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# THE REACTION OF ACTIVE NITROGEN WITH ETHYLENE[1]

BY J. VERSTEEG[2] AND C. A. WINKLER

ABSTRACT

Reinvestigation of the active nitrogen–ethylene reaction has confirmed hydrogen cyanide as the principal product. Smaller quantities of ethane, cyanogen, acetylene, and methane have also been found and the variations in amounts of these products with ethylene flow rate have been established. No significant amount of polymeric material was found.

The reaction of active nitrogen with ethylene has been investigated previously in this laboratory (3) but under conditions such that the results were rendered quantitatively uncertain by the formation of considerable amounts of unidentified polymer. Further experience with reactions of similar type (1) has made it possible to reduce the extent of polymer formation to negligible proportions. The ethylene reaction has therefore been reinvestigated with the improved technique to establish the essential features of the reaction on a more reliable quantitative basis, and to provide a more detailed examination of the reaction products.

## EXPERIMENTAL

The apparatus and procedure were identical in all essentials with those used in the earlier studies mentioned above. Formation of the troublesome hydrogen cyanide polymer encountered previously was very largely prevented by eliminating water vapor from the system, and by careful sublimation of the cyanide below its melting point from the main product trap into a bulb containing calcium chloride.

Hydrogen cyanide was estimated both by weight and by titration (6). Cyanogen was determined by alkaline hydrolysis followed by determination of the resulting cyanide (7). A hydrocarbon fraction which was separated cleanly from hydrogen cyanide and cyanogen by distillation at 116° C. was analyzed for acetylene and ethylene by absorption in the manner described by Brooks *et al.* (2). The residual gas was assumed to be ethane. Small amounts of $C_3$ hydrocarbon might also have been present, although no indication of them was obtained in Podbielniak distillations of three of the hydrocarbon fractions. Also, an average carbon balance of 95% to 96% was obtained, disregarding carbon not accounted for in traces of polymer that were formed

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and in possible $C_3$ or higher hydrocarbons. (The carbon balance in the previous study of the reaction was of the order of 70%.) Methane was determined by combustion over the cupric oxide – ferric oxide catalyst of Brooks *et al.* (2).

## RESULTS AND DISCUSSION

The results of the study have been summarized in Fig. 1. The curve for hydrogen cyanide production confirms the main feature of the reaction observed in the previous study; the remainder of the curves represent new information.

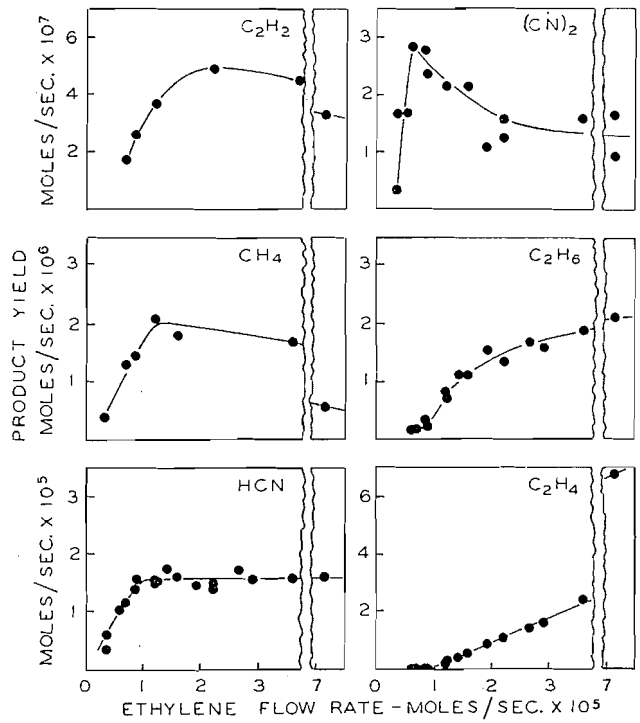



FIG. 1. Rate of formation of various products in the ethylene – nitrogen atom reaction, as a function of the ethylene flow rate.

The present study in itself would not seem to demand serious revision of the earlier reaction mechanism, which assumed as a primary step

$$C_2H_4 + N \rightarrow HCN + CH_3 \cdot .$$

However a recent study of the nitrogen atom reaction with propylene (5) has given strong indication that the ethylidene radical is formed in the initial step of that reaction, thus

$$C_3H_6 + N \rightarrow CH_3\,CH{:} + CH_2N$$
$$\downarrow$$
$$HCN + H .$$

The analogous reaction with ethylene, though less favorable energetically

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than that to form the methyl radical, would lead to the primary production of the methylene radical,

$$C_2H_4 + N \rightarrow CH_2{:} + CH_2N \downarrow HCN + H\,.$$

No decision between the two possibilities would yet seem possible.

The production of ethane and methane can be reasonably accounted for by reactions of atomic hydrogen with ethylene, and either methyl or methylene radicals, respectively. The observed increase in amount of ethane and decrease in amount of methane with increased flow rate of ethylene presumably correspond to the increasingly preferred reaction of hydrogen atoms with ethylene at the expense of methane formation.

Formation of the observed small amounts of acetylene, and the decrease in these amounts with increased ethylene flow, may be explained by some dehydrogenation of ethylene according to the reactions (cf. 4, p. 262)

$$C_2H_4 + H \rightarrow C_2H_3 + H_2\,,$$
$$C_2H_3 + H \rightarrow C_2H_2 + H_2\,.$$

The formation of cyanogen, with a maximum value at approximately the ethylene flow rate beyond which ethylene is in excess of the nitrogen atoms (determined from hydrogen cyanide production), would seem to be best explained by the reactions

$$C_2H_4 + N \rightarrow [C_2H_4N]^*,$$
$$[C_2H_4N]^* + N \rightarrow [C_2H_4N_2]^*,$$
$$[C_2H_4N_2]^* \rightarrow C_2N_2 + 2H_2\,.$$

This implies that the collision complex is sufficiently stable to suffer an appreciable number of collisions with a second nitrogen atom. The high rate at which ethylene is attacked by atomic nitrogen, compared with, say, the relatively slow attack on ethane (1), makes it seem reasonable to attribute comparative ease of formation and correspondingly significant stability to the ethylene – nitrogen atom complex.

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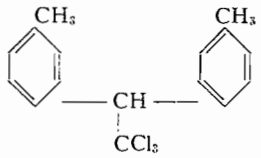
# ON THE OXIDATION OF 1,1,1-TRICHLORO-2,2-*BIS*-(*p*-TOLYL)-ETHANE[1]

By Yvon Perron

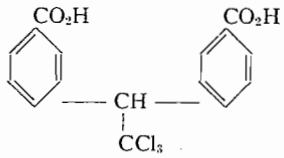

## ABSTRACT

The condensation of benzene with chloral hydrate in the presence of concentrated sulphuric acid gave rise to 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane. The oxidation of this condensation product with potassium dichromate in dilute sulphuric acid at the boiling temperature yielded 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene, the structure of which was shown by its oxidative degradation to 4,4′-dicarboxybenzophenone. When the oxidation of the same condensation product was carried out in the cold, with the aid of chromium trioxide in glacial acetic acid and acetic anhydride, 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane was obtained in a good yield. This last compound was converted to the dichloroethylenic-dicarboxylic acid upon refluxing with a methanolic solution of sodium hydroxide. The corresponding amide derivatives of both the dichloro and trichlorodicarboxylic acids were also prepared.


In connection with the syntheses of some DDT analogues, 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane and its amide derivative were needed. Haskelberg and Lavie (2) have previously reported the synthesis of this trichlorodicarboxylic acid. According to their procedure, chloral hydrate was first condensed with toluene, as described earlier by Fischer (1), and 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane (I) was obtained.

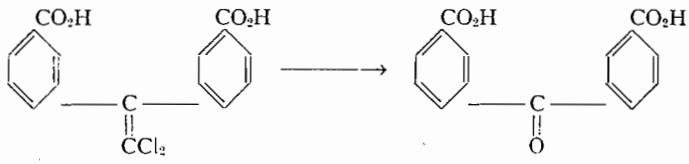


I



II

This compound was in turn oxidized with the aid of potassium dichromate and dilute sulphuric acid at the boiling point of the mixture. These authors claimed to have obtained by this procedure a 20% yield of 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (II). However, all attempts to prepare this trichlorodicarboxylic acid by the procedure described have failed in our hands. It seemed that under such a drastic condition of oxidation, as employed by these authors, there was, together with the conversion of the methyl groups to carboxyl groups, a concurrent loss of a molecule of hydrogen chloride and the product so obtained was 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene (III).



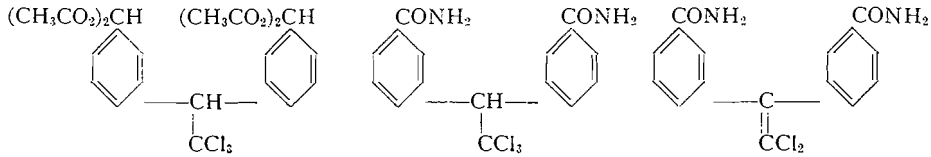
III IV

[1] *Manuscript received October 6, 1952.*
*Contribution from the Department of Chemistry, University of Montreal, Montreal, Que.*

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That the compound obtained, when the procedure described by Haskelberg and Lavie was followed, had really Structure III was shown by elemental analyses and also by the fact that on further oxidation with chromic anhydride in glacial acetic acid at the boiling point of the solvent, it gave rise to 4,4′-dicarboxybenzophenone (IV).

In view of this result a modified method for the preparation of the dicarboxylic acid II was desirable, and in this respect, the oxidation of 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane under milder conditions was attempted.




V VI VII

We have previously reported (4) that Compound I in glacial acetic acid and acetic anhydride, when oxidized at 5° C. with chromium trioxide, gave rise to the tetraacetate of 1,1,1-trichloro-2,2-*bis*-(*p*-aldehydophenyl)-ethane (V). The same reaction was carried out at 15° C. instead of 5° C., and under this condition a good yield of the desired trichlorodicarboxylic acid (II) was obtained. Furthermore, we have found that the omission of acetic anhydride from the reaction mixture led to the ethylenic-dicarboxylic acid (III).

1,1,1-Trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (II), upon refluxing with a methanolic solution of sodium hydroxide, was converted to the ethylenic-dicarboxylic acid (III), the melting point of which was undepressed upon admixture with the dicarboxylic acid obtained by the procedure described by Haskelberg and Lavie. The dicarboxylic acids II and III, heated under reflux with thionyl chloride and then treated with concentrated aqueous ammonia, gave rise respectively to 1,1,1-trichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethane (VI) and 1,1-dichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethylene (VII).

## EXPERIMENTAL

*1,1,1-Trichloro-2,2-bis-(p-tolyl)-ethane (I)*

This product was prepared according to Fischer (1).

In a 250 ml. round-bottomed flask, equipped with a mechanical stirrer and a thermometer, chloral hydrate (41 gm.) and toluene (50 gm.) were introduced. The reaction flask was immersed in an ice-bath and the mixture was cooled to 5° C. To this mixture which was mechanically stirred, concentrated sulphuric acid (150 gm.) was added dropwise from a dropping funnel. The stirring was continued for three hours, at room temperature, after the addition of acid had been completed. A semisolid product separated from the reaction mixture. The contents of the reaction flask was poured on crushed ice, and the solid was filtered off and washed thoroughly with cold water to get rid of the excess chloral and sulphuric acid. It was then freed from excess toluene by

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trituration with ethanol (50 ml). The crude product was finally recrystallized from 95% ethanol, from which white platelets, m.p. 89° C., were obtained. Yield, 58%.

*Oxidation with Potassium Dichromate and Sulphuric Acid*

The oxidation of 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane with potassium dichromate and sulphuric acid was carried out as described by Haskelberg and Lavie (2).

Potassium dichromate (38.3 gm.), 1,1,1-trichloro-2,2-*bis*-(*p*-tolyl)-ethane (13.3 gm.), and water (75 cc.) were introduced into a 500 ml. reaction flask. To this mixture sulphuric acid (85 gm.) was added slowly with stirring. When half of this quantity was added the mixture was heated to the boiling point and the addition was continued at the boiling temperature. The reaction mixture was allowed to cool and it was then poured into 1 liter of cold water. The solid material was collected by filtration and ground with 5% sulphuric acid (150 cc.). The precipitate was filtered off, washed with cold water, and extracted with a 5% aqueous sodium hydroxide solution (100 cc.). The alkaline solution was freed from insoluble residue by filtration and then acidified with a 10% sulphuric acid solution. The precipitated dicarboxylic acid was dissolved in boiling 50% aqueous ethanol and the resulting solution was decolorized with charcoal. After many recrystallizations from that solvent, 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene separated as colorless needles melting at 278° C. (dec.). Yield, 22%. Calc. for $C_{16}H_{10}O_4Cl_2$: C, 56.97; H, 2.96; Cl, 21.06%; neut. equiv., 337. Found: C, 56.88; H, 2.97; Cl, 21.15%; neut. equiv., 339.

*1,1,1-Trichloro-2,2-bis-(p-carboxyphenyl)-ethane (II)*

1,1,1-Trichloro-2,2-*bis*-(*p*-tolyl)-ethane (15 gm.), acetic anhydride (125 cc.), and glacial acetic acid (125 cc.) were introduced in a 500 ml. reaction flask equipped with a mechanical stirrer and a thermometer. The resulting solution was cooled to 15° C. and concentrated sulphuric acid (25 cc.) was added slowly, from a dropping funnel, with cooling and stirring. After the addition of acid had been completed, the solution was allowed to cool again to 15° C. Chromic anhydride (25 gm.) was then added, in small portions, at such a rate that the temperature did not rise above 20° C. The contents of the reaction flask was kept stirred over a period of 30 min. after all the chromium trioxide had been added. The reaction mixture was then poured on crushed ice. This caused the separation of a brown precipitate which was collected by filtration and subsequently washed with small quantities of cold water until the washings were colorless. The solid was extracted at room temperature with a 2% sodium hydroxide solution (200 cc.) and the insoluble material was removed by filtration. The resulting aqueous solution was acidified with 10% sulphuric acid (100 cc.) which caused the precipitation of the organic diacid. The crude material was filtered off, washed several times with small quantities of cold water, and recrystallized from 75% aqueous dioxane or 50% aqueous ethanol. After three recrystallizations, there was obtained a white crystalline product melting at 283° C. (dec.). Yield, 75%. Calc. for $C_{16}H_{11}O_4Cl_3$: C, 51.48; H,

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2.90; Cl, 28.51%; neut. equiv., 373.5. Found: C, 51.45; H, 2.96; Cl, 28.45%; neut. equiv., 374.

*1,1-Dichloro-2,2-bis-(p-carboxyphenyl)-ethylene (III)*

A mixture of 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (1.5 gm.) and a 7% methanolic solution of sodium hydroxide (25 cc.) was refluxed for 10 hr. The methanol was then distilled off under reduced pressure and the solid residue was dissolved in water (25 cc.). The resulting aqueous solution was acidified with a 10% sulphuric acid solution, which caused the precipitation of the free dicarboxylic acid. The white precipitate was filtered off and washed with small quantities of cold water until the washings were neutral to litmus. It was then dissolved in boiling 50% aqueous ethanol. On cooling, 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene crystallized out as colorless needles. After three recrystallizations from that solvent the product melted at 277–278° C., either alone or in admixture with a sample of the dicarboxylic acid obtained by the dichromate – sulphuric acid oxidation. Calc. for $C_{16}H_{10}O_4Cl_2$: C, 56.97; H, 2.96; Cl, 21.06%; neut. equiv., 337. Found: C, 56.90; H, 2.98; Cl, 21.10%; neut. equiv., 338.

*4,4'-Dicarboxybenzophenone (IV)*

Chromic anhydride (1 gm.) and 1,1-dichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethylene (0.7 gm.) were dissolved in glacial acetic acid (40 cc.). The resulting solution was refluxed gently for two hours after which time the contents of the reaction flask was poured into cold water (100 cc.). This caused the precipitation of the expected ketone. The precipitate was filtered off and washed thoroughly with cold water, until the washings were colorless. After recrystallization from a large volume of 95% ethanol the product was obtained as colorless microcrystalline needles melting over 360° C. (dec.) as reported previously by Limpricht (3). Yield 50%. Calc. for $C_{15}H_{10}O_5$: C, 66.67; H, 3.70%; neut. equiv., 270. Found: C, 66.49; H, 3.81%; neut. equiv., 270.

*1,1,1-Trichloro-2,2-bis-(p-carboxamidophenyl)-ethane (VI)*

A mixture of 1,1,1-trichloro-2,2-*bis*-(*p*-carboxyphenyl)-ethane (2 gm.) and freshly distilled thionyl chloride (15 cc.) was heated under reflux for three hours, after which time the solid material had completely dissolved. The unreacted thionyl chloride was distilled off and the residual yellow oil dissolved in ether. The ethereal solution was added cautiously from a dropping funnel, to a concentrated aqueous ammonia solution. This caused the separation of a yellowish precipitate which was removed by filtration and subsequently washed with cold water. The crude 1,1,1-trichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethane thus obtained was recrystallized from methanol, from which it separated as colorless plates, melting at 261–62° C. (dec.). Yield, 90%. Calc. for $C_{16}H_{13}O_2N_2Cl_3$: C, 51.68; H, 3.49; Cl, 28.66; N, 7.53%. Found: C, 51.59; H, 3.52; Cl, 28.60; N, 7.48%.

*1,1-Dichloro-2,2-bis-(p-carboxamidophenyl)-ethylene (VII)*

This amide was prepared exactly as described above for 1,1,1-trichloro-2,2-*bis*-(*p*-carboxamidophenyl)-ethane. The product so obtained was recrystallized from methanol from which it separated as colorless rectangular plates

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melting at 256–57° C. Yield, 95%. Calc. for $C_{16}H_{12}O_2N_2Cl_2$: C, 57.31; H, 3.58; Cl, 21.19; N, 8.35%. Found: C, 57.26; H, 3.63; Cl, 21.24; N, 8.38%.

ACKNOWLEDGMENTS

We are indebted to the Office de Recherches Scientifiques de la Province de Québec for a grant in aid, and also to Dr. R. Barré for his stimulating interest in this work.

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# N-BENZOYLPHENYLHYDROXYLAMINE AS A REAGENT FOR TIN[1]

By D. E. Ryan and G. D. Lutwick

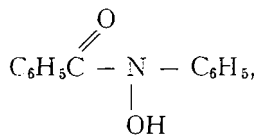
ABSTRACT

N-Benzoylphenylhydroxylamine precipitates tin quantitatively from stannic chloride solutions; complete precipitation is obtained in solutions varying from 1 to 8% in concentrated hydrochloric acid. The reagent reduces stannic to stannous tin before forming the addition compound $(C_{13}H_{11}O_2N)_2\ SnCl_2$; this compound is stable and may be used as a weighing form for tin. Tin can be determined readily in brasses; copper, lead, and zinc do not interfere.

## INTRODUCTION

The gravimetric methods for the determination of tin all require ignition to stannic oxide; the oxide, in addition to the disadvantage of a high conversion factor, must be heated to a high temperature and has a marked tenacity for water. The present investigation was undertaken in the attempt to find a reagent that would precipitate a complex from stannic solutions that could be dried at 110°C.

Of 25 compounds tested in preliminary experiments the N-benzoyl derivative of phenylhydroxylamine,



seemed to offer the greatest possibilities. It reacted with stannic chloride solutions to give complete precipitation of the tin and the resulting compound was stable with a melting point of 171°C. This paper is a report on the use of N-benzoylphenylhydroxylamine as a reagent for tin.

## EXPERIMENTAL

### *Preparation*

N-Benzoylphenylhydroxylamine was prepared by reacting benzoyl chloride with phenylhydroxylamine following the method of Bamberger (2). However, in the precipitation of the N-benzoyl derivative from ammonia (in which the monobenzoyl compound is dissolved to separate it from any dibenzoyl that may have been formed during the reaction) Bamberger neutralized by means of sulphuric acid. It was found that, because of oxidation and heat of reaction, the neutralized solution was distinctly yellow in color and contained, in addition to precipitated reagent, a reddish brown oil that solidified, contaminating the desired product.

The use of 3*N* hydrochloric acid to neutralize the ammonia resulted in a colorless solution and eliminated the formation of the oil. One recrystallization from hot water gave a white crystalline product with a melting point of 121° C. In recrystallizing from hot water, since prolonged heating caused some decompo-

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sition, 0.6 gm. of the reagent was added for each 100 ml. of boiling water and the solution, after being filtered, was cooled in an ice bath.

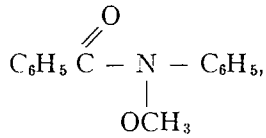
*Properties*

N-Benzoylphenylhydroxylamine is a white crystalline solid melting at 121° C. It is only slightly soluble in water at 25° C., the solubility being 0.04 gm. per 100 ml.; the solubility in hot water is approximately 0.5 gm. per 100 ml. The reagent reacts much the same as does cupferron but it is more stable towards heat, light, and air; it has been used by Shome (3) to precipitate iron, copper, aluminum, and titanium but the complexes are more easily decomposed by acids than the cupferron derivatives. Reaction occurs, in these compounds, by replacement of the hydrogen of the oxime by the metal and co-ordination to the oxygen of the carbonyl grouping; such is not the case with tin, however, in which an addition rather than an inner complex compound is formed.

*Nature of Reaction*

The precipitated benzoylphenylhydroxylamine tin compound was found to contain 19.28% tin and 11.3% chlorine; the theoretical percentages for a compound having the composition $(C_{13}H_{11}O_2N)_2SnCl_2$ are 19.27 for tin and 11.5 for chlorine. The hydroxylamine apparently reduces stannic to stannous tin before forming the addition compound; complexes precipitated from stannous and stannic chloride solutions have the same composition with a melting point of 171° C.

That the metal is not linked to the oxygen and the hydrogen of the oxime plays no part other than that of reducing the stannic tin is shown by the ready formation of similar compounds by the O-methyl ether of benzoylphenylhydroxylamine,



with stannous chloride solutions; no reaction occurs with stannic chloride solutions.

*Methods*

1. *Ignition to the Oxide*

To aliquots of a standard solution of stannic chloride were added varying amounts of concentrated hydrochloric acid and the solutions were diluted to 100 ml. Three milliliters of a 10% solution of benzoylphenylhydroxylamine in ethyl alcohol was added slowly, with stirring. The solutions were then cooled in an ice bath for one hour and the precipitates were filtered through S & S No. 589 white ribbon filter paper, washed with ice water, and ignited to the oxide. The results are shown in Table I.

Table I shows that tin can be quantitatively precipitated by means of benzoylphenylhydroxylamine from solutions varying from 1 to 8% in concentrated hydrochloric acid. Incomplete precipitation at higher concentrations of the acid is neither caused by an increase in the stability of $SnCl_6''$ with increasing chloride ion concentration nor by failure of reduction to take place; complete precipitation was obtained from solutions 15% in chloride (from sodium chloride) while only

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TABLE I

PRECIPITATION OF TIN BY BENZOYLPHENYLHYDROXYLAMINE AND SUBSEQUENT WEIGHING AS THE OXIDE

| Tin taken, mgm. | Tin recovered, mgm. | Remarks |
|---|---|---|
| 9.45 | 9.45 | Solution 1% in concentrated HCl |
| 9.45 | 9.45 | Solution 1% in concentrated HCl |
| 9.45 | 9.38 | Solution 5% in concentrated HCl |
| 9.45 | 9.45 | Solution 5% in concentrated HCl |
| 9.45 | 9.35 | Solution 8% in concentrated HCl |
| 9.45 | 9.45 | Solution 8% in concentrated HCl |
| 8.34 | 8.03 | Solution 10% in concentrated HCl |
| 9.76 | 9.77 | Tin determined in brass sample after dissolving approximately 0.1 gm. of the brass in concentrated HCl and a few drops of $HNO_3$ |
| 11.09 | 11.11 | Tin determined in brass sample after dissolving approximately 0.1 gm. of the brass in concentrated HCl and a few drops of $HNO_3$ |
| 12.5 | 12.4 | Sample of $(Et_3N)_4\ SnCl_4$ analyzed for tin |
| 33.0 | 33.3 | Sample of $(EtNH_2)_6\ SnCl_4$ analyzed for tin |
| 25.8 | 26.2 | Sample of $(Et_3N)_2\ SnCl_4$ analyzed for tin |

slight precipitation was obtained from stannous solutions 15% in concentrated hydrochloric acid.

Although copper can be quantitatively precipitated by benzoylphenylhydroxylamine at pH 3.6 – 6.0, no interference was encountered from copper, lead, or zinc in precipitating tin from brass solutions containing 7% of concentrated hydrochloric acid. Copper was determined successfully in the filtrates from the tin precipitation, after neutralizing with ammonia, by the method of Shome (3).

The tin addition compounds were prepared by W. R. Trost (4) and were analyzed by dissolving the compounds in 5% hydrochloric acid and following the usual procedure.

2. *Weighing as the Complex*

To aliquots of a standard solution of stannic chloride were added 10 ml. of concentrated hydrochloric acid and the solutions were diluted to approximately 200 ml. From a separatory funnel was added, dropwise and with stirring, 5 ml. of a 1% solution of the reagent in alcohol for each 10 mgm. of tin present plus 8 ml. in excess. The solutions were cooled in an ice bath for four hours, the precipitates filtered on a filter crucible, washed with a few milliliters of ice water, and dried at 110° C. The weight of the precipitate was multiplied by the theoretical factor 0.1927 to obtain the weight of tin. Results are shown in Table II.

It is essential that the reagent concentration be closely regulated because of the slight solubility of the reagent and the necessity of excess reagent for complete precipitation. The first four results in Table II were obtained by adding 225 ml. of a saturated aqueous solution of the reagent to precipitate the tin; to avoid the addition of the large volume necessary for greater quantities of tin a 1% solution of the reagent in ethyl alcohol was found to be satisfactory and all other results were obtained using the above procedure.

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TABLE II

PRECIPITATION OF TIN BY BENZOYLPHENYLHYDROXYLAMINE AND WEIGHING AS THE COMPLEX $(C_{13}H_{11}O_2N)_2\ SnCl_2$

| Tin taken, mgm. | Tin recovered, mgm. | Tin taken, mgm. | Tin recovered, mgm. |
|---|---|---|---|
| 4.79 | 4.78 | 4.57 | 4.60 |
| 4.79 | 4.74 | 10.02 | 9.98 |
| 4.79 | 4.80 | 10.02 | 10.03 |
| 4.79 | 4.78 | 11.50 | 11.54 |
| 4.57 | 4.60 | *11.50 | 11.45 |
| 4.57 | 4.51 | 23.00 | 23.08 |
| 4.57 | 4.57 | *23.00 | 23.01 |
| 4.57 | 4.59 | | |

**These results were obtained, independently, by a member of this laboratory.*

## DISCUSSION

Cupferron and neocupferron (the ammonium salts of nitrosophenyl and nitrosonaphthyl hydroxylamine respectively) react with stannous and stannic tin by replacement of the hydrogen of the oxime grouping to give complexes of the type $SnC_2$ and $SnC_4$ (1). That the N-benzoyl derivative of phenylhydroxylamine does not behave similarly but forms an addition compound can probably be attributed to its greater basicity. The fact that the replacement of the hydrogen of the oxime does not occur with tin is important; it suggests the possibility of preparing reagents that will permit separations from elements that do require the presence of a replaceable hydrogen for reaction. Thus the O-methyl ether of benzoylphenylhydroxylamine reacts with tin (II) and antimony (III) but does not react with iron or copper. Further investigations of N-benzoylphenylhydroxylamine for separating and determining tin have been discontinued, for the present, in order to investigate more fully these possibilities.

## ACKNOWLEDGMENTS

We take this opportunity to thank Mr. L. S. Theobald (Imperial College, London), who suggested this problem to one of us, and Dr. W. J. Chute, who co-operated in the preparation of various organic compounds.

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# KINETIC STUDIES OF A REDOX POLYMERIZATION[1]

By R. M. Brown[2] and C. A. Winkler

ABSTRACT

Kinetic studies of a redox-initiated polymerization have indicated activation energies of 9.7 kcal. per mole for the decomposition of the initiating system, approximately 6 kcal. per mole for the propagation reaction, and 9.0 kcal. per mole for the consumption of MTM-4 in the emulsion system. Lower polymerization temperatures raised the gel point without shortening the polymer chains, apparently by decreasing the proportion of cross-linking to propagation reactions. Two types of nonmercaptan termination have been found to occur to appreciable extents: mutual termination of free radicals and a termination process involving the emulsifier.

## INTRODUCTION

The introduction of low temperature redox polymerization systems has improved significantly the physical properties of synthetic elastomers (5, 19, 21). The improvement may be ascribed to increased regularity in configuration of the polymer chains (2, 7, 9, 12, 15). The present paper describes some experiments in which the effect of temperature on several aspects of the reaction kinetics has been examined, using a typical redox polymerization recipe.

## EXPERIMENTAL

The standard bottle technique for emulsion polymerization (13) was used, with end-over-end rotation at 35 r.p.m. in a water bath controlled to ± 0.02°C. The polymerization recipe was slightly modified from one of Mitchell, Spolsky, and Williams (16), and consisted of:

| Component | Parts by weight |
|---|---|
| Butadiene* | 75.0 |
| Styrene* | 25.0 |
| Cumene hydroperoxide* (68%) | 0.24 |
| Dresinate 731* (dry wt.) | 4.70 |
| Sodium hydroxide | 0.11 |
| Mixed tertiary mercaptan* (MTM-4) | Variable (0.00 to 0.20) |
| Kalex sodium* (dry wt.) | 0.15 |
| Dextrose | 0.50 |
| $FeSO_4.7H_2O$ | 0.028 |
| $Na_3PO_4.12H_2O$ | 0.34 |
| Distilled water | 180 |
| Di-*tert*-butyl hydroquinone* (shortstop) | 0.40 |

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The Dresinate 731 emulsifier and the sodium hydroxide were combined in a stock solution. The activator, consisting of an organic complex of ferrous iron

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which was sensitive to oxygen, was prepared in a stock solution by dissolving the sodium phosphate, ferrous sulphate, dextrose, and Kalex sodium in about 20 parts of the water charge and boiling exactly 10 min. The activator solution, when stored under oxygen-free nitrogen, could be kept indefinitely without change in effectiveness.

The shortstop, di-*t*-butyl hydroquinone, was prepared as a suspension using the same emulsifying agent present in the latex.

The components were charged into 1-oz. bottles in the order: water, soap solution, activator solution, styrene solution of mercaptan, styrene solution of cumene hydroperoxide, and, finally, an excess of butadiene, which was allowed to evaporate to the desired weight, to expel air from the bottle.

*Analytical Methods*

Self-sealing Butyl rubber* gaskets under each bottle cap allowed repeated insertion of a hypodermic needle for purposes of injecting shortstop or withdrawing a sample of latex (8). The extent of polymerization was determined on the basis of solids content of the latex (11) correcting for known nonpolymer solids in the recipe.

The residual mercaptan in the latex at any desired conversion was determined by amperometric titration with silver nitrate according to the method of Kolthoff and Harris (14). Satisfactory sampling of the latex for this purpose proved impossible and it was necessary to coagulate and titrate the whole contents of a bottle, except for a 1 ml. sample removed for determination of percentage conversion.

The intrinsic viscosity of the polymer product was measured by determining the flow times of polymer solutions at 24.8°C. in a modified Ubbelohde viscometer having a large solution reservoir to allow measurements at several concentrations by successive dilutions in the viscometer. The vistex method of Henderson and Legge (10) was followed using 80/20 (by volume) toluene–isopropanol as solvent and pure toluene as diluent to obtain the several solutions required for the determination of the kinematic flow time in pure toluene. Since the viscometers were designed with reasonably long flow times, kinetic energy corrections were neglected and results recorded as intrinsic flow times.

## RESULTS AND DISCUSSION

*The Polymerization Reaction*

Persistent difficulty in obtaining a reproducible rate of reaction was encountered in the preliminary work with this polymerization system. No definite cause for this difficulty was identified, but with further experience with the system, reproducibility between individual bottles of a particular experiment of $\pm$ 1.5% conversion was achieved. The rate of polymerization continued to vary from experiment to experiment, but enough polymerizations were observed to give good average values for the polymerization rate under various conditions.

Typical rate curves for the polymerization reaction at various temperatures are plotted in Fig. 1. In contrast to the inhibition period often observed in poly-

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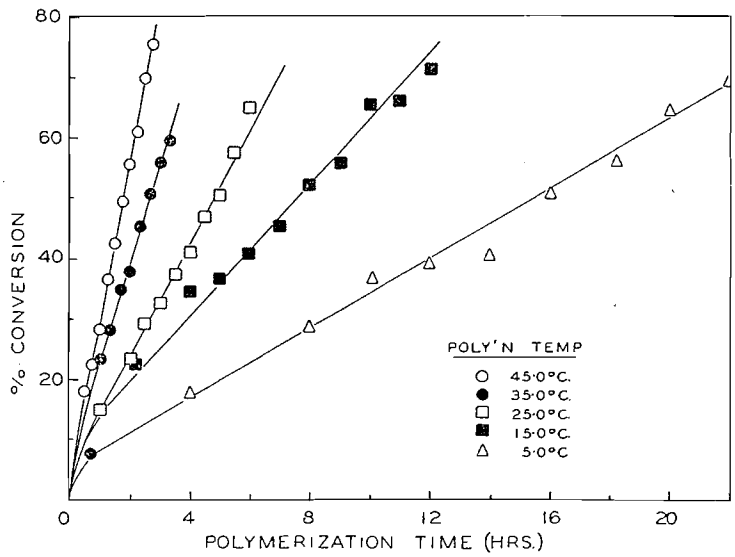



FIG. 1. The rate of polymerization at various temperatures.

merizations of the Mutual recipe system (3), the present system displayed a very fast initial reaction in all experiments. The amount of this initial surge was variable, but usually amounted to an intercept of 6 – 10% conversion when the zero order portion of the rate curve was extrapolated back to zero time. This fast reaction appears to be dependent on the initiating system as a whole, since when either the peroxide, or the activator, or both were omitted from the charge, no polymerization took place at all. If these components were then added to the emulsified charge by syringe, the usual polymerization curve was obtained. The initial surge was unaffected by the elimination of mercaptan from the charge, or substitution of potassium laurate for the Dresinate emulsifier.

The actual consumption of activator during the course of polymerization was slight. Table I indicates that the polymerization rate becomes sensitive to acti-

TABLE I

THE DEPENDENCE OF POLYMERIZATION RATE ON ACTIVATOR CONCENTRATION
Polymerization temperature = 25.0°C
Polymerization time = 5.50 hr.
No mercaptan charged.

| Activator (fraction of normal*) | % Conversion |
|---|---|
| 0.25 | 33.8 |
| 0.50 | 50.5 |
| 0.75 | 55.0 |
| 1.00 | 55.5 |

**Normal charge refers to that quoted in the polymerization recipe.*

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vator concentration at an activator charge below one half of that normally used. In spite of this sensitivity at low activator concentration, a uniform rate of polymerization up to high conversions was observed using one quarter the normal activator charge.

An Arrhenius plot for the average zero order rates of polymerization between 10% and 65% conversion at five different temperatures yielded a value of 9.7 kcal. per mole for the activation energy of the process which is rate controlling during the zero order portion of polymerization. This is of the same order of magnitude as the activation energy of 11.1 kcal. per mole found for the free radical reaction of $Fe^{++}$ and cumene hydroperoxide by Fordham and Williams (6).

The polymerization has been found to become first order in respect of monomer when reaction has proceeded to such an extent that the concentration of monomer becomes the rate-controlling factor, i.e. beyond 65 – 70% conversion. In this region of reaction no separate monomer phase exists, hence the monomer concentration at the site of reaction is given by the total monomer remaining in the system. The rates indicated by the first order plots in Fig. 2 permit an estimate

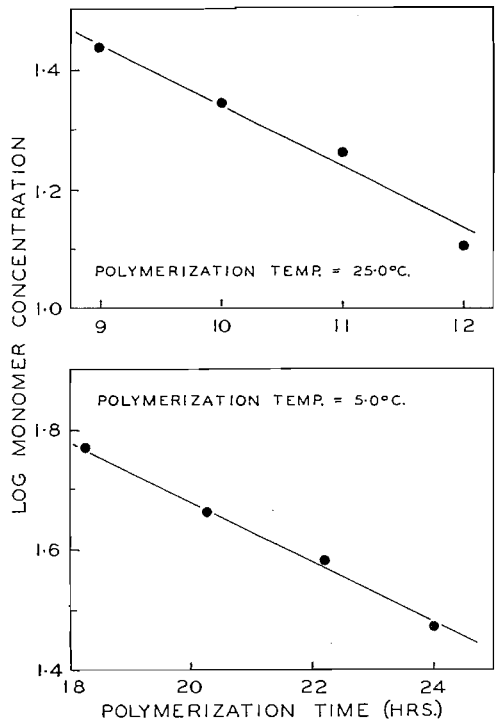



FIG. 2. First order plot of monomer disappearance at high conversions.

of 6 kcal. per mole for the activation energy of the reaction responsible for disappearance of monomer, i.e., the propagation reaction. This value is very approximate since the first order reaction can be followed only over a short range.

*Termination Reactions*

Typical analytical data for the disappearance of MTM-4 during the course of

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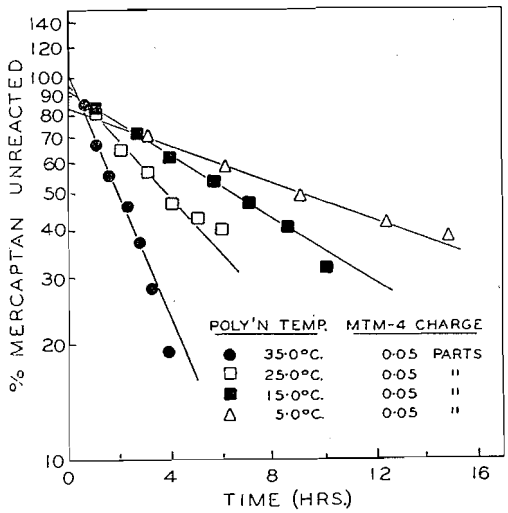



FIG. 3. The rate of mercaptan disappearance at various temperatures.

the polymerization at various temperatures are plotted in Fig. 3. The reaction of MTM-4 as a chain transfer agent in this emulsion showed first order kinetics up to about 60% conversion in a manner similar to the behavior of mercaptans of the Mutual system. However, anomalous behavior was observed during the early stages of reaction. It was found that the rate of mercaptan disappearance did not keep up with the rate of polymerization during the fast initial polymerization. In spite of this, the polymer formed during this stage of reaction was of low molecular weight rather than high. Hence a mode of termination other than by mercaptan would appear to play a major role in the initial stage of polymerization. Higher mercaptan consumption occurred during the initial surge of polymerization, the lower the temperature. This suggests that the nonmercaptan terminating reaction has or is controlled by an activation energy greater than that governing MTM-4 chain transfer. An Arrhenius plot of the zero-time intercepts obtained from a large-scale plot of Fig. 3 indicates a value of about 0.9 kcal. per mole for the activation energy difference of the two terminating processes.

An Arrhenius plot for the first order rate of MTM-4 disappearance at different temperatures gave an activation energy of 9.0 kcal. per mole for the over-all process of MTM-4 consumption. This is not an activation energy for the isolated reaction between the growing free radical and the mercaptan molecule. It is, rather, a measure of the temperature dependence of the over-all process that involves transport of the mercaptan molecule from the oil droplet in the emulsion to the monomer–polymer particle, and its subsequent reaction with the growing free radical.

From this value and the difference in activation energy of the two terminating processes, the second terminating process is found to be controlled by an activation energy of about 9.9 kcal. per mole. This is in reasonable agreement with the value of 9.7 kcal. per mole obtained for the production of free radicals by the

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initiating system, as indicated by the polymerization reaction. This suggests that the early nonmercaptan termination is, in reality, mutual termination of free radicals and is controlled by the concentration, hence rate of production, of free radicals in the same sense as the rate of the polymerization reaction itself. The existence of an appreciable amount of mutual termination during the fast initial polymerization is to be expected when it is considered that this fast reaction indicates an abnormally high concentration of initiating and growing free radicals.

Evidence that considerable nonmercaptan termination is operating in this system throughout the course of polymerization is given by a comparison of degrees of polymerization calculated from mercaptan consumption data and from intrinsic viscosity data. In a system in which all termination is by mercaptan chain transfer, the weight average degree of polymerization that would be attained in the total absence of cross-linking and branching reactions may be calculated from mercaptan consumption data as shown by Bardwell and Winkler (1):

$$\bar{y}_{w_\alpha} = 2(e^{r\alpha} - 1)/r^2\alpha R_0,$$

$\alpha$ = fractional extent of conversion of monomer to polymer,
$\bar{y}$ = average degree of polymerization, i.e. average number of structural units per polymer chain,
$\bar{y}_{w_\alpha}$ = weight average degree of polymerization at conversion $\alpha$,
$R_0$ = initial mercaptan concentration (as moles per mole of initial monomer),
$r$ = regulating index (4) = $-d \ln R/d\alpha$.

Statistical mechanical considerations relate the various primary degrees of polymerization (1):

$$\bar{y}_v \doteq \frac{1.85}{2.00}\bar{y}_w.$$

Hence, $\bar{y}_v$ for the polymer chains that would be formed in the total absence of branching or cross-linking, i.e. the primary polymer chains, can be evaluated provided all termination is by mercaptan chain transfer. At very low conversions, where the extent of cross-linking is small, the degree of polymerization calculated from viscosity data and from mercaptan consumption data should be of the same order, but the viscosity degree of polymerization should rapidly become larger than the $\bar{y}_v$ calculated from mercaptan disappearance as the reaction proceeds to the gel point.

A comparison of $\bar{y}_v$ calculated from mercaptan consumption data and from intrinsic viscosity data is made in Fig. 4 for a polymerization at 35°C. Molecular weights are calculated from intrinsic viscosity values in toluene using the relation:

$$[\eta] = 5.25 \times 10^{-4} \times M_v^{0.67}$$

which has been established for GR-S polymerized at 50°C. (18). Structural heterogeneity of butadiene–styrene copolymer does not vary greatly with polymerization temperature (15), and this equation should be reasonably valid for polymer formed at 35°C. An average molecular weight of the structural unit of the copolymer of 59.4 has been used to calculate average degrees of polymerization from the viscosity molecular weights.

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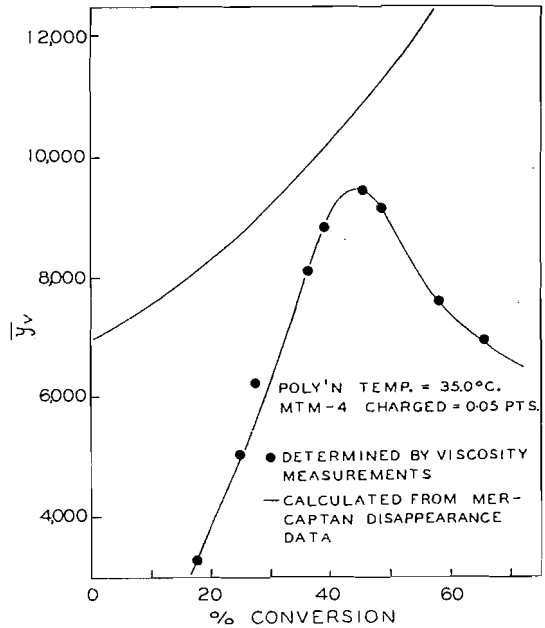



FIG. 4. Comparison of the average degrees of polymerization determined by viscosity measurements, using the equations:

$$[\eta] = 5.25 \times 10^{-4}\ M_v^{0.67},$$
$$\bar{y}_v = M_v/59.4,$$

with those calculated from kinetic data for the disappearance of mercaptan using the equations:

$$\bar{y}_v = 0.92\,\bar{y}_w = 0.92 \times 2(e^{r\alpha} - 1)/\alpha r^2 R_0$$

where $R_0 = 1.39 \times 10^{-4}$ moles mercaptan per mole initial monomer,
$r = 1.88$ for polymerization at 35.0°C. from Figs. 1 and 3.

In Fig. 4, the actual molecular weights indicated by viscosity measurements are seen to be much lower than the primary molecular weights suggested by mercaptan consumption data, in spite of the existence of extensive cross-linking that must be present in the polymer just prior to, and at the gel point. Thus, the mercaptan consumption cannot be a true indication of the primary molecular weights, and extensive termination by other means must occur. Comparison of the molecular weights at low conversion, i.e., 20% conversion, suggests that mercaptan terminates less than half of the polymer chains formed, since the average degree of polymerization calculated from mercaptan consumption data is about twice that indicated by viscosity measurements. Accurate comparisons of this type at very low conversions to obtain quantitative information about the extent of mercaptan termination are precluded in this system by the anomalous behavior of the polymerization and mercaptan chain transfer reaction rate in this region.

The nonmercaptan termination operating during the main course of reaction appears to arise from at least two sources as indicated by investigation of the effect of recipe constituents on the intrinsic viscosity–conversion curve. The nature of the emulsifier and the concentration of the activator have both been found to affect the viscosity–conversion curve (Fig. 5*A*) in such a way as to

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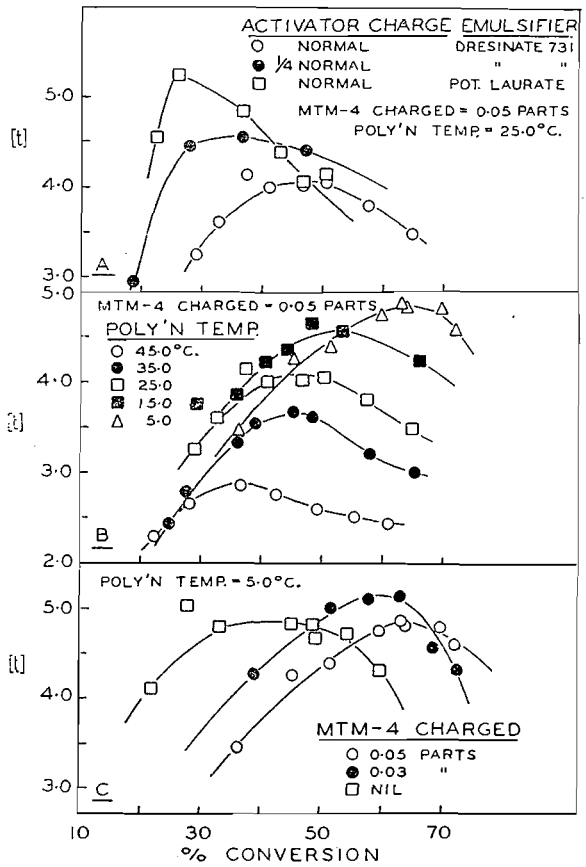



FIG. 5. The effect of polymerization variables on the viscosity–conversion relationship.

indicate clearly that they are responsible for considerable termination in the system. A reduction of the amount of this termination by changing the emulsifier and by reducing the concentration of activator has resulted in lower gel points in a manner analogous to the effect of reduced mercaptan concentration.

The emulsifier probably terminates by a chain transfer mechanism similar to the reaction of mercaptan. The chemical nature of the emulsifier and the fact that polymerization proceeds at a fast rate support this suggestion. If the emulsifier were merely terminating without simultaneously initiating, it would drastically lower the free radical concentration, hence the rate of polymerization.

It is conceivable that some constituent of the activator could act as a chain transfer agent, but it is much more likely that the activator affects the polymer molecular weight by its effect on the free radical concentration in the polymerizing system, i.e., through influencing mutual termination. A lowering of the free radical concentration in the system, such as that produced by a decrease in the activator charge, should reduce the rate of mutual termination relative to the

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rate of polymerization since the former depends on $[R^{\bullet}]^2$ whereas the latter is dependent on $[R^{\bullet}]$.

The difference of only 1 kcal. per mole between the activation energies of the processes that are rate controlling for mercaptan chain transfer and mutual termination explains the greater extent of mutual termination in this system than in the persulphate-initiated system. The two termination reactions are allowed to compete on a practically equal basis, and there will always be a relatively large proportion of mutual termination in this system, even in the presence of larger amounts of mercaptan. This makes the calculation of primary molecular weights of redox-produced polymer from mercaptan consumption data a doubtful procedure under the usual conditions of mercaptan concentration.

*The Cross-linking Reaction*

Further investigation of the viscosity–conversion relationship of polymer produced in this system has given qualitative information about the cross-linking reaction. Since gelation occurs when there is, on the average, one cross-link per primary chain (20), the gel point depends on the number of primary chains, hence on the average primary chain length, as well as on the total number of cross-links in a system. In considering gel point data it is important to distinguish between effects arising from variation of the amount of cross-linking and effects arising from variation of the primary chain length. The intrinsic viscosity of the polymer before and at the gel point is helpful in drawing this distinction.

The viscosity characteristics of the polymer formed in this investigation have been found to be markedly affected by polymerization temperature, as illustrated in Fig. 5*B*. Low temperatures allow the production of soluble polymer up to higher conversions where the kinetics of the termination reactions result in higher primary molecular weights. Below the gel points the relatively small differences in polymer viscosities at the same conversion suggest that the size of the primary polymer chains is comparable for the different polymerization temperatures. This primary polymer chain length is not completely controlled in these polymerizations since both the mutual termination and mercaptan chain transfer reactions are temperature sensitive. In any case a comparison of the viscosities gives only an approximate indication of the relative primary chain lengths, since varying amounts of branching and cross-linking are present in the different polymers, especially close to the gel point.

When the gel point is raised by using a larger amount of chain transfer agent instead of a decrease of temperature, much shorter polymer chains are formed at the same conversion, as indicated by the polymer viscosities below the gel point presented in Fig. 5*C*. The reduction in chain length produced by the additional chain transfer agent is usually sufficient to counteract the effect of increased conversion on the chain length, with the result that the peak of the viscosity–conversion curve is usually lower in spite of the fact that it occurs at higher conversions.

This contrast between the effect of polymerization temperature and concentration of a chain transfer agent is evidence that the reduction in gelation achieved by lowering temperature is a result of a reduction in the amount of cross-linking

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and not a result of a decrease in polymer chain length. The fact that this is a temperature effect on the amount of cross-linking suggests that the rate of cross-linking relative to the rate of propagation is decreased with lowering temperature, i.e., the cross-linking reaction has a higher activation energy than the propagation reaction. Morton and Salatiello have observed a similar dependence of gel point on polymerization temperature in the polymerization of butadiene in a Mutual recipe system (17). The quantitative treatment applied by these workers cannot be extended to this redox system because of a mixed nature of the terminating processes operating.

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# HYDROXYLATION AND EPOXIDATION OF RAPESEED OIL DERIVATIVES WITH SUBSEQUENT PYROLYSIS AND AMMONOLYSIS[1]

By O. L. Mageli,[2] E. W. Patteson,[3] and E. Y. Spencer[4]

ABSTRACT

A method was developed to follow the hydroxylation of rapeseed oil and erucic acid derivatives with peracetic acid. Peracetic acid prepared *in situ* was found to be equally as effective as the preformed acid in hydroxylation of methyl erucate. Among the compounds synthesized were ethyl 13,14-dihydroxybehenate, methyl 13,14-oxidoerucate, ethyl 13,14-diacetoxybehenate, and methyl 13,14(14,13)-hydroxyacetoxybehenate which were subsequently pyrolyzed at approximately 300° C. with *p*-toluenesulphonic acid as catalyst. The first compound yielded mainly the corresponding ketone with a small amount of the oxido derivative, the chief product of the second compound was also the ketone with some unsaturated material, the third compound yielded 43% of the diene, while the last one yielded 60%. Ammonolysis of the oxido compound or the bromohydrin to yield the corresponding aminohydroxy derivative under pressure with liquid ammonia and ammonium bromide was unsuccessful. A new compound oxidoerucamide, m.p. 101.5°, was synthesized.

## INTRODUCTION

The semidrying oil from rapeseed has a high proportion of mono-unsaturated fatty acids and is particularly rich in the glyceride containing the $C_{22}$ fatty acid, erucic acid (22). It appeared, therefore, of interest to study the acids of this oil, and especially erucic acid, to increase their unsaturation or form amino derivatives through the intermediate steps of hydroxylation and epoxidation.

A number of reagents have been used to hydroxylate unsaturated fatty acids. Organic peracids are particularly efficient. Of these performic and peracetic acid are the most useful and offer a number of advantages (19). The use of peracetic acid also allows the isolation of the epoxy or oxirane derivatives of the unsaturated acids (7). Advantage was taken of this to prepare oxidoerucic acid as an intermediate in ammonolysis investigation. The use of both *in situ* and preformed peracids was examined. The preparation of preformed acids is lengthy and loss of active oxygen occurs on storage so that preparation *in situ* was usually employed.

Owing to the variation in time for peracid oxidations to proceed to completion, the rate of peracetic acid oxidation of methyl erucate with and without catalyst was studied. Earlier attempts in this laboratory (13) to follow the hydroxylation by means of iodine numbers using Wijs solution were unsuccessful owing to the difficulty of obtaining representative samples from the heterogeneous reaction mixture and the insolubility of more completely

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hydroxylated material in the Wijs solution. Attempts to determine residual peroxide with ceric sulphate (17) were finally abandoned when it was shown that the rate of decomposition of the peroxide was nonlinear (13). The rate of hydroxylation was finally studied by destruction of unreacted peroxide and peracid with zinc dust and determining the residual unsaturation by employing a modified Rosenmund–Kuhnhenn iodine reagent (2) to overcome the insolubility problem.

Peracid oxidation of unsaturated vegetable oils does not appear to go to completion (18) by contrast with the oxidation of isolated single fatty acid esters. Performic acid oxidation of rapeseed oil triglycerides according to a modified procedure of Greenspan (9) was therefore investigated to determine whether some polymerization occurs during the hydroxylation.

Since the use of peracetic acid allows the production of glycols, oxido compounds, mono and diesterified glycols, pyrolysis of these would indicate the possibility of producing ketones or introducing conjugated diene systems. Crowder and Elm (4) found that pyrolysis of both hydroxyacyloxy and diacyloxy stearic acid as well as the epoxy compound yielded varying amounts of the conjugated diene. This is in agreement with others (14).

With the production of oxidoerucic acid, the possible introduction of an amino group at the center of a $C_{22}$ chain by ammonolysis appeared of interest. Although ethylene and propylene oxide react readily with ammonia, very little work has apparently been done on the epoxides of unsaturated fatty acids. One reaction to introduce nitrogen at the position formerly occupied by the double bond was carried out by Bauer and Bähr (1) by reacting oxidoerucic acid with hydrazine hydrate in a bomb. However no further work along this line has been reported.* The lack of literature, of course, may be due to the relatively unreactive nature of this oxido compound as was demonstrated in this laboratory.

## METHODS AND MATERIALS

The rapeseed oil was that obtained by expeller expression. Initially erucic acid was isolated essentially by the method of Dorée and Pepper (5). Later the methyl esters of rapeseed oil were prepared by the method of Hilditch (11) and methyl erucate separated by fractional distillation in a Podbielniak column at 244° C., 10 mm.

### *Performic Acid Oxidation*

Performic acid was prepared *in situ* and both 30% and 90% hydrogen peroxide were employed. The method of performic acid oxidation was essentially that of Greenspan (9). In the preparation of large batches of hydroxylated rapeseed oil acids for the isolation of dihydroxybehenic acid by fractional crystallization, the following method was used: 200 gm. of rapeseed oil acids were added to 600 ml. of 90% formic acid in a three-necked flask. To

**Since the preparation of the original draft of the manuscript a paper has been cited by G. W. Pigulevskii and I. L. Kuranova in Doklady Akad. Nauk. S.S.S.R. 82: 601. 1952, in which the authors outline the synthesis of an aminohydroxy compound derived by the treatment of epoxyoleic acid with aqueous ammonia for 12 hr. at 130° C.*

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100 ml. of formic acid were added hydrogen peroxide in 5% excess and enough concentrated sulphuric acid to give a final sulphuric acid content of 1% by weight. The performic acid mixture was then added rapidly to the vigorously-stirred mixture of fatty acids and formic acid. The temperature was maintained at 40° C. for three and one-half hours. Cooling was necessary initially. The hydroxylated fatty acids were separated by addition of water and filtering. To complete the hydrolysis of the formoxy ester and yield the dihydroxy compound, the mixture was heated with *N* sodium hydroxide. After neutralization and washing, 13,14-dihydroxybehenic acid was crystallized several times from dioxane. Normally the lower melting isomer (m.p. 101° C.) was isolated. However in one instance when 5*N* sodium hydroxide was used for hydrolysis, the higher melting hydroxylated acid (m.p. 132–3° C.) was isolated. This was not investigated further in this work.

*Peracetic Acid Oxidation*

Preformed peracetic acid was used for the oxidation of fatty acids and their esters when it was desired to isolate the epoxy derivatives. The peracetic acid solution was prepared by the method of Swern, Findley, and Scanlan (21).

Oxidations with peracetic acid prepared *in situ* were carried out according to the method of Swern *et al.* (20). The amount of hydrogen peroxide employed was calculated on the basis of 1.2 moles per mole of unsaturation. Glacial acetic acid and hydrogen peroxide were used in the ratio of 20:1.

Contrary to the statements of Greenspan (9) and Swern *et al.* (21) to the effect that the hydroxyacetoxy compounds could be isolated in high yields using this procedure, the chief product isolated was identified as the dihydroxy compound both by melting point and hydroxyl value.

The method of Greenspan and MacKellar was used to standardize peracetic acid solution in the presence of hydrogen peroxide using ceric sulphate (10).

The rate of peracetic acid hydroxylation was determined by removing quantitatively a 2 ml. sample of the rapidly-stirred reaction mixture from a three-necked flask maintained at constant temperature. The sample was then transferred to a 15 ml. centrifuge tube containing 10 ml. of dioxane. Two to three grams of zinc dust were added, the tube corked, shaken thoroughly, and allowed to stand for one hour with intermittent shaking. The mixture was then centrifuged and a 2 ml. sample was removed from the supernatant liquid for an iodine number determination by the modified Rosenmund–Kuhnhenn method (2).

Epoxy oxygen was determined by the method of Findley *et al.* (6) based on the quantitative consumption of hydrogen chloride required to open the oxirane ring.

Hydroxyl values were estimated by the acetic anhydride – pyridine method of Ogg *et al.* (15).

Carbonyl oxygen was determined by the potentiometric method of Knight and Swern (12) using hydroxylamine. Rinsing down the flask with water toward the end of the titration, as suggested, altered the pH considerably.

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The use of aldehyde-free ethanol was found to be more suitable. The hydroxylamine reagent when prepared with aldehyde-free ethanol and stored in the refrigerator was stable up to four days and thus its daily preparation was not necessary.

Unsaturation was originally determined by the Wijs iodine–chloride method. However, it was later replaced by the Rosenmund–Kuhnhenn method as modified by Benham and Klee (2). By the use of mercuric acetate catalyst complete addition to conjugated systems was obtained.

Conjugated dienes were also determined by ultraviolet absorption (3) using a Beckman model DU spectrophotometer. A correction was made for the higher molecular weight material.

*Pyrolysis*

(*a*) *Vertical column method.*—The column of Pyrex glass tubing was 1 in. by 20 in. and jacketed to maintain temperatures between 100° C. and 300° C. Originally the column was filled with Berl saddles coated with the catalyst, sodium bisulphate, or *p*-toluenesulphonic acid. Later the latter catalyst was dissolved in the starting material. The system was maintained at 7 mm. and volatile products were collected in a dry-ice trap.

(*b*) *Batch method.*—The process was similar to that of Crowder and Elm (4). The system was maintained at a reduced pressure and the 250 ml. reaction flask was plunged into a Wood's metal bath at 280°–285° C. After seven to eight minutes the flask was removed from the bath and allowed to cool.

For molecular weight determinations the cryoscopic method of Gay (8) was used. Cyclohexane was purified by shaking with concentrated sulphuric acid and recrystallized four or five times to a freezing point depression constant of 21.3. Reagent grade naphthalene and a Beckmann thermometer were employed in determining the constant.

The ammonolysis investigations were carried out in an Aminco hydrogenator bomb. Nitrogen was determined by a micro-Kjeldahl method.

## RESULTS AND DISCUSSION

The rate of oxidation of methyl erucate with peracetic acid prepared *in situ* and with varying concentrations of sulphuric acid as catalyst was readily followed by the method outlined and is shown in Fig. 1.

Rapeseed oil was hydroxylated with performic acid, then saponified and esterified with ethanol. The esters were then fractionally distilled. The mean molecular weight of each fraction was determined and included in Table I. The higher molecular weights indicated that some polymerization had occurred. The hydroxyl value of the polymeric residue was very low, about one-tenth of the theoretical value for the completely hydroxylated rapeseed oil triglycerides. Therefore, the molecular weight of the residual material was not accounted for by unsaponified hydroxylated erucin.

Through the intermediate of the reaction of peracetic acid on methyl and ethyl erucate the following compounds were synthesized: methyl 13,14-oxido-

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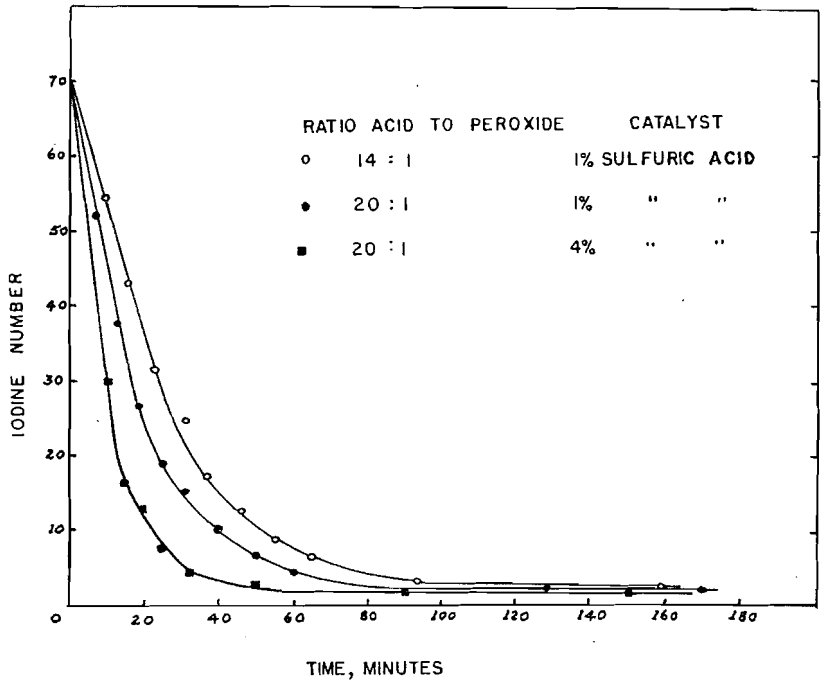



FIG. I

TABLE I

MOLECULAR WEIGHT DETERMINATIONS ON HIGH-VACUUM DISTILLATES AND RESIDUES FROM RAPESEED OIL HYDROXYLATION

| Material | Fraction | Mean mol. wt. | Pressure, mm. Hg $\times 10^{-2}$ | Temp. range, ° C. |
|---|---|---|---|---|
| Rapeseed oil after hydroxylation and methyl esterification | 1* | 92 | 48–50 | 150–155 |
| | 2 | 76 | 29 | 175–180 |
| | 3 | 361 | 27 | 210–215 |
| | 4 | 366 | 29 | 225–235 |
| | Residue | 1116 | | |
| Residue from a similar run only at lower vacuum | Residue after using lower vacuum | 1263 | 1.5–2.0 | 230<br>Hydroxyl value 1.4%<br>Theoret. hydroxyl value 14.2% based on iodine No. Sap. equiv. 281. |

**The residue was about 40%. The main portions of the distillate were in fractions No. 3 and No. 4, 20–25% each.*

erucate, methyl and ethyl 13,14-diacetoxybehenate, methyl 13,14(14,13)-hydroxyacetoxybehenate, and ethyl 13,14-dihydroxybehenate. These were subjected to pyrolysis by both a continuous and batch method in the presence of a catalyst as outlined under Methods. The results are summarized in Table II.

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TABLE II

PYROLYSIS OF HYDROXYLATED DERIVATIVES OF ERUCIC ESTERS

| Starting material | Method* | Temp., °C. | Catalyst,** % | Product |
|---|---|---|---|---|
| Ethyl 13,14-dihydroxybehenate | *C* | 205–210 | *** | Epoxy O 0.49% (11.7% oxido compds.)<br>Carbonyl O 3.0% (71.7% ketones)<br>Dienes 1.87% |
| | *B* | 215–230 | 0.2 | Largely ethyl 13-ketobehenate |
| Ethyl 13,14-diacetoxybehenate | *C* | 290 | 0.2 | Iodine No. 1.3 (theoret. 138.7 for complete conversion to diene) |
| | *B* | 340–360 | 0.1 | Iodine No. 60.3 |
| Methyl 13,14-oxidoerucate | *B* | 290–305 | 0.2 | Epoxy O 0.28% (Starting material 4.04%)<br>Iodine No. 17.6<br>Carbonyl O 2.03% (48% ketones) |
| Methyl 13,14-hydroxyacetoxybehenate | *B* | 330–370 | 0.2 | Conjugated diene 60.5%<br>Carbonyl O 0.81% (19% ketones) |

**B—batch pyrolysis.*
*C—column pyrolysis.*
***p-Toluenesulphonic acid.*
****Berl saddles coated with sodium bisulphate instead of p-toluenesulphonic acid.*

Pyrolysis of both dihydroxy and epoxy derivatives appeared to yield largely ketonic material with no significant amount of conjugated diene. The diacetoxy derivative yielded some diene while the hydroxyacetoxy derivative on pyrolysis yielded as much as 60% diene, the chief by-product was still the ketone. This is largely in agreement with the results of Crowder and Elm (4), except that they obtained some unsaturation on pyrolysis of the epoxy derivative. The batch method with *p*-toluenesulphonic acid as catalyst was found to give more favorable yields of desired products than the continuous method. This was probably due in part to the higher temperature of the batch process.

The attempt to produce 13,14(14,13)-hydroxyamino derivatives either by ammonolysis of oxido or bromohydrin derivatives was unsuccessful. Treatment of epoxide ethyl esters of rapeseed oil with concentrated aqueous ammonia at 60° C. for 24 hr. largely resulted in the production of the ammonium salt of the epoxy acids. Using liquid ammonia in a bomb at 75° C. for three and one-half hours and ammonium chloride as a possible catalyst resulted in recovery of largely unchanged starting material. More strenuous conditions at 165° for five and one-half hours yielded largely polymerized material. When benzene was used as an inert solvent at this higher temperature, only unchanged material was recovered. The use of a new derivative, oxidoerucamide, at the same temperatures also did not yield the desired product. Treatment of the bromohydrin of methyl erucate with liquid ammonia at 150° for six hours also yielded a polymer and a test for bromide.

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Apparently the oxido derivative of the compounds investigated is relatively inert to ammonolysis under mild conditions, with liquid or aqueous ammonia. Under more severe reaction conditions with liquid ammonia the ring is evidently broken with the resultant loss in epoxy oxygen but polymerization follows without the production of the aminohydroxy derivative.

Oxidoerucamide was prepared by peracetic acid oxidation of erucamide, essentially according to the procedure of Roe *et al.* (16) for the epoxidation of oleamide. After several recrystallizations from ethanol a 65% yield of pure product was obtained, m.p. 101.5°. Analysis—N 3.90%, theoretical 3.96%; epoxy oxygen 4.50%, theoretical 4.53%. The product was also obtained by treatment of ethyl oxidoerucate with liquid ammonia.

## ACKNOWLEDGMENTS

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# FREE RADICALS BY MASS SPECTROMETRY

## III. RADICALS IN THE THERMAL DECOMPOSITION OF SOME BENZENE DERIVATIVES[1]

By K. U. Ingold[2] and F. P. Lossing[3]

ABSTRACT

The following benzene derivatives have been pyrolyzed in a free radical mass spectrometer: benzene, toluene, benzaldehyde, anisole, diphenyl, phenyl ether, and benzyl ether. The products and intermediates were analyzed, particular attention being paid to the formation (and stability) of any aromatic free radicals found. The phenyl, benzyl, phenoxy, and benzoyl radicals, as well as atomic carbon, were detected. The first two could be obtained abundantly and are fairly stable below 1150°. The oxygenated radicals were much less abundant and appeared to be less stable.

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## INTRODUCTION

The use of modified mass spectrometers for the detection and identification of free radicals formed by thermal dissociation has been described by various authors (3, 8, 14, 15, 19). However, the method has been applied only to light radicals such as methylene, methyl, and ethyl. It was thought to be of interest to try to extend the method to the study of heavier radicals such as phenyl and benzyl.

Evidence for the existence of the phenyl radical was first obtained in 1933 by Dull and Simons (2) from the thermal decomposition of tetraphenyl lead and the subsequent reaction of the phenyl radical with mercury. The radical has also been produced by the photochemical decomposition of tetraphenyl lead (13). In 1934 Horn and Polanyi (9) produced the phenyl radical by the diffusion flame method; it was detected by reaction with iodine. However, Paneth and Lautsch (17) who repeated this work did not detect any free radicals.

In view of the conflicting opinions about the phenyl radical, Glazebrook and Pearson (6) studied the radicals produced in the photolysis of aromatic ketones with the aid of tellurium mirrors. In the absence of tellurium, the photolysis of acetophenone gave some evidence for the presence of diphenyl, benzil, and dibenzoyl ethane. In the presence of tellurium, $Ph_2Te$, $Me_2Te$, and PhMeTe were identified, the ketone molecule having split into phenyl and methyl radicals which then reacted with the tellurium. The occurrence of benzil suggests the intermediate formation of the benzoyl radical ($C_6H_5CO$) which can dissociate to a phenyl radical and carbon monoxide. The photolysis of benzophenone also yields active fragments, and it can be argued by analogy that it undergoes simple fission like acetophenone.

The radical has also been detected in solution both by the decomposition

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of benzene diazonium chloride (28) and by the action of copper bronze on phenyl iodide (18).

In 1949 Schüler and Reinebeck (20) decomposed a number of benzene derivatives by electron impact into both excited and unexcited radicals. Both identical (i.e. radical) and characteristic emission spectra were observed. The phenyl radical was found in benzene and a number of monosubstituted benzenes, including toluene. The benzoyl radical was detected in acetophenone and benzophenone, and some evidence for the existence of radicals in benzaldehyde was obtained from the absorption spectra. No radicals were detected in anisole.

The benzyl radical ($C_6H_5CH_2$) was first prepared by Paneth and Lautsch (17) in 1935 by decomposing tetrabenzyl tin, dibenzyl ketone, and also by the reaction of benzyl chloride with sodium vapor. It has also been found in the thermal decomposition of toluene by mirror techniques (7) and by the formation of dibenzyl (24). The benzyl radical has also been produced in the decomposition of some substituted toluenes (1, 12, 16, 25, 27) and by the production of free radicals in the presence of toluene (26).

## EXPERIMENTAL

A description of the free radical mass spectrometer used in this work has been given in previous papers (14, 15). The compound to be studied was carried, at a partial pressure of a few microns of mercury, through the tubular quartz reactor in a stream of helium at total pressures of a few millimeters. Since the compounds with two aromatic nuclei had very low vapor pressures, the mixture of helium and the compound was made by passing the helium through a trap containing the compound at a suitable temperature. Since the lines to the mass spectrometer were not heated, this temperature had to be below room temperature. Even by this method it was not possible to pick up enough benzophenone or benzil to permit the study of their decompositions, and the maximum partial pressure of benzyl ether which could be obtained was quite low. In order to reduce condensation of the reactants on the water-cooled wall of the reactor, it was necessary to preheat the cooling water above room temperature.

The detection of the radicals was made, using 50 volt electrons, by subtraction of the spectra of any compounds of higher molecular weight which were found to be present in significant amounts. To give greater precision, these spectra were obtained at temperatures just below the decomposition temperatures of the reactants. Attempts to detect phenyl and benzyl at low electron energies by the method of Eltenton (3) gave negative results. This was surprising and can only be explained by a very low ionization cross section for these radicals at the low electron energies required to eliminate the mass 77 and 91 peaks from the spectra of the parent compounds. In the absence of confirmation of the presence of the radicals by the low electron energy method, it was of great importance to ensure that peaks of mass 77 and 91 were due to ionized phenyl and benzyl and not produced by electron

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impact from some substance of higher molecular weight. Fortunately, the dimeric forms such as diphenyl and dibenzyl were present only in trace amounts, and in the spectra of these the parent molecular ion is many times more abundant than the fragments at mass 77 and 91. It has been assumed that what remains of the parent radical peak after subtraction of the contributions from all known products of higher molecular weight can be attributed to the radical itself. It might be noted that in the most unfavorable cases the contribution to the radical peak from substances of higher molecular weight is never more than 90–95%. In more favorable cases, it may be as low as 50%. There still remains a rather remote possibility that at least a portion of these radical peaks could be due to some unsuspected molecular species in whose spectrum the 77 and 91 peaks are by far the most abundant, and for which the parent molecular ion is practically absent.

*Material for Pyrolysis*

The benzene used was Nichols Reagent Grade, the toluene was Phillips' Research Grade. The benzaldehyde, anisole, and diphenyl were supplied by the Matheson Co. The phenyl ether used was obtained from Dr. Theodor Schuchardt G.m.b.H. Gorlitz, and the benzyl ether was obtained from the Eastman Kodak Co.

## RESULTS

The thermal decomposition of benzene, toluene, benzaldehyde, anisole, diphenyl, phenyl ether, and benzyl ether were studied. The phenyl, benzyl, phenoxy ($C_6H_5O$), and benzoyl radicals were identified in these decompositions, and in two cases methyl radicals were found. Without considerable modification of the present apparatus, it was found to be impossible to measure the sensitivity of the instrument to these radicals by the method used for methyl (15), owing to the large number of products formed, and to the difficulty of preventing the heavier products and reactants from condensing or adsorbing in the cooler parts of the reactor. In the absence of any such relationship, the sensitivities of the radicals were assumed to be all the same with 50 volt electrons and to be equal to two-thirds the sensitivity of benzene. This assumption is not likely to be in error by more than a factor of two, if one can use the case of methyl and methane as an analogy (15). For other materials whose sensitivities were not measured the same assumed sensitivity was used; in the tables the use of this value is indicated by an asterisk. For carbon, the sensitivity value is purely arbitrary, and the pressures given in the tables are useful only as a rough guide to the relative amounts of carbon formed at different temperatures.

*Benzene*

The products found in the pyrolysis of benzene at three temperatures are given in Table I. A fairly large proportion of the reaction appears to go directly to carbon and hydrogen. Only a trace of the phenyl radical was found. Of the other products, acetylene was the most abundant.

*Toluene*

Benzyl radicals were found in abundance in the pyrolysis of toluene, as

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TABLE I

DECOMPOSITION PRODUCTS OF BENZENE (He PRESSURE = 7.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

| Products | 1350° C. | 1400° C. | 1450° C. |
|---|---|---|---|
| Hydrogen | 2.68 | 3.62 | 4.96 |
| Carbon* | 0.05 | 0.10 | 0.23 |
| Methane | 0.01 | 0.03 | 0.06 |
| Acetylene | 0.09 | 0.06 | 0.01 |
| Ethylene | 0.01 | 0.02 | 0.03 |
| Butadiyne | 0.02 | — | — |
| Phenyl* | — | 0.01 | 0.01 |
| Initial benzene | 4.34 | 4.34 | 4.34 |
| Remaining benzene | 3.30 | 2.82 | 2.12 |

**Denotes use of assumed sensitivity as described in text.*

shown in Table II. Methyl and a trace of phenyl radicals were also present at the two lower temperatures. Acetylene and butadiyne were the most important hydrocarbon fragments. It should be noted that since tolyl radicals are isomeric with benzyl radicals, the possibility that the radicals of mass 91 are tolyl radicals cannot be ruled out.

TABLE II

DECOMPOSITION PRODUCTS OF TOLUENE (He PRESSURE = 7.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

| Products | 1150° C. | 1225° C. | 1300° C. |
|---|---|---|---|
| Hydrogen | 1.77 | 4.40 | 8.02 |
| Carbon* | 0.04 | 0.08 | 0.15 |
| Methyl | 0.05 | 0.06 | — |
| Methane | 0.07 | 0.13 | 0.11 |
| Acetylene | 0.11 | 0.48 | 1.06 |
| Ethylene | 0.11 | 0.16 | 0.13 |
| Ethane | 0.01 | 0.03 | 0.03 |
| Butadiyne | 0.11 | 0.50 | 0.79 |
| Phenyl* | 0.01 | 0.01 | — |
| Benzyl* | 0.27 | 0.14 | 0.02 |
| Benzene | 0.16 | 0.26 | 0.25 |
| Diphenyl* | Trace | Trace | Trace |
| Dibenzyl* | Trace | Trace | Trace |
| Initial toluene | 2.5 | 2.5 | 2.5 |
| Remaining toluene | 1.6 | 0.8 | 0.19 |

**Denotes use of assumed sensitivity as described in text.*

*Benzaldehyde*

The major products from the decomposition of benzaldehyde at 1100° and 1400° C. were hydrogen, carbon monoxide, and benzene. Other products were carbon, methane, acetylene, ethylene, formaldehyde, butadiyne, and diphenyl. There is some evidence for the formation of acrolein and 1,5-hexadiyne-3-ene. Phenyl radicals and a trace of benzoyl radicals were detected.

Carbon monoxide was evolved from the furnace at high temperatures even

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after the benzaldehyde flow had been stopped, indicating that some polymerization had also occured. This effect persisted after the experiments with benzaldehyde were completed, and at high temperatures interfered with the measurement of the 28 peak in the subsequent compounds (see note in Table V).

*Anisole*

Anisole was pyrolyzed at 800° and above; the products at 800° are listed in Table III. A trace of benzyl alcohol and diphenyl were also found. Phenyl and methyl radicals were abundant, the phenoxy radical was also present in small amounts.

TABLE III

DECOMPOSITION PRODUCTS OF ANISOLE (He PRESSURE = 2.8 MM.)
PARTIAL PRESSURES IN MICRONS Hg

| Products | 800° C. | Products | 800° C. |
|---|---|---|---|
| Hydrogen | 0.30 | Phenyl* | 0.05 |
| Methyl | 0.06 | Phenoxy* | 0.01 |
| Methane | 0.11 | Phenol* | 0.09 |
| Ethylene | 0.03 | Benzene | 0.28 |
| Ethane | 0.02 | Toluene | 0.03 |
| Carbon monoxide | 0.37 | | |
| Formaldehyde | 0.04 | Initial anisole* | 0.61 |
| Butadiyne | 0.02 | Remaining anisole* | 0.24 |

**Denotes use of assumed sensitivity as described in text.*

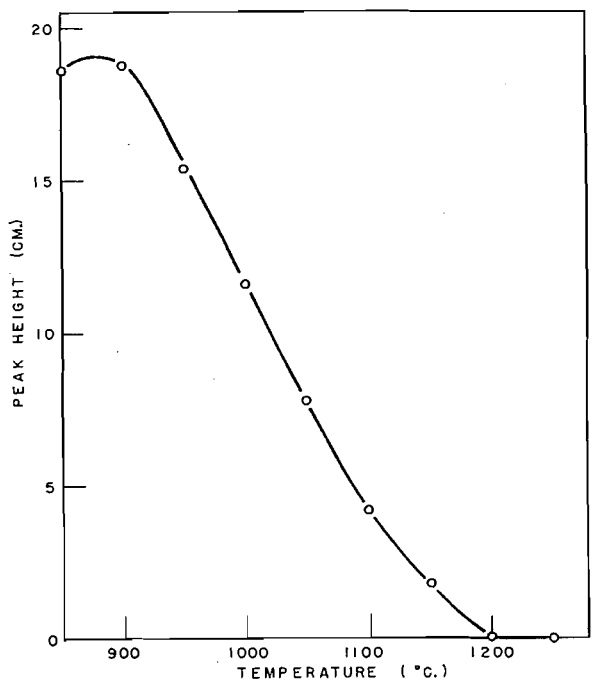



FIG. 1. The thermal decay of phenyl radicals produced from anisole.

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The phenyl radical concentration decreased with increase of temperature (Fig. 1), being completely absent at 1200° and above.

*Diphenyl*

Diphenyl was decomposed from 1300° to 1500°C. At these high temperatures only a trace of phenyl was observable. Other products detected included hydrogen, carbon, acetylene, ethylene, butadiyne, and benzene.

*Phenyl Ether*

The major products of the decomposition of phenyl ether at four different temperatures are given in Table IV. Other products with the following masses were detected:

118, possibly vinylphenyl ether,
76, possibly 1,5-hexadiyne-3-ene,
66, possibly 1-hydroxybutadiyne.

Traces of the phenoxy radical and phenol were also detected.

TABLE IV

DECOMPOSITION PRODUCTS OF PHENYL ETHER (He PRESSURE = 8.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

| Products | 970° C. | 1040° C. | 1130° C. | 1175° C. |
|---|---|---|---|---|
| Hydrogen | 1.08 | 1.96 | 2.84 | 2.68 |
| Carbon* | 0.01 | 0.04 | 0.05 | 0.08 |
| Methane | — | 0.02 | 0.03 | 0.03 |
| Acetylene | 0.03 | 0.22 | 1.03 | 1.19 |
| Ethylene | 0.05 | 0.15 | 0.08 | 0.12 |
| Carbon monoxide | 0.44 | 1.24 | 1.28 | 1.39 |
| Butadiyne | 0.07 | 0.06 | 0.17 | 0.29 |
| Phenyl* | 0.03 | 0.10 | 0.08 | 0.07 |
| Benzene | 0.28 | 0.54 | 0.56 | 0.47 |
| Diphenyl* | 0.02 | 0.02 | 0.03 | 0.03 |
| Initial $(C_6H_5)_2O$* | 0.93 | 0.93 | 0.93 | 0.93 |
| Remaining $(C_6H_5)_2O$* | 0.42 | 0.11 | 0.03 | 0.02 |

**Denotes use of assumed sensitivity as described in text.*

*Benzyl Ether*

The decomposition products of benzyl ether at three different temperatures are given in Table V. In addition to the products listed some acetylene and benzyl alcohol were detected. There appeared to be little or no toluene present. Both benzoyl and phenyl radicals were present in small quantities, but free benzyl was abundant, being present in this compound in a larger ratio to the other products than in the decomposition of toluene. This is probably due to the fact that this compound can be decomposed at a much lower temperature where the benzyl radical is fairly stable. It should be noted that, at the highest temperature studied, viz. 1290° C., the amount of benzyl present shows a marked decrease.

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TABLE V

DECOMPOSITION PRODUCTS OF BENZYL ETHER (He PRESSURE = 8.0 MM.)
PARTIAL PRESSURES IN MICRONS Hg

| Products | 860° C. | 1050° C. | 1290° C. |
|---|---|---|---|
| Hydrogen | 0.10 | 0.25 | 0.54 |
| Methane | — | 0.01 | 0.02 |
| Ethylene | 0.01 | 0.03 | 0.02 |
| Carbon monoxide | 0.02 | 0.10 | See note |
| Formaldehyde | — | 0.02 | 0.04 |
| Butadiyne | 0.01 | 0.01 | 0.01 |
| Phenyl* | 0.005 | 0.005 | 0.004 |
| Benzyl* | 0.05 | 0.05 | 0.01 |
| Benzene | 0.01 | 0.03 | 0.03 |
| Benzoyl* | 0.004 | 0.01 | 0.002 |
| Benzaldehyde* | 0.03 | 0.03 | — |
| Dibenzyl | Trace | Trace | Trace |
| Initial $(C_6H_5.CH_2)_2O$* | 0.078 | 0.078 | 0.078 |
| Remaining $(C_6H_5CH_2)_2O$* | 0.05 | 0.03 | 0.004 |

*Note: As previously described in the text, the carbon monoxide measurement was invalidated by the decomposition of benzaldehyde polymers.*
**Denotes use of assumed sensitivity as described in text.*

## DISCUSSION

*Benzene*

Although the photolysis (11, 29) and mercury photosensitized (4) decomposition of benzene have been fairly thoroughly investigated, there have been very few examinations of the uncatalyzed thermal decomposition, the only one of note being that of Hein and Mesée (7*b*) who, by the use of mercury vapor, were able to detect radicals. The results of their microanalysis gave no clue as to the nature of the organic residue, but they concluded that the mercuriated phenyl groups were partially hydrogenated by the hydrogen set free in the pyrolysis. The present investigation shows that while phenyl radicals are undoubtedly a product they are present in such small amounts that they cannot play any important part in the reaction. The only important process appears to be a direct decomposition to hydrogen and free carbon. Small amounts of butadiyne and some lower hydrocarbons are also formed. The trace of methane which was found is rather surprising; it might arise either by the direct action of hydrogen on the free carbon present in the reactor, or by the breakdown of various unsaturated primary products, being detected only because it is rather more stable than the majority of hydrocarbons.

*Toluene*

The pyrolysis of toluene has been rather more thoroughly investigated than that of benzene. Jost and Müffling (10) found that $Hg(CH_3)_2$ had no effect on the rate of decomposition at 690°, and therefore concluded that the reaction is not a chain process. By the use of mercury vapor, Hein and Mesée (7) isolated mercury dibenzyl from which they concluded that the first step in the decomposition of toluene is the rupture of one of the C–H

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bonds in the methyl group. More recently Szwarc (24) has confirmed this result by the isolation of dibenzyl as a product of the reaction. The only other products reported by Szwarc are hydrogen, methane, and benzene; he suggests the following mechanism for the decomposition of toluene in the temperature range 738° to 864° C.

$$C_6H_5CH_3 \rightarrow C_6H_5.CH_2 + H \quad (1)$$

$$C_6H_5.CH_3 + H \rightarrow C_6H_5.CH_2 + H_2 \quad (2)$$

and

$$C_6H_5.CH_3 + H \rightarrow C_6H_6 + CH_3 \quad (3a)$$

$$C_6H_5.CH_3 + CH_3 \rightarrow CH_4 + C_6H_5.CH_2 \quad (3b)$$

or

$$C_6H_5.CH_3 + H \rightarrow C_6H_5 + CH_4 \quad (4a)$$

$$C_6H_5CH_3 + C_6H_5 \rightarrow C_6H_6 + C_6H_5.CH_2 \quad (4b)$$

$$2\ C_6H_5.CH_2 \rightarrow (C_6H_5.CH_2)_2 \quad (5)$$

Neither ethane nor diphenyl were found, either or both of which might have been expected from the dimerization of the radicals produced in reactions (3*a*) and (4*a*) respectively. In the present experiments which were carried out some 300° to 450° higher, small amounts of both methyl and phenyl radicals were detected, as well as their dimers. Only a trace of dibenzyl was detected at all temperatures, and the benzyl radical, though abundant at the lowest temperatures, was found to decrease markedly with rise of temperature, evidently being unstable above 1150°. A rough value of 68 ± 4 kcal. was obtained for the temperature coefficient of the disappearance of the benzyl radical. The presence of carbon and various unsaturated hydrocarbons, e.g. acetylene and butadiyne, in the products shows that at least some of the benzene nuclei are being broken at this temperature, so this temperature coefficient may correspond to breakdown of the benzyl radical. But, because of the relatively high degree of decomposition with which it is necessary to work in the present method, other alternative reactions which lead to disappearance of the radical, such as disproportionation or hydrogen abstraction from compounds other than toluene, will occur simultaneously. It is therefore not possible to assign this value to any one particular reaction.

The present results are in general agreement with those of Szwarc when it is remembered that they were done at temperatures several hundred degrees higher where some of the benzene nuclei are ruptured, but it also seems possible that at these high temperatures direct breakdown to a phenyl and a methyl radical occurs

$$C_6H_5.CH_3 \rightarrow C_6H_5 + CH_3\,. \quad (6)$$

*Benzaldehyde*

The thermal decomposition of gaseous benzaldehyde has been studied by Smith and Hinshelwood (21) in a static system. The chief products were benzene and carbon monoxide, but some diphenyl was also formed. The reaction was approximately first order and was partially inhibited by nitric oxide. From the results of their inhibition experiments Smith and Hinshelwood concluded that the mechanism of decomposition must involve two kinds of radical, one of which can only propagate the chain after itself decomposing

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to give a smaller radical, and that the chains are broken by recombination of two different kinds of radical. Their proposed mechanism of decomposition is given below.

$$C_6H_5CHO \rightarrow C_6H_5 + CHO \quad (7)$$
$$CHO \rightarrow CO + H \quad (8)$$
$$H + C_6H_5CHO \rightarrow C_6H_6 + CHO \quad (9)$$
$$H + CHO \rightarrow H_2 + CO \quad (10)$$

However, Steacie (23) suggests that reaction (9) is unlikely compared with

$$H + C_6H_5CHO \rightarrow H_2 + C_6H_5CO, \quad (11)$$
$$C_6H_5CO \rightarrow C_6H_5 + CO\,. \quad (12)$$

Although the present experiments were done at a considerably higher temperature, they seem, nevertheless, to be in general agreement with the modified mechanism which replaces reaction (9) by reaction (11) and (12). The benzoyl radical is undoubtedly one of the products, but it is not nearly as plentiful as phenyl and must therefore be rather less stable. Once again at these high temperatures some of the benzene nuclei are broken down to carbon and various unsaturated hydrocarbons.

However, by analogy with toluene it is to be expected that the $C_6H_5C(O)-H$ bond will be much more readily broken than the $C_6H_5$-CHO bond, for the benzoyl radical will be resonance stabilized in the same manner as benzyl. The mechanism given by Smith and Hinshelwood was derived from a comparison with the mechanisms proposed for the decomposition of simple aliphatic aldehydes, e.g. acetaldehyde and propionaldehyde, but it seems doubtful that such mechanisms can be extended to include benzaldehyde. Another possible reaction scheme which covers the experimental data is therefore given.

$$C_6H_5CHO \rightarrow C_6H_5CO + H \quad (13)$$
$$C_6H_5CO \rightarrow C_6H_5 + CO \quad (12)$$
$$C_6H_5 + C_6H_5CHO \rightarrow C_6H_6 + C_6H_5CO \quad (14)$$
$$H + C_6H_5 \rightarrow C_6H_6 \quad (15)$$
$$C_6H_5 + C_6H_5CO \rightarrow C_6H_5COC_5H_5 \quad (16)$$

Reactions (11) and (15) will remove the H atoms formed in the primary step. Diphenyl will be formed by the dimerization of phenyl radicals.

It is quite probable that some of the reaction goes by a direct molecular rearrangement to benzene and carbon monoxide

$$C_6H_5CHO \rightarrow C_6H_6 + CO\,. \quad (17)$$

*Anisole*

The thermal decomposition of anisole from 482° to 707° C. was studied in a flow system by Freĭdlin *et al.* (5). They concluded that the reaction proceeds primarily to phenol with the probable formation of a free alkyl radical, and simultaneously undergoes rearrangement to benzyl alcohol. Some benzene and toluene were also found. In the present investigation methyl, phenyl, and phenoxy radicals were detected. These, by dimerization and hydrogen abstraction, give rise to ethane, methane, diphenyl, and some of the benzene

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and phenol. Toluene comes from the recombination of methyl and phenyl radicals. Several primary steps appear possible.

$$C_6H_5OCH_3 \rightarrow C_6H_6 + CO + H_2 \quad (18)$$
$$C_6H_5OCH_3 \rightarrow C_6H_5 + CH_3O \quad (19)$$
$$C_6H_5OCH_3 \rightarrow C_6H_5O + CH_3 \quad (20)$$

The methoxy radical was not detected and apparently decomposes at these temperatures to formaldehyde and a hydrogen atom. To account for the proportions of the products found would require that about half the phenoxy radicals formed react together, with one ring rupturing and the other forming a phenyl.

$$2\ C_6H_5O \rightarrow C_6H_5. + 2CO + C_4H_5 \quad (21)$$

The $C_4H_5$ could then give rise to carbon, hydrogen, ethylene, and butadiyne. Only a trace of benzyl alcohol was detected, so that at these temperatures it is either much less stable than anisole or, as is more probable, only a small part of the reaction goes by a "carbinol-type" rearrangement.

A plot of the peak height due to the phenyl radical as a function of the temperature is given in Fig. 1. From this curve a temperature coefficient of $39 \pm 3$ kcal. was obtained for the disappearance of the phenyl radical. It is difficult to assign this value to a given reaction since, over this temperature range, hydrogen abstraction (low $E$) and actual breakdown of the phenyl radical (high $E$) are probably in competition.

*Diphenyl*

The decomposition of diphenyl at high temperatures can be represented by:

$$C_6H_5.C_6H_5 \rightarrow 2C_6H_5 \rightarrow H_2 + C + C_2H_2 + C_2H_4 \text{ etc.}, \quad (22)$$
$$C_6H_5 + RH \rightarrow C_6H_6 + R. \quad (23)$$

*Phenyl Ether*

The decomposition of phenyl ether has previously been studied only at low temperatures (22) (440°–490° C.). In the present experiments the stoichiometric relationship above 1100° was found to be

$$C_6H_5.O.C_6H_5 \rightarrow CO + 2H_2 + C_2H_2 + \tfrac{1}{2}C_6H_6 + \text{unsaturated hydrocarbons and carbon.} \quad (24)$$

Below 1100° there is very much less acetylene.

The most important primary step is presumably breakdown to a phenyl and a phenoxy radical, but the presence of vinylphenyl ether in the products shows that one of the rings can break open before the C–O bond is broken. Diphenyl arises from the recombination of two phenyl radicals, and benzene and phenol are formed from phenyl and phenoxy respectively by hydrogen abstraction. At 970° the amount of carbon monoxide formed does not correspond to the amount of phenyl ether decomposed, and much of the oxygen must be present in other compounds such as 1-hydroxybutadiyne and vinylphenyl ether. Above 970° almost all the oxygen appears as carbon monoxide.

A temperature coefficient of $47 \pm 3$ kcal. was obtained for the disappearance of the phenyl radical. As explained for anisole this probably represents a compound value for decomposition and hydrogen abstraction. This value was

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obtained at a higher temperature where more breakdown and less abstraction would be expected, so that a larger temperature coefficient is not altogether unexpected.

*Benzyl Ether*

The primary step in the decomposition of benzyl ether is presumably the breaking of a C–O bond:

$$(C_6H_5CH_2)_2O \rightarrow C_6H_5CH_2 + C_6H_5CH_2O\,. \qquad (25)$$

The $C_6H_5CH_2O$ radical can undergo a number of different reactions, some of which are listed below.

$$C_6H_5CH_2O \rightarrow C_6H_5 + H.CHO \qquad (26)$$
$$C_6H_5CH_2O \rightarrow C_6H_6 + CO + H \qquad (27)$$
$$C_6H_5CH_2O \rightarrow C_6H_5CO + H_2 \qquad (28)$$
$$C_6H_5CH_2O \rightarrow C_6H_5CHO + H \qquad (29)$$

All the products shown (except H atoms) were found. The benzoyl radical might also give benzaldehyde by hydrogen abstraction, or alternatively benzaldehyde might give the radical by loss of a hydrogen atom.

The virtual absence of toluene in the products proves that the direct molecular rearrangement to toluene and benzaldehyde does not occur.

$$(C_6H_5CH_2)_2O \rightarrow C_6H_5CH_3 + C_6H_5CHO \qquad (30)$$

Moreover, it means that the benzyl radical does not readily abstract hydrogen atoms.

To sum up the analytical data given in this paper, it may be noted that hydrogen, carbon, and unsaturated hydrocarbons form a larger proportion of the products as the temperature is increased, and in those compounds which have to be cracked at high temperatures. The phenyl and benzyl radicals can be obtained copiously below about 1150° C.; the best sources were found to be anisole and benzyl ether respectively. The phenoxy and benzoyl radicals appear to be less stable and could not be obtained in large amounts from any of the compounds studied.

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# THE ULTRAVIOLET ABSORPTION SPECTRA OF NITROGUANIDINE DERIVATIVES[1]

By A. F. McKay and C. Sandorfy[2]


## ABSTRACT

The ultraviolet absorption spectra of the ammonia and amine addition products of 1-nitro-2-nitramino-2-imidazoline verify the linear structure *A* for these compounds. Also the ethanol addition product is considered on the basis of

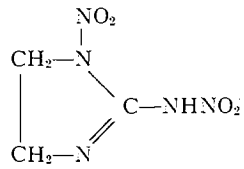
$$NO_2NHCH_2CH_2NH{-}C(=NR){-}NHNO_2$$

*A*

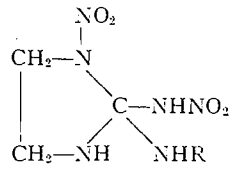
its absorption spectrum to be N-β-nitraminoethyl-N-nitro-*o*-ethylisourea. The relative effects of the nitramino and nitroguanidine chromophores on the absorption spectra of several nitroguanidine derivatives are discussed.


## INTRODUCTION

In 1948 the reaction of 1-nitro-2-nitramino-2-imidazoline with amines was described (6). It was found that one mole equivalent of ammonia, or amines, combined with 1-nitro-2-nitramino-2-imidazoline (I) to give addition products. These addition products were assigned a cyclic structure (II). The only evi-



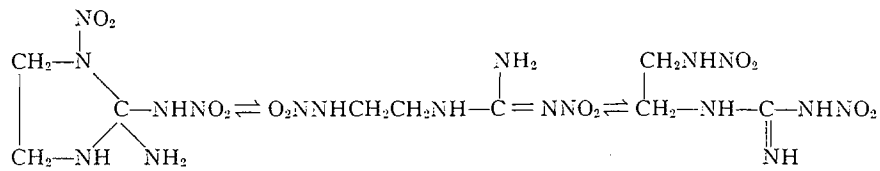
I



II

R = H or alkyl

dence for this structure was that the ammonia addition product gave a low yield (26%) of 1,3-dinitro-2-imidazolidone, on nitration. Later titration data (1) indicated that the ammonia addition product was a monobasic acid which acquired a second acidic function on standing in alkali for 90 hr. On this basis the ammonium addition compound of 1-nitro-2-nitramino-2-imidazoline was represented as an equilibria mixture (III–V) which was considered to be predominantly displaced towards III. Since the ammonia addition



III IV V

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[2] *National Research Council of Canada Postdoctorate Fellow.*

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product of 1-nitro-4-methyl-2-nitramino-2-imidazoline behaved as a bifunctional acid on titration it was assigned a linear structure VI. Finally,

$$NO_2NHCH_2CH(CH_3)NHC(=NH)—NHNO_2$$

VI

potentiometric titration of the *n*-propylamine addition product indicated it possessed one acidic group and it was assigned (2) the cyclic structure, 1-nitro-2-nitramino-2-*n*-propylaminoimidazolidine (II, R = $n-C_3H_7$). More recently (5) it has been shown that both the ammonia addition products of 1-nitro-2-nitramino-2-imidazoline and 1-nitro-4-methyl-2-nitramino-2-imidazoline possess almost identical ultraviolet absorption spectra. Moreover, on the basis of these absorption spectra linear structures V and VI respectively were assigned to these addition products. Now the ultraviolet absorption spectra of several compounds of this series have been determined and the results agree with linear structures for these adducts.

## RESULTS AND DISCUSSION

All of the compounds having a nitroguanidine group displayed two absorption maxima at 205 mμ and 269–271 mμ (cf. Table I and Reference 5). Compounds possessing a primary nitramino group exhibit a maximum at 227–235 mμ (4) with a second increase in absorption beginning at 210 mμ (cf. Curve *A*, Fig. 1). The absorption spectrum of 1-nitro-2-nitramino-2-imidazoline is mainly of the nitroguanidine type (compare Curves *A* and *B* of Fig. 2). The effect of replacing the hydrogen at position 1 by a nitro group has been to double the $E_{max}$ of the absorption maximum at 206 mμ. There has also been an increase in the molar extinction coefficient of the minimum.

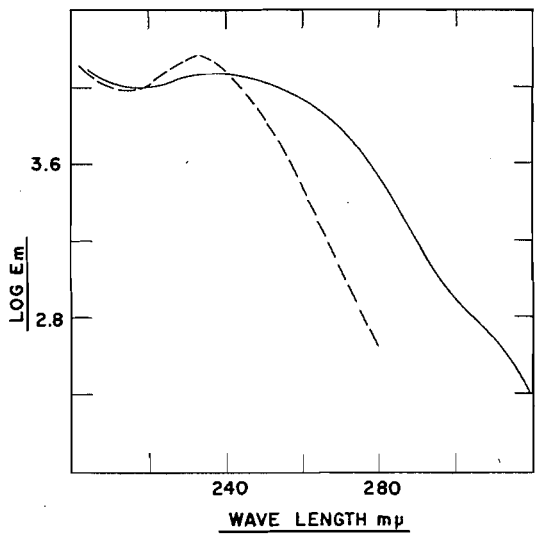



FIG. 1. Curve *A* – – – 1,3-Dinitraminopropane (water).
Curve *B* —— N-β-Nitraminoethyl-N′-nitrourea (water).

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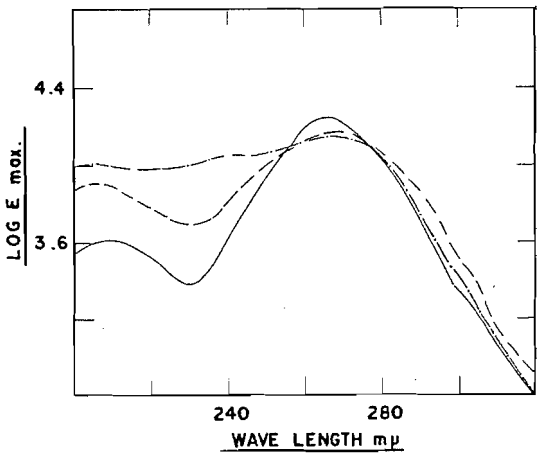



FIG. 2. Curve *A* —— 2-Nitramino-4(or 5)-methyl-2-imidazoline (water).
Curve *B* – – – 1-Nitro-2-nitramino-2-imidazoline (water).
Curve *C* – · – N-β-Nitraminoethyl-N′-methyl-N″-nitroguanidine (water).

TABLE I

2-NITRAMINO-2-IMIDAZOLINES

| Compound | Solvent | Absorption maxima | | | |
|---|---|---|---|---|---|
| | | λ, mμ | log $E_{max}$ | λ, mμ | log $E_{max}$ |
| 1-β-Hydroxyethyl-2-nitramino-2-imidazoline | Water | 204 | 3.66 | 269 | 4.26 |
| 1-Methyl-2-nitramino-2-imidazoline | Water | 208 | 3.60 | 268 | 4.17 |
| 2-Nitramino-4(or 5)-methyl-2-imidazoline | Water | 209 | 3.62 | 265 | 4.25 |
| 1-Nitro-2-nitramino-2-imidazoline | Water | 206 | 3.91 | 268 | 4.17 |

The ammonia and amino addition compounds of 1-nitro-2-nitramino-2-imidazoline (cf. Table II) have three absorption maxima at 205, 223–240, and 269–271 mμ. The ultraviolet absorption spectra of these compounds are a composite of the absorption spectra of the nitramino (VII) and nitroguanidino chromophores (VIII). Therefore 1-nitro-2-nitramino-2-imidazoline must add ammonia or amines with simultaneous opening of the ring to give compounds

$-NHNO_2$

VII

$$N=C(-NH-)-NHNO_2$$

VIII

of structure IX. The two chromophores, viz. nitramino and nitroguanidino

$$NO_2NHCH_2CH_2NH-C(=NR)-NHNO_2$$

IX

R = H, $CH_3$, $C_2H_5$.

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groups, are insulated by two saturated carbons and their effect would be expected to be additive, which it is. On the other hand, if amino and ammonia addition products of 1-nitro-2-nitramino-2-imidazoline possess the proposed (1, 2, 6) cyclic structures, carbon 2 would be saturated and the spectra ought to be purely of the nitramine type.

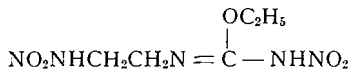
TABLE II

ABSORPTION SPECTRA OF LINEAR SUBSTITUTED NITROGUANIDINES

| Compound | Absorption maxima | | | | | |
|---|---|---|---|---|---|---|
| | λ, mμ | log $E_{max}$ | λ, mμ | log $E_{max}$ | λ, mμ | log $E_{max}$ |
| N-β-Nitraminoethyl-N′-nitroguanidine* | | | 232 | 4.13 | 271 | 4.30 |
| N-β-Nitramino-α-methylethyl-N′-nitroguanidine* | | | 232 | 4.08 | 271 | 4.26 |
| N-β-Nitraminoethyl-N′-methyl-N″-nitroguanidine** | 205 | 4.02 | 240 | 4.05 | 269 | 4.17 |
| N-β-Nitraminoethyl-N′-ethyl-N″-nitroguanidine** | 205 | 4.04 | 239 | 4.05 | 269 | 4.16 |
| N-β-Nitraminoethyl-N′-phenyl-N″-nitroguanidine** | | | 223 | 4.13 | 271 | 4.20 |

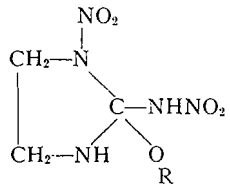
*Solvent, alcohol. Measurements taken from Reference 5.
**Solvent, water.

The height of the 230–240 mμ band depends on the overlap of this band with the strong neighboring band at 268 mμ. If the nitroguanidino band is shifted towards longer wave lengths, the overlap decreases rapidly and a minimum appears at the position of the former maximum. However, this minimum has a surprisingly high $E$ value (ca. 7000) which corresponds fairly well to the absorption of one nitramino group. Then this band coalesces with the 205 mμ band to give a broad apparent band at about 220 mμ. This effect is observed in the spectrum of N-β-nitraminoethyl-N′-phenyl-N″-nitroguanidine (Curve *A*, Fig. 3). A similar effect is apparent in the spectrum of N-β-nitraminoethyl-N′-nitro-*o*-ethylisourea (X) (Curve *B*, Fig. 3).



X

For the latter compound X the following structure (XI, R = $C_2H_5$)



XI

was previously (6) suggested. Also the *n*-propyl alcohol addition product of 1-nitro-2-nitramino-2-imidazoline was assigned (3) this structure (XI, R =

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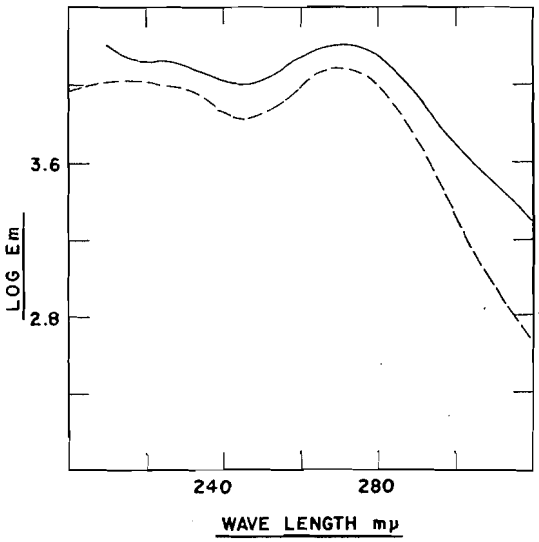



FIG. 3. Curve *A* —— N-β-Nitraminoethyl-N′-phenyl-N″-nitroguanidine (water).
Curve *B* – – – N-β-Nitraminoethyl-N′-nitro-*o*-ethylisourea (water).

$n$C$_3$H$_7$) on the basis of potentiometric titration data. However, this cyclic structure seems to be invalidated by the ultraviolet absorption spectra. In the cyclic structure, the two nitramino groups are insulated from each other by a tetrahedral carbon atom and the spectrum should be a pure nitramine spectrum with no 269 mμ band. Since a strong band is present at 271 mμ, it testifies to the existence in this compound (ethanol addition product of 1-nitro-2-nitramino-2-imidazoline) of the chromophore

$$\mathrm{HN{=}C(Y){-}NHNO_2}$$

which is to be considered as a unique system of mobile electrons. One may consider the spectra of the compounds in Table I as due to this chromophore.

At 205–209 mμ both the nitramino and nitroguanidino groups absorb but the greater part of the absorption is due to the nitramino group as indicated by the extinction of the pure nitroguanidines.

The spectrum of N-β-nitraminoethyl-N′-nitrourea is closer to the nitramine type except for the unusual width of the 236 mμ band. This spectrum (Curve *B*, Fig. 1) indicates clearly that a band due to the chromophore

$$\mathrm{-NH{-}\overset{\overset{O}{\|}}{C}{-}NHNO_2}$$

is hidden under the long wave length wing of the 236 mμ band. Its approximate position would be between 260 to 280 mμ.

## EXPERIMENTAL

The spectra were measured on a Cary ultraviolet spectrophotometer. The compounds were analytically pure samples.

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ACKNOWLEDGMENT

The authors are very grateful to Dr. R. N. Jones of the National Research Council, Ottawa, for the use of the Cary Spectrophotometer and for his kind interest in this work.

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# THE FISSION YIELD OF $Te^{134}$[1]

By L. Yaffe,[2] Alison E. Day,[3] and Betsy A. Greer[4]

ABSTRACT

The fission yield of $Te^{134}$ has been found to be 6.48% ± 0.47%. This makes the cumulative yield of $I^{134}$ 7.71% using Glendenin's value of 0.19 as the independent fractional chain yield of $I^{134}$. This value, since it is very close to that found by Thode for $Xe^{134}$, offers additional confirmation of the 54 min. iodine assignment to mass 134.

## INTRODUCTION

The fission yield concept was first introduced by Anderson, Fermi, and Grosse (1). It may be defined as the probability of a given nuclide being formed in fission. Owing to the work of many in the Plutonium Project (19) and others, the shape of the fission yield – mass curve is now well-known. For thermal neutron fission the curve is double-humped, showing that asymmetric fission is much more probable (600:1) than symmetric.

The data from which this curve is obtained are radiochemical and the errors which may be involved are usually quite large. In general, relative measurements may have an error of ± 5% and absolute measurements are probably no better than ± 10%. Thode and his collaborators have refined these measurements by use of the mass spectrometer where the precision is very great.

They determined (13) the yields of some of the Kr and Xe isotopes formed in fission and found that the yields of $Xe^{133}$ and $Xe^{134}$ were too high above the smooth mass–yield curve to be explained by experimental error. The yields determined by Thode were the cumulative yields for the chain. For example, a certain mass chain may consist of the following members, $A$, $B$, $C$, and $D$;

$$A \xrightarrow{\beta^-} B \xrightarrow{\beta^-} C \xrightarrow{\beta^-} D \text{ (stable)}.$$

$B$, for example, may be formed directly at the moment of fission or may be formed by the decay of its precursor $A$. Similarly for $C$ and $D$, although the probability of the nuclide being formed as a primary fission fragment decreases as the stable end member is approached.

The yield of the nuclide formed directly as a fission fragment at the moment of fission is usually known as the *independent* yield, while that due to independent yield formation plus decay from its precursors is called the *cumulative* yield. The cumulative yield is most accurately determined by a mass spectrographic determination of the stable end member of the chain.

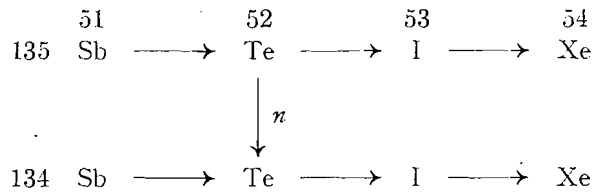
Glendenin (3, 5) has invoked the Mayer (14) nuclear shell hypothesis in an attempt to explain the high yields found by Thode for the 134 chain. He suggested that if a primary fission product is formed with one neutron, for example,

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*Contribution from the Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ont. Issued as A.E.C.L. No. 21.*
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greater than that which composes a stable nuclear shell, the nucleus might de-excite by neutron emission of the last loosely-bound neutron, rather than by normal negaton decay.

In the case of the 134 and 135 chains,



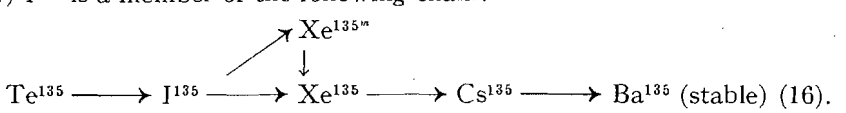

$_{52}Te^{135}$ has 83 neutrons in its nucleus, one more than the stable 82 shell, and the nuclear de-excitation may take place by neutron emission to the 134 chain. Such a mechanism would set up perturbations which would distort the smooth curve and produce anomalies. Recently (17) this suggestion has been extended to include primary fission fragments with one, three, five, and seven neutrons greater than that found in the stable shell, since these neutrons are all rather loosely bound.

Recently other anomalies have been found. Glendenin *et al.* (8) have found that mass 100 has a yield higher than that suggested by the smooth mass–yield curve. They follow the suggestion made by Thode (20) and others (15) that a stable shell may be a preferred mode of fission and suggest that the mass 100 particle is the complementary fragment of the mass 134 particle which is formed by a preferred mode of fission (e.g., $_{52}Te^{134}$ — 82 neutrons) in high yield.

When these anomalies began showing up it seemed advisable to re-investigate the yield of the earlier members of the 134 chain. The yield of $I^{134}$ had been investigated previously by Katcoff *et al.* (11) and Yaffe and Mackintosh (23) who obtained yields of 5.7%. Glendenin (4) suggested that these results might be low because of poor exchange between the radioactive iodine atoms and the inert iodine carrier atoms used as a diluent. Such exchange difficulties had previously been noted by Glendenin *et al.* (7).

The independent yield of $I^{134}$, i.e., the amount formed directly in fission as distinct from that by $Te^{134}$ decay, had been found by Glendenin (5). He calculated the activity expected from $I^{134}$ decaying from $Te^{134}$ after a known irradiation period. He then measured the $I^{134}$ extracted at a certain time, the difference being due to the $I^{134}$ formed in an independent manner. From this, the independent yield relative to some reference (5.6% for $I^{135}$ in this case) may be calculated. He obtained an independent yield of 1.0% representing the fraction $0.19 \pm .03$ of the total chain yield. This figure will have to be revised slightly for the following reasons:

(1) $I^{135}$ is a member of the following chain:




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(2) Mass spectrographic evidence (20) gives the yield of $Cs^{135}$ as 6.75% (using the fission yield of $I^{131}$, 3.14%, as a reference).

(3) The independent yield of $Cs^{135}$ must be very small, (*a*) on the basis of any of the charge distribution in fission theories and (*b*) because the independent fission yield of its precursor $Xe^{135}$ has been shown (2, 10) to be small (2.7% of the chain yield).

(4) By difference one gets the fission yield of $I^{135}$ to be 6.57%, in good agreement with the results obtained by Pappas (18) i.e., 6.2%, which is higher than the value of 5.6% used by Glendenin.

(5) Glendenin used a yield of 5.0% for $Te^{134}$ in his determination. The present work as well as data obtained from nuclear closed-shell effects in fission suggest a higher value. However, this operated only as a small correction factor and in the opposite direction to the other correction.

For the purposes of this paper the value obtained by Glendenin has been used.

Let us consider the formation of the various fission products which occur in the 134 chain during the fission process, and between the end of the irradiation and the separation of the $I^{134}$ (which is to be measured) from the $Te^{134}$,

$$134\quad Sb \xrightarrow[<\ 10\ \text{min.}]{} Te \xrightarrow[44\ \text{min.}]{} I \xrightarrow[52.5\ \text{min.}]{} Xe\ (\text{stable})\ (16).$$

Let $N$ = number of fissions per sec.,
$Y_{Te}$ = fission yield of Te,
$Y_i$ = independent fission yield of I,
$X_1$ and $X_2$ = number of atoms of $Te^{134}$ and $I^{134}$ respectively at any time $t$ during irradiation,
$T$ = time of irradiation,
$\lambda_1$ and $\lambda_2$ = disintegration constants of $Te^{134}$ and $I^{134}$ respectively.

*During irradiation.* —

$$\frac{dX_1}{dt} = Y_{Te}N - X_1\lambda_1$$

[1] and
$$X_1 = \frac{Y_{Te}N}{\lambda_1}(1 - e^{-\lambda_1 T}),$$

$$\frac{dX_2}{dt} = X_1\lambda_1 + Y_iN - X_2\lambda_2$$

[2] so that
$$X_2 = \frac{N(Y_{Te} + Y_i)}{\lambda_2}(1 - e^{-\lambda_2 T}) - \frac{Y_{Te}N}{\lambda_2 - \lambda_1}(e^{-\lambda_1 T} - e^{-\lambda_2 T})$$

after substituting from equation [1].

*Between the end of irradiation and separation of I from Te.* — Let the number of Te atoms at any time $t$, measured from the end of the irradiation, $= X_1' = X_1e^{-\lambda_1 t_1}$. Similarly the number of I atoms $= X_2' = X_2e^{-\lambda_2 t_1}$ + growth of I from Te since the end of irradiation.

*Growth of I after irradiation.* —

$$\frac{dX_2'}{dt} = X_1\lambda_1e^{-\lambda_1 t_1} - X_2'\lambda_2,$$

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$$X_2' = \frac{\lambda_1}{\lambda_2 - \lambda_1} X_1(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}),$$

$$\text{total } X_2' = X_2 e^{-\lambda_2 t_1} + \frac{\lambda_1}{\lambda_2 - \lambda_1} X_1(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}),$$

and substituting from equations [1] and [2] gives

$$X_2'\lambda_2 = NY_i(1-e^{-\lambda_1 T})(e^{-\lambda_2 t_1}) + NY_{Te}\left\{\left[\frac{\lambda_2}{\lambda_1 - \lambda_2}e^{-\lambda_1 T} - \frac{\lambda_1}{\lambda_1 - \lambda_2}e^{-\lambda_2 T} + 1\right]e^{-\lambda_2 t_1}\right.$$

$$\left. + \frac{\lambda_2}{\lambda_2 - \lambda_1}(1 - e^{-\lambda_1 T})(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1})\right\} \qquad [3]$$

which is equal to the measured disintegration rate of $I^{134}$ at time $t_1$, measured from the end of the irradiation.

If $T \gg 1/\lambda_1$ and $T \gg 1/\lambda_2$, then equation [3] simplifies to:

$$X_2'\lambda_1 = N\left\{(Y_i + Y_{Te})e^{-\lambda_2 t_1} + Y_{Te}\frac{\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1})\right\}. \qquad [4]$$

The above treatment assumes that the measured disintegration constant is equal to the "effective" decay constant within the pile for both $I^{134}$ and $Te^{134}$. This means that their capture cross sections are taken to be small.

If $N$, the fission rate, is known or measured, the above equation is soluble. However, a reference of known fission yield can be irradiated simultaneously and treated in the same manner. For this purpose we have used $Ba^{139}$ (fission yield — 6.3%) which occurs in the following mass chain (16):

$$^{139}\text{Xe} \xrightarrow[41\text{ sec.}]{} \text{Cs} \xrightarrow[9.7\text{ min.}]{} \text{Ba} \xrightarrow[85\text{ min.}]{} \text{La (stable)}.$$

If the disintegration rates of the two are compared, the fission rate cancels out and $Y_{Te}$ is then found in terms of the $Ba^{139}$ yield. We here assumed its independent yield to be negligibly small compared to that of its precursor, $Cs^{139}$. This will be true on any reasonable charge distribution in fission theory.

## EXPERIMENTAL

### (*a*) *Irradiation*

Accurately weighed samples of uranyl nitrate hexahydrate (10 – 20 mgm.) were irradiated in various positions in the Chalk River NRX nuclear reactor for known lengths of time. The neutron spectrum in these positions was predominantly thermal. Two samples of uranyl nitrate were used in each irradiation, one for the $Ba^{139}$, the other for the $I^{134}$ determination. The salt was enclosed in small sealed quartz ampoules. Irradiation times varied from 1 hr. to 16 hr.

### (*b*) *Chemical Separation*

#### (i) *Iodine*

The silica tube was crushed in a beaker containing 2 *M* sodium carbonate to which a weighed amount of potassium iodide had been added as a carrier. A few milliliters of 5% sodium hypochlorite solution was added and the solution heated for at least five minutes to ensure completion of reaction ($I^-$ to $I^{+7}O_4$). The solution was then transferred to a separating funnel containing enough

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nitric acid to render the solution acid, the iodate reduced to iodine with hydroxylamine hydrochloride, and extracted into carbon tetrachloride. The iodine was further reduced ($I_2$ to $I^-$) using sulphurous acid, and the organic layer discarded. The iodide was then reoxidized with a sodium nitrite – nitric acid mixture and extracted with carbon tetrachloride. The sodium nitrite oxidation and sulphurous acid reduction cycle was repeated twice.*

The reduced solution was finally acidified with 6 *N* nitric acid. In some cases the solution was then placed on a weighed counting tray which contained excess silver nitrate. The tray was then heated under an infrared lamp and the dried silver iodide was weighed and the activity measured. In other cases the reduced solution was made up to a standard volume, an aliquot taken and treated in the above manner to obtain an activity measurement. This produced essentially a "weightless" source. The iodide content of the stock solution was determined gravimetrically, again precipitating silver iodide.

(ii) *Barium*

The barium was separated by a method described previously (9). This consisted of separation of the barium from the uranium and other fission products by several chloride, chromate, and nitrate separations with appropriate hold-back carriers added. In some cases the barium was precipitated finally as the sulphate, slurried with acetone, and transferred to a weighed counting tray. The weight of the barium sulphate whose activity was measured was then obtained. In experiments where the specific activity was very high, the final barium nitrate precipitate was dissolved in water and made up to a standard volume. An aliquot was then taken and dried on a counting tray. This produced essentially a weightless source.

The barium content of the stock solution was then obtained gravimetrically by a barium sulphate precipitation.

(*c*) *Measurements*

All activity measurements were made using "end-window" Geiger counters with window thicknesses of about 3 mgm. per cm.$^2$ Where relevant, the following correction factors were made.

(i) *Self-absorption*

In some cases when the samples were not weightless, self-absorption curves were obtained (21). This correction was applied only in Experiments 1 – 9 inclusive.

(ii) *External Absorption*

Absorption of the $\beta$ rays in the counter window and air gap between sample and counter window was corrected for in the following manner. Decay curves were obtained through various thicknesses of aluminum and absorption curves obtained from these. A slight extrapolation back to "zero absorption" was made to correct for any loss due to absorption.

(iii) *Back-scattering Corrections*

In cases of measurement of actual samples, conditions were such that

* *This method is almost identical with that used by Glendenin and Metcalf (6) and was the only method of many tried which gave complete exchange between active atoms and added inactive carrier atoms. These methods included addition of iodine in any or all of its many valence states and oxidation and reduction by various reagents.*

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"saturation back-scattering" (22) was obtained in all cases. Corrections were made by measuring certain samples in identical "geometry" with no sample backing at all and then with "saturation" backing.

(iv) *Coincidence Losses*

A quench unit with a delay time of 600 μsec. was present in the circuit at all times and appropriate corrections were made where relevant.

(v) *Radioactive Decay*

Decay curves were obtained from measurements extending over at least 24 hr. The required activity (52.5 min. for $I^{134}$ and 85 min. for $Ba^{139}$) was obtained from the background due to other active isotopes by the usual "peeling-off" technique. The straight line obtained from the semilogarithmic plot was extrapolated back to zero time which is defined as the removal of the desired element from its precursors (the first carbon tetrachloride extraction in the case of the iodine, and the first chloride precipitation in the case of the barium).

(vi) *Chemical Recovery*

For low specific activities the material which was to be measured directly on the counting tray was weighed. For high specific activities a small aliquot was placed on the counting tray and a chemical analysis performed on the remainder. The yield was then obtained by comparison with the amount of inactive carrier initially used.

## RESULTS

The results are listed in Table I.

TABLE I

| Expt. No. | Irrad'n. pos'n. | Time of irrad'n., $T$ (hr.) | $t_1$. Time in minutes between end of irrad'n. and sep'n. | | Corrected counts/min./mgm. $UO_2(NO_3)_2.6H_2O$ at zero time | | Fission yield, % |
|---|---|---|---|---|---|---|---|
| | | | $I^{134}$ | $Ba^{139}$ | $I^{134}$ | $Ba^{139}$ | |
| 1 | Thermal column | 16.00 | 40.0 | 36.2 | 93.1 | 72.2 | 6.70 |
| 2 | " | 9.00 | 81.5 | 98.5 | 39.4 | 27.9 | 6.05 |
| 3 | " | 16.33 | 59.0 | 46.0 | 102.1 | 86.4 | 6.46 |
| 4 | " | 16.05 | 46.8 | 51.3 | 68.8 | 55.0 | 6.04 |
| 5 | " | 15.65 | 62.5 | 45.0 | 76.1 | 65.3 | 6.61 |
| 6 | " | 10.34 | 31.2 | 45.2 | 80.7 | 58.0 | 6.42 |
| 7 | " | 16.55 | 29.3 | 41.3 | 93.7 | 72.5 | 6.07 |
| 8 | " | 15.94 | 32.3 | 35.2 | 115.7 | 85.2 | 6.80 |
| 9 | " | 16.75 | 39.7 | 57.8 | 100.9 | 64.5 | 6.87 |
| 10 | Self-serve | 8.00 | 104.0 | 84.2 | $2.26 \times 10^6$ | $1.66 \times 10^6$ | 6.85 |
| 11 | " | 8.05 | 57.3 | 59.0 | $2.76 \times 10^6$ | $2.22 \times 10^6$ | 6.08 |
| 12 | " | 8.00 | 85.0 | 86.1 | $3.91 \times 10^6$ | $3.04 \times 10^6$ | 6.27 |
| 13 | " | 5.00 | 77.7 | 87.5 | $5.08 \times 10^6$ | $3.50 \times 10^6$ | 6.58 |
| 14 | " | 5.00 | 72.8 | 71.2 | $2.24 \times 10^6$ | $2.22 \times 10^6$ | 5.76 |
| 15 | " | 5.00 | 54.3 | 54.0 | $4.73 \times 10^6$ | $4.24 \times 10^6$ | 5.56 |
| 16 | " | 5.00 | 79.3 | 84.5 | $4.88 \times 10^6$ | $3.38 \times 10^6$ | 6.81 |
| 17 | " | 5.00 | 41.0 | 40.7 | $3.31 \times 10^6$ | $2.88 \times 10^6$ | 5.81 |
| 18 | " | 5.00 | 63.2 | 67.3 | $7.98 \times 10^6$ | $5.39 \times 10^6$ | 7.08 |
| 19 | " | 5.00 | 52.8 | 42.5 | $8.01 \times 10^6$ | $6.34 \times 10^6$ | 6.81 |
| 20 | " | 1.00 | 63.7 | 63.7 | $3.36 \times 10^6$ | $2.66 \times 10^6$ | 6.64 |
| 21 | " | 1.00 | 63.2 | 84.0 | $2.23 \times 10^6$ | $1.53 \times 10^6$ | 6.61 |
| 22 | " | 1.00 | 80.7 | 107.3 | $1.84 \times 10^6$ | $1.08 \times 10^6$ | 7.60 |
| | | | | | | Average: | $6.48 \pm 0.47$ |

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## DISCUSSION

The fission yield of $Te^{134}$ was found to be 6.48% ± 0.47% using Glendenin's (5) value of 0.19 as the independent fractional yield of $I^{134}$. This gives a value for the cumulative yield of $I^{134}$ of 7.71%. This agrees well with recent work by Pappas (18) who got values of 7.0% and 7.9% respectively.

No real genetic proof exists for the mass assignment of 134 for the 44 min. tellurium and the 52.5 min. iodine. The assignment is still on a tentative basis, although recent work by Katcoff, Miskel, and Stanley (12) on the range of fission fragments makes the assignment a highly probable one. The other possibility is mass 132. Thode *et al.* (13) found values of 4.6% and 8.2% respectively for the cumulative yields of the 132 and 134 chains (normalized to 3.1% for mass chain 131). Since the yield of the 54 min. iodine is much higher than the yield of the 132 chain and very close to that of the 134, this is considered additional evidence for the mass assignment.

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# THE KINETICS OF COAGULATION OF AN EMULSION[1]

By G. Brady, L. Mandelcorn, and C. A. Winkler

ABSTRACT

Under suitable conditions, the coagulation of GR-S latex by sulphuric acid has been found to exhibit second order rate characteristics, and to be represented by the equation,

$$C = \frac{C_0}{1 + k\,(H^+)'\,C_0 t}$$

where $C$ is the concentration of polymer at time $t$, $C_0$ is the initial concentration of polymer, and $(H^+)'$ is the concentration of $H^+$ ion in excess of the critical concentration necessary to initiate coagulation. Coagulation is accompanied by desorption of soap from the surface of the latex particles, and the variation of surface tension resulting from this follows the equation $\log \gamma = A - B \log t$, where $\gamma$ is the surface tension and $A$ and $B$ are constants. Appropriate adjustment of the temperature was found to stabilize the emulsion markedly in the presence of acid. A mechanism for the coagulation process is considered.

The phenomenon of coagulation of colloidal systems is analogous in many respects to a chemical reaction, proceeding at a definite rate dependent on temperature and concentration. Frequently, however, it is a diffusion-controlled process to which the standard kinetic methods based on equilibrium between reactants, activated complex, and products cannot be applied. It is only when the probability of coalescence of the particles taking part in a collision is reduced, that is when the particles are relatively stable, that an equilibrium state can be postulated.

Statistical treatment of the problem by Smoluchowski and others (1, 6, 15, 16) has yielded the relation

$$[1] \qquad n = \frac{n_0}{1 + k\,\epsilon\,n_0 t}$$

to represent the number of particles $n$ present at time $t$ in a monodisperse system which at time $t = 0$ consists of $n_0$ primary particles. In this expression, $\epsilon$ is a numerical constant of value $0 \leqslant \epsilon \leqslant 1$, which depends on the charge or other stabilizing factors of the particle, and $k$ is equal to $4\pi DR$, where $D$ is the diffusion coefficient of the primary particle and $R$ is the radius of its sphere of attraction. $R$ is defined as the distance to which two particles must approach for coalescence, which must be equal to at least twice the radius of the primary particles. This equation has been found to be generally valid when $\epsilon \approx 1$ (9, 19, 21), that is, for uncharged particles, but has been found to be in poor agreement with experiment in many cases where the charge on the particles has been only partially neutralized (slow coagulation) (3, 4, 7).

With emulsions the particles are generally stabilized by emulsifiers adsorbed at the interface between the internal phase and the external suspending

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medium. Coagulation of emulsions results when this film is removed or weakened sufficiently to decrease the stability of the particles to a value below the critical threshold potential. The process is more complicated than with particles which are simply charged, in that the rate of removal of the adsorbed film may be a rate-controlling factor. Also, observations by Lewis (10) and Powis (13) indicate that the primary process in emulsion coagulation may be an adherence of the particles in which their physical identity in the resulting aggregate is retained. This may be followed by coalescence of these particles into a single mass, or by disintegration of the aggregates before coalescence is achieved. Thus it is probable that the simple mechanism postulated by von Smoluchowski may not apply rigorously to this type of system.

In this paper are presented results for coagulation of GR-S latex, type II, with sulphuric acid. Experiments were made to determine the rate of coagulation and its dependence on the concentrations of latex and acid, and on temperature. Efforts were also made to determine the rate of desorption of soap during the coagulation and to seek a correlation between this phenomenon and the rate of coagulation.

## EXPERIMENTAL AND RESULTS

### *Determination of Rate of Coagulation*

The rate of coagulation was determined by centrifuging the coagulated material from the system. By adjusting the speed and time of centrifuging, particles of any desired size could be separated from the emulsion. Preliminary experiments demonstrated that at the acid concentrations used, a centrifuging time of one minute at 3000 r.p.m. offered the best conditions for determining the rate of coagulation in 100-fold diluted latex. Experiments were made using acid concentrations of $N/10$, $N/20$, $N/30$, $N/40$, $N/60$, and $N/90$ sulphuric acid (based on total volume). Samples (25 cc.) of 50-fold diluted latex, containing 0.1152 gm. coagulable solids, were placed in 8-in. test tubes, 25 cc. of acid added from a burette, and the whole immersed in a thermostat at 30°C. $\pm$ 0.05°C. After appropriate time intervals samples were removed and centrifuged for one minute at 3000 r.p.m. The coagulum formed at the top in the form of a skin which was removed and placed on a weighed filter paper. Paper and coagulum were then dried in a vacuum oven at 60°C. for 30 min. and weighed.

Fig. 1 illustrates the results obtained from these experiments. With $N/90$ sulphuric acid, coagulation was negligible, whereas at a concentration of $N/10$ sulphuric acid, the emulsion was coagulated very quickly. At higher acid concentrations (not shown in the figure) the curves did not differ appreciably from that obtained with $N/10$ sulphuric acid. Thus $N/10$ and $N/90$ sulphuric acid may be taken as the limiting concentrations which define a region of slow coagulation. (It should be understood that this applies only to the centrifuging conditions and concentrations used in these experiments.)

The intermediate curves indicate that coagulation occurred in two stages. Addition of acid caused an immediate increase in particle size represented by

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the portion of the curves from zero time to point $A$; from $A$ to $B$ a period of induction was apparent. At $B$ the second stage commenced and the coagulation proceeded slowly and steadily. The sharp rise to $A$ in all probability represented coagulation of the larger particles of the latex and it was only at $B$ that all particles had grown to a size large enough to be centrifuged out.

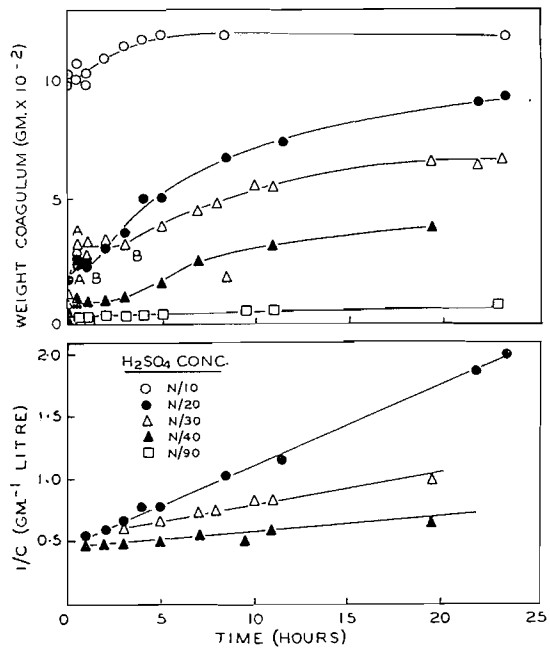



FIG. 1. Weight of coagulum formed vs. time. Variation of $1/C$ with time.

The portions of the curves beyond point $B$, for $N/20$, $N/30$, and $N/40$ acids, gave good linear relations when the reciprocal of the polymer concentration was plotted against time, indicating that coagulation occurred by a second order process. The rate constants, in gm.$^{-1}$ liter-hr., calculated from the slopes of these lines were 0.064, 0.029, and 0.012 for $H^+$ ion concentrations of 0.050, 0.033, and 0.025 gm. equiv. per liter respectively. From this it follows that the coagulation reaction may be represented by an equation of the form

$$[2] \qquad -\frac{dc}{dt} = k''c^2$$

where $k''$ is a function of the acid concentration. The rate constants proved to be linearly related to the concentration of the coagulating ion (Fig. 2). The line of Fig. 2 can be represented by the equation

$$[3] \qquad k'' = k'(H^+ - H_0^+)$$

where $H_0^+$ is the "threshold concentration", corresponding to the intercept

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on the $H^+$ ion concentration axis. Combination of equations [2] and [3] gives

$$-\frac{dc}{dt} = k'c^2(H^+)'$$

where $(H^+)' = (H^+ - H_0{}^+)$. Integration of this equation gives

[4] $$c = \frac{c_0}{1 + k'c_0(H^+)'t}$$

where $c_0$ is the initial concentration of polymer. This expression gives the variation of $c$ as a function of the initial concentration of polymer $c_0$, the acid concentration, and the time.

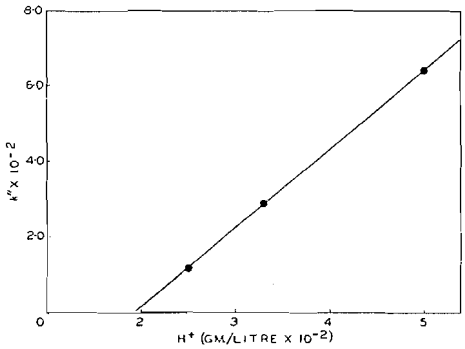



FIG. 2. Rate constant as a function of the $H^+$ ion concentration.

The value of $H_0{}^+$ from Fig. 2 is $1.92 \times 10^{-2}$ gm. per liter. Below this concentration the coagulation rate should fall to zero. Experimentally, the value obtained for the minimum acid concentration necessary for coagulation is about $10^{-2}$ gm. per liter ($N/90$ sulphuric acid).

*Surface Tension of Coagulating Latex*

Heller and Oppenheimer (5) had noted that, during coagulation, the surface tension of latex emulsions decreased markedly, denoting an increase of soap in solution due to its desorption from the particles of the internal phase. They made no attempt to investigate this effect kinetically, however, and accordingly experiments were undertaken to compare the rate of desorption with the rate of coagulation.

The measurement of surface tension requires extreme precautions against contamination of the surface by impurities. In particular all glassware must be scrupulously cleaned, and this was accomplished by immersing it in concentrated nitric acid – sulphuric acid at 90°C. for two hours, washing thoroughly with redistilled water, steaming for 15 min., and finally rinsing again in redistilled water. A Cenco Du Nouy tensiometer was used for surface tension determinations. The platinum ring was flamed before and after each reading to ensure volatilization of any material collected on it. The temperature was

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controlled at 30°C. ± 1°C. with a thermostatic jacket surrounding the Petri plate used to hold the samples.

A 20 ml. sample of latex, diluted 50 times with redistilled water, was poured into the Petri plate and to this was added 20 ml. of $N/10$, $N/15$, or $N/35$ sulphuric acid which, based on total volume, gave a 100-fold dilution of the latex and normalities of $N/20$, $N/30$, and $N/70$ for the acid. These solutions were then covered and allowed to stand without agitation. At various times the cover was removed and the surface tension measured. The surface was swept with a platinum wire a few minutes before each reading to remove flakes of coagulum from the surface.

The results of these experiments are illustrated in Fig. 3. It is seen that at all concentrations of acid used a large decrease in surface tension took place. The curves indicate that desorption of soap occurred for as long as 23 hr.

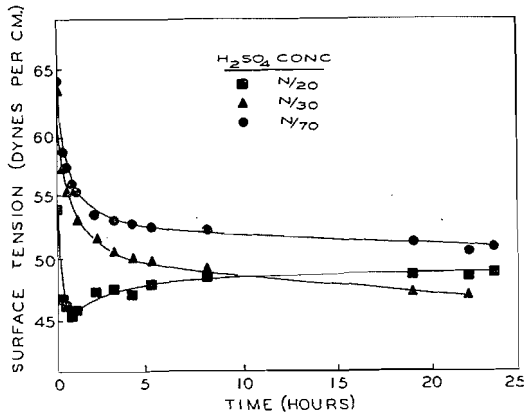



FIG. 3. Surface tension vs. time during coagulation.

*Effect of Temperature*

Data for coagulation at different temperatures (Table I) show that an increase of temperature to 32°C. accelerated coagulation but further increase to 34°C. markedly stabilized the system. Treatment of latex at higher tempera-

TABLE I

COAGULATION OF GR-S LATEX, TYPE II, AT DIFFERENT TEMPERATURES. 100-FOLD DILUTE LATEX AND $N/40$ $H_2SO_4$

| Temperature (°C.) | Time (hr.) | Wt. coagulum (mgm.) |
|---|---|---|
| 30 | 3.00 | 37.8 |
| 30 | 12.25 | 53.8 |
| 30 | 18.50 | 66.9 |
| 32 | 2.50 | 33.4 |
| 32 | 12.00 | 62.5 |
| 32 | 18.00 | 70.7 |
| 34 | 2.50 | 3 |
| 34 | 12.00 | 3 |

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tures in the presence of coagulating agents also resulted in stabilization of the particles (Table II). For example, latex to which has been added $N/40$ sul-

TABLE II

SUMMARY OF DATA FOR COAGULATION OF GR-S LATEX, TYPE II, AT DIFFERENT TEMPERATURES

| Temperature $T_1$ (°C.) | Time (hr.) at $T_1$ | Temperature $T_2$ (°C.) | Time (hr.) at $T_2$ | Total time (hr.) | Weight coagulum (mgm.) |
|---|---|---|---|---|---|
| 30 | 3 | — | — | 3 | 37.9 |
| 30 | 10 | — | — | 10 | 52.1 |
| 49 | 60 | 30 | 10 | 70 | 22.8 |
| 60 | 60 | 30 | 3 | 63 | 3.5 |
| 60 | 60 | 30 | 10 | 70 | 7.1 |
| 30 | 18 | — | — | 18 | 77.7 |
| 30 | 3 | 49 | 15 | 18 | 45.5 |
| 30 | 3 | 60 | 15 | 18 | 40.5 |

phuric acid was held for 60 hr. at 60°C. and then at 30°C. for three hours with the result that the weight of coagulated material was virtually negligible. Alternatively, if latex was coagulated at 30°C. for three hours, and then the temperature raised to 49°C., coagulation was again seriously retarded. Preheating of latex without addition of acid had no effect on either the coagulation velocity or the particle size.

It might be noted that Maron *et al.* (12) have also observed increased stabilization of latex with high temperature treatment in the presence of electrolytes, while critical phenomena of the type indicated above have been observed with soap solutions (17, 18, 20).

## DISCUSSION

The equation derived for the coagulation of GR-S latex is

$$c = \frac{c_0}{1 + k'(\mathrm{H}^+)'c_0t}. \qquad [4]$$

This equation is significant in that it bears a close resemblance to the Smoluchowski equation

$$\sum_{j=1}^{\infty} n_j = \frac{n_0}{1 + k \epsilon n_0 t} \qquad [1]$$

where $k = 4\pi DR$. It should be possible to obtain equation 4 as a particular case of equation 1. If the left-hand side of equation 1 is written as

$$\sum_{j=1}^{\infty} n_j = \sum_{j=1}^{m} n_j + \sum_{j=m}^{\infty} n_j$$

and if it is assumed that all particles $\geq n_m$ are removed by centrifuging, then $\sum_{j=1}^{m} n_j$ represents the concentration of particles remaining in the system. Further, $m$ must be large since only particles of large mass are removed by the centrifuge, and therefore $\sum_{j=m}^{\infty} n_j$ must be small compared with $\sum_{j=1}^{m} n_j$. Neglecting the former, equation 1 becomes

$$\sum_{j=1}^{m} n_j = \frac{n_0}{1 + k \epsilon n_0 t}$$

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which when transformed into weight concentrations gives

$$[5] \qquad \sum_{j=1}^{m} c_j = c = \frac{c_0}{1 + k'''\epsilon_0 c_0 t}.$$

In the Smoluchowski equation $k$ is the rate constant for coagulation of uncharged particles. For partially charged particles it is multiplied by $\epsilon$. Since $k = 4\pi DR$ is the rate constant when all collisions are effective, it is essentially the collision number, and the rate can be expressed by analogy with chemical kinetics as

$$\text{Rate constant} = Ze^{-E/RT}$$

where $Z = k = 4\pi DR$, and $e^{-E/RT} = \epsilon$ expresses the fraction of effective collisions, that is the fraction of collisions in which the colliding particles have enough kinetic energy to overcome the repulsive forces of the partially neutralized particles. From Fig. 2 it is evident that $\epsilon = e^{-E/RT}$ is a linear function of the effective $H^+$ ion concentration and may be put equal to $k''(H^+)'$. Substituting in equation 5 gives

$$c = \frac{c_0}{1 + k'(H^+)'c_0 t}$$

which is equivalent to equation 4.

Hence, it appears that coagulation of GR-S latex exhibits the same characteristics as coagulation of a monodisperse sol, to which the Smoluchowski equation is applicable. The portion from zero time to point $A$ in the curves of Fig. 1 represents an initial fast coagulation of all particles. In this initial agglomeration of particles the aggregates appear to be loose, and require time to reach equilibrium stability. The section $OB$ of the curves exhibits a large degree of irregularity. The experiments are difficult to reproduce and the results are semiquantitative only, but they suggest an initial unstable aggregation, from which portions of the particles may detach themselves and diffuse away. This is in agreement with the suggestion of Lewis (10) that coagulating particles adhere initially to each other without immediate coalescence. At $B$, the products presumably have attained internal equilibrium and the coagulation proceeds smoothly from this point.

The soap desorption accompanying the coagulation exhibits the properties of a rate process (Fig. 3) and it is interesting to enquire into the mechanism of this effect.

The amount of emulsifier which can be adsorbed by the suspended particles is clearly a function of the extent of surface of the particles, and the decrease in surface area when coagulation occurs should lead to a desorption of the emulsifier molecules (or ions) from the surface. The surface area of the particles as a function of time may be calculated from the Smoluchowski equation, and if it is assumed that the number of adsorbed molecules, $\sigma$, per unit surface area remains constant, the number of molecules desorbed will be given by the difference between the surface area of the particles at zero time and at time $t$ multiplied by $\sigma$. Thus if $k$ particles each of radius $r_1$ and volume $v_1$ with total

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volume $4/3\pi r_1^3 k$ coalesce to form one particle of radius $r_k$ and volume $4/3\pi r_k^3$, the radius $r_k$ is equal to $k^{1/3} r_1$. If $n_k$ denotes the concentration of $k$-particles, the surface area of a $k$-fold particle is $4\pi k^{2/3} r_1^2 n_k$. The number of particles $n_k$ as a function of time is given by the Smoluchowski equation as

$$\frac{n_0 (at)^{k-1}}{(1 + at)^{k+1}}$$

where $a = 4\pi DRn_0\epsilon$. By summing over the $k$'s and letting $\alpha = at/(1 + at)$, the total surface area of the suspended particles is obtained:

$$[6] \qquad S_T = \frac{4\pi r_1^2 n_0}{(1 + at)^2} \sum_{k=1}^{\infty} k^{2/3} \alpha^{k-1}.$$

The number of molecules removed from the surface of the particles during coagulation is then given by

$$[7] \qquad \begin{aligned} c &= \sigma(S_0 - S_T) \\ &= c_0 - \sigma \frac{4\pi r_1^2 n_0}{(1 + at)^2} \sum_{k=1}^{\infty} k^{2/3} \alpha^{k-1} \end{aligned}$$

which may be written as

$$[8] \qquad c_0 - c = \sigma \frac{4\pi r_1^2 n_0}{(1 + at)^2} \sum_{k=1}^{\infty} k^{2/3} \alpha^{k-1}.$$

The series in equation 8 cannot be evaluated analytically; in the range of small $\alpha$,* however, the series converges rapidly and to a reasonable approximation, neglecting higher terms,

$$[9] \qquad c_0 - c = \sigma \frac{4\pi r_1^2 n_0}{(1 + at)^4} (1 + 3.6\, at).$$

For moderate concentrations of emulsifier the surface tension can be represented by

$$[10] \qquad \log \gamma = b \log(c_0 - c) + \log m$$

where $b$ and $m$ are constants. Substitution for $c_0 - c$ in equation 10 and appropriate expansion of the logarithms gives the relation

$$[11] \qquad \log \gamma = A - B \log t.**$$

Fig. 4 is a plot of log $\gamma$ against log $t$. The agreement between the predicted linearity and the experimental behavior is probably adequate, in view of the approximations involved in the calculations and the accuracy of the experimental work.

To account for the observed stabilization effect with change of temperature, consideration may be given to the soap adsorbed on the latex particles, in

* *If values for the "molecular weight" of the latex particles and of E are taken as 600,000 and 7 kcal. respectively, both of which seem reasonable enough, $\alpha$ is readily calculated to be of the order $10^{-2}$.*

** *For certain values of $\alpha$ the summation may be replaced by an integration, and it can be shown that the same relation between $\gamma$ and $t$ is obtained.*

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solution, and in micellar form. These three forms are in equilibrium and can be represented by the following scheme:

$$\underset{C_A}{\text{adsorbed soap}} \underset{(A)}{\overset{k_1}{\underset{k_2}{\rightleftarrows}}} \underset{C_F}{\text{free soap}} \underset{(B)}{\overset{k_3}{\underset{k_4}{\rightleftarrows}}} \underset{C_M}{\text{micellar soap}}.$$

Under normal conditions, when most of the soap is adsorbed, $k_2$ is greater than $k_1$. Above the critical concentration for micelle formation (14), $k_3$ is much greater than $k_4$, and any added soap increases the micelle concentration without altering the concentration of free soap. Also, $k_2$ is greater than $k_3$ since when soap is added to the emulsion it is adsorbed by the particles and surface saturation of the particles is attained at the critical concentration for micelle formation (11). However, since the processes of micelle formation and adsorption are similar, it may be assumed that $k_2/k_3$ will be less than $k_2/k_1$.

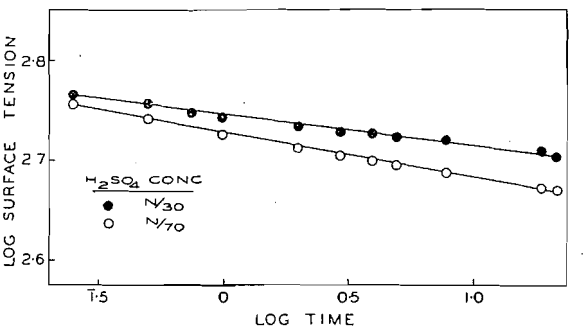



FIG. 4. Log $\gamma$ vs. log $t$.

When coagulating agent is added to the emulsion, the critical concentration for micelle formation is lowered (2, 14). This results in an increase of $K_3$, the equilibrium concentration for process $B$, and in $k_3$, since $K_3 = k_3/k_4$. Consequently the concentration of free soap $C_F$ is decreased, and soap is desorbed from the particles to readjust the equilibrium $K_A$. This desorption leads to coagulation, with an attendant decrease in surface. However, a decreased surface for adsorption will increase $K_A$ since less surface is presented to the emulsifier and therefore the decreased surface leads to a further desorption of soap. The extent to which the soap is removed from solution into the micelles will depend on the relative magnitudes of $k_2$ and $k_3$. As the decrease of surface increases the concentration of free soap in solution, the rate of coagulation will be controlled by the rate of removal of this soap into the micelles; if this free soap is not removed it will prevent further coalescence, since the rate of adsorption $k_2C_F$ will increase. The rate of removal of soap by micellization is $k_3C_F$, and thus to have coagulation $k_3$ must be greater than $k_2$. $k_3$ depends on the decrease of critical concentration resulting from addition of coagulating agent, and therefore the coagulation velocity can be associated with the effect of the coagulating agent on the critical concentration.

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The critical temperature effect is particularly interesting when viewed in this way, and may be explained by the effect of temperature on the rate constants. Increased temperature causes an increase in the critical concentration for micelle formation (8) and this effect is more marked in the presence of electrolytes (20). An increase in temperature also results in a decrease in adsorption, i.e. $k_1$ and $k_4$ are increased. At the critical temperature when the micelles break up, there is a sharp increase in $C_F$, the free soap, which is available for stabilization of the latex particles by adsorption, and coagulation is thus arrested.

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# PHTHALIDE FORMATION

## II. CONDENSATIONS WITH 3-HYDROXY-4-METHYLBENZOIC ACID[1]

By E. H. Charlesworth, H. J. Anderson, and N. S. Thompson

ABSTRACT

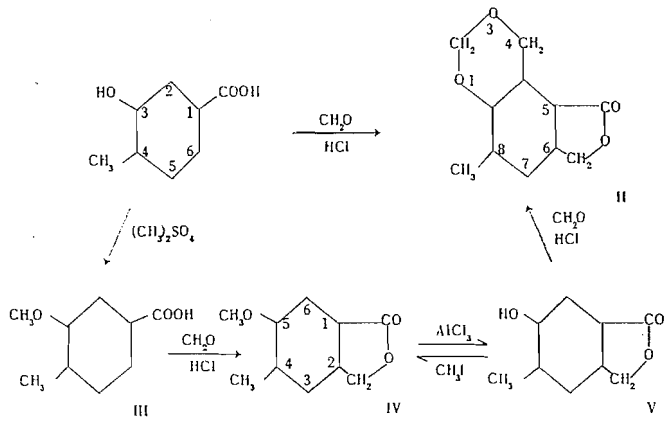
The condensation of 3-hydroxy-4-methylbenzoic acid with aqueous formaldehyde and hydrochloric acid yields the lactone of 6-hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic acid. This dioxanylphthalide has also been produced in a similar type of condensation from 5-hydroxy-4-methylphthalide which can be obtained by demethylation with aluminum chloride of 5-methoxy-4-methylphthalide.

Proof of the presence of the *m*-dioxane and phthalide rings in the condensation product has been obtained by opening these rings in succession. The action of alkaline permanganate opens the phthalide ring to yield a substituted phthalic acid. Acid hydrolysis then opens the *m*-dioxane ring with loss of formaldehyde and the formation of a new phthalide ring. Successive steps of decarboxylation, methylation, and oxidation of the new phthalide yield the known 3-methyl-4-methylphthalic acid.

## INTRODUCTION

The literature contains a fairly extensive number of condensations in which methoxy-substituted benzoic or toluic acids have been condensed with formaldehyde and hydrochloric acid to yield phthalides or in some cases chloromethylphthalides. Condensations with the corresponding hydroxy-substituted acids are on the other hand comparatively rare, the explanation presumably being that in most cases only amorphous high melting products of diphenylmethane or Bakelite structure are isolated.

When 3-hydroxy-4-methylbenzoic acid (I) is condensed in the usual manner with formaldehyde and hydrochloric acid, a crystalline compound (m.p. 165°C.) is obtained. This product has been identified as the lactone of 6-hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic acid (II).



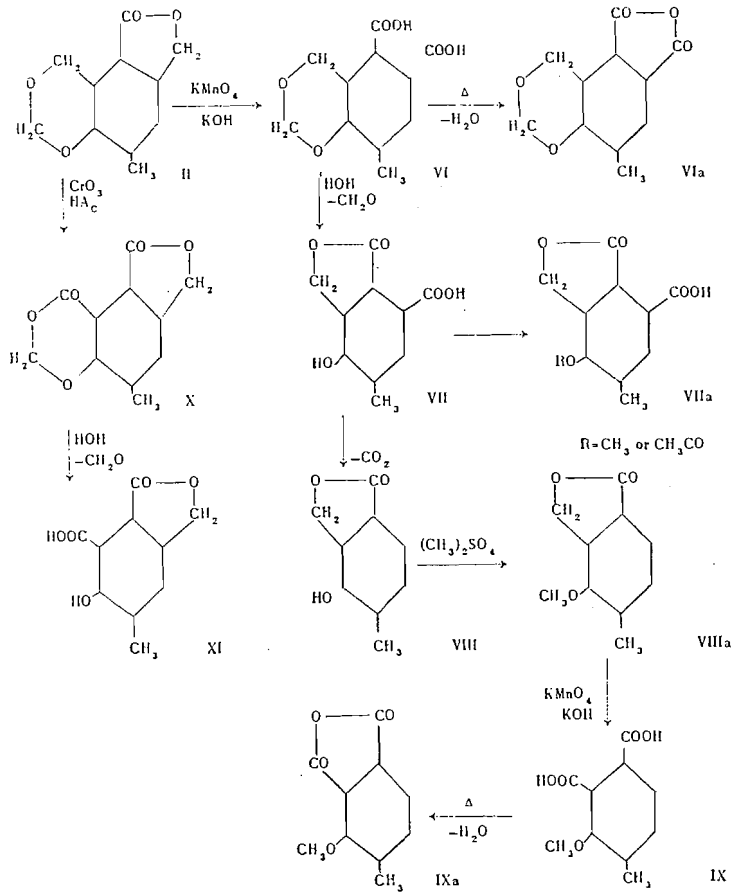

The structure of this dioxanylphthalide (II) is supported by the following

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alternative synthesis. 5-Methoxy-4-methylphthalide (IV) was prepared from 3-methoxy-4-methylbenzoic acid (III) by the method of Charlesworth, Rennie, Sinder, and Yan (7). By demethylation of IV with hydriodic acid or better with aluminum chloride (anhydrous) in dry benzene the hydroxyphthalide (V) was obtained. Tests indicated that the demethylating agents had not broken the phthalide ring and this was proved by remethylation to the methoxyphthalide (IV) by the method of Irvine (9). When the hydroxyphthalide (V) was condensed with formaldehyde and hydrochloric acid, a product identical with the dioxanylphthalide (II) was obtained, thus completing the cycle. This substance (II) gave a stong fluorescence in the phthalide test with resorcinol and sulphuric acid. It gave also a reddish-orange precipitate with phloroglucinol and sulphuric acid which Mehta and Ayyar (10) have used as a test for the *m*-dioxane ring.

The presence of the *m*-dioxane and phthalide rings in II has been shown by degradative oxidation following the classical methods of Borsche and Berkhout (1) and more recently of Buehler and his coworkers (2, 3, 4, 5, 6). Oxidation of II with alkaline permanganate opened the phthalide ring and gave the ortho dibasic acid (VI) which readily formed the anhydride (VI*a*).




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Acid hydrolysis of VI opened the dioxane ring with elimination of formaldehyde and the formation of the hydroxylactone (VII). Decarboxylation with quinoline and copper chromite gave the hydroxyphthalide (VIII). Oxidation of the methyl ether (VIII*a*) with alkaline permanganate opened the new phthalide ring and yielded the dicarboxylic acid (IX) whose orientation has been previously established by Simonsen and Rau (11).

When the dioxanylphthalide (II) was oxidized with chromic oxide and acetic acid the methylene ether – ester (X) was produced. This is the usual first step in the opening of *m*-dioxane rings. Alkaline hydrolysis of this ether–ester according to the method of Borsche and Berkhout (1) splits off formaldehyde, but the acid (XI) has not yet been isolated in pure form.

## EXPERIMENTAL

3-Hydroxy-4-methylbenzoic acid (I), 3-methoxy-4-methylbenzoic acid (III), and 5-methoxy-4-methylphthalide (IV) were made as described by Charlesworth, Rennie, Sinder, and Yan (7) in the first paper in this series.

*The Lactone of 6-Hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic Acid (II)*

3-Hydroxy-4-methylbenzoic acid (20 gm.), formaldehyde solution (100 ml., 40%), and concentrated hydrochloric acid (100 ml.) were heated on the water bath for one hour. The acid did not appear to go into solution, but a definite reaction occurred. After cooling and dilution, the solid product was filtered and washed with water. It was crystallized from alcohol from which it separated as fine white needles (14 gm.) melting sharply at 165°C. Found: C, 63.9; H, 4.86%; mol. wt. (Rast method), 195; neut. equiv., 201. Calc. for $C_{11}H_{10}O_4$: C, 64.0; H, 4.86%; mol. wt., 206; neut. equiv., 206. On warming this substance with resorcinol and concentrated sulphuric acid followed by sodium hydroxide solution, the greenish fluorescence characteristic of the phthalide ring developed. When warmed with phloroglucinol and strong sulphuric acid a reddish precipitate was formed which Mehta and Ayyar (10) have used to confirm the presence of the *m*-dioxane ring.

*5-Hydroxy-4-methylphthalide (V)*

This product was produced by demethylation of the corresponding methoxyphthalide (IV). Two methods were employed:

(*a*) Hydriodic acid (27 ml., sp.gr. 1.7) and acetic anhydride (27 ml.) were carefully mixed in an atmosphere of carbon dioxide and added to a mixture of 5-methoxy-4-methylphthalide (2 gm.) and washed and dried red phosphorus (2 gm.). The mixture was refluxed gently for three hours in an atmosphere of carbon dioxide, cooled, diluted with water, and filtered to remove phosphorus. The filtrate was evaporated under reduced pressure by a slow current of carbon dioxide. A resinous precipitate formed, which on crystallization from alcohol gave a small amount of a white crystalline solid melting at 190–195°C.

(*b*) More successful results were obtained employing the method introduced by Fernholz and Finkelstein (8) using anhydrous aluminum chloride.

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5-Methoxy-4-methylphthalide (1.8 gm.), anhydrous aluminum chloride (1.4 gm.), and dry benzene (40 ml.) were heated on a water bath. After refluxing for eight hours the brown oil, which had settled out slowly, solidified. After cooling, this solid material was broken up, filtered, and washed first with benzene and then with water. On crystallization from alcohol it separated in fine white needles (0.6 gm.), which melted at 195–197° and were identical with the product formed by method (*a*). Further recrystallization raised the melting point to 205°C. The compound was soluble in hot water and very soluble in hot alcohol, ether, acetone, and benzene. It yielded a strong phthalide test with resorcinol and sulphuric acid. Found: C, 65.7; H, 5.02%. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.88%.

*5-Methoxy-4-methylphthalide (IV)*

A mixture of 5-hydroxy-4-methylphthalide (0.2 gm.), dry silver oxide (0.5 gm.), and methyl iodide (10 gm.) was refluxed gently for an hour. The excess methyl iodide was removed by distillation and the residue extracted with hot alcohol. The extract was concentrated and, on cooling, glistening white needles which melted at 143–146°C. separated. A mixed melting point proved the substance identical with 5-methoxy-4-methylphthalide, produced by direct condensation of 3-methoxy-4-methylbenzoic acid with formaldehyde and hydrochloric acid (7).

*Condensation of 5-Hydroxy-4-methylphthalide*

A mixture of 5-hydroxy-4-methylphthalide (0.5 gm.), formaldehyde solution (5 ml., 40%), and concentrated hydrochloric acid (8 ml.) was heated for an hour on the water bath. After cooling and dilution the solid was filtered off. It crystallized from alcohol in the form of needles (0.4 gm.), which melted at 164–165°C. and which mixed melting point showed to be identical with the lactone of 6-hydroxymethyl-1,3-benzodioxane-8-methyl-5-carboxylic acid described above.

*1,3-Benzodioxane-8-methyl-5,6-dicarboxylic Acid (VI)*

The dioxanylphthalide II (6.0 gm.) was dissolved in potassium hydroxide (10 gm.) in water (300 ml.) by allowing the mixture to stand overnight. The solution was cooled in an ice bath to 5–10°C. and maintained at this temperature during the oxidation. A solution of potassium permanganate (24 gm.) in water (700 ml.) was added slowly over a period of one hour. The resulting green solution was allowed to regain room temperature and to stand overnight. The manganese dioxide was filtered off, washed with water, and the combined filtrates acidified with hydrochloric acid, litmus being employed as indicator. The solution was concentrated to about 300 ml. by evaporation on a hot plate at 80°C. and acidified with hydrochloric acid, with Congo red as indicator. The white, chalky, crude acid was separated by filtration and purified by dissolving in sodium bicarbonate and treating with Norite. On acidification a sufficiently pure acid (4.0 gm.) was obtained for further reactions. It was recrystallized for analysis from acetone. The pure acid melted at 199–200°C. with loss of water. Found: C, 55.3; H, 4.17%; neut. equiv., 120. Calc. for $C_{11}H_{10}O_6$: C, 55.5; H, 4.20%; neut. equiv., 119.

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*The Anhydride of 1,3-Benzodioxane-8-methyl-5,6-dicarboxylic Acid (VIa)*

The aforementioned acid VI (1.1 gm.) was heated on an oil bath at 202–205° until the violent evolution of water vapor had subsided. Continued heating or higher temperature was avoided, as it caused evolution of formaldehyde and resin formation. The solidified mass was extracted with boiling toluene and filtered hot. On cooling, the anhydride separated in masses of yellow needles (0.5 gm.). A second crystallization from toluene gave a pure product which melted at 193–194°C. Found: C, 60.0; H, 3.69%. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.64%.

The anhydride can also be formed by dissolving the acid (1.2 gm.) in hot acetic anhydride (1.9 ml.). The solution was evaporated to half its volume on the hot plate and, on cooling, crystals of the anhydride separated. These were filtered, washed with anhydrous ether, and crystallized as before from toluene.

*The Lactone of 3-Hydroxymethyl-4-hydroxy-5-methyl-1,2-phthalic Acid (VII) and Its Derivatives (VIIa)*

The dicarboxylic acid VI (6.0 gm.) was heated under reflux for six hours with concentrated hydrochloric acid (100 ml.) and water (100 ml.). Formaldehyde was evolved during the heating. The yellow needles formed were collected and recrystallized from a mixture of alcohol and petroleum ether. The recrystallized material (4.5 gm.) melted at 269–270°C. Found: C, 57.4; H, 3.87%; neut. equiv., 200. Calc. for $C_{10}H_8O_5$: C, 57.7; H, 3.84%; neut. equiv., 208.

The 4-methyl ether of this acid was formed by treatment in the usual manner in sodium hydroxide solution with dimethyl sulphate. It crystallized from acetone in fine white needles which melted at 154–155°C. Found: C, 59.3; H, 4.71%. Calc. for $C_{11}H_{11}O_5$: C, 59.4; H, 4.50%.

The 4-acetyl derivative of the above acid was prepared in the usual manner by treatment of the potassium salt with acetic anyhydride. The crude acetate was crystallized first from alcohol and then from acetone. The purified material melted at 189–190°C. Found: C, 57.5; H, 4.02%. Calc. for $C_{12}H_{10}O_6$: C, 57.6; H, 4.03%.

*3-Hydroxy-4-methylphthalide (VIII)*

The monocarboxylic acid VII (4.8 gm.) was dissolved in pure quinoline (40 ml.) and copper chromite (0.01 gm.) added. The mixture was heated on an oil bath at 185°C. as long as carbon dioxide was evolved. The cooled quinoline solution was acidified with dilute hydrochloric acid (1 : 1) and extracted with ether. Removal of the ether left a yellow oily material which was purified by repeatedly treating the solution in dilute sodium hydroxide with Norite. After acidification the recovered phthalide (2.1 gm.) was crystallized from water and melted at 190–191°C. Found: C, 65.6; H, 4.84%. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.88%.

*3-Methoxy-4-methylphthalide (VIIIa)*

The 3-methyl ether of the phenolic phthalide (VIII) was obtained by repeated methylation with methyl sulphate and sodium hydroxide. After acidification and several crystallizations from a mixture of acetone and water

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it melted at 119–120°C. Found: C, 67.0; H, 5.60%. Calc. for $C_{10}H_{10}O_3$: C, 67.4; H, 5.62%.

*3-Methoxy-4-methylphthalic Acid (IX)*

3-Methoxy-4-methylphthalide (1.1 gm.) was dissolved in sodium hydroxide solution (10 ml., 10%). To this stirred solution finely powdered potassium permanganate (1.0 gm.) was added gradually at such a rate that the temperature did not rise above 22°C. The solution was allowed to stand at room temperature for 24 hr. The manganese dioxide was decomposed by the gradual addition of sodium bisulphite and after acidification the solution was extracted thoroughly with ether. The white solid left after removal of the ether was triturated with sodium bicarbonate solution. A residue (0.3 gm.) of unoxidized phthalide was left. The bicarbonate solution was treated with activated charcoal, filtered, and acidified with hydrochloric acid. The acid thus obtained was crystallized thrice from water and finally from a mixture of acetone and chloroform from which it separated in small prisms (0.3 gm.) which melted at 172–173°C. Found: C, 57.1; H, 5.07%. Calc. for $C_{10}H_{10}O_5$: C, 57.1; H, 4.76%. A mixed melting point of this acid with an authentic sample prepared by the method of Simonsen and Rau (11) gave no depression.

*The Anhydride of 3-Methoxy-4-methylphthalic Acid (IXa)*

When the dibasic acid (IX) was heated at 160° on an oil bath until bubbling ceased, the anhydride was produced. When recrystallized from toluene it melted at 133–134°. Simonsen and Rau (11) reported a melting point of 135°C. A mixed melting point with a sample prepared by the method of these authors confirmed the identity of the above anhydride.

*The Lactone of 6-Hydroxymethyl-8-methyl-1,3-benzodioxane-4-one-5-carboxylic Acid (X)*

The dioxanylphthalide II (2.0 gm.) was dissolved in warm glacial acetic acid (12 ml.) and the solution allowed to regain room temperature. A saturated solution of chromium trioxide (3.0 gm.) in water was diluted with glacial acetic acid (5 ml.) and gradually added to the phthalide solution at such a rate that the temperature did not exceed 70°. The mixture was allowed to stand at room temperature for 36 hr., heated to 50° on the hot plate, and again cooled. After four hours it was diluted with water (250 ml.) and allowed to stand overnight. The precipitate was removed by filtration, washed thoroughly with water, dried, and extracted with cold acetone (50 ml.) which removed any unreacted dioxanylphthalide. The residue was dissolved in the minimum of boiling acetone and filtered. Two thirds of the acetone was evaporated and on cooling, white crystals which melted at 240–245°C. were obtained. A further crystallization from acetone and finally from water afforded a pure product (0.12 gm.) which melted at 249–250°C. Found: C, 59.9; H, 3.67%; mol. wt., 211. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.64%; mol. wt., 220.

When the above methylene ether – ester (X) was hydrolyzed on the water bath with 20% sodium hydroxide solution a strong odor of formaldehyde was noticed, but the ortho hydroxy acid (XI) has not yet been isolated in pure form.

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# THE DIELECTRIC BEHAVIOR OF VAPORS ADSORBED ON SILICA GEL[1]

By J. A. Snelgrove,[2] H. Greenspan,[3] and R. McIntosh[4]

ABSTRACT

Experiments to determine the dielectric constants of adsorbed butane, ethyl chloride, and water on an activated silica at frequencies up to 3.7 Mc. per sec. are reported. No Debye-type dispersion was observed for the polar adsorbates down to −30° C., the lowest temperature employed. Mixtures of ethyl chloride and water, and of butane and water, were also studied. The assumption that adsorption of ethyl chloride and water occurs with both adsorbates sharing two types of sites sufficed to explain the findings for this system. No explanation was apparent to account for the behavior of the butane-water system.

Formulae due to Kurbatov and to Snelgrove and McIntosh have been used to interpret the results obtained with polar adsorbates. On the assumption that the adsorbates have densities equivalent to those for the liquid state at the same temperature, it is concluded that adsorbed water undergoes oscillatory motion. The first quantities of ethyl chloride adsorbed behave as though the molecules may rotate freely within an angle of 98°. The ethyl chloride adsorbed nearer the saturation pressure shows oscillatory motion, as a negligible temperature coefficient of the molar polarization is observed.

## INTRODUCTION

In previous publications (5, 6), data have been presented which are characteristic of the dielectric behavior of water, ethyl chloride, and butane when adsorbed on a porous silica gel. It was shown that for all the adsorbates linear sections of the plots of capacitance change vs. volume adsorbed were obtained; that the several linear sections for each substance indicated an abrupt alteration of the electrical properties of the adsorbed material; and that the apparent change of electrical properties occurred at a quantity of adsorbate on the surface which did not vary with temperature for a given adsorbate and which did not appear to be related to the cross-sectional area of the adsorbed species. In addition, up to a frequency of 100 kc. per sec., no Debye–type dispersion was found down to − 15°C. in the case of adsorbed water, and − 30°C. in the case of ethyl chloride.

An explanation of the sudden change of dielectric properties was sought. There was no particular support for the view expressed by Kurbatov (3) that the observed change marks the completion of the unimolecular layer. The phenomenon was therefore attributed to adsorption on different types of site, and the density of the adsorbed phase was assigned a value which would yield a "reasonable" absolute value of the polarization.

Other unexpected results were observed. The temperature coefficient of the dielectric constant of the polar adsorbates was found to have anomalous values when compared with bulk (liquid) matter. Moreover, the behavior

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*Contribution from the Chemistry Department, University of Toronto, Toronto, Ont.; based on theses presented by J. A. Snelgrove and H. Greenspan as part of the requirements for the degrees of Ph.D. and M.A., respectively, of the Graduate School, University of Toronto.*
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exhibited differed for each linear section along an isotherm. The most difficult observation to explain was the high apparent value of the polarization, indicating a contribution from the orientational part to the total polarization, in combination with a zero or very small temperature coefficient. It was pointed out that this difficulty could be avoided through the assignment of the density of the adsorbate. Such a practice, however, is not particularly helpful in extending our knowledge of the adsorbed state, and indeed, would have to be abandoned as soon as the knowledge of this factor is obtained. Information concerning the density of the adsorbate can already be derived for nonpolar materials (6) and at sufficiently high frequencies the same method could be applied for polar adsorbates.

In the present paper measurements are reported similar to those referred to, but the frequency range has been extended to 3.7 Mc. per sec. This is about the upper limit which can be investigated using the form of cell and housing which has been developed. The difficulty arises from errors introduced by leads. As the electrical system, once calibrated, is quite satisfactory up to this frequency, a description of the system will be given.

Using this apparatus three chief findings were made. First, the dielectric loss factor, while increasing at the higher frequencies, did not appear to be near a maximum, although the higher frequency range permitted a better elimination of the contribution of d-c. conductance to the loss tangent in the case of water than had previously been achieved.

Second, mixtures of adsorbed ethyl chloride and water may be treated as adsorbing on two types of site, both adsorbates competing for the two types of site. Alternatively, the adsorption data are shown to be consistent with the equation given by Tompkins (8) for adsorption on a heterogeneous surface which possesses a very wide distribution of the energies of the sites. If this view is adopted, it may be seen that both water and ethyl chloride are distributed over the various types of site in the same way.

Third, the adsorption of butane and water has presented a result for which we can offer no explanation. It is found that the position of the abrupt change of slope from one linear section to the next for butane isotherms on gel with varying quantities of water is displaced up to a limiting quantity of water added. Beyond this quantity no further displacement is observed, a behavior quite different than that of ethyl chloride adsorbed on gel of various water contents. In addition, it is also found that the equilibrium pressure of the butane, for any given quantity adsorbed, continues to increase with additional water in the gel.

Some reinterpretation of results reported earlier is attempted. This is based on formulae which are now available, and which express the orientational polarization of an oscillating dipole and a dipole which is free to rotate within a given cone angle, but cannot rotate through larger angles. Kurbatov (4) developed expressions for the polarizations of such molecules when oscillation or rotation may take place in three dimensions. In the following paper (7) the cases of dipoles restricted to oscillate or rotate in the plane of the adsorbing

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surface are considered. The importance of the model of an oscillating dipole is the prediction of a zero temperature coefficient of the polarization, although the contribution from the orientational polarization need not be zero. Thus some of the effects attributed to the density may now be explained in terms of the oscillating dipole. A rotating dipole shows a temperature coefficient of the polarization. Information now available is not sufficient to state that the model of the oscillator is to be preferred to density adjustment, or vice versa. The oscillator model offers greater specificity, and, in conjunction with the detection and study of Debye dispersion, should assist greatly in the interpretation of dielectric measurements.

## EXPERIMENTAL

The adsorption assembly, cell, and pressure gauges have been adequately described (6), and need not be shown in detail here. However, a somewhat novel and very convenient arrangement was used for the measurement of the amount of water adsorbed. It is shown diagrammatically in Fig. 1. The

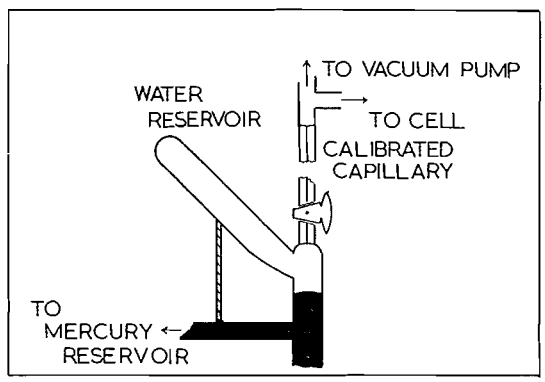



FIG. 1. Diagram of water doser.

design has the advantage that the water need be freed of dissolved gases only once, and a single filling is sufficient for many experimental runs. The mercury displaces water into the calibrated capillary, which is then isolated by means of the stopcock from the main volume, eliminating the need of temperature regulation. The level is read by means of a telescope and a Beckmann thermometer scale, and the desired amount of water is allowed to distill into the cell. To prepare for a new addition, it is only necessary to lower the mercury below the side-arm, allowing some of the trapped water to enter the capillary, and then raise it again to the desired level. Usually a difference in height of about 5 cm. of capillary was used, and the volume of material adsorbed for a single admission was known to $\pm 0.3\%$. No correction was needed for the residual water vapor in the connecting lines over the low relative pressure range investigated.

*Measurement of Capacitance Change*

The bridge system employed for measurements up to 100 kc. per sec. has

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already been described (6). A resonance circuit was used above this frequency. It consisted of a coil, the measuring condenser and the test cell in parallel with one another and with the coil, and a vacuum tube voltmeter connected across the common terminals of the circuit. A high resistance in series with the grid of the voltmeter tube assured negligible current drain by the voltmeter branch even at high frequencies. Neither of the condensers of the mesh was free from residuals, and these were sufficient to cause significant errors at the higher frequencies. The effect of the residuals was also dependent upon the setting of the condenser, in the case of the measuring condenser, and the value of capacitance of the test condenser. The measuring condenser, a General Radio Type 722, was found to have an apparent capacity, which could be related to its true, or low frequency value of capacity, by the relation

$$C_a = C_t(1 + \omega^2 L C_t)$$

where $L$ is the series inductance of the condenser, $C_a$ and $C_t$ are the apparent and the true value of the capacitance, respectively.

Now if the reading of this measuring condenser is determined at resonance, and if any change is brought about in the capacitance of the test cell branch, a new setting of the measuring condenser is required to re-establish resonance. The difference between any two such readings may be corrected by the above formula to yield the true value of the capacitance change which occurred. However, the measured change thus obtained arises from the condenser in the test arm and the effect of residuals of that condenser. It was therefore necessary to obtain the values of the inductance and capacitance of the leads of the test cell. The capacitance of the leads, including the connections through the cell housing, was determined over the frequency range and varied from 48.82 to 48.25 $\mu\mu$f. The effect of the series inductance and resistance of the leads on the capacitance of known condensers, of values covering the range expected with the test cell, was determined at various frequencies. The apparent capacitance was expressed in terms of the true by means of the formula given above. This practice resulted in values of $L_T$, where this is the series inductance of the test cell, which varied slightly both with frequency and value of the condenser at the end of the leads. As the variation was slight, showing that the effect of the series resistance was small, the procedure was adopted of using a value of $L_T$ which was appropriate to the frequency and value of capacitance of the test cell. Under the worst conditions, that is a high capacitance at the end of the leads and at the highest frequencies, the correction term was about 70 $\mu\mu$f. in about 600 $\mu\mu$f. for the test cell. Application of the correction reduced the error to less than 1 $\mu\mu$f. It may be added that over the frequency range where both the bridge and resonance systems could be employed, the data obtained agreed within 0.1 $\mu\mu$f.

The variation of the equivalent shunt conductance of the test cell branch was determined by evaluating the conductance of the circuit when only degassed adsorbent was in the cell and when a known quantity of adsorbate had been added. The standard method of obtaining the conductance from the shape of the resonance peak was employed. The change of conductance

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for a given addition of adsorbate can then be considered as arising from the connection of a condenser across the test branch, the capacitance of which is that caused by the addition of the adsorbate, and the shunt conductance of which is that necessary to account for the observed conductance change. In the present investigation the changes of conductance were very small, and the total shunt conductance of the composite dielectric is reported.

These procedures are applications of the principles discussed by Hartshorn and Ward (2).

*Oscillator and Vacuum Tube Voltmeter*

The signal was supplied by a series-fed Hartley oscillator, employing a 6J5 tube, and having a frequency range from 0.100 to 3.70 Mc. per sec. It was operated at fixed and calibrated frequencies, obtained by changing the coil of the tank circuit or by varying the tuning condenser. The oscillator was coupled to the resonant circuit by means of a cathode follower circuit, employing a 6J5 tube and a coil. The cathode follower served to isolate the oscillator. A regulated power supply was used.

The voltage across the resonant circuit was measured by means of a bridge-type vacuum tube voltmeter (2) in conjunction with a moving coil galvanometer having a sensitivity of 0.0029 $\mu$amp. per mm. The self-compensating action of the bridge-type circuit, the use of type 957 tubes of low interelectrode capacitance, and the use of batteries as power source enabled the optimum sensitivity of the galvanometer to be utilized.

*Results with Water*

The increased frequency at which the electrical properties of the adsorbed water were measured resulted in little new information. The main finding arising from measurements made at 0.6° C. was that some conduction dispersion was apparent in the results obtained up to 0.1 Mc. per sec. which were reported earlier. This dispersion led to slightly high values of the polarization. Whereas values of the polarization per cubic centimeter of 1.047 and 0.952 have been reported for the first and second linear sections respectively using formula (*a*) of the paper by McIntosh, Rideal, and Snelgrove (6), these should be reduced to 1.02 and 0.900 as determined from the measurements at higher frequencies. In view of the difficulty of interpreting results, this change does not alter materially what can be deduced concerning the adsorbed state of water. As pointed out previously (6), a value of the polarization per cubic centimeter greater than one is not an absurdity, since an incorrect assignment of the density of the adsorbate can account for such values. The values stated here are based upon a density of 1.0 gm. per cc.

The high polarization per cubic centimeter along both linear sections, in conjunction with a zero temperature coefficient, may now be interpreted by means of the models of oscillating dipoles. The choices are either a dipole which may oscillate in three dimensions, or a dipole which oscillates in the plane of the adsorbing surface. The correction factor $a$ of the Kurbatov formula (4), or of the formula given in the following paper (7), may be evaluated by employing the known refractive index of water and the value of its

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permanent dipole moment of 1.87 debyes. On this basis the value of $a$ is 0.159 along the second linear section, where it is possible to assign the normal liquid density. The two formulae yield respectively 5.9 and 1.1 for $\beta^2$. These values lead to 3400 cal. per mole and 640 cal. per mole, respectively, for the energy of the oscillator. Here $\beta^2$ is $\omega^2 I/2kT$ where $\omega$ is the frequency of oscillation and $I$ is the moment of inertia of the dipole. $E$ is $\omega^2 I/2$.

Since it has been pointed out by De Boer (1) that a physically adsorbed polyatomic molecule should lie flat on the surface, the values for the oscillator constrained to the plane would appear preferable.

If measurements can be obtained at sufficiently high frequencies for $\omega$ to be determined, since the orientational polarization observed leads to $\mu^2/\omega^2 I$, a comparison of $\mu^2/I$ between molecules in the adsorbed state and in the gaseous state should be possible.

One further result of the tests at higher frequencies is the recognition that Debye-type dispersion is just becoming discernible for moderate quantities of adsorbed water. As shown in Fig. 2, where the loss tangent of the composite

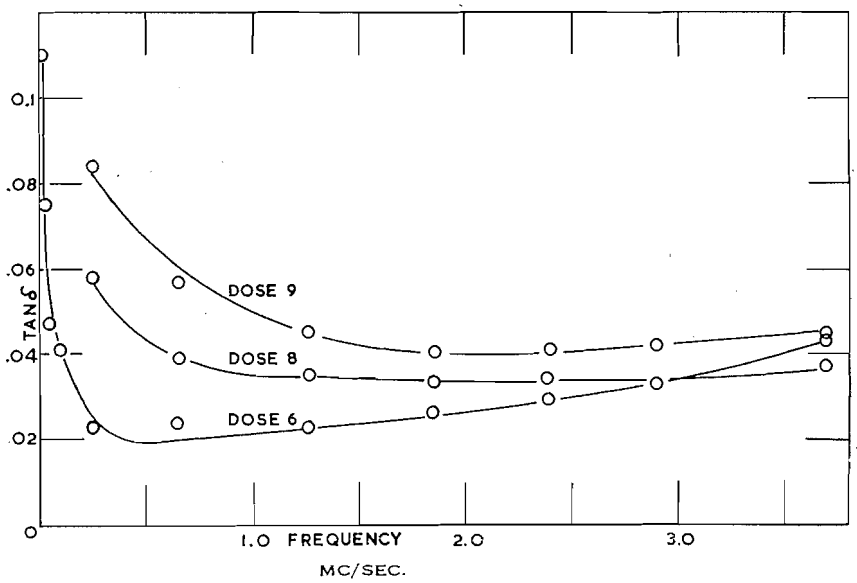



FIG. 2. Loss tangent of cell filled with silica and various quantities of adsorbed water.

dielectric is plotted against frequency, a minimum is observed for the sixth addition of water. With further adsorbate, conduction dispersion has masked the effect. The observations again serve to emphasize the necessity for measurements at very high frequencies, and at lower temperatures. Silica gel and water appear to be an inconvenient system for study at lower temperatures. An isotherm at −30° C. was abandoned because of the long time lags and the finding that the initial part of the first linear section was identical with the corresponding section at higher temperatures.

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*Results with Ethyl Chloride*

Three isotherms were measured at +30°, 0°, and −30° C. The electrical measurements were made at frequencies up to 3.7 Mc. per sec. No Debye-type dispersion was noted even at the lowest temperatures. The data obtained were sufficiently similar to those reported earlier (6) that it is not necessary to quote them here. Again, assigning the normal liquid state value of the density at each temperature, a temperature coefficient of the molar polarization was observed along the first linear region, while a negligible temperature coefficient was observed along the second linear region.

In view of the formulae due to Kurbatov (4) and ourselves (7), the ethyl chloride adsorbed over the pressure range where the dielectric data reveal a temperature coefficient may be considered as a rotating dipole within a given cone angle or given angle of arc. The value of this angle, $\Omega^0$, is 98°, whether the motion is considered possible in three dimensions, or is restricted to the adsorbent plane.

Along the second linear region the adsorbate must be considered to oscillate. The value of $\beta^2$ deduced by the Kurbatov formula is 4.8, which results in a value of the energy of 2800 cal. per mole. The value of $\beta^2$ deduced on the assumption of oscillations constrained to a plane is 0.84, and the value of the energy is 490 cal. per mole.

*Ethyl Chloride – Water Results*

Four isotherms were determined at 0.1° C. with the quantity of water in the gel varying from 0 to 250 cc. expressed as gas at N.T.P. The data are shown in Fig. 3 as plots of $\Delta C$ vs. volume of ethyl chloride adsorbed. It was found that the same initial and final slopes were obtained except at the highest moisture content, where even the first addition of ethyl chloride results in a lower value of the capacitance increment than found on dry silica. The position of the discontinuity of slope, obtained from the intersection of the linear sections, shifted progressively to lower quantities of ethyl chloride adsorbed. The shift of this position was not linear in the quantity of water adsorbed. It became less dependent on this quantity as the water content was increased.

To account for the observations an analysis based on an assumption of two types of adsorption site has been employed. It was postulated that both ethyl chloride and water are adsorbed on these two types of sites, and that for each site the polarizability of the molecule is characteristic. Since the experimental observations, both for water and ethyl chloride, showed a slight but regular change in the slope of formula (*a*) (Reference (6)) for each addition of adsorbate, it was possible to compute the fraction of each addition of adsorbate associated with the respective types of sites. (The trend in slope, although observable and quite regular if sufficient significant figures are employed, does not invalidate the assertion that linear sections of the plots exist to the precision with which the results have been given in tables and figures of this and other publications.) The computation of the fraction associated with each type of site also involves the assumption that the polarization may be accounted for as the sum of the polarizations associated with each type of site

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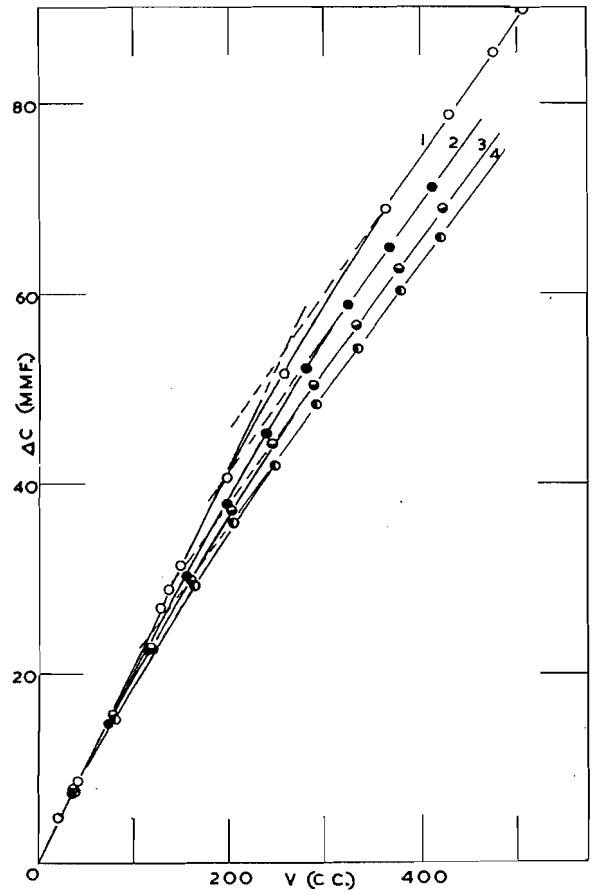



FIG. 3. Dielectric data for ethyl chloride and water systems at 0.1° C.

multiplied by the volume fraction of each addition adsorbed on each type of site.

Using the results obtained for the adsorbates separately, a calculation was made of the amount of ethyl chloride and water which would adsorb on each type of site as a function of the total amount adsorbed. These values were then applied to the isotherms for ethyl chloride on gel of varying water content. The results are given in Table I and it can be seen that the total volume ad-

TABLE I

| $H_2O$ content of gel, cc. at N.T.P. | $H_2O$ adsorbed on Type I, cc. at N.T.P. | $C_2H_5Cl$ adsorbed on Type I, cc. at N.T.P. | Total adsorbed on Type I, cc. at N.T.P. |
|---|---|---|---|
| Nil | Nil | 234 | 234 |
| 85 | 79 | 155 | 234 |
| 175 | 140 | 101 | 241 |
| 250 | 180 | 71 | 251 |

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sorbed on one of the types of site remains substantially constant, although the comparative quantities of water and ethyl chloride are quite different. Here the amount of water on Type I is calculated from the electrical data for water alone, while the value for ethyl chloride was obtained with the dry gel. The approximate constancy of the figures of the final column suggests that the treatment is a fair approximation.

To attempt to confirm this rationalization, the total volume adsorbed was considered to be given by an equation of the Langmuir form for two types of sites, that is

$$V = \frac{b_1 V_1 p}{1 + b_1 p} + \frac{b_2 V_2 p}{1 + b_2 p}.$$

The appropriate values of $V_1$ and $V_2$ for an isotherm at a given value of water content were then obtained by taking 234 cc. and subtracting the amount of

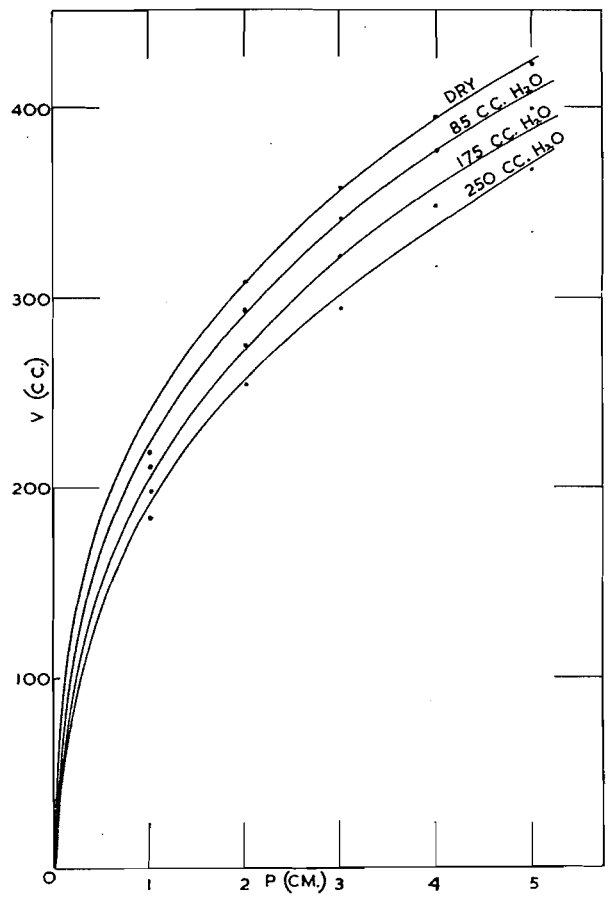



FIG. 4. Adsorption data of ethyl chloride – water systems.
Curves represent experimental values.
Points represent calculated values.

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water on Type I sites, and by taking 466 cc., a value obtained from the saturation value for ethyl chloride on the dry gel in conjunction with the quantity on Type I sites, and subtracting the amount of water on Type II sites. From the isotherm for the dry gel $b_1$ and $b_2$ were evaluated, and these values were then employed for the isotherms of wet gels. The approximate agreement of theory and experiment is indicated in Fig. 4. The treatment is approximate, but serves to show that the electrical results for ethyl chloride in the presence of adsorbed water are semiquantitatively accounted for on the postulate that water and ethyl chloride are adsorbed on the same types of sites. The assumption of two types of sites appears sufficient to account for the nature of the observations.

The adsorption data for ethyl chloride, both on dry and wet gel, show the best agreement with theory when the Bradley–De Boer–Palmer equation is employed. This form of adsorption isotherm has been shown by Tompkins (8) to arise when nonlocalized monolayers are established on a surface with sites of a wide range of energies. This description of the system is inconsistent with the two site theory outlined above, but offers another possible explanation for the gradual change of polarization of the adsorbate with increasing surface concentration.

The slopes of the plots of the Bradley–De Boer–Palmer equation are independent of moisture content of the gel. Since the slope is related to the width of the distribution curve of the sites of various energies, and to the volume required to complete the unimolecular layer, it follows that the water must be distributed on the numerous types of sites in the same way as the ethyl chloride.

*Butane and Water Mixtures*

The adsorbates butane and water were studied in the same way as ethyl chloride and water at 0.1° C. The results, which are given in Table II and

TABLE II

DIELECTRIC DATA FOR BUTANE ON SILICA AT 0.1° C.

| Water content of gel, cc. at N.T.P. | Dielectric constant using formula (*a*) | | Refractive index squared |
|---|---|---|---|
| | First linear section | Second linear section | |
| Nil | 1.79 | 1.74 | 1.81 |
| 44.6 | 1.74 | 1.72 | 1.81 |
| 89.1 | 1.74 | 1.70 | 1.81 |
| 167 | 1.70 | 1.68 | 1.81 |
| 361 | 1.70 | 1.62 | 1.81 |

represented graphically in Figs. 5 and 6, are very different. In the butane–water system the slope of the initial part of the $\Delta C$ vs. volume adsorbed plot did not change with increased moisture content. Moreover, beyond a moisture content of 167 cc. of water (as vapor at N.T.P.), there was no further change in the position of the intersection of the two linear sections of the plot, although

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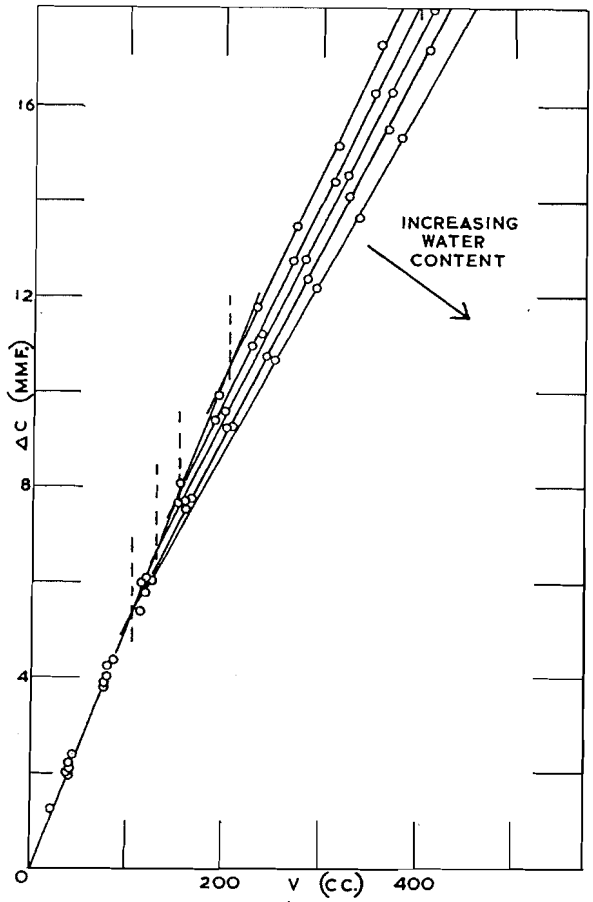



FIG. 5. Dielectric data for butane–water system at 0.1° C.

the isotherm is altered as shown in Fig. 6.

As can be seen from Table II, there is a variation of the apparent dielectric constant of the adsorbed material with moisture content for both sections of the data. In view of earlier discussions concerning nonpolar adsorbates (6), it appears necessary to explain the observed change in terms of a density variation. In this case it appears that the adsorbed film changes density to a limiting value along the first section, but that the value continues to alter along the second section. Such a view leads to speculation concerning the arrangement of the water and butane molecules in the adsorbent gel. With the present information, however, we have been unable to develop any self-consistent theory, particularly in view of the two facts that ethyl chloride and water appear to compete for the same sites, and that the isotherm continues to alter with increasing water content of the gel, while the electrical data over the range of low butane adsorption remain unaltered. It should be pointed out also that the butane–water data do not conform with the Bradley–De Boer–Palmer equation.

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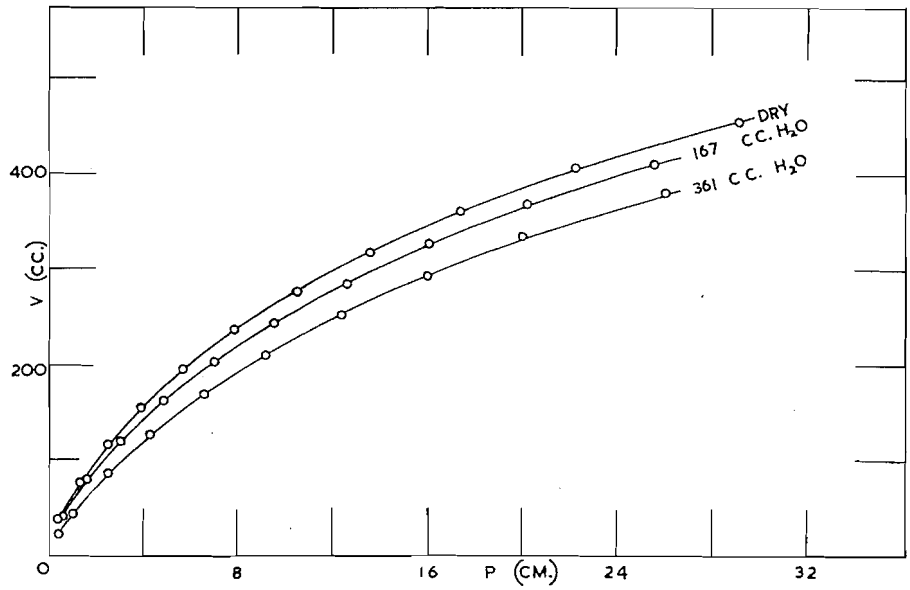



FIG. 6. Adsorption data for butane–water system at 0.1° C.

Clearly, such information must eventually be related with the abrupt change of apparent dielectric properties which has now been firmly established for a variety of systems, and concerning which no adequate comprehension can be claimed.

ACKNOWLEDGMENT

We are indebted to Prof. R. H. McKay of the Physics Department for valuable discussions and advice.

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# THE ORIENTATIONAL POLARIZATION OF ADSORBED POLAR MOLECULES[1]

By J. A. Snelgrove[2] and R. McIntosh[3]

ABSTRACT

The orientational polarization of a polar molecule adsorbed on a solid surface is deduced for two cases. First, the molecule oscillates in the plane of the surface about some equilibrium position. A zero temperature coefficient of the polarization is deduced. Second, the molecule may rotate freely in the plane within some given angle, but cannot incline to any greater extent from the equilibrium position under the influence of the field. The normal temperature coefficient is obtained with this model.

The derivation of these formulae is based upon the procedures of Kurbatov who considered oscillation and rotation to be possible in three dimensions. The models employed here are considered preferable on the grounds that a physically adsorbed polyatomic molecule would presumably lie flat in the plane of the adsorbing surface.

## INTRODUCTION

Recently Kurbatov (3) has derived several formulae for the orientational polarization of adsorbed polar molecules. He has treated two cases: one, a dipolar molecule which is attached to the surface at one end, and which may oscillate in three dimensions about some mean position in space; two, the dipolar molecule may rotate freely within a given cone angle, but cannot pass beyond the limits of the particular cone. Both these models would appear to be of value in explaining the observed behavior of adsorbed polar molecules. The first leads to the conclusion that a contribution to the over-all polarization from the orientational polarization may exist although a zero temperature coefficient of the polarization is also found. This is quite distinct from the case of a freely rotating dipole.

The second model leads to an expression for the orientational polarization which contains the absolute temperature in the same form as the Debye formula (2). The normal temperature coefficient has also been shown to result in the case of a dipolar molecule which may rotate freely in the plane of the adsorbing surface (4). The rotating dipole may be treated more generally in the manner developed by Kurbatov, and the angle on the plane, within which the molecule may rotate freely, may be deduced. The formula involved is identical with that given by Kurbatov, and no deduction of this particular case need be given.

It is also possible to consider the case of a polar molecule which is constrained to oscillate in the plane of the adsorbing surface. The result is somewhat different from that given by Kurbatov. The zero or negligible temperature coefficient of polarization is again deduced, but quite different values of the restoring energy are derived using the formula. Thus, the assumption of oscillations in three

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*Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont. Taken from a thesis presented in partial fulfillment of the requirements for the Ph.D. degree of the Graduate School, University of Toronto.*

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dimensions may lead to an energy term for the oscillator of 5000 cal. per mole (5), whereas oscillation in a plane with an energy of 500 cal. per mole results in the same value of the orientational polarization.

In view of the considerations stressed by DeBoer (1), and because of the general experimental evidence through heat of adsorption, it seems reasonable to expect that polyatomic molecules, which are physically adsorbed, will lie in the plane of the adsorbing surface. On this basis, the formula derived below is to be preferred to that given by Kurbatov.

Because of the intrinsic interest of the model and because the work of Kurbatov is not readily available in the English language, the development of the formula is given quite fully. It follows closely the procedure employed by Kurbatov, and the symbols employed are, where possible, the same as those used by him.

## ORIENTATIONAL POLARIZATION OF A DIPOLE CONSTRAINED TO OSCILLATE IN A PLANE

Consider an adsorbed dipole $\mu$ which can execute small rotational oscillations of angular frequency $\omega$ about an equilibrium position in a plane. The oscillations are assumed to be simple harmonic. The particular plane considered has a given orientation, but for the system as a whole the planes are assumed to be orientated randomly. If, on application of a field $F$, the dipole oscillates about a new equilibrium position inclined with respect to the original position, the potential energy of the dipole will be altered. The change of potential energy arises from the displacement to the new equilibrium position and the force of attraction to the former equilibrium position, and from the inclination in the new equilibrium position with respect to the applied field. Hence, following Kurbatov and employing Boltzmann statistics, the probability of the dipole having a new equilibrium orientation between $\Omega$ and $\Omega + d\Omega$ with respect to the position when no field is acting is proportional to

$$e^{-\beta^2\Omega^2} e^{(\mu F \cos x)/kT} d\Omega$$

for small values of $\Omega$. Here, $\beta^2 = \omega^2 I/2kT$, where $I$ is the moment of inertia of the dipole with respect to the axis of rotation, and $k$ is the Boltzmann constant per molecule. Here $\mu \cos x$ gives the component of the dipole in the direction of the field, which is taken to be along the $x$ axis. The relation among $\cos x$, $\Omega$, and the orientation of the plane is given by

$$\cos x = \cos \psi \cos \theta \cos \Omega + \sin \theta \sin \Omega.$$

The position of the normal line to this particular plane is defined by the angles $\theta$ and $\psi$ with the coordinate axes, $\psi$ being the azimuthal angle.

The probability of the dipole being within the angle between $\Omega$ and $\Omega + d\Omega$ is thus proportional to $e^{-\beta^2\Omega^2} e^{\alpha \cos x} d\Omega$, where $\alpha$ is $\mu F/kT$. The total moment of such dipoles in the direction of the field for all values of $\Omega$ is

$$A \int_0^{2\pi} e^{-\beta^2\Omega^2} e^{\alpha \cos x} \mu \cos x \, d\Omega,$$

where $A$ is a constant depending upon the number of dipoles. The mean value

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of the projection of the moment in the direction of the field for such dipoles in the plane, the orientation of which is given by $\theta$, $\psi$, is

$$(a) \qquad \bar{m}_{\theta,\psi} = \frac{A\int_0^{2\pi} e^{-\beta^2\Omega^2} e^{\alpha\cos x}\,\mu\cos x\,d\Omega}{A\int_0^{2\pi} e^{-\beta^2\Omega^2} e^{\alpha\cos x}\,d\Omega}.$$

The integrals may be evaluated by a procedure which is illustrated by using the numerator. Where $\alpha \ll 1$, that is for weak fields, the exponential term involving $\alpha$ may be expanded in a series and only the first two terms retained. The numerator then becomes

$$\int_0^{2\pi} e^{-\beta^2\Omega^2}(1 + \alpha\cos\psi\cos\theta\cos\Omega)(1 + \alpha\sin\theta\sin\Omega) \times (\mu\cos\psi\cos\theta\cos\Omega + \mu\sin\theta\sin\Omega)d\Omega.$$

Neglecting terms in $\alpha^2$ and rewriting as constants the terms not involving $\Omega$, we have

$$(b) \qquad \int_0^{2\pi} e^{-\beta^2\Omega^2}(1 + k_1\cos\Omega + k_2\sin\Omega)(k_3\cos\Omega + k_4\sin\Omega)d\Omega$$

where $\alpha\cos\psi\cos\theta = k_1$, $\alpha\sin\theta = k_2$, $\mu\cos\psi\cos\theta = k_3$, and $\mu\sin\theta = k_4$. The integral may be evaluated term by term. First extend the upper limit to infinity. This introduces no serious error for values of $\beta^2 \geqslant 0.1$, that is, for sufficiently rigid binding of the dipole, owing to the rapid convergence of the functions being integrated. A graphical test of this statement was made for $\beta^2 = 0.1$, and the areas arising in each term are less than 1% of the area for the appropriate term up to the limit $2\pi$. A method of evaluating the integrals is as follows

$$e^{-\beta^2\Omega^2 + i\Omega} = e^{-\beta^2\Omega^2}(\cos\Omega + i\sin\Omega).$$

The real part is $e^{-\beta^2\Omega^2}\cos\Omega$ and the imaginary part is $ie^{-\beta^2\Omega^2}\sin\Omega$.

Now let $z = \beta\Omega - i/2\beta$ and

$$\int_0^{\infty} e^{-\beta^2\Omega^2 + i\Omega}\,d\Omega = \frac{1}{\beta}e^{-1/4\beta^2}\int_0^{\infty} e^{-z^2}\,dz + \frac{1}{\beta}e^{-1/4\beta^2}\int_{-i/2\beta}^{0} e^{-z^2}\,dz.$$

Hence $\int_0^{\infty} e^{-\beta^2\Omega^2}\cos\Omega\,d\Omega$ is given by the real part of the above equation, while $i\int_0^{\infty} e^{-\beta^2\Omega^2}\sin\Omega\,d\Omega$ is given by the imaginary part. To deal with the imaginary part the substitution $z = iv$ is made, and the integral becomes

$$i\frac{1}{\beta}e^{-1/4\beta^2}\int_0^{1/2\beta} e^{v^2}\,dv.$$

Here the exponential is expanded and the first two terms of the series are retained.

By employing these procedures and evaluating each term in (*b*), one obtains for the numerator of (*a*)

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$$\frac{k_3\sqrt{\pi}}{2\beta}e^{-1/4\beta^2} + k_4e^{-1/4\beta^2}\left(\frac{1}{2\beta^2}+\frac{1}{24\beta^4}\right) + \frac{k_1k_3\sqrt{\pi}}{4\beta}\left(1+e^{-1/\beta^2}\right) + \frac{k_2k_4\sqrt{\pi}}{4\beta}\left(1-e^{-1/\beta^2}\right) + \frac{k_2k_3+k_1k_4}{2}e^{-1/\beta^2}\left(\frac{1}{\beta^2}+\frac{1}{3\beta^4}\right).$$

The denominator becomes

$$\frac{\sqrt{\pi}}{2\beta} + \frac{k_1\sqrt{\pi}}{2\beta}e^{-1/4\beta^2} + k_2e^{-1/4\beta^2}\left(\frac{1}{2\beta^2}+\frac{1}{24\beta^4}\right).$$

Now let

$$\frac{\sqrt{\pi}}{2}e^{-1/4\beta^2} = k_5, \quad e^{-1/4\beta^2}\left(\frac{1}{2\beta}+\frac{1}{24\beta^3}\right) = k_6, \quad \frac{\sqrt{\pi}}{4}\left(1+e^{-1/\beta^2}\right) = k_7,$$

$$\frac{\sqrt{\pi}}{4}\left(1-e^{-1/\beta^2}\right) = k_8, \quad \frac{1}{2}e^{-1/\beta^2}\left(\frac{1}{\beta}+\frac{1}{3\beta^3}\right) = k_9, \quad \frac{\sqrt{\pi}}{2} = k_{10}.$$

Then $\bar{m}_{\theta,\psi}$ becomes

$$(c) \qquad \frac{k_5\mu\cos\psi\cos\theta + k_6\mu\sin\theta + k_7\alpha\mu\cos^2\psi\cos^2\theta + k_8\alpha\mu\sin^2\theta}{k_{10}+k_5\alpha\cos\psi\cos\theta+k_6\alpha\sin\theta} + \frac{2k_9\alpha\mu\cos\psi\cos\theta\sin\theta}{k_{10}+k_5\alpha\cos\psi\cos\theta+k_6\alpha\sin\theta}.$$

To evaluate $\bar{m}$, the mean value of the component of the dipole in the direction of the field, on the assumption of uniform adsorption density, the averaging process is given by

$$(d) \qquad \bar{m} = \frac{\int_0^{\pi}\int_0^{2\pi}\bar{m}_{\theta,\psi}\sin\psi\,d\theta\,d\psi}{\int_0^{\pi}\int_0^{2\pi}\sin\psi\,d\theta\,d\psi}.$$

The exact integration of all the terms in $(d)$ arising through $\bar{m}_{\theta,\psi}$ is not possible but if we use the first two terms of the binomial expansion of the denominator in $(c)$, the equation

$$\bar{m}_{\theta,\psi} = \frac{1}{k_{10}}\left(k_5\mu\cos\psi\cos\theta + k_6\mu\sin\theta + k_7\alpha\mu\cos^2\psi\cos^2\theta + k_8\alpha\mu\sin^2\theta + 2k_9\alpha\mu\cos\psi\cos\theta\sin\theta\right)\left(1-\frac{k_5}{k_{10}}\alpha\cos\psi\cos\theta - \frac{k_6}{k_{10}}\alpha\sin\theta\right)$$

results. Again terms in $\alpha^2$ are neglected and the integral is evaluated term by term. Finally, there is obtained

$$(e) \qquad \bar{m} = \frac{\alpha\mu}{3}\left(1-\frac{1}{2}e^{-1/\beta^2} - \frac{1}{2}e^{-1/2\beta^2} - 6e^{-1/2\beta^2}\left(\frac{1}{2\beta}+\frac{1}{24\beta^3}\right)^2\Big/\pi\right).$$

In the limits when $\beta^2 = 0$ (free rotation) and $\beta^2 = \infty$ (rigid binding), this reduces as expected to

$$\bar{m} = \frac{\alpha\mu}{3} \text{ and } \bar{m} = 0, \text{ respectively.}$$

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When the first two exponential terms of equation (*e*) are expanded into a series and the first two terms are retained,

$$\bar{m} = \frac{\alpha\mu}{3}\frac{3}{4\beta^2} = \frac{\mu^2 F}{2\omega^2 I}.$$

The contribution of the orientational component to the total polarization is

$$(f) \qquad P_\mu = \frac{2\pi N}{3}\frac{\mu^2}{\omega^2 I}$$

which is independent of temperature. This result is to be compared with that obtained by Kurbatov where oscillation is possible in three dimensions, namely

$$(g) \qquad \frac{8\pi N}{9}\frac{\mu^2}{\omega^2 I}.$$

It should be noted that the lack of a temperature term is rigorous only for reasonably large values of $\beta^2$. With $\beta^2$ as small as 0.1 the polarization, as calculated from equation (*e*), is less at 350° A. by about 10% than that at 300° A., while if the Debye form of the equation were involved, the reduction would be about 15%. With $\beta^2 = 0.2$ there is virtually no change of the orientational polarization for such a temperature change.

For any given temperature the orientational polarization may be conveniently expressed by means of the Debye term and a correction factor designated as $a$ by Kurbatov, that is,

$$\bar{m} = \frac{a\mu^2 F}{3kT}.$$

The correction factor varies from a value of one when $\beta^2 = 0$, to zero when $\beta^2 = \infty$. In Fig. 1 are shown the values of $a$ as a function of $\beta^2$ for oscillation in three dimensions, and for oscillation restricted to a plane. The value of $a$ for the oscillator in the plane (curve 2) lies below that for the model treated by

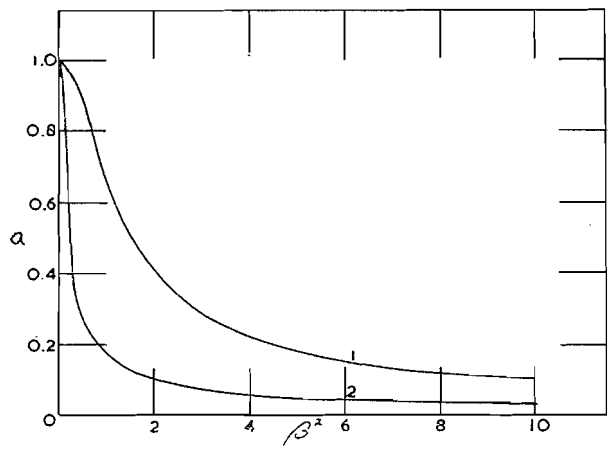



FIG. 1. Correction factors to Debye term for oscillating dipoles as a function of $\beta^2$.

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Kurbatov (curve 1). This leads to values of $\beta^2$ which are much less for the oscillations in the plane than for the model examined by Kurbatov at any given measured value of the orientational polarization. Cases in point have been presented for several adsorbates on activated silica (5).

## FREE ROTATION WITHIN A GIVEN ANGLE ON A PLANE

The orientational polarization of a dipolar molecule which can rotate freely within a given angle on the adsorbing plane, but which cannot rotate beyond this angle, may be developed by a similar modification of Kurbatov's treatment. The necessary relations are:

$$(h) \qquad \bar{m}_{\theta,\psi} = \frac{A\int_0^{\Omega^\circ} e^{\alpha\cos x}\,\mu\cos x\,d\Omega}{A\int_0^{\Omega^\circ} e^{\alpha\cos x}\,d\Omega}$$

$$(i) \quad \text{and} \qquad 4\pi\bar{m} = \int_0^{2\pi}\int_0^{\pi} \bar{m}_{\theta,\psi}\sin\psi\,d\psi\,d\theta.$$

The formula deduced is the same as that given by Kurbatov, namely,

$$(j) \qquad \bar{m} = \frac{\mu^2 F}{3kT}\left(1 - \cos^4\frac{\Omega^0}{2}\right)$$

where $\Omega^0$ is the limiting inclination of the dipole on either side of its equilibrium position in the plane. The correction factor to the Debye term, designated by the symbol $a_1$, is shown as a function of the angle $\Omega^0$ in Fig. 2. It may be noted

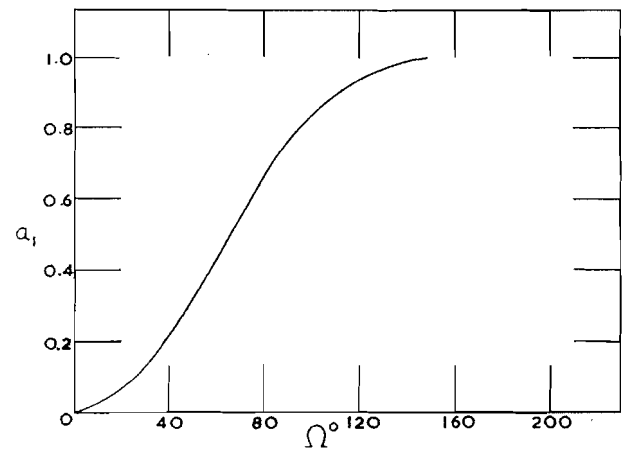



Fig. 2. Correction factor to Debye term for rotating dipoles as a function of limiting angle for free rotation $\Omega^0$.

that for rotation through an angle of 180°, the correction factor is one, in agreement with the result given by McIntosh, Rideal, and Snelgrove (4) for free rotation on a plane. Furthermore, it is seen that the normal temperature coefficient is predicted.

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## CONCLUSIONS

On the basis of these formulae it is possible to interpret the experimental observations of the polarization of adsorbed molecules as arising either from oscillating dipoles or from freely rotating dipoles within some given angle of permitted rotation. In the former case no temperature coefficient is to be expected; in the latter, the normal temperature variation will be observed. It must be remembered, however, that values of the restoring energy or of the angle within which free rotation is possible both depend upon the absolute value of the total polarization which is computed from the experimental results. The absolute value of this quantity depends upon an arbitrary assignment of the density of the adsorbed phase. The uncertainty in this factor can only be eliminated by a determination of the polarization at such high frequencies that any contribution from orientational polarization is negligible.

## ACKNOWLEDGMENT

We are indebted to Prof. R. H. McKay of the Physics Department for valuable discussions.

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# THE DECOMPOSITION OF SOLID POTASSIUM PERCHLORATE BY 50 KILOVOLT X RAYS[1]

By H. G. Heal[2]

ABSTRACT

Potassium perchlorate crystals are decomposed by 50 kv. X rays. The main products of the primary decomposition are chlorate and chloride, but small amounts of unidentified oxidizing substances are also formed. The chlorate decomposes by a secondary reaction to chloride. These reactions are approximately of the first order. The average amount of X-ray energy absorbed by the salt per $ClO_4^-$ ion decomposed is $19 \pm 2$ ev.

## INTRODUCTION

In recent years interest in the decomposition of solid salts by ionizing radiation has been stimulated by the increasing use of the Szilard–Chalmers method for separating radioisotopes. This method makes use of the change in the state of chemical combination of atoms, caused by the recoil accompanying an $(n,\gamma)$ reaction, to separate these atoms from the bulk of the material. Solid salts containing complex ions, e.g. permanganates, chromates, and perchlorates, have given excellent results in Szilard–Chalmers separations. When the samples are irradiated in a nuclear reactor, however, the Szilard–Chalmers effect is often accompanied by partial decomposition of the nonradioactive bulk of the salt. This is due in the main to $\gamma$ rays, which are, of course, unavoidably present at high intensities. It can seriously impede the separation of the radioactive isotope that is sought.

It is now being recognized that such decompositions, although a nuisance from the technical standpoint, are actually quite interesting problems in their own right. Burton in 1947 (3) pointed out the need for more work in this neglected field. The present paper describes an investigation with the object of finding out something about the mechanism of a typical decomposition of this kind. This work differs from most previous researches in the field in having as its principal aims the study of the reaction kinetics and energy utilization.

Newton (8) observed, but did not investigate in detail, the decomposition occurring when potassium chlorate or perchlorate is irradiated in a nuclear reactor for the separation of $Cl^{36}$ by the Szilard–Chalmers effect. The decomposition of potassium bromate associated with Szilard–Chalmers separation of $Br^{82}$ has also been studied (2). It is appropriate to mention, in addition, the work of Günther, Lepin, and Andreev (6) on the X-ray decomposition of barium azide, that of Allen and Ghormley on the decomposition of barium nitrate by Van de Graaff electrons (1), and that of Müller and Brous (7) on the decomposition of sodium azide by slow electrons.

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## EXPERIMENTAL METHODS

Irradiations in a nuclear reactor suffer from the drawback of mixing several kinds of radiation effects, and the energy absorbed cannot be measured easily. Low-voltage beryllium-windowed X-ray tubes provide a means of administer-

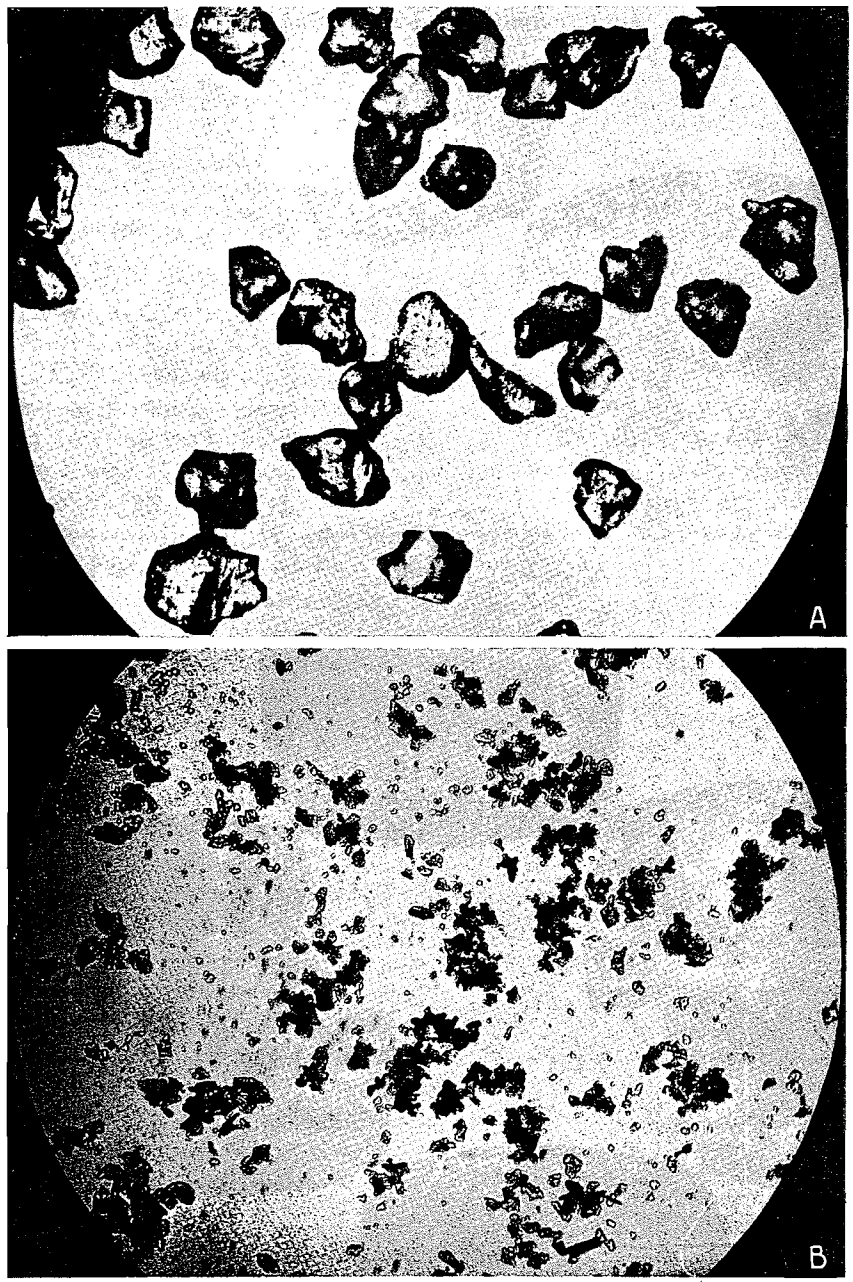



FIG. 1 *A*. Photomicrograph ( × 35) of potassium perchlorate grains before irradiation.
*B*. $KClO_4$ grains ( × 35) after 60 hr. irradiation.

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ing doses of radiation comparable with those obtainable in such a reactor, but consisting only of one kind of radiation. They can be operated with light shielding, and in a manner permitting of accurate dosage measurement. In this investigation a Machlett AEG-50-T tube with tungsten target, beryllium window, and 5 mm. focal spot was employed. It was run at 50 kvp., 50 ma., using full-wave rectified but unfiltered high-voltage. The voltage and milliamperage were maintained within 2% of these values during the irradiation by manual adjustment.

*Preparation of Potassium Perchlorate Samples*

Reagent grade potassium perchlorate was recrystallized several times from double distilled water. It was ground and sifted through 200- and 325-mesh screens, the grains which fell between these two sizes being selected for the irradiation. In this way grains within an average diameter of about 0.1 mm., and fairly uniform in size (as Fig. 1*A* shows), were obtained. Uniform grains were required because of the possibility that the course of the reaction might depend on the grain size. Samples of this material averaging 1 mgm. were weighed by a semimicro balance sensitive to 0.01 mgm., into the irradiation cell shown in Fig. 2*B*. This was made from two ½-in. square microscope cover

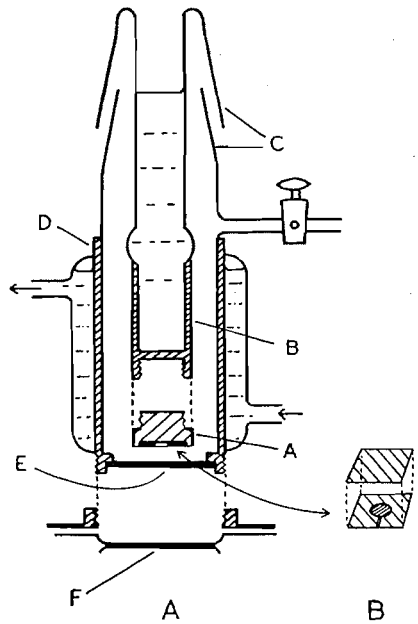



FIG. 2. *A*. Irradiation equipment.
*B*. Irradiation cell.

glasses. One, about 0.2 mm. thick, had a circular depression of 5 mm. diameter etched in its center by hydrofluoric acid, with a fine channel leading from this depression to the edge of the glass, to permit free passage of gases. The sample was spread out over the bottom of this depression with a microspatula. The other cover glass, 0.1 mm. thick, was then placed over the sample. In this way

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the salt was held in place in a layer one grain thick. This arrangement was required to guarantee reproducible conditions of irradiation, and also to prevent scattering of the grains of salt in the decrepitation which occurs during irradiation. The whole "sandwich" was fastened with a clip of steel wire to the under side of the copper block, (*A*) in Fig. 2*A*, which was screwed into the thimble *B*. The 0.1 mm. thick cover glass faced the X-ray tube.

A few larger samples, about 5 mgm., were used for the qualitative identification of products. These were also irradiated in a thin layer between two cover glasses.

*Procedure in Irradiations*

The ground joint *C* (Fig. 2*A*) was greased with Apiezon *L* and connected. The vessel was evacuated to 0.0001 mm. pressure, and then filled with purified helium (99.99% He) at a pressure between 0.3 and 0.7 atmosphere. This was mainly for the purpose of conducting heat away from the sample during irradiations. Actually, rough calculations later carried out to determine the rate of heat loss from the salt by radiation suggest that this precaution was unnecessary: it seemed that even in a high vacuum the temperature of the salt could hardly rise more than about 2° above that of the surroundings. It was shown that with other conditions equal, the yields of chloride and chlorate obtained in typical irradiations of potassium perchlorate did not alter significantly when a high vacuum was substituted for the helium atmosphere during irradiation. The brass jacket (*D*) and inner thimble (*B*) of Fig. 2*A* were kept at 25° throughout the irradiations by circulating water. The distance between the sample and the window *F* of the X-ray tube was about 1 cm. The axis of the thimble (*B*) passed through the centers of the sample and the X-ray tube window. *E* in Fig. 2*B* is a 1 mm.-thick beryllium window soldered in a monel ring, which is soldered to the brass casing *D*. The glass to metal joint is made with vacuum wax.

*Analytical Methods*

The irradiated potassium perchlorate was analyzed for chloride, chlorate, and other oxidizing agents. Chloride was determined by titration with silver nitrate. Chlorate was measured by means of its ability to oxidize ferrous ion in hot acid solution, and other oxidizing agents by the oxidation of ferrous ion in the cold. Perchlorate does not oxidize ferrous ion in solution under any conditions.

The various substances described here as "other oxidizing agents" were not fully identified. The total amount of these was always small compared with the amounts of chloride and chlorate. Absorption spectra of the solutions suggested that chlorite and hypochlorite ions were present.

A typical sample was analyzed as follows. The irradiated salt was washed with a few drops of water into a 5 ml. beaker, and the solution weighed. After the solution had been mixed, an aliquot, usually 0.2 ml., was taken by means of a micropipette and added directly to an excess of 14 m*M* ferrous sulphate in 0.8 *N* sulphuric acid, to which a drop of 2 *N* sulphuric acid had been

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added. The solution was left to stand a minute or two. Then 0.5 ml. of saturated *o*-phenanthroline solution and 1 ml. of 2 *M* sodium acetate were added. The volume was made up to 5 ml., and the color intensity measured with a Klett–Summerson photoelectric colorimeter, using a green filter. This gave the total number of equivalents of all oxidizing agents except chlorate, which does not oxidize ferrous ion under these conditions. For the determination of chlorate, another aliquot, generally 0.02 ml., was added to 0.05 ml. of the same acid ferrous solution in a short piece of 7 mm. diameter glass tubing sealed at one end. This was then drawn out in a flame and sealed off. A similar capsule containing only the ferrous solution was prepared to serve as a blank. The two were immersed in boiling water for an hour. They were then cut open. The contents were washed out and analyzed for residual ferrous ion as described above. This gave the total equivalents of all oxidizing agents including chlorate, from which the chlorate was determined by difference. Air oxidation of the blank was appreciable but not serious, while the reduction of chlorate was not quite complete. A correction, amounting to 8%, which had been determined with the aid of standard chlorate samples, was added to all results to compensate for incompleteness of reduction of chlorate ion.

Chloride was determined on the portion of the original solution remaining after withdrawal of these aliquots. It was transferred by pipette, together with washings, to a 1 ml. beaker, and evaporated down to about 0.2 ml. under an infrared lamp. The solution was titrated with 0.025 *M* silver nitrate from a microburette. The end point was determined electrometrically. One electrode was a piece of silver wire. The other was a platinum wire dipping into dilute potassium nitrate solution in a small vessel which communicated by a fine capillary with the titration vessel. This probably functioned as an oxygen electrode, and maintained a satisfactorily constant potential during titrations. The e.m.f. was measured with a vacuum tube voltmeter (Beckman pH meter). In order to eliminate any danger of the solution in the titration beaker flowing up into the tip of the burette and into the reference electrode, its density was increased by the addition of a drop of 16% pure potassium nitrate solution to each sample.

It was established by blank experiments that chloride and chlorate did not interfere with the chlorate determinations, nor chlorate and perchlorate with the chloride determinations.

*Measurement of Energy Absorbed by the Sample*

The shape of the energy spectrum of radiation emitted by the X-ray tube target was calculated by means of De Waard's formula (4). Only the continuous spectrum was considered, since the voltage applied to the tube was insufficient to excite the *K* lines of tungsten, and the intensities of the other lines are negligibly small. Fig. 3*A* shows $I_\lambda$ plotted against the wave length. $I_\lambda$ is a function such that the total energy flux in the wave length range $\lambda$ to $\lambda + d\lambda$ is equal to $I_\lambda\, d\lambda$. The reduction in intensity due to absorption in the two beryllium windows and the cover glass was calculated for a series of wave lengths, using tabulated values of the mass absorption coefficients. For this

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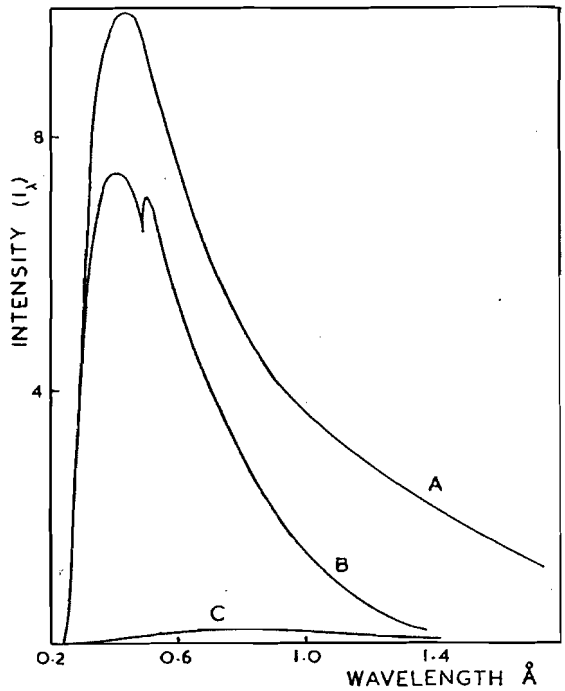



FIG. 3. *A*. Energy spectrum of X rays from tungsten target at 50 kv.
*B*. Spectrum of X rays striking the salt.
*C*. Spectrum representing energy absorbed in potassium perchlorate samples as a function of X-ray wave length.

purpose it was necessary to know the chemical composition of the cover glass. This information was kindly supplied by the makers. The shape of the "filtered" spectrum, as it impinged on the sample, is shown in Fig. 3*B*. By similar methods the fraction of the incident energy absorbed by the sample at a variety of wave lengths could then be calculated. Fig. 3*C* shows a function (of the same kind as $I_\lambda$) of the energy absorbed by the sample, plotted against wave length. The areas under 3*A* and 3*B* represent the relative total energy fluxes in the unfiltered and filtered beam respectively, while the area under 3*C* represents, in its correct proportion, the energy absorbed by the sample. Under the conditions of the experiments, wave lengths around 0.8 Å contribute most energy to the salt, although the peak in the total flux emitted by the tube comes at about 0.4 Å.

The total flux at the position of the sample was determined calorimetrically. The block *A* in Fig. 2*B* was removed and a silver disk 5 mm. in diameter and 0.5 mm. thick was placed in the exact position usually occupied by the sample, being supported by the leads of a copper–constantan thermocouple soldered to its back. The cold junction of the circuit was made by soldering the other end of the constantan lead to the thimble *B* of Fig. 2*B*. With the vessel highly evacuated, the e.m.f. developed by the thermocouple in the full X-ray beam was measured. It corresponded to a temperature rise in the silver disk of

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nearly 6°C. The X-ray beam was switched off, and a cooling curve plotted. The cooling of the disk followed Newton's law of cooling within the error of measurement. The disk was detached and weighed. Knowing its mass and specific heat, it was possible to calculate the rate of heat loss by the disk at the equilibrium temperature reached by it in the X-ray beam, in calories per second. This was, of course, equal to the rate of energy input from the X-ray beam. Since the incident energy was for all practical purposes totally absorbed by the disk, the same figure gave the total energy flux in the beam, over a cross section equal to the area of the disk. With the aid of area measurements on the graphs of Fig. 3, it was then a simple matter to calculate the absolute rate of energy absorption in the sample. A possible objection to this method of calculation arises when the actual mechanism of energy absorption is more closely considered. The primary process by which an X-ray quantum is absorbed is the production of a photoelectron, which is actually the effective agent in ionizing and exciting the medium. The energy of a photoelectron corresponding to the peak wave length in Fig. 3*C* is in the region of 10 kv. to 20 kv., and the range of such an electron is of the order of 1 mgm. per cm.$^2$ of aluminum, or rather less. Since the thickness of the sample is only about 5 mgm. per cm.$^2$, some photoelectrons must evidently escape from the surfaces of the sample without producing their full complement of ionization and excitation. For samples of this thickness, loss is of the order of 5% of the total energy absorbed by the sample. It must be remembered, however, that the sample is enclosed between glass plates which have roughly the same stopping power both for X rays and for electrons as the sample itself. This means that the loss of electrons from the surfaces of the sample is fairly exactly compensated by the entry of electrons from the glass plates into the sample.

The correctness of the absorption calculations was tested by substituting for the 0.1 mm. cover glass filter a cover glass of the same material but twice the thickness. The reduction in yield of $Cl^-$ and $ClO_3^-$ thereby caused was determined. The observed yield was smaller by a mean factor of 1.8 than previously, whereas the calculations predicted a reduction by a factor of 1.7. This agreement was considered adequate for an investigation not aiming at the highest accuracy.

## RESULTS AND DISCUSSION

Potassium perchlorate darkens in color to golden brown in the first few minutes of irradiation. Thereafter the color changes but slowly. There is a tendency to lighten somewhat in very long irradiations. This color is presumably due to displaced and trapped electrons. In other respects the appearance of the grains remains unchanged up to four hours' irradiation at 50 kv., 50 ma. The grains then decrepitate and fall to a fine powder (Fig. 1*B*). The irradiated samples dissolve in water with effervescence, unless they have been irradiated for a very long time, when the effervescence becomes scarcely noticeable.

### *Kinetic and Energetic Features of the Decomposition*

Fig. 4 represents the number of moles of $ClO_3^-$, $Cl^-$, and other products

(expressed as $ClO_2^-$) formed in one mole of $KClO_4$ during irradiation for periods up to 60 hr.

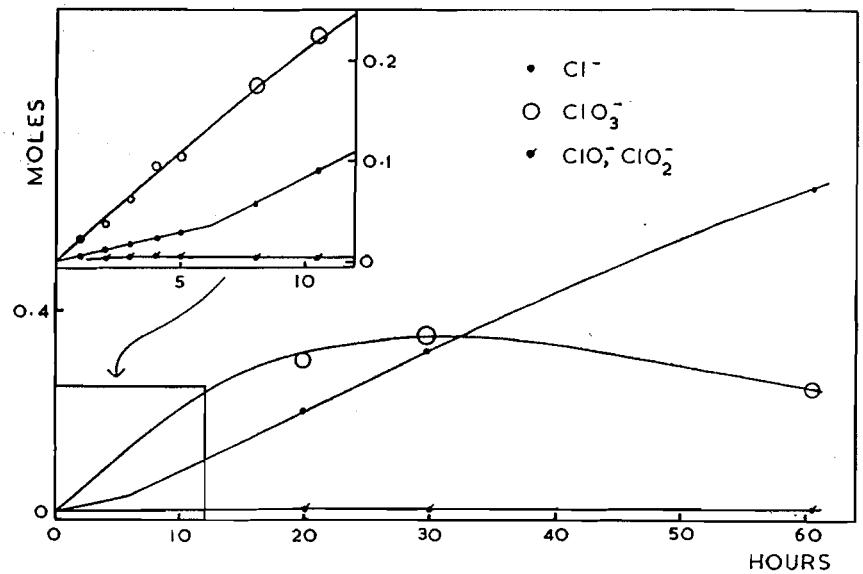



FIG. 4. Diagram showing the yields of chloride, chlorate, and other products obtained in irradiation of 1 mole of potassium perchlorate for various periods.
(*Insert*) A magnified portion of the main diagram, showing yields in the first 12 hr. irradiation. The size of the circles for chlorate ion represents the estimated possible analytical error. The analytical errors in the determination of chloride and other products are smaller than the size of the circles.

The following conclusions emerge from a study of Fig. 4:

(1) $Cl^-$ and $ClO_3^-$ are both formed directly from $ClO_4^-$ under irradiation, at first in the ratio of about 1 mole to 4 moles. $Cl^-$ is not formed solely as a secondary product resulting from the decomposition of $ClO_3^-$ first formed, although it is probably formed by this mechanism also. These facts are shown by the formation of $Cl^-$ at a constant rate at the very beginning of the irradiation. The rapid increase in the amount of $ClO_3^-$ present during the first four hours does not apparently affect the rate of formation of $Cl^-$. In other words, at the beginning of irradiation, when the crystal lattice is substantially that of pure potassium perchlorate, the reactions

$$KClO_4 \rightarrow KClO_3 + \tfrac{1}{2}O_2,$$
$$KClO_4 \rightarrow KCl + 2O_2$$

proceed simultaneously, the first being about four times as likely as the second.

(2) There is a secondary decomposition of $ClO_3^-$ to $Cl^-$ and $O_2$. This is shown by the fact that the amount of $ClO_3^-$ in the sample passes through a maximum and then decreases again as irradiation continues. It is noteworthy that this secondary decomposition of $ClO_3^-$ does not give rise to significant amounts of $ClO_2^-$ and $ClO^-$, although they do appear to be formed in quite

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large amounts in the direct irradiation of potassium chlorate.* The only obvious explanation of this difference is the different physical state of the material in the two cases.

(3) About five hours after irradiation commences, the rate of $Cl^-$ formation is suddenly approximately doubled, while the rate of formation of $ClO_3^-$ does not change. This phenomenon occurs at the same time as the breakdown of the crystals of potassium perchlorate to a fine powder, and may therefore be connected with the increase of surface area or with the rearrangement of the crystal lattice.

Because of the break in the $Cl^-$ curve (Fig. 4) it is clear that the kinetics of the reaction cannot be completely explained by any simple mechanism. The portion of the $Cl^-$ curve before the break is, however, small compared with the whole curve, and as a first approximation can be neglected. If this is done, the following simple picture will explain roughly the shapes of the curves in Fig. 4. The decomposition of potassium perchlorate is approximately of the first order, with velocity constant (under the special conditions of these experiments) equal to 0.0371 $hr.^{-1}$ This velocity constant includes a contribution of 0.011 arising from the decomposition to $Cl^-$, whereas the rest, 0.0260, comes from decomposition to $ClO_3^-$ (other modes of decomposition being neglected). Fig. 5 shows that the logarithm of the quantity of potassium perchlorate in

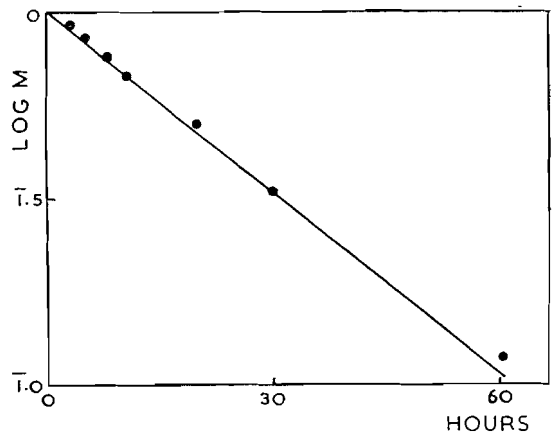



FIG. 5. Logarithm of the number of moles ($M$) of potassium perchlorate left undecomposed after various periods of irradiation of 1 mole potassium perchlorate.

the sample, when plotted against time, gives a good straight line, as required for a first order reaction. The $ClO_3^-$ also decomposes by an approximately first order reaction to $Cl^-$. If a value for the velocity constant of this decompo-

* *In some preliminary experiments on the irradiation of crystalline potassium chlorate under the same conditions as the irradiation of potassium perchlorate described here, chloride, hypochlorite, and chlorite all appeared to be formed in comparable and continuously increasing amounts. The reaction products from this irradiation were tentatively identified by their absorption spectra in aqueous solution and by the reaction with silver nitrate, but the identification is not yet complete or altogether satisfying.*

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sition equal to 0.0200 is adopted, the shape of the $ClO_3^-$ curve is not badly described, and the same is true of the $Cl^-$ curve (Fig. 6).

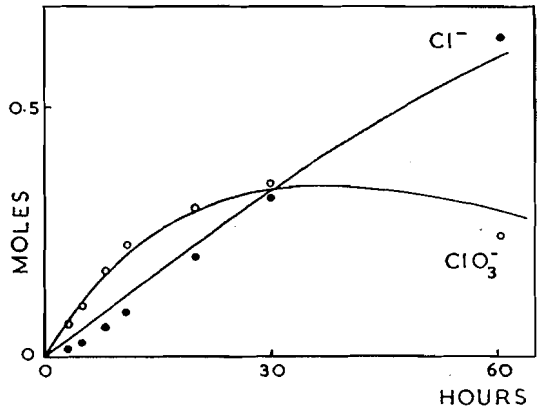



FIG. 6. The curves represent calculated yields of chlorate and chloride from irradiation of 1 mole potassium perchlorate for various periods, assuming first-order decomposition of $ClO_4^-$ and $ClO_3^-$. The points represent experimentally determined yields.

By comparing the total number of $ClO_4^-$ ions decomposed per unit time, during the first four hours of the reaction, with the rate of energy absorption determined calorimetrically, one obtains for the average energy required to decompose a $ClO_4^-$ ion the figure of 19 ± 2 ev. This corresponds to 440 kcal. per mole $KClO_4$. $\Delta H$ for the reaction

$$KClO_4 \rightarrow KCl + 2O_2$$

is 7.9 kcal., while for the reaction

$$KClO_4 \rightarrow KClO_3 + \tfrac{1}{2}O_2$$

$\Delta H$ is 22.2 kcal. Therefore the over-all utilization of energy in the decomposition is quite inefficient. It is more legitimate to compare the energy required for the decomposition with that required to raise the perchlorate ion from the ground state to its first excited level, which is at least 5.4 ev.* The energy of activation for the decomposition may be greater than this, but cannot well be less, since electronic excitation or ionization of $ClO_4^-$ is the only possible way in which decomposition can be initiated. Thus it follows that at least 30% of the energy absorbed is used in activating the decomposition. The figure of 19 ev. absorbed per molecule decomposed is of the same order as that found for radiation-induced reactions in gases and aqueous solutions.

*The Mechanism of the Decomposition of Potassium Perchlorate*

Photoelectrons resulting from the primary absorption process travel through the perchlorate lattice, where they may either split off electrons from $ClO_4^-$ ions: —

$$ClO_4^- \rightarrow ClO_4 + e \qquad [1]$$

or excite $ClO_4^-$ ions electronically without electron loss: —

$$ClO_4^- \rightarrow ClO_4^{-*}. \qquad [2]$$

* *This figure can be deduced from the fact that the ultraviolet absorption of the $ClO_4^-$ ion in aqueous solution begins around 2300 Å. Exact figures for the wave lengths of absorption bands in solid potassium perchlorate do not seem to be available.*

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Both processes presumably occur, and it becomes necessary to decide whether either or both leads to decomposition. The fact that ions found in the solution of irradiated salt cannot be assumed to be necessarily present in the solid adds to the difficulty of this problem.

Reaction [1] would give $ClO_4$, which is not now believed to exist as a chemical entity. It is difficult to account for the electrons which would be set free in this reaction, if it occurred. They could either be recaptured by $ClO_4$, with no net reaction, or trapped at lattice imperfections, giving rise to color centers. Since the color of the salt does not darken further after a very few minutes' irradiation, and is never very dark, there can be but small numbers of trapped electrons. Reaction [1] is therefore believed to contribute little, if at all, to the over-all decomposition, and reaction [2] must be accepted as the starting point of the decomposition.

A difficulty is encountered if it is supposed that decomposition occurs uniformly throughout the lattice. It would then be necessary to postulate the reaction

$$ClO_4^- \rightarrow ClO_4^{-*} \qquad [2]$$

followed by

$$ClO_4^{-*} \rightarrow ClO_3^- + O \qquad [3]$$

occurring at an ordinary lattice site, i.e. away from imperfections. The oxygen could not easily escape from the point where it was formed. Even if [3] could take place, it is hardly reasonable to suppose that an arrangement consisting of a chlorate ion with an oxygen atom held close to it by the surrounding lattice could persist in this state without reverting to a perchlorate ion, since all our knowledge indicates that the necessary electronic rearrangement would occur instantly and spontaneously in such circumstances. Moreover, in view of the large size of the oxygen atom and the low temperature, one cannot reasonably assume that oxygen atoms could diffuse away from the point where they were formed at an appreciable rate. The alternative is to postulate that decomposition takes place at lattice imperfections and surfaces. Here we are faced with an apparent difficulty in explaining the relatively efficient energy utilization in the reaction. Only a minute fraction of the primary excitation can occur in the neighborhood of imperfections and surfaces, whereas the energy utilization observed requires that at least one third the $ClO_4^-$ ions excited decompose.

The solution of this problem is probably to be found in the "exciton" theory first advanced by Frenkel (5). According to this, a point of electronic excitation, or "exciton", in a crystal lattice can travel considerable distances through the lattice by successive excitation and de-excitation of adjacent ions: alternatively, the excitation cannot a priori be regarded as localized at any particular lattice point. We can postulate that the excitons formed in the potassium perchlorate lattice travel until they reach an imperfection (most probably an internal crack or edge dislocation), at which point room is available for the excited $ClO_4^-$ to dissociate. Hence chloride and chlorate would accumulate in internal cracks, weakening the crystal structure. The oxygen gas formed in the same places would build up a pressure. Eventually these combined factors would lead to violent rupture of the crystal, as observed.

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According to this explanation, blocks of chloride and chlorate lattices, or a mixture of the two, should be built up in limited regions inside the potassium perchlorate crystal and on its surface, probably at first in a fragmentary condition, as long as they are only a few ions thick. On account of the closer packing of ions in potassium chloride, as compared with potassium chlorate, and the resulting higher lattice energy, an arrangement in which the potassium chloride and potassium chlorate lattices are entirely separate would be more stable than a potassium chlorate lattice in which $ClO_3^-$ ions were replaced at intervals by $Cl^-$ ions. Probably, therefore, chloride and chlorate would accumulate at imperfections and surfaces in the form of blocks of pure chloride and pure chlorate.

Since only the exact energy of excitation of a $ClO_4^-$ ion could easily be transferred to adjacent $ClO_4^-$ ions, only excitation originally produced in $ClO_4^-$ can be effective in bringing about decomposition of $ClO_4^-$ at lattice imperfections and surfaces. Thus the rate of decomposition of $ClO_4^-$ should be proportional to the total amount of $ClO_4^-$ present, and independent of the other substances (neglecting minor factors). The same is true of the decomposition of $ClO_3^-$. The experimentally observed first order decompositions are therefore in agreement with the hypothesis just advanced. The increase in the rate of chloride formation with the break-up of potassium perchlorate crystals is probably connected in some way with the sudden increase of free surface, which it is reasonable to suppose would encourage dissociation of $ClO_4^-$ to $Cl^-$ rather than to $ClO_3^-$, since more room would be available for escape of oxygen atoms. The same "explanation" can be given for the fact that $ClO_3^-$ as formed in the perchlorate decomposes almost entirely to $Cl^-$, whereas in large crystals of potassium chlorate, $ClO^-$ and $ClO_2^-$ are also formed in considerable amounts. It must be admitted, however, that there are objections to this description of the process which can hardly be answered without further experimental work.

## ACKNOWLEDGMENTS

I wish to acknowledge the help given by my wife and by Dr. T. J. Hardwick with the calculations required for this work.

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NOTE

## THE PYROLYSIS OF CALCIUM SALTS OF CARBOXYLIC ACIDS

By C. C. Lee and J. W. T. Spinks

Recently, Bell and Reed (1) reported that the $C^{13}$ content of the carbonyl-carbon atom of the acetaldehyde obtained in the pyrolysis of a mixture of barium acetate, enriched with $C^{13}$ in the carboxyl group, and barium formate is approximately normal. This requires the fission of the carbon–carbon bond in the acetate. A free radical mechanism was suggested to interpret the results. A similar tracer technique has been applied in our laboratory in the study of such pyrolyses.

Calcium acetate labelled with $C^{14}$ in the carboxyl group and an equimolar quantity of unlabelled calcium benzoate, *p*-toluate, phenylacetate, or *n*-valerate were dissolved in water, evaporated to dryness to give an intimate mixture, and then dry distilled. In each experiment, the liquid product was taken up in ether, thoroughly washed with water to remove acetone, dried over anhydrous sodium sulphate, and treated with decolorizing charcoal. The ether was then removed and the residue fractionated. The unsymmetrical ketones obtained were converted to the corresponding semicarbazones and their radioactivity determined. The results (Table I) indicate that the fission of the carbon–carbon

TABLE I

Radioactivity data

Semicarbazones of unsymmetrical ketones obtained by pyrolysis of mixed calcium salts

| Compound | Observed activity,[a] counts/min. | | Activity/millimole,[b] counts/min. | | % of acetate activity in ketone | |
|---|---|---|---|---|---|---|
| | Run I | Run II | Run I | Run II | Run I | Run II |
| $CH_3COONa$ | 3390 | 3366 | 278 | 276 | | |
| $C_6H_5(CH_3)CNNHCONH_2$ | 22.2 | 22.8 | 3.93 | 4.03 | 1.4 | 1.5 |
| $p$-$CH_3C_6H_4(CH_3)CNNHCONH_2$ | 19.2 | 22.8 | 3.67 | 4.36 | 1.3 | 1.6 |
| $C_6H_5CH_2(CH_3)CNNHCONH_2$ | 484 | 483 | 92.5 | 92.3 | 33.3 | 33.4 |
| $CH_3(CH_2)_3(CH_3)CNNHCONH_2$ | 335 | 327 | 53.0 | 51.7 | 19.1 | 18.7 |

[a] *At "infinite thickness".*
[b] *Observed activity × molecular weight × 10⁻³.*

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bond in the acetate accounts for the formation of almost all of the acetophenone and *p*-methylacetophenone, about four fifths of the *n*-amyl methyl ketone, and about two thirds of the benzyl methyl ketone.

The above findings render unsatisfactory any mechanism involving heterolytic cleavage of the carbon–carbon bond since the predominance of a carbonium ion or a carbanion of the $CH_3^+$ or $CH_3^-$ type is very unlikely. A mechanism involving an aldol type of reaction, as suggested by Miller, Cook, and Whitmore (3), is also questionable. Aside from the fact that an aldol condensation between salts of carboxylic acids is improbable, no aldol condensation can account for the formation of diaryl ketones from the pyrolysis of salts of aromatic acids. A free radical mechanism as suggested by Bell and Reed (1) remains attractive. In the formation of acetophenone, for example, the reaction sequence may be written:

| | |
|---|---|
| Initiation | $CH_3COOM \rightarrow CH_3\cdot + \cdot COOM \qquad M = \frac{1}{2}Ca$ |
| Chain continuation | $CH_3\cdot + C_6H_5COOM \rightarrow CH_3COC_6H_5 + MO\cdot$ |
| | $CH_3COOM + MO\cdot \rightarrow CH_3\cdot + M_2CO_3$ |
| Termination | $2CH_3\cdot \rightarrow CH_3CH_3$, or $CH_4 + CH_2$: etc. |
| | $2\ MO\cdot \rightarrow (MO)_2$ |
| | $MO\cdot + \cdot COOM \rightarrow M_2CO_3$ |

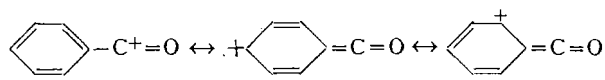
Clarification of certain questionable aspects is still needed before the free radical chain can be accepted as the sole mechanism. In the homolytic cleavage of the carbon–carbon bond, other things being equal, one would expect the benzyl radical to be more readily formed than the methyl radical (5). However, in the formation of benzyl methyl ketone, if only the radical mechanism operates, our results would indicate a two-thirds predominance of the methyl over the benzyl free radical. The detailed study of the pyrolysis of trimethylacetic acid by Miller *et al.* (3) certainly renders impossible any satisfactory explanation of the multitude of products without assuming the presence of some free radicals. To explain, on a free radical basis, the formation of the main product of the reaction, the unsymmetrical *t*-butyl *iso*-butyl ketone, a rearrangement from a tertiary carbon radical (*t*-butyl radical) to a primary carbon radical (*iso*-butyl radical) is necessary. Established rearrangements involving free radicals (6,7), however, indicate an opposite trend in that primary radicals tend to rearrange to the tertiary state.

A polar mechanism operating in conjunction with one of the free radical type may be considered. The first step may be the formation of an acyl carbonium ion followed by an $S_E2$ type of decarboxylation (2,4) with the acyl carbonium ion acting as the electrophilic component.

$$R\text{–}COOM \rightarrow R\text{–}C^+\text{=}O + MO^-$$

$$R\text{–}C^+\text{=}O + R'\text{–}COOM \rightarrow R\text{–}\overset{\overset{O}{\|}}{C}\text{–}R' + M^+ + CO_2$$

where R and R′ may be the same or different, aliphatic or aromatic, and M is a metal such as calcium or barium, etc. When R is aromatic, resonance of the type



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would greatly increase the probability of its formation over that of the methyl acyl carbonium ion, $CH_3-C^+=O$, accounting for the exclusive carbon–carbon cleavage of the acetate when it is pyrolyzed with benzoate or *p*-toluate. However, on the basis of hyperconjugation, $CH_3-C^+=O$ would be expected to have a greater probability of formation than either $C_6H_5CH_2-C^+=O$ or $CH_3(CH_2)_3-C^+=O$. Resonance interpretations alone thus fail to account for the preferred cleavage of the carbon–carbon bond of acetate in the pyrolytic production of benzyl methyl ketone and *n*-amyl methyl ketone. A possibility may be that this pyrolysis may proceed through both polar and free radical mechanisms, the observed results being the composite of the two.

A two-step mechanism in which an acyl carbonium ion is produced by a fairly rapid reversible process followed by a rate-controlling $S_E2$ displacement may also be considered.

$$R-COOM \rightleftarrows R-C^+=O + MO^-$$

$$R-C^+=O + R'-COOM \xrightarrow{\text{slow}} R-\overset{\overset{O}{\|}}{C}-R' + M^+ + CO_2$$

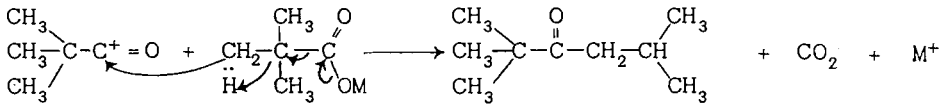
Considering first the pyrolysis of calcium acetate with calcium benzoate or toluate, it is seen that the $S_E2$ displacement of $C_6H_5-C^+=O$ on calcium acetate would involve a backside attack on the methyl carbon with Walden inversion, whereas the displacement of $CH_3-C^+=O$ on calcium benzoate or toluate would of necessity proceed by a frontal attack on a carbon of the nucleus. These two reactions, being quite different in nature, might be expected to proceed at very different rates, and this, rather than the relative probability of formation of the two onium ions in the first step, might account for the observed exclusive carbon–carbon cleavage in acetate.

The preferred cleavage of the carbon–carbon bond of acetate in the pyrolysis with phenylacetate and *n*-valerate may be explained in terms of this mechanism on the basis of a difference in the steric factor. The attack of $CH_3-C^+=O$ on phenylacetate or *n*-valerate would be expected to have a lower entropy of activation than the alternative process involving the attack of $C_6H_5CH_2-C^+=O$ or $CH_3(CH_2)_3-C^+=O$ on acetate.

Finally, the difference in the extent of carbon–carbon cleavage of acetate in its pyrolysis with phenylacetate and *n*-valerate could be attributed to a difference in activation energy. The cleavage of the carbon–carbon bond in phenylacetate would be expected to require a lower energy of activation then carbon–carbon cleavage in *n*-valerate since this bond in phenylacetate is one carbon atom removed from the aromatic nucleus. Moreover, the observation of Bell and Reed (1) might be similarly explained for the activation energy required for carbon–carbon cleavage in barium acetate should be lower than that for carbon–hydrogen cleavage in barium formate.

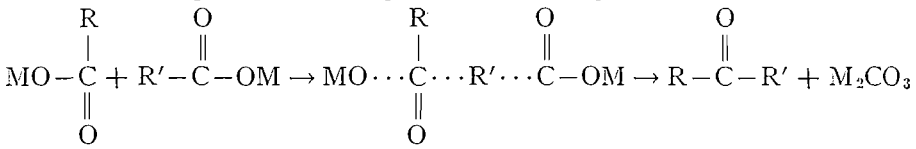
Steric considerations would also render an interpretation for the formation of the major product in the pyrolysis of trimethylacetic acid (3). The *t*-butyl group may hinder the approach of the acyl carbonium ion in the $S_E2$ decarboxylation. A carbon atom $\beta$ to the carboxyl instead of the $\alpha$-carbon atom is then attacked.

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The polar mechanism involving an acyl carbonium ion may further afford at least one explanation for the well-known fact that in the ketonic pyrolysis of salts of carboxylic acids, lithium, barium, and calcium salts proceed more smoothly than sodium and potassium salts. Relatively speaking, metals of the first group have a greater affinity for electrons than those of the second. The splitting off of $MO^-$, and hence the production of the acyl carbonium ion, is thus favored where M is the less basic metals.

Possibly, one may criticize the mechanism outlined on the basis that the formation of an onium ion usually is slow compared to its subsequent reaction to give the final product. Instead of the two-stage mechanism, the decarboxylation reaction might conceivably proceed in one step as follows:



The reaction may involve either heterolytic or homolytic cleavage of the bonds concerned. The arguments presented above, based on the two-step mechanism, should apply equally well to the one-step interpretation.

We are grateful to the National Research Council of Canada for financial assistance, and to Dr. A. N. Bourns of McMaster University, Hamilton, Ont., for helpful comments.

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# THE RATE OF DEHYDRATION OF COPPER SULPHATE PENTAHYDRATE AT LOW PRESSURES OF WATER VAPOR[1]

BY G. B. FROST AND R. A. CAMPBELL[2]

ABSTRACT

The rate of dehydration of copper sulphate pentahydrate has been determined over a range of low pressures of water vapor. It has been found that as the pressures are increased, the rate at first drops very rapidly; this drop is followed by a period of marked acceleration, which is followed in turn by a gradual decline. Copper sulphate pentahydrate has been found to be similar in this respect to manganous oxalate dihydrate, which has been hitherto regarded as unique in its behavior. The observed effects are probably due to amorphous to crystalline transitions occurring during induction periods, the durations of which have also been found to depend on water vapor pressure.

## INTRODUCTION

The kinetics of the dehydration of copper sulphate pentahydrate at low pressure has been studied by Garner and Tanner (4), Hume and Colvin (5), Smith and Topley (7), and others. Although these investigations were carried out with different objects in view, and by somewhat different methods, all of them involved, ultimately, the determination of the rate of loss of water per unit area of reaction interface, under conditions where the liberated water molecules were removed very rapidly from the reaction zone. In the determination of these rates, consideration was given to the influence of such factors as the self-cooling of the crystals, and the impedance effect of the layer of reaction product formed around the decomposing crystal. The values obtained are in very satisfactory agreement.

In the course of these studies, Smith and Topley made a careful investigation of the effect of water vapor at low pressures on the rate of dehydration of single crystals of copper sulphate pentahydrate. Crystals, nucleated artificially over their entire surface, were suspended from a quartz spiral balance, and the rate of loss of water determined, either by a static method in which the crystal was exposed to water vapor maintained at a constant pressure, or by a flow method in which hydrogen containing water vapor at a known partial pressure was circulated over the crystal. They found that a gradual, but very marked, decrease in rate occurred as the pressure of water vapor was increased over a range of very low values. At a pressure of 0.04 mm., the rate (expressed as loss in weight per unit area per unit time) was found to be about one-tenth of the rate in vacuum. They did not carry out rate measurements at pressures higher than approximately this value.

[1] *Manuscript received August 5, 1952.*
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Smith and Topley also pointed out that, for some other hydrated salts, the relationship between rate of dehydration and water vapor pressure might be more complex. A great deal of interest has been shown in one of these cases, namely, the dehydration of manganous oxalate dihydrate, which has been studied independently by Topley and Smith (8) and by Volmer and Seydel (9). Both of these groups of workers used an experimental technique similar to that used by Smith and Topley, and determined the rates of dehydration, both when the dehydration took place in an atmosphere of water vapor at constant pressure, and when the dehydration occurred in an initially evacuated system, the pressure being allowed to build up as the dehydration progressed.

In this case, it was not found possible to express the rate in terms of the loss of water per unit time per unit interfacial area, as had been done for copper sulphate pentahydrate crystals. This was partly due to the fact that the low solubility of this salt hydrate prevented the growth of single crystals large enough to be artificially nucleated over their surface. Consequently, the comparison of rates at various water vapor pressures had to be made by somewhat arbitrary methods. Topley and Smith compared the rates of loss per decigram of material, corresponding to 20% decomposition. Volmer and Seydel compared rates at maximum values read from experimentally determined loss-in-weight versus time curves. The results of the two investigations are in qualitative agreement as regards the shape of the curve obtained. A plot of the experimental values tabulated by Topley and Smith for static experiments at 75.9° C. is shown in Fig. 1.

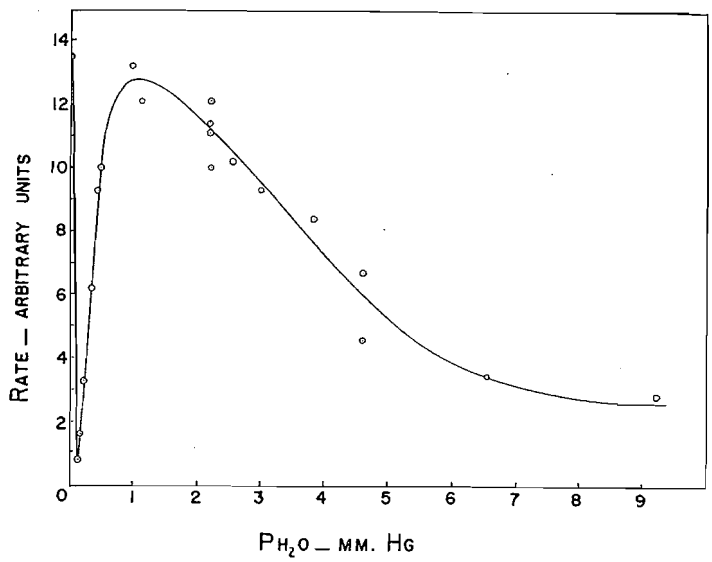



FIG. 1. The dependence of the dehydration rate of aggregates of small crystals of manganous oxalate dihydrate on water vapor pressure (from the data of Topley and Smith).

It will be observed that, as the pressure of water vapor is increased, the rate at first falls in very much the same way as it does with copper sulphate

pentahydrate crystals. This drop, however, is followed by a period of rapid increase to a value comparable to that in vacuum. After passing through a maximum, the rate then gradually declines. The deviation of individual experimental values from the curve drawn is probably due to small differences between the measured pressures and those existing in the actual reaction zone. These deviations are not particularly significant, since it is the qualitative aspect of the curve which is of interest.

Topley and Smith and Volmer and Seydel have given quite different explanations for the over-all aspects of this curve. These need not be discussed here. It will suffice to say that the latter workers found that an amorphous product of relatively high energy content was formed on vacuum dehydration of this salt. They suggested that the formation and ultimate crystallization of this amorphous product is a determining factor in the dehydration mechanism. However, copper sulphate pentahydrate is also known to yield an X-ray amorphous product on low pressure dehydration (6). If the reaction mechanism is to be explained in terms of the role played by such an amorphous intermediate, it might be expected that both salts would have similar relationships in the dependence of dehydration rate on water vapor pressure. The desirability of extending the data for copper sulphate pentahydrate over a wider pressure range has been pointed out by Colvin and Hume (1).

Frost, Moon, and Tompkins (3) have determined the fractional amounts of energy-rich amorphous material formed at a series of dehydration pressures, from copper sulphate pentahydrate and zinc sulphate hexahydrate. Although they did not make kinetic measurements, their results suggest that both of these salts should show the type of rate dependence on pressure which has been observed for manganous oxalate dihydrate. On the basis of their work, the possibility suggests itself that the manganous oxalate dehydration, rather than being unique, may be typical of a group of heterophase reactions in which amorphous intermediates occur.

The purpose of this paper is to report the results of some rate measurements which have been carried out with the foregoing considerations in mind.

## EXPERIMENTAL METHOD

Experiments were carried out both with finely divided samples and with small single crystals of copper sulphate pentahydrate. To obtain the fine samples, the salt of reagent grade was recrystallized twice and screened, the portion that passed through 60 but not 80 mesh being used. Microscopic examination showed that a fairly large proportion of the aggregate consisted of small well formed triclinic crystals of linear dimensions about 0.2 mm. Other crystals, however, were irregular in form and variable in size. A very rough estimate would indicate that the crystals used were about twice the size of those used by Topley and Smith in their experiments on manganous oxalate dihydrate.

Single crystals, weighing approximately 0.05 gm., were grown slowly from small crystals at room temperature. In the selection of these crystals, those having numerous facets were rejected. The dimensions were measured with

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a travelling microscope. The surfaces were activated by rubbing with copper sulphate monohydrate enmeshed in cloth.

The apparatus used did not differ in any important respect from that described in detail by Smith and Topley (7) for their static experiments.

The sample was contained in a small rectangular basket made from 100 mesh copper screen and was suspended from a quartz spiral balance by means of a fine platinum wire. The sensitivity of the spiral was 2.03 mgm. per mm. and was found to be uniform over the extensions used. The spiral was placed in a case of glass tubing 60 cm. long enclosed in a constant temperature cabinet fitted with windows for observation. The spiral case was connected at the top, by a ground joint, to either the vacuum system, or to the source of constant water vapor pressure. It was connected at the bottom, by a ground joint, to the reaction vessel which contained the suspended sample. This reaction vessel was surrounded by a constant temperature bath. Except where otherwise indicated, dehydrations were conducted at a bath temperature of $40 \pm 0.5°$ C.

Water vapor at the desired constant low pressures was obtained by adjusting the temperature of ice crystals deposited on glass wool. These were contained in a small bulb connected to the line by a large stopcock. The bulb was immersed in a Dewar flask containing one of several suitable ice–salt eutectic mixtures. Furfural and ethylchloroacetate at their respective freezing points were found suitable in maintaining temperatures below $-21.0°$ C. No variation in the pressures so obtained was observed during the time required for experimental readings.

Pressures were read on an oil manometer by means of a cathetometer mounted on a rigid support, the apparatus being assembled so that the same cathetometer could be used for readings of either pressure or spiral extensions. Control experiments, in which one arm of the manometer was connected with the base of the spiral case, indicated that there was no source of error in pressure readings due to pressure gradient through the system.

X-ray powder photographs were made of the dehydration product resulting from all experiments with finely divided crystals.

## EXPERIMENTAL RESULTS

### *Preliminary Experiments with Finely Divided Crystals*

Topley and Smith obtained their initial results with manganous oxalate dihydrate by suspending a small weight of fine crystals in a closed and initially evacuated space, and observing both the loss in weight of the crystals and the rise in pressure in the system as the dehydration proceeded. It was considered desirable to carry out this same procedure with copper sulphate pentahydrate crystals. In order to induce nucleation, the crystals were exposed to full vacuum until 10% dehydration to the monohydrate stage occurred. Water vapor pressure was then allowed to build up in the system, and readings of weight loss and pressure taken. The results obtained are shown in Fig. 2.

It will be observed that, following an induction period, the water vapor first accelerates, then retards the net rate of decomposition. By taking the

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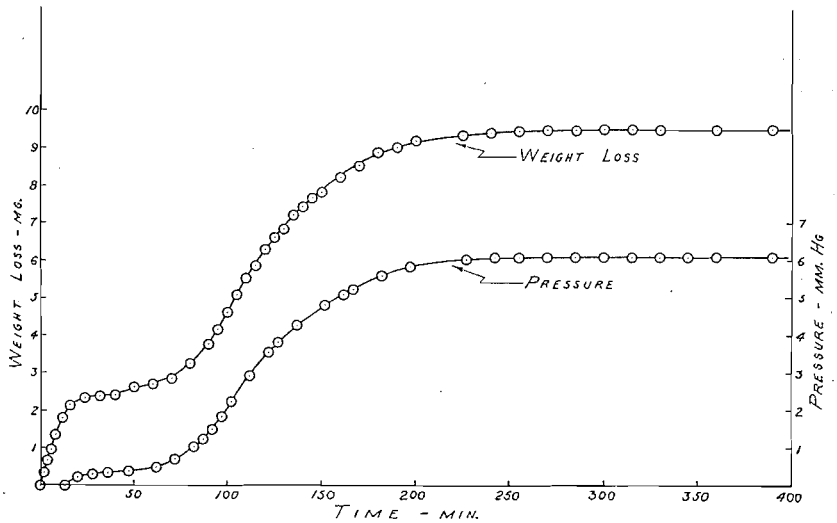



FIG. 2. The change in weight loss, and pressure, during the dehydration of fine crystals of copper sulphate pentahydrate in a closed, initially evacuated space.

slope of the weight loss curve over small intervals, and plotting the values so obtained against the pressure at the mid-points of the intervals, the curve shown in Fig. 3 was obtained.

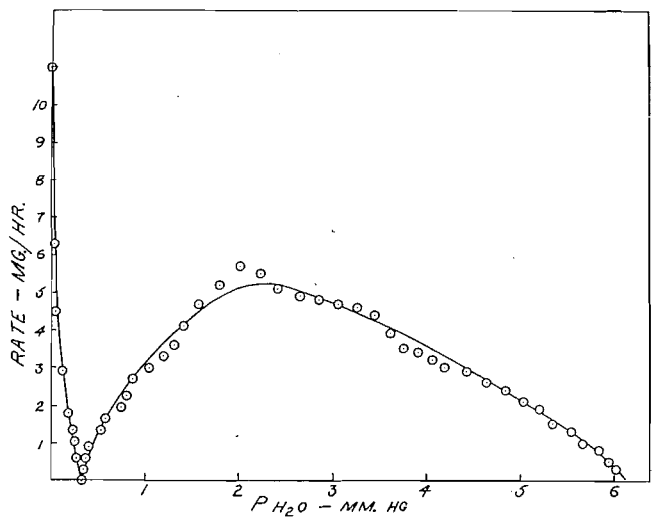



FIG. 3. The dependence of rate of weight loss upon pressure, determined from the data of Fig. 2.

This curve is similar in form to that obtained by Topley and Smith. It is obvious, however, that a similar type of curve would result if either the rate of change of weight loss, or the rate of change of pressure, was plotted against time.

Similar experiments were carried out at several dehydration temperatures.

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It was found that, as the temperature of the reacting crystals was lowered, the minimum in rate became sharper and displaced toward the region of lower pressure. Also, the induction period became longer; at 30° C., nearly twelve hours elapsed before an observable increase in pressure or weight loss occurred. At 50° C., the induction period was scarcely observable.

*Experiments with Finely Divided Crystals at Constant Water Vapor Pressures*

A few experiments were carried out under nearly vacuum conditions. In these, the sample was suspended from the spiral, and the system, apart from the spiral case and reaction vessel, evacuated to approximately $10^{-6}$ mm. The stopcock connecting the spiral case to the vacuum system was then opened and readings started, the pumps being kept in operation throughout the duration of the experiment. After about fifteen minutes, the pressure in the reaction vessel fell to about 0.002 mm. and remained constant at that value.

In experiments conducted at constant pressures of water vapor, the sample was dehydrated as above until 10% decomposition to the monohydrate composition had occurred. The system was then shut off from the pumps, and the sample exposed to the source of water vapor.

In all, 12 experiments were carried out at pressures ranging from 0.002 mm. to 4.57 mm. The weight-loss versus time curves for five of these experiments are shown in Fig. 4, the other curves obtained being entirely similar in type.

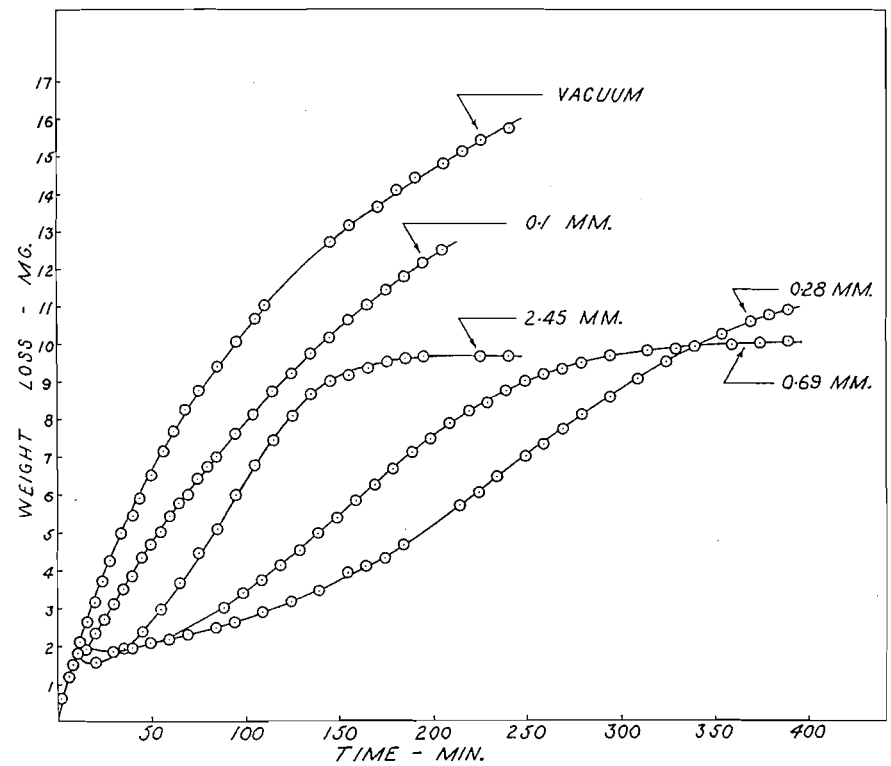



FIG. 4. The change in weight loss of fine crystal aggregates during dehydration at a series of constant water vapor pressures.

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The readings recorded cover the entire dehydration period, and include the period of nucleation under vacuum.

It will be observed that these curves fall into two groups. At pressures of 0.002 mm. and 0.1 mm., the rate of loss in weight decreases gradually, and the dehydration proceeds without a break in the rate curve until the monohydrate composition is reached. Furthermore, the rate of dehydration at any given time is lowered with increase in water vapor pressure. X-ray powder photographs have shown that the products obtained under these conditions are amorphous.

The other group of curves are distinctly different in character. They are coincident with the former group up to the point where the pumps are shut off and the system is exposed to water vapor at constant pressure. An induction period then sets in, following which the rates increase over a period of time. The rates then gradually decline, the curves flattening at approximately the trihydrate composition. X-ray powder photographs show trihydrate lines for these end products. The most interesting aspect of this second group of curves lies in the fact that the over-all slopes of the curves in the period following the induction period depend upon the pressure at which the dehydration was conducted. In Fig. 4, these slopes are seen to increase sharply as the pressure is increased from 0.28 mm. to 2.45 mm.

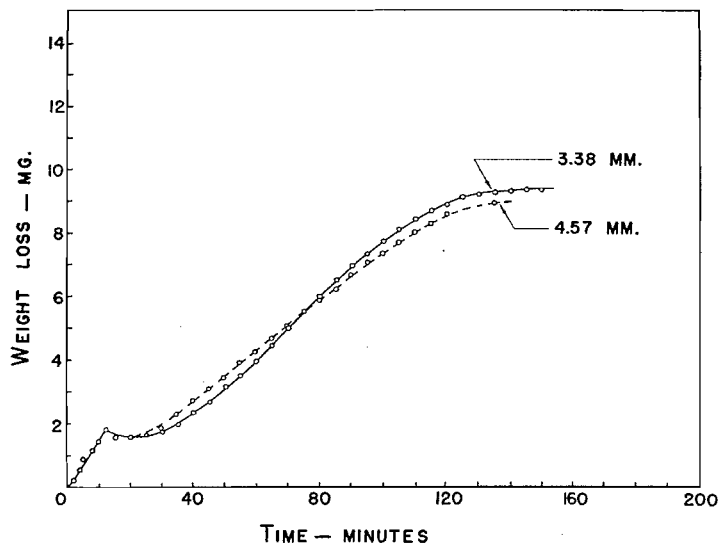



FIG. 5. The change in weight loss of fine crystal aggregates during dehydration in the range of pressure when the rate becomes lowered by pressure increase.

It has been found, however, that there is a limit in pressure beyond which this increase in rate does not occur. This is shown by the two experiments for which data are plotted in Fig. 5. The slope of the portions of the curve following the induction period is lower for the experiment conducted at 4.57 mm. than for that carried out at 3.38 mm. This result has been found to be reproducible both in experiments with finely divided crystals and with single crystals.

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In Table I, the rates of dehydration at corresponding water vapor pressures are tabulated. Those given under method *A* were calculated on the basis of the observation that, in all experiments, the loss in weight varies almost linearly with time over a range of fractional decomposition ranging from 0.2 to 0.4 (complete decomposition corresponding to the removal of four water molecules from the pentahydrate lattice, i.e., to a weight loss of 28.8%). This method is very similar to that used for manganous oxalate by Topley and Smith who, as has been mentioned, compared rates corresponding to 20% decomposition.

TABLE I

DEHYDRATION RATES AT 40° C.

| Sample wt., mgm. | Pressure water vapor, mm. Hg | Rate, Method *A*, mgm./hr./dgm. | Rate, Method *B*, mgm./hr./dgm. | X-ray powder photograph |
|---|---|---|---|---|
| 62.0 | 0.002 | 10.53 | 19.38 | No lines |
| 62.0 | 0.10 | 6.84 | 7.90 | No lines |
| 62.0 | 0.28 | 3.15 | 3.65 | Trihydrate lines |
| 62.3 | 0.69 | 4.03 | 4.11 | Trihydrate lines |
| 62.0 | 0.69 | 4.16 | 4.46 | Trihydrate lines |
| 62.0 | 1.18 | 3.74 | 4.37 | Not determined |
| 62.0 | 1.22 | 4.21 | 4.68 | Trihydrate lines |
| 62.0 | 2.45 | 7.32 | 7.75 | Trihydrate lines |
| 62.0 | 2.62 | 7.85 | 8.33 | Trihydrate lines |
| 62.0 | 3.38 | 9.36 | 9.88 | Not determined |
| 62.0 | 4.57 | 8.15 | 8.30 | Not determined |
| 62.2 | 4.57 | 8.30 | 8.50 | Trihydrate lines |

The rates tabulated under method *B* were determined for each curve by finding the slope over small intervals and determining the point of inflection. In other words, the rates so tabulated are those prevailing at the point where the rate begins to decline owing, presumably, to the impedance effect.

Both of these methods are arbitrary, and are particularly so when applied to the two curves which show a gradual decrease in rate throughout. However, for these curves the only feature which is of immediate concern is that the rate drops rapidly with increasing pressure.

The rates determined by methods *A* and *B* are shown plotted against corresponding pressures in Fig. 6 and Fig. 7 respectively.

A comparison of these curves with that shown in Fig. 1 shows clearly that the effect of increasing water vapor pressure on dehydration rate is qualitatively similar in the two cases.

*Experiments with Single Crystals*

A series of experiments were carried out in which single crystals weighing approximately 50 mgm. were subjected to the procedures which have been described.

When nucleated crystals were placed in an initially evacuated space and allowed to dehydrate while the pressure increased, the results obtained were similar to those shown in Fig. 3.

Dehydrations at constant pressure were carried out over a range of pressures

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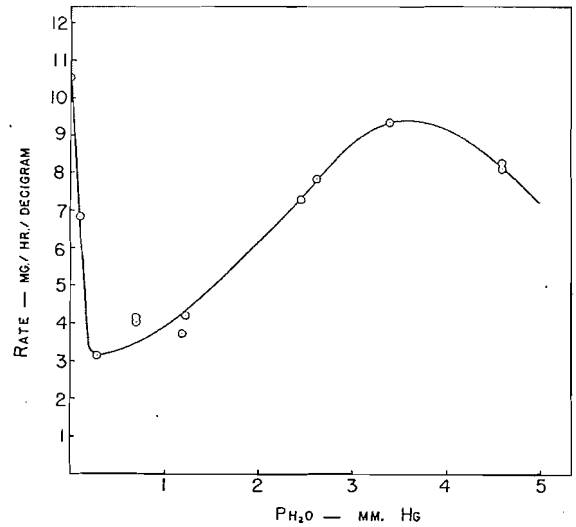



FIG. 6. The dependence of rate upon pressure (method *A*).

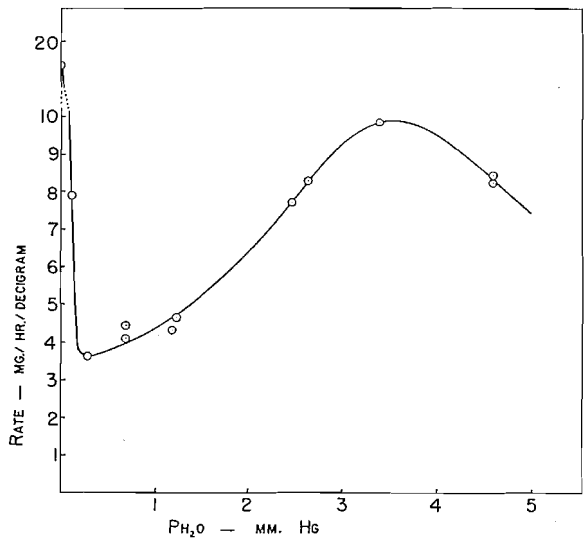



FIG. 7. The dependence of rate upon pressure (method *B*).

from nearly vacuum to 4.60 mm. The results of four experiments are shown in Fig. 8. It will be seen that the rates are very much slower, the dehydration extending over two days in some cases.

These experiments were carried out with the hope that the rates might be expressed as loss in weight per unit time per unit area, the interfacial areas at different stages of decomposition being calculated from the linear dimensions of the crystal by making the assumption that the reaction is propagated inwards in a uniform manner.

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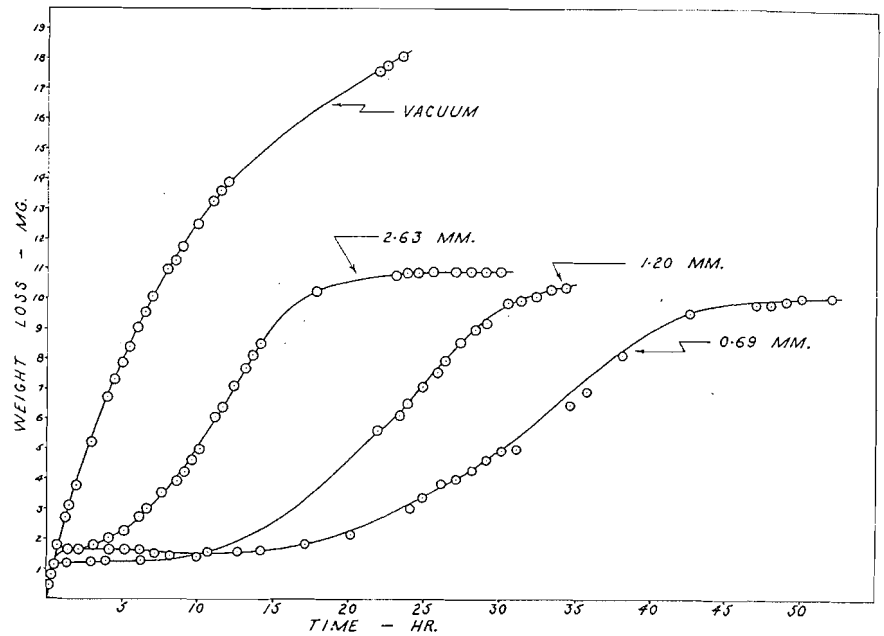



FIG. 8. The change in weight loss of single crystals during dehydration at a series of constant water vapor pressures.

In order to test this assumption the following experiment was carried out. Several small crystals were prepared and selected as has been described. These were placed in a small tube which was connected to the vacuum system through a ground joint and a large stopcock. The tube was surrounded by a Dewar flask containing water at 40° C. A crystal was also placed on the spiral pan housed in the spiral case as has been described. The water vapor pressure was then adjusted to one of a series of values. The crystals in the tube and the crystal on the spiral pan were therefore subjected to identical conditions of temperature and pressure. At suitable intervals during the dehydration periods, the proper stopcocks were closed, the system opened, and one of the crystals removed for microscopic examination. The tube was then replaced, the air pumped out, the sample again exposed to the water vapor for a definite time, and a second crystal removed, the whole operation being then repeated a number of times. Since constant conditions were maintained, it was assumed that the loss in weight of any one of the crystals in the tube corresponded to that of the crystal on the spiral basket.

Microscopic examination of crystals dehydrated to various stages under nearly vacuum conditions confirmed the findings of previous workers that the reaction proceeds at an interface which moves into the crystal as the reaction proceeds. Fairly satisfactory correlation was obtained between the percentage weight loss as determined from the spiral extension and that estimated from the position of the interface. In view of the experiments of Smith and Topley, who were able to calculate their rates to zero impedance, it would appear

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likely that dehydrations carried out at pressures to the left of the minimum shown in Fig. 6 or in Fig. 7 are of this type.

However, microscopic examination of crystals dehydrated to various stages at pressures greater than those corresponding to the minimum rate gave no evidence of such correlation. In most cases the position of the interface could be estimated only in the very early stages of decomposition, and all traces of an interface disappeared long before the decomposition was complete. It appeared from these experiments that nucleation developed through the entire crystal very shortly after the decomposition commenced, probably during the induction period. This marked difference in behavior is of interest and is undoubtedly related to the distinct difference in character between the types of dehydration curves to which reference has been made.

In view of these experiments, it was necessary therefore to evaluate rates by the methods used in the case of finely divided crystals. When these rates were plotted against pressure, curves were obtained similar to those shown in Fig. 6 and Fig. 7.

## DISCUSSION

The similarity in rate–pressure dependence, which these experiments have shown to exist for manganous oxalate dihydrate and copper sulphate pentahydrate, clarifies our understanding of the processes involved to the extent of removing the difficulty in interpretation which has arisen as a consequence of regarding these salt hydrates as being different in behavior. The comment which follows is intended to bring into relief certain features which we regard as pertinent, rather than to suggest explanations which differ in any fundamental way from those which have been already offered (1, 8, 9).

We believe that the key to the interpretation of the observed dependence of rate upon pressure shown in Figs. 6 and 7 lies in the fact that the durations of the induction periods shown in Figs. 4 and 8 are also pressure dependent, and furthermore, that the curves are very nearly linear following these induction periods. These curves show qualitatively, but clearly, that the induction periods become shorter as the pressure becomes greater. This is also the case in the experiments shown in Fig. 5 although the subsequent rates show an inverse relationship with pressure.

Experiment has shown that the breakdown of the copper sulphate pentahydrate lattice at low pressure results in the formation of a product which does not diffract X rays. This product is relatively stable. It may be prepared in the laboratory, and some of its properties studied. However, its exact nature is as yet unknown. Experiment shows that the orientation of this amorphous product into a stable lattice occurs in the presence of traces of water vapor (3).

Upon low pressure dehydration, when water molecules are continually drawn away from the reaction zone, the amorphous product has the stoichiometrical composition of the monohydrate. The group of weight-loss versus time curves obtained at very low pressures represent dehydrations of this type. The pentahydrate lattice breaks down into amorphous monohydrate, the

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gradual decrease in rate being due to increasing impedance and diminishing interfacial area.

The same process must be assumed to occur in all other cases up to the point where the sample is exposed to water vapor at constant pressure. At this stage (following in some cases a slight increase in weight due to adsorption) the induction period sets in during which there is little observable change in weight. It has been pointed out that microscopic examination of crystals dehydrated to this stage shows the reaction zone to have advanced far into the crystal. It is probable, therefore, that during the induction period the pentahydrate lattice continues to collapse into the amorphous product, but that the liberated water molecules are retained in the amorphous layer in sufficiently large numbers to make the weight loss undetectable by the method used. As the water vapor pressure in the region external to the crystal is increased, the pressure gradient between the crystal and its surroundings is reduced. Hence the rate of removal of water molecules is lowered and the effectiveness in inducing crystallization is increased.

When crystallization occurs, the escape of water molecules will be facilitated by a decreased adsorption and through the development of spaces between the small crystals through which water molecules may pass. The induction period will be followed, therefore, by a period during which water molecules will escape at a nearly linear rate, this rate being eventually decreased as the impedance effect of the crystalline layer increases. This, of course, is what has been observed in the loss-in-weight versus time curves which have been reported in the foregoing.

On the basis of this view, the center of interest shifts from the effect of pressure on the rate following the induction period, to the effect of pressure on the induction period itself. In other words, the rate of escape of water molecules from the reaction zone will be increased in proportion to the extent to which crystallization has occurred. But this extent of crystallization will depend upon a diminishing pressure gradient, or consequently upon increase of external water vapor pressure. It is interesting to note that in those experiments in which crystals were allowed to dehydrate into a closed and initially evacuated space, the long induction period observed at 30° C. is practically nonexistent at 50° C. In other words, at the higher temperature, water vapor is produced rapidly enough to cause rapid crystallization of the amorphous product and the consequent release of water molecules from the reaction zone.

While these considerations may be helpful in arriving at a qualitative explanation of the results obtained, it must be emphasized that the observed changes in rate occur with changes in external pressure of only 2 or 3 mm. This sensitivity to water vapor over this small range is very surprising. A more definite knowledge of the nature of the amorphous product might throw light on the nature of the processes of nucleation and crystallization which appear to be dependent upon these small changes in pressure.

Mention should also be made of the fact that under the experimental conditions, in which dehydrations were conducted at a definite static pressure of water vapor, the end crystalline product was trihydrate instead of mono-

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hydrate as might have been expected. Frost, Moon, and Tompkins (3) carried out dehydrations over substantially the range of pressures used in this work, and obtained mixtures of crystalline pentahydrate along with crystalline and amorphous monohydrate and with only slight evidence of trihydrate formation. However, their dehydration pressures were obtained by means of a throttled stopcock device, under which condition there would be a movement of water molecules away from the reaction interface.

The stability of the trihydrate phase at pressures far below those corresponding to the tri–monohydrate equilibrium (16 mm. at 40° C.) has been observed by other workers and is consistent with the finding of Cooper, Colvin, and Hume (2) that the rates of nucleation and propagation of the trihydrate are much slower than those of the pentahydrate. From this point of view, the curves of Figs. 4 and 8 level off at the induction period of the crystalline trihydrate to crystalline monohydrate transition.

## ACKNOWLEDGMENTS

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# THE FISSION YIELD OF $I^{131}$ IN THE THERMAL NEUTRON FISSION OF $U^{235}$[1]

By Rosalie M. Bartholomew, F. Brown, R. C. Hawkings, W. F. Merritt, and L. Yaffe[2]

ABSTRACT

The fission yield of $I^{131}$ has been investigated using improved extraction techniques and disintegration rate measurements. The value obtained for the fission yield is $(3.1 \pm 0.1)\%$. This is relative to a $Ba^{140}$ reference fission yield of 6.1%. The half-life for $I^{131}$ has been determined and found to be $8.05 \pm 0.01$ days.

## INTRODUCTION

Recent reports (16, 11) of fine structure in the fission yield – mass curve obtained from thermal fission of $U^{235}$ have made advisable a redetermination by improved radiochemical techniques of the yields of some of the nuclides formed in fission. The mass 131 chain has been used by Thode *et al.* (16) as their standard and thus an accurate knowledge of the chain yield is necessary. This paper deals with an improved determination of the yield of the last radioactive member of this chain, $I^{131}$.

All previous measurements of the fission yield of $I^{131}$ have been with reference to the yield of $Ba^{140}$. The normalization values assumed vary from worker to worker. For comparison purposes, we have normalized all earlier values for $I^{131}$ to a $Ba^{140}$ yield of 6.1% (9). This is currently believed to be the best value and has been used as the reference in this work.

On this basis the following results have been obtained by other investigators: Anderson, Fermi, and Grosse (2)—2.4%, Grummitt and Wilkinson (13)—1.4%, Yaffe and Mackintosh (21)—2.4%, Engelkemeir, Seiler, Steinberg, and Winsberg (7)—2.8%.

It has recently become evident that the fluctuations and possibly low values quoted above can be improved by better chemical extraction methods and better disintegration rate measurements, both of which were used in this work.

The nuclide $I^{131}$ was first identified by Livingood and Seaborg (15) and first found as a fission product by Abelson (1). Recent values for the half-life are $8.02 \pm .03$ days by Sinclair and Emery (18) and $8.1409 \pm .0062$ days by Sreb (19), although no experimental details have been published of Sreb's work.

The $I^{131}$ decay scheme is extremely complex and is still a matter of some dispute, although probably the best scheme is that recently proposed by Bell and Graham (3). Owing to the complexity of the decay scheme and the fact that about 1% of the $I^{131}$ disintegrations go to a metastable state of $Xe^{131}$ with a half-life of about 12 days (5), the accurate measurement of the disintegration rate presents a problem.

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*Contribution from Chemistry and Physics Branches, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 26.*
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## EXPERIMENTAL

### (*a*) *Irradiation*

Accurately weighed samples (10–20 mgm.) of uranyl nitrate hexahydrate were irradiated in sealed quartz ampoules in the NRX nuclear reactor. Separate samples were used for the $Ba^{140}$ and $I^{131}$ determinations. The ampoules were arranged so that they were very close together and thus received the same neutron irradiation. The samples used were of such a size that self-shielding was negligible.

The position chosen in the reactor was one where the neutrons were predominantly thermal. The length of irradiation was 48 hr. in two experiments and 96 hr. in the third.

### (*b*) *Chemical Extraction*

#### (i) *Iodine*

The iodine was extracted from the irradiated uranium about one week after the end of irradiations. This allowed the $Te^{131}$ parent of the $I^{131}$ to decay essentially completely.

The chemical separation method used was one which had been shown to give complete interchange between the radioactive iodine and the added carrier. The method is essentially that of Glendenin and Metcalf (10) which has been modified slightly by Yaffe, Day, and Greer (20). The iodine carrier is added as KI to an alkaline solution of the uranium salt. The KI is oxidized to $I^{+7}$ with sodium hypochlorite, reduced to $I_2$ with hydroxylamine hydrochloride, further reduced to $I^-$ with sulphur dioxide, and oxidized to $I_2$ with sodium nitrite – nitric acid mixture. This cycle was repeated several times, finally leaving the iodine in the reduced state. Full details are given in Reference 20. The final reduced solution was made slightly alkaline with lithium hydroxide and made up to a standard volume.

#### (ii) *Barium*

The barium was extracted by a method described previously (12). Using this method the barium was separated from the uranium and other fission products by several chloride, chromate, and nitrate precipitations with the addition of appropriate hold-back carriers. The final barium nitrate precipitate was dissolved in water and made up to a standard volume. Aliquots were taken from this for measurement purposes.

### (*c*) *Source Preparation for Measurement*

From the master solution, aliquots were pipetted out with calibrated micropipettes and deposited on thin films. The area over which the source was to be spread was previously wetted by placing on it and then removing a drop of 5% insulin. The films used were of laminated Zapon-formvar (100 $\mu$gm. per cm.$^2$) sputtered with 25 $\mu$gm. per cm.$^2$ gold on either side.

#### (i) *Barium*

The aliquot of the barium nitrate solution was placed on the film and dried using an infrared lamp. This gave essentially a "weightless" source, i.e., self-absorption was negligible.

#### (ii) *Iodine*

The aliquot of iodide solution was added to a solution of silver nitrate already

present on the film. Approximately two equivalents of $Ag^+$ were used per equivalent of $I^-$. This excess usually resulted in the precipitation of some silver oxide but has been found to give a more stable precipitate of silver iodide. Attempts to reduce the silver concentration resulted in loss of radioactive iodine. A good source appears uniformly gray to black on the film—all others were discarded.

A sample on the film was heated for 15–20 min. prior to each measurement using a 250 watt infrared lamp at a distance of 15–20 cm. This technique was adopted to get rid of the xenon decay products formed from the iodine. This is not too important with $I^{131}$ since only about 1% decays to an active xenon daughter. All other iodine products had decayed before extraction. This is very important, however, in the measurement of the other iodine isotopes and this technique will be described in a forthcoming publication.

*(d) Measurements*

All activities were measured using the $4\pi$ $\beta$-counting technique as described by Borkowski (4) and Hawkings, Merritt, and Craven (14). This counter has the advantage of very great stability, low resolving time, and does not require the use of major correction factors. Small corrections, of the order of one per cent, are made for coincidence losses and for loss of $\beta$ particles in the film holding the sample. These corrections can be made with good accuracy.

*(e) Radioactive Growth and Decay*

Decay curves for $I^{131}$ were followed for many half-lives in subsidiary experiments as shown in Table II and a very accurate value of the half-life obtained. Each half-life shown represents a separate irradiation and extraction. The activity in the iodine sample after extraction consisted principally of $I^{131}$ since the other iodine isotopes had almost completely decayed away.

(i) $I^{131}$ is formed as a member of the following chain

$$\xrightarrow{a} Te^{131m} \xrightarrow{30\ \text{hr.}} \qquad \xrightarrow{b} Te^{131} \xrightarrow[25\ \text{min.}]{} I^{131} \xrightarrow[8.0\ \text{days}]{}$$

where $a$ and $b$ are the fractional yields of $I^{131}$ from the parent isomers.

$$a/b = 87/13 \quad (8)$$

If the sample of uranium is irradiated for a time $t_0$ and then allowed to decay for a time $t_1$ (measured from the end of irradiation), then the number of atoms of $I^{131}$, $N_I$, present at time $t_1$ can be shown to be

$$N_I = Y_{131}N\left\{\left(\frac{b+a}{\lambda_3}\right)(e^{-\lambda_3 t_1} - e^{-\lambda_3(t_0+t_1)}) + \frac{a\lambda_2}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_1)}(e^{-\lambda_1 t_1} - e^{-\lambda_3 t_1} - e^{-\lambda_1(t_0+t_1)} + e^{-\lambda_3(t_0+t_1)}) + \left(\frac{(b+a)}{\lambda_3-\lambda_2} - \frac{a\lambda_2}{(\lambda_2-\lambda_1)(\lambda_3-\lambda_2)}\right)(e^{-\lambda_2 t_1} - e^{-\lambda_3 t_1} - e^{-\lambda_3(t_0+t_1)} + e^{-\lambda_3(t_0+t_1)})\right\}$$

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where $Y_{131}$ = fission yield of $I^{131}$,
$N$ = fission rate,
$\lambda_1$ = decay constant of $Te^{131m}$ (30 hr.),
$\lambda_2$ = decay constant of $Te^{131}$ (25 min.),
$\lambda_3$ = decay constant of $I^{131}$.

This is based on the reasonable assumption that the independent fission yield of $I^{131}$ is negligibly small.

The above equation may be expressed in the following form

$$N_I = Y_{131} N k_1$$

where the value of $k_1$ may be calculated from the experimental data and known constants involved.

Then the disintegration rate is $N_I\lambda_3 = Y_{131} N k_1 \lambda_3$.

(ii) $Ba^{140}$

$$Ba^{140} \xrightarrow[12.8 \text{ days}]{\beta^-} La^{140} \xrightarrow[40 \text{ hr.}]{\beta^-} Ce^{140}$$

Since the daughter of the $Ba^{140}$ is shorter-lived than the parent, a "growth" curve rather than a decay curve results if one plots the ratio $(Ba^{140} + La^{140})_t / (Ba^{140})_{t_0}$ against time. The symbols $Ba^{140}$ and $La^{140}$ refer to the disintegrations per unit time from these nuclides, while $t$ and $t_0$ refer to the actual time of measurement and the time of separation of the $Ba^{140}$ from the $La^{140}$ respectively; $t_0$ is the actual time of the last barium nitrate separation. The growth curve was plotted using the best values available for the half-lives.

The half-life of $La^{140}$ was checked experimentally using neutron-irradiated 'spec-pure' lanthanum oxide. A value of 40.2 ± 0.1 hr. was obtained by a least squares fit over 12 half-lives. Source reproducibility was guaranteed by taking repeated aliquots from a master solution. Special precautions were taken to prevent evaporation of the master solution. A value of 12.8 days (6) was taken for the half-life of $Ba^{140}$.

Using the theoretical growth curve based on the above half-lives, the disintegration rate of $Ba^{140}$ at the time of separation was calculated. The constancy of this value, as shown in Table I, where observations were made over a wide variation in the ratio $La^{140}/Ba^{140}$, shows that the soft radiations of $Ba^{140}$ were counted with good efficiency.

The disintegration rate of $Ba^{140}$ was then corrected back to the end of irradiation using a half-life of 12.8 days. This then gives

$$N_{Ba}\lambda_{Ba} = Y_{140} N$$

where $N_{Ba}$ and $\lambda_{Ba}$ are the number of atoms of $Ba^{140}$ and its decay constant respectively. $Y_{140}$ is the fission yield of $Ba^{140}$ and $N$ again the fission rate. Using this, the fission yield of $I^{131}$ ($Y_{131}$) is calculated as follows

$$Y_{131} = \frac{(N_I\lambda_3)\, Y_{140}}{k_1\lambda_3(N_{Ba}\lambda_{Ba})}.$$

*(f) Chemical Yields*

The chemical yields were determined by gravimetric analyses of the solutions.

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Silver iodide and barium sulphate were precipitated, using standard analytical methods.

## RESULTS

TABLE I

| Time elapsed between separation and measurement ($t - t_0$) in hours | Theoretical ratio of $La^{140}/Ba^{140}$ | $Ba^{140}$ concentration at $t_0$ (dis./sec./ml. $\times 10^{-5}$) |
|---|---|---|
| 4 | 0.07 | 4.76 |
| 27 | 0.39 | 4.77 |
| 140 | 1.01 | 4.76 |
| 800 | 1.15 | 4.77 |
| 1650 | 1.15 | 4.78 |

The results of the half-life determinations are given in Table II.

TABLE II

| Period of measurement (days) | Weighting factor | Observed half-life (days) |
|---|---|---|
| 27 | 1.000 | 8.058 |
| 27 | 1.000 | 8.068 |
| 27 | 1.000 | 8.050 |
| 50 | 1.852 | 8.062 |
| 69 | 2.556 | 8.055* |
| 35 | 1.296 | 7.980 |

**This sample of $I^{131}$ was not obtained from the fission of $U^{235}$, but was prepared by the neutron irradiation of tellurium.*

The results were weighted using factors directly proportional to the period over which the measurement took place. The observed half-lives shown are the best values obtained by a least squares fit.

The weighted average for the half-life of $I^{131}$ is 8.05 ± .01 days. Owing to the long period of time taken for the measurements, the care to avoid any $Xe^{131}$ contribution, and the stability of the equipment used, this value is considered to be reliable.

The fission yield data are shown in Table III. The value obtained is (3.10 ± .01)% relative to a yield of 6.1% for $Ba^{140}$.

TABLE III

| Expt. No. | Length of irradiation, $t_0$ (hr.) | Time between end of irradiation and chemical separation, $t_1$ (hr.) | | Dis./sec./mgm. uranyl nitrate at time of separation | | Fission yield in per cent (relative to $Ba^{140}$ + 6.1%) |
|---|---|---|---|---|---|---|
| | | $Ba^{140}$ | $I^{131}$ | $Ba^{140}$ | $I^{131}$ | |
| 1 | 48.0 | 126.3 | 123.0 | $3.500 \times 10^5$ | $1.840 \times 10^4$ | 3.10 |
| 2 | 48.0 | 179.8 | 207.0 | $4.108 \times 10^5$ | $1.585 \times 10^4$ | 3.12 |
| 3 | 96.0 | 111.0 | 253.0 | $4.640 \times 10^5$ | $2.840 \times 10^4$ | 3.09 |
| | | | | | Average | 3.10 ± .01 |

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It is exceedingly difficult to assess any systematic errors which may be carried along. We are suggesting a value of $(3.1 \pm 0.1)\%$ for the $I^{131}$ fission yield. The error quoted is 10 times the standard deviation and is probably greater than any systematic error present. This agrees well with a recent unpublished value of 3.0% obtained by Pappas and Coryell (17).

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# THE BIOGENESIS OF ALKALOIDS

## VII. THE FORMATION OF HORDENINE AND N-METHYLTYRAMINE FROM TYROSINE IN BARLEY[1]

By Edward Leete[2] and Léo Marion

ABSTRACT

Feeding *dl*-tyrosine-2-$C^{14}$ to sprouting barley resulted in the formation of radioactive hordenine and N-methyltyramine in the roots. Isolation and degradation of these alkaloids showed that all the activity was located in the $\alpha$-carbon atom of the side chain, thus indicating that tyrosine is a precursor of N-methyltyramine and hordenine.

It has been shown previously (6) that tyramine is a precursor of hordenine in sprouting barley, the hordenine being formed by stepwise methylation via N-methyltyramine (4). It seemed highly likely that the source of tyramine in the roots was tyrosine, since it is well established that this conversion can be brought about by a variety of bacteria and by the kidney tissue of animals.

This hypothesis was tested by feeding *dl*-tyrosine-2-$C^{14}$ to sprouting barley and then, after a suitable period of time, isolating the N-methyltyramine and hordenine from the roots. These alkaloids were found to be radioactive and degradation as previously described (6) showed that all the activity of both alkaloids was located in the $\alpha$-carbon atom of the side chain (see Table I). The higher activity of the N-methyltyramine was again observed, indicating a stepwise methylation. Since no tyramine could be detected in the extracts from the roots, it thus seems that tyramine has only a transient existence in the normal growth of the roots. It is immediately methylated to N-methyltyramine, while further methylation to hordenine takes place more slowly.

The source of hordenine in the roots of barley has now been clearly established, but this can only be considered as a preliminary step in determining the function of this alkaloid in the physiology of the plant.

The indole alkaloid gramine is produced in the leaves of the strain of barley used in this investigation (Charlottetown No. 80) and in view of the recent suggestion of Robinson (7) that tyrosine may be a source of indole we examined the leaves of the sprouting barley which had been fed with the radioactive tyrosine. The leaves were found to be radioactive, as also was the methanol extract of the leaves. However, the crude gramine isolated from the extract was found to be completely inactive. It has been shown that tryptophane is a precursor of gramine (1) and other workers have shown that tryptophane is synthesized by the condensation of indole and serine in *Neurospora* (8, 9, 10). Thus, had the tyrosine-2-$C^{14}$ been converted to indole by Robinson's mechanism, gramine should have been obtained in which radioactivity was located in the $\alpha$-position of the indole nucleus. At least this would be the case if it be assumed that any indole produced would be converted to

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[2] *Holder of a Postgraduate Travelling Fellowship from the Goldsmiths' Company of London, England.*

tryptophane and thence to gramine. The biosynthesis of tryptophane in barley leaves is being investigated.

## EXPERIMENTAL

*Preparation of dl-Tyrosine-2-$C^{14}$*

$C^{14}$-Methyl labelled sodium acetate (1.64 gm.) was converted to bromoacetic acid by the method of Fields *et al.* (2). The crude bromoacetic acid was dissolved in water (5 ml.) and sodium carbonate (1.2 gm.) added to the solution. The mixture was warmed to 60° and after the addition of sodium cyanide (1.1 gm.) dissolved in a little water, maintained at 60° for 15 min., and then refluxed for five minutes. The resulting brown solution was cooled to 0°, concentrated hydrochloric acid (2.5 ml.) added, and the solution evaporated to dryness *in vacuo*. The residue was extracted with absolute alcohol and the filtered extract on evaporation yielded crystalline cyanoacetic acid. The crystalline acid was suspended in ether and to the suspension was added a solution of excess diazoethane in ether; after the solution had stood for five minutes it was filtered and the ether evaporated off on the water bath. The ethyl cyanoacetate-2-$C^{14}$ thus obtained was a yellow oil. It was used to synthesize *dl*-tyrosine-2-$C^{14}$ by the method of Fields *et al.* (3). The yield of *dl*-tyrosine was 1.826 gm. (50.3% based on sodium acetate).

*Administration of dl-Tyrosine-2-$C^{14}$ to the Barley*

Barley (Charlottetown No. 80, 720 gm.) was grown as previously described (4). On the sixth day of sprouting a solution of *dl*-tyrosine-2-$C^{14}$ (506.75 mgm.) in distilled water (600 ml.) containing concentrated hydrochloric acid (0.40 ml.) was fed to the barley. The administered tyrosine had a specific activity of $3.31 \times 10^4$ disintegrations per minute per millimole and a total activity of $9.40 \times 10^7$ disintegrations per minute. The low pH of the solution had no apparent effect on the growth of the barley and after one day in contact with the roots the nutrient solution was neutral.

*Isolation of the Alkaloids from the Roots*

On the 11th day of sprouting the shoots and roots of the barley were separated. The crude alkaloids from the roots were obtained by established methods (5, 6). The roots (80.4 gm.) which had been extracted with hot methanol for 48 hr. still had a high residual activity of 765 disintegrations per minute per mgm. Paper chromatography of the crude extract (6) followed by a survey of the radioactivity of the developed chromatogram showed that the activity of the extract was located in spots coincident with N-methyltyramine and hordenine detected by Millons reagent. There was no trace of radioactivity in the position where tyramine would occur on the chromatogram. Chromatography of the extract on alumina (6) yielded hordenine (0.0996 gm. with a specific activity of $1.61 \times 10^5$ disintegrations per minute per millimole) and N-methyltyramine (0.0678 gm. with a specific activity of $6.12 \times 10^5$ disintegrations per minute per millimole). Both the hordenine and N-methyltyramine were diluted with inactive alkaloids, and subsequent degradations were carried out with these diluted samples. Degradations were carried out as previously

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described and the specific activities of the derivatives and degradation products of the alkaloids are summarized in Table I.

TABLE I

| Derivative[3] | Disintegrations per minute per millimole[4] | |
|---|---|---|
| | From hordenine | From N-methyltyramine |
| Alkaloid | $1.61 \times 10^5$ | $6.12 \times 10^5$ |
| Picrate | $1.69 \times 10^5$ | $6.72 \times 10^5$ |
| Hydrochloride | $1.70 \times 10^5$ | $6.38 \times 10^5$ |
| Platinochloride | $2 \times 1.69 \times 10^5$ | $2 \times 6.07 \times 10^5$ |
| Hordenine methiodide | $1.57 \times 10^5$ | $6.38 \times 10^5$ |
| O-Methylhordenine methiodide | $1.62 \times 10^5$ | $6.07 \times 10^5$ |
| Trimethylamine platinochloride[5] | 0 | 0 |
| Anisic acid[6] | 0 | 0 |
| Homoanisaldehyde oxime[7] | $1.71 \times 10^5$ | $6.57 \times 10^5$ |
| Anisic acid[8] | $1.60 \times 10^5$ | $6.10 \times 10^5$ |

[3] *The preparation of all the derivatives was carried out exactly as described previously (6).*
[4] *The radioactive measurements were determined on thin samples, making the usual corrections for self-absorption, etc.*
[5] *Obtained from the Hofmann degradation of the O-methylhordenine methiodide.*
[6] *Obtained by the oxidation of p-vinylanisole from the Hofmann degradation.*
[7] *Obtained by oxidation of the p-vinylanisole with mercuric oxide and iodine.*
[8] *Obtained by oxidation of the homoanisaldehyde oxime.*

### *Isolation of Gramine from the Shoots*

The shoots (55.75 gm.) which had been dried at room temperature were extracted as previously described (1). The residue (28.8 gm.), obtained by evaporation of the crude methanol extract, was assayed and found to have an activity of 34.6 disintegrations per minute per mgm., or a total activity of $1.00 \times 10^6$ disintegrations per minute. Crude gramine (0.281 gm.) isolated from the extract by the usual method (1) was found to be inactive.

ACKNOWLEDGMENT

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# THE REACTION OF ACTIVE NITROGEN WITH ACETYLENE[1]

By J. Versteeg[2] and C. A. Winkler

ABSTRACT

The main products of this reaction were hydrogen cyanide and polymer that contained approximately 32% nitrogen. Yields of these substances increased to constant values with increase of acetylene flow rate. Some cyanogen and methane were also formed. The yield of cyanogen passed through a maximum with increased flow rate of acetylene, but the methane yields were quite erratic.

Previous studies in this laboratory have served to outline the main features of several reactions involving the attack of active nitrogen on paraffin and olefine hydrocarbons (1, 3, 6, 8). The present paper summarizes the results of a similar study with acetylene, with an interpretation in terms of atomic nitrogen as the reactive species in active nitrogen (cf. 6).

## EXPERIMENTAL

The apparatus and general experimental and analytical techniques were identical with those described in the earlier papers. Hydrogen cyanide and cyanogen were estimated by an adaptation of the method of Wallis (9), acetylene by absorption in potassium iodomercurate (4), and methane and hydrogen by combustion (2).

## RESULTS AND DISCUSSION

The reaction was accompanied by a very bright flame, more reddish in color than similar flames with other hydrocarbons studied in this laboratory. The size of the flame was unaffected by hydrocarbon flow rate in the range used, and the flame was always located in the immediate vicinity of the hydrocarbon jet. The temperature indicated by a thermocouple in the center of the reaction vessel was approximately 165°C., but the true reaction (flame) temperature was probably much higher than this value.

The main products were hydrogen cyanide and a brown polymer that accumulated, for the most part, on the wall of the reaction vessel. A small amount of polymer of darker color was also deposited in two consecutive liquid nitrogen traps in the main pumping line. No ethylene or ethane was detected among the products.

Preliminary experiments showed that formation of polymer in one experiment reduced the amount of reaction in a subsequent experiment, presumably because the concentration of nitrogen atoms available for reaction with acetylene was reduced by their reaction with polymer. Prior to each experiment, the apparatus following the discharge tube was therefore cleaned thoroughly with chromic acid, followed by water, potassium hydroxide solution, and copious amounts of water. It was then poisoned with dilute phosphoric acid solution in the usual way.

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The yields of the various products as a function of the flow rate of acetylene are shown in Fig. 1.* At very low flow rates of acetylene, corresponding to at

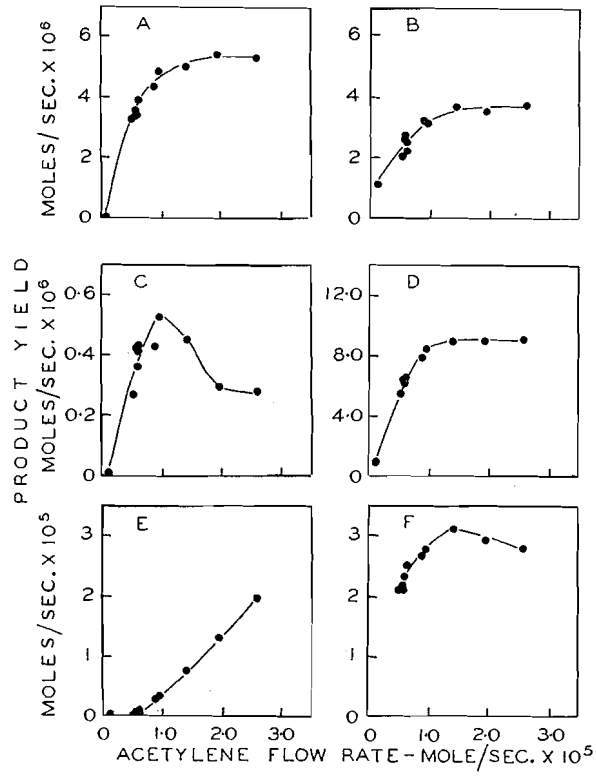



FIG. 1. Relation between yields of products and flow rate of acetylene.
Curve *A*—hydrogen cyanide.
Curve *B*—polymer (plotted as acetylene lost).
Curve *C*—cyanogen.
Curve *D*—total nitrogen reacted.
Curve *E*—acetylene (recovered).
Curve *F*—total hydrogen in noncondensable gases (i.e. as $H_2$ and $CH_4$).

least a sevenfold excess of nitrogen atoms, negligible yields of hydrogen cyanide, cyanogen, or methane were obtained. The acetylene that reacted at these flow rates presumably appeared almost entirely as polymer. From appropriate carbon balances for the system at various flow rates, the curve for polymer formation (Fig. 1*B*) was plotted.

The identity of the polymer has not been established with any certainty. From its rather mottled color it may be inferred that it was not entirely homogeneous. Two samples, one from the reaction vessel, the other from the traps, were obtained by washing some of the more loosely held polymer from the glass surface with distilled water. Dumas nitrogen analyses** showed that the material from the

**The maximum yield of cyanogen corresponds approximately to a flow rate of acetylene just sufficient to react with the nitrogen atoms present, as estimated from the hydrogen cyanide produced in experiments with ethylene under similar conditions (8).*

***We are indebted to Mr. A. J. Matuszko for the analyses.*

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reaction vessel contained 32% nitrogen, while that from the traps contained 16% nitrogen. A hydrogen balance at an acetylene flow rate of $1.2 \times 10^{-5}$ mole per second indicated that the polymer contained only about 20% of the hydrogen originally present in the acetylene that was converted to polymer. Hence, the ratio of carbon to hydrogen in the polymer was probably about five to one.

The polymer was quite insoluble in the usual organic solvents and in dilute acids and alkalies. When heated to about 900°C. in a stream of nitrogen, no cyanogen was detectable but considerable hydrogen cyanide was formed. The residue, amounting to about 50% of the polymer taken, closely resembled graphite in appearance. It would seem, therefore, that the polymer contained little or no paracyanogen, which should decompose completely to cyanogen at 860°C. (7). On the other hand, it has been found (5) that the pyrolysis of methyl or ethyl cyanide at 865°C. and 675°C. respectively produces hydrogen cyanide and considerable amounts of carbon and tar, but no cyanogen. It is suggested, therefore, that the polymer contained nitrogen in a structure analogous to that of a nitrile, and that the monomer from which the polymer was derived may be regarded as a complex formed by collision of a nitrogen atom* with the acetylene molecule.

From the known amounts of hydrogen cyanide, cyanogen, and polymer produced, together with the approximate values for the nitrogen content (assumed to be 32%) and the carbon–hydrogen ratio of the polymer, the curve for total nitrogen reacted was obtained (Fig. 1*D*). The shape of this curve is reasonably explained if all the available acetylene is consumed at acetylene flow rates below about $0.6 \times 10^{-5}$ mole per sec., while at flow rates above $1.2 \times 10^{-5}$ mole per sec. all available nitrogen atoms are consumed. The curve for recovery of acetylene (Fig. 1*E*) is consistent with such an interpretation. In the range of acetylene flow rates between $0.6 \times 10^{-5}$ and $1.2 \times 10^{-5}$ mole per sec. recovery of acetylene increased slightly until at the upper limit of the range the recovery increased at approximately the same rate as the flow rate (quite apparent in larger scale plot). These observations would appear to imply incomplete reaction in the range of flow rates cited, whereas the small flame size observed in all the experiments would indicate complete consumption of one or other reactant over the entire range of flow rates used. The apparent contradiction can be resolved if it is assumed that nitrogen atoms may be removed from the gas stream by reaction with polymer on the wall. At sufficiently low acetylene flow rates there would still be enough nitrogen atoms present to react with all the hydrocarbon. At sufficiently high acetylene flow rates, nitrogen atoms would be almost completely consumed before significant reaction with the polymer on the wall could occur. At intermediate flow rates of acetylene, however, the extent to which nitrogen atoms were removed by the wall reaction would depend upon the acetylene flow rate. The variable nitrogen atom concentration then available for reaction with acetylene would make the relation between acetylene flow rate and product formation appear to change gradually from one of complete nitrogen atom consumption to one corresponding to complete hydrocarbon consumption. Such

**If, for example, the $N_3$ molecule is a reactive species in active nitrogen, formation of such a complex might be represented by $N_3 + C_2H_2 \rightarrow [C_2H_2N] + N_2$.*

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behavior is in marked contrast to the sharply defined conditions for complete hydrocarbon or complete nitrogen atom consumption in the ethylene reaction (3, 8), where virtually no polymer is formed.

Analyses for methane in the noncondensable products gave quite erratic results, from $0.3 \times 10^{-6}$ to $1.8 \times 10^{-6}$ mole per sec. The yields of hydrogen were also erratic, in the range zero to $2.3 \times 10^{-6}$ mole per sec. However, the total hydrogen in the noncondensable gases gave the regular relation with acetylene flow rate shown in Fig. 1*F*.

One experiment, at an acetylene flow rate of $1.08 \times 10^{-5}$ mole per sec., was made with the reaction vessel wrapped in glass wool, so that the temperature indicated by the thermocouple rose to 209°C. Increase in the yields of hydrogen cyanide (10%), cyanogen (35%), and hydrogen (8%), and in consumption of acetylene (25%), were then observed; the polymer yield decreased (25%). No change occurred in the total amount of nitrogen combined in nitrogenous products. The significance of the observed changes is difficult to assess, in view of the uncertainty in the true reaction temperature and in the effect that changes in amount and composition of the polymer on the surface might have on the gas phase reactions. No attempt was made, therefore, to make a more elaborate study of the effect of temperature on the reaction.

A mechanism for the acetylene – nitrogen atom reaction can be formulated in the same way that has been suggested for other reactions of similar type. Collision of a primary acetylene – nitrogen atom complex with a second nitrogen atom would readily account for the cyanogen observed in the products. On the other hand, as indicated previously, the conditions of formation and properties of the polymer obtained are perhaps most satisfactorily accounted for by polymerization of the complex. Decomposition of the complex could, of course, yield hydrogen cyanide. The reactions concerned would be represented

$$C_2H_2 + N \rightarrow [C_2H_2N] \qquad [1]$$

followed by

$$[C_2H_2N] + N \rightarrow (CN)_2 + H_2, \qquad [2]$$

$$n[C_2H_2N] \rightarrow (C_2H_2N)_n, \qquad [3]$$

$$[C_2H_2N] \rightarrow HCN + CH. \qquad [4]$$

The shape of the cyanogen curve (Fig. 1*C*) is similar to that observed with ethylene and may be explained in the same way.

The erratic, small amounts of methane found were probably due to reactions of the methyne radical derived from reaction [4]. The lack of reproducibility in the methane values suggests that the polymer might be involved in reactions of the type

$$CH + (RNH)_n \rightarrow CH_2 + (RN)_nH_{n-1}$$

or

$$CH + H_2 \rightarrow CH_3,$$

$$CH_3 + (RNH)_n \rightarrow CH_4 + (RN)_nH_{n-1}.$$

The relatively low hydrogen content of the polymer is in accord with the occurrence of such reactions. The regularity of the total hydrogen content of the noncondensable gases (Fig. 1*F*) compared with the erratic yields of free hydrogen might be accounted for by an erratic consumption of free hydrogen for the production of methane.

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A point of interest is the possible difference between the complexes of ethylene and acetylene with nitrogen atoms, such that the acetylene but not the ethylene complex is capable of polymerization. The obvious implication is that the ethylene complex is not a free radical whereas the acetylene complex has free radical character. It is tentatively suggested that the difference may be due to expulsion of a hydrogen atom from the ethylene molecule, but not from the acetylene molecule when the complexes are formed,

$$C_2H_4 + N \rightarrow [C_2H_3N] + H,$$
$$C_2H_2 + N \rightarrow [C_2H_2N]^{\cdot}.$$

Such a concept makes no fundamental alteration necessary in the reaction mechanisms proposed previously for the reactions with olefines or paraffins.

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# ISOLATION OF THE ALDOBIURONIC ACID, 3-(XYLOPYRANOSYL)-α-D-GLUCURONOPYRANOSIDE, FROM WHEAT STRAW HOLOCELLULOSE AND SYNTHESIS OF ITS β-ISOMER[1]

By C. T. Bishop

ABSTRACT

Extraction of wheat straw holocellulose with 4% potassium hydroxide removed a polysaccharide fraction containing D-xylose (77.2%), L-arabinose (6.9%), and uronic acid anhydride (7.9%). Hydrolysis of this polysaccharide with dilute acid produced a degraded polysaccharide which was precipitated by ethanol after removing free D-xylose from the hydrolyzate by fermentation with *Hansenula suaveolans*. Prolonged hydrolysis of the degraded polysaccharide yielded an aldobiuronic acid which was shown to be 3-(xylopyranosyl)-α-D-glucuronopyranoside. The β-isomer of this compound was synthesized from D-glucurone and D-xylose and its structure was confirmed by degradative studies after methylation. The enzyme β-glucuronidase did not hydrolyze the α- or β-isomers of this aldobiuronic acid.

Uronic acids, when found in polysaccharides, are attached to the main structure of the molecule by a glycosidic bond through their $C_1$ carbon atoms. Because this glycosidic bond is greatly stabilized by the uronic carboxyl group, hydrolysis of a polysaccharide cleaves the other labile glycosidic bonds first. The acid resistant residue consists of a uronic acid linked glycosidically to one of the carbon atoms of a monosaccharide. An examination of the structure of such compounds, known as aldobiuronic acids, reveals exactly how two monomeric components of the polysaccharide are joined.

Complex acids consisting of D-xylose units joined to D-glucuronic acid have been found in the hemicelluloses of hardwoods (2, 19), pear cell wall (6), and New Zealand flax (18). However, the position at which the D-glucuronic acid is attached to the D-xylose has never been definitely established. This report discusses the isolation of an aldobiuronic acid from a wheat straw polysaccharide and the determination of its structure.

Fig. 1 shows the procedure for hydrolysis of the polysaccharide used in this work and isolation of the barium uronates. Analysis of the original polysaccharide showed that it was composed predominantly of D-xylose units together with smaller amounts of L-arabinose and uronic acid anhydride. After hydrolysis and addition of methanol some of the large excess of D-xylose precipitated with the barium uronates. This difficulty was overcome by removing D-xylose from the hydrolyzate by specific fermentation with *Hansenula suaveolans* (24). Preliminary experiments, using known mixtures, showed that D-glucuronic or D-galacturonic acid could be recovered quantitatively when added to fermentations of D-xylose with this yeast.

The uronic acid content of the precipitate, barium salt "*A*", was 15.1%, and complete methylation, followed by hydrolysis, yielded mono-, di-, and tri-methyl-D-xyloses and a trimethyl hexuronic acid. These results showed

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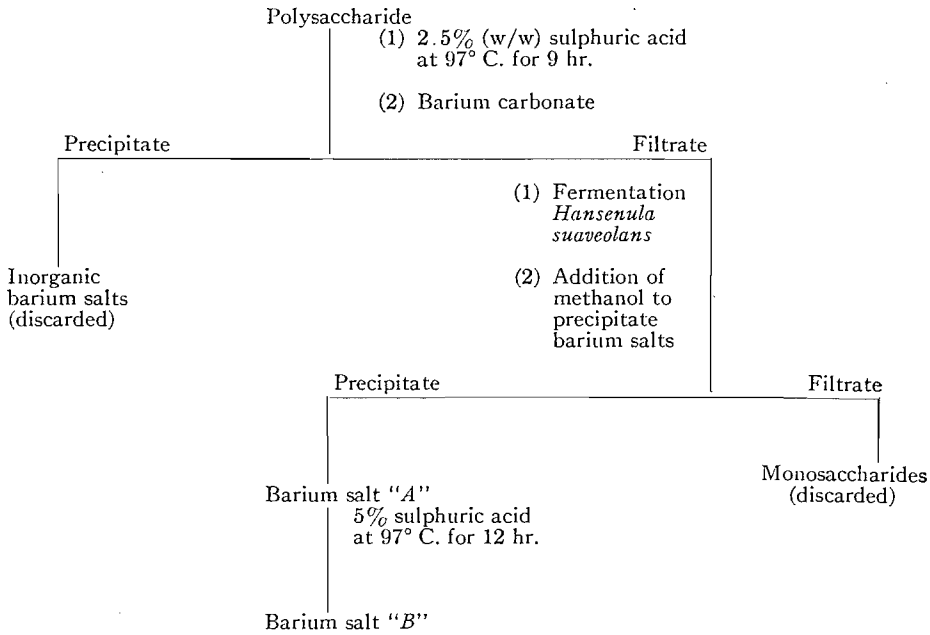


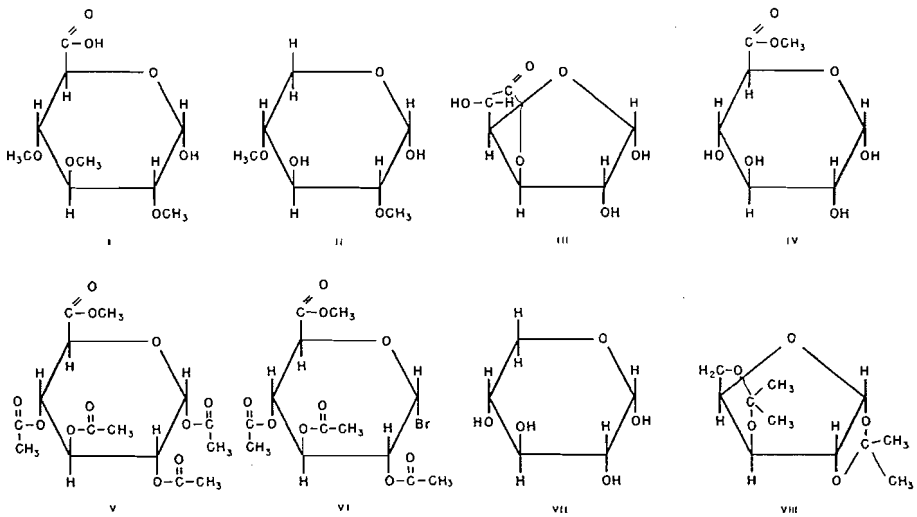

FIG. 1. Hydrolysis of polysaccharide and isolation of the barium uronates.

that barium salt "*A*" was not the salt of an aldobiuronic acid but was a larger molecule containing at least three D-xylose units together with a uronic acid residue. This compound was similar to the uronic acid complex isolated by McIlroy (18) from New Zealand flax.

Further hydrolysis of barium salt "*A*" and isolation of the barium uronates gave barium salt "*B*". Analysis showed that this was the salt of an aldobiuronic acid. In the original polysaccharide and in barium salt "*A*" the molar ratios of methoxyl to uronic acid anhydride contents approached unity. However, in barium salt "*B*" the ratio was 0.35 showing that only one-third of the uronic acid anhydride units contained a methyl group. A similar mixture of methylated and nonmethylated uronic acids was found in quince seed mucilage by Renfrew and Cretcher (20). The products of methylation and hydrolysis of barium salt "*B*" were 2,3,4-trimethyl-D-glucuronic acid (I) and 2,4-dimethyl-D-xylose (II). The identification of these two compounds showed that the aldobiuronic acid was composed of D-glucuronic acid linked glycosidically from its $C_1$ to the $C_3$ of a D-xylose unit. The configuration of the glycosidic bond was established by synthesizing the β-isomer and comparing its rotation with that of the naturally occurring aldobiuronic acid.

The aldobiuronic acid, 3-(xylopyranosyl)-β-D-glucuronoside was synthesized from D-glucurone and D-xylose. D-glucurone (III) was converted to its methyl ester (IV) which was fully acetylated to the 1,2,3,4-tetraacetyl derivative (V) and then brominated to yield α-bromo-2,3,4-triacetyl-D-glucuronic acid methyl ester (VI). D-xylose (VII) was converted to 1,2-3,5-diacetone-D-xylofuranose (VIII) from which 1,2-monoacetone-D-xylofuranose (IX) was obtained by

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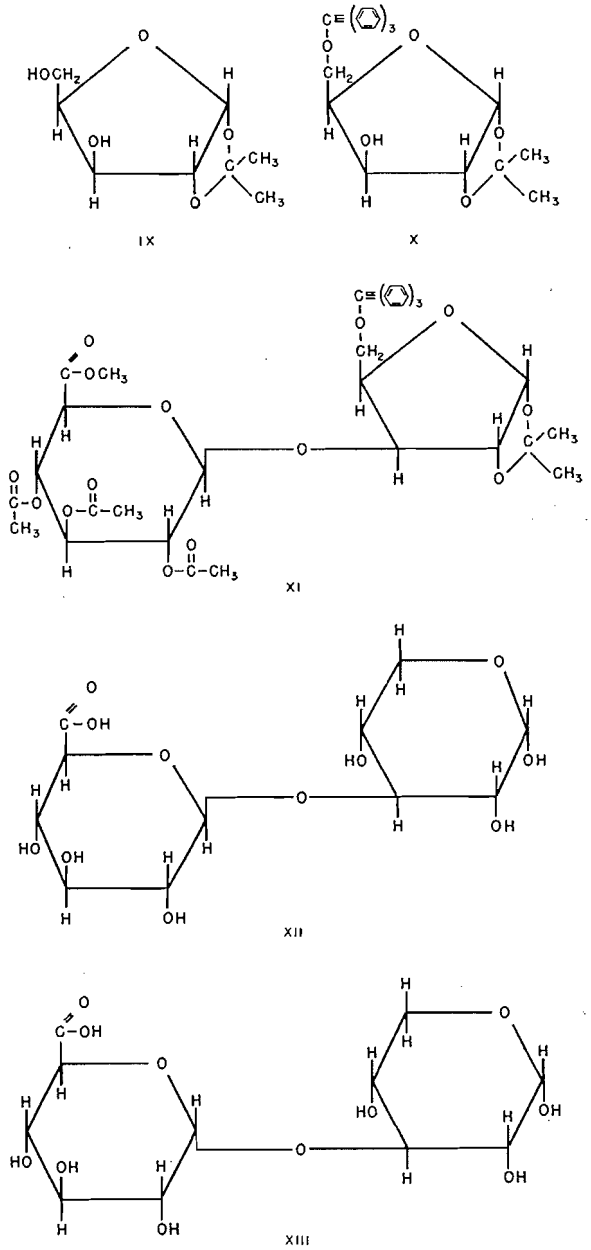
partial hydrolysis. The primary hydroxyl group at $C_5$ was then blocked by condensation with triphenylchloromethane yielding 1,2-monoacetone-5-trityl-D-xylofuranose (X) in which only the $C_3$ hydroxyl was free to react. Condensation with the $\alpha$-bromo-2,3,4-triacetyl-D-glucuronic acid methyl ester (VI) in the presence of silver oxide formed the glycosidic bond at $C_3$ of the D-xylose. The condensation product (XI) was freed of its trityl and acetone groups by acid hydrolysis. Alkali saponification removed the methyl ester and acetyl groups to yield the aldobiuronic acid 3-(xylopyranosyl)-$\beta$-D-glucuronoside (XII). The structure of this compound was confirmed by the same methylation techniques used on the natural aldobiuronic acid. The products of hydrolysis after complete methylation were the same; i.e. 2,3,4-trimethyl-D-glucuronic acid and 2,4-dimethyl-D-xylose.

The specific rotations of the natural and synthetic aldobiuronic acids were not the same. The unsubstituted products were not strictly comparable because approximately one-third of the natural aldobiuronic acid contained a methoxyl group. However, a comparison could be based on rotations of the fully methylated aldobiuronic acids.

| | Natural aldobiuronic acid | Synthetic aldobiuronic acid |
|---|---|---|
| Unsubstituted | $[\alpha]_D^{27}$ +18.5 ($c$ = 3.28 in water) | $[\alpha]_D^{27}$ −3.97 ($c$ = 1.76 in water) |
| Methylated | $[\alpha]_D^{28}$ +12.4 ($c$ = 1.67 in chloroform) | $[\alpha]_D^{28}$ −4.79 ($c$ = 2.25 in chloroform) |

Because in both aldobiuronic acids the D-glucuronic acid was joined glycosidically to $C_3$ of the D-xylose, the differences in specific rotations could be caused only by a difference in configuration of the glycosidic link. Because $\alpha$-bromo-2,3,4-triacetyl-D-glucuronic acid methyl ester (VI), when condensed with alcohols in the presence of silver oxide, yields only $\beta$-glucuronides (15), the glycosidic bond in the synthetic aldobiuronic acid must possess the $\beta$-con-

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figuration. Therefore, the natural aldobiuronic acid (having a different specific rotation) must contain an α-glycosidic bond. This conclusion is also in agreement with Hudson's rules of nomenclature (13) where the more dextrorotatory member of an α–β pair in the D-series is designated as α. The aldobiuronic acid isolated from the wheat straw polysaccharide is therefore 3-(xylopyranosyl)-α-D-glucuronoside (XIII).

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In aldobiuronic acids the carboxyl group, while greatly stabilizing the glycosidic bond, is itself easily removed by hot mineral acids. Consequently hydrolysis of these compounds by chemical means is always attended by considerable decomposition and poor yields. These difficulties prompted an investigation of the action of the enzyme β-glucuronidase on the two aldobiuronic acids prepared in this work. β-glucuronidase will liberate D-glucuronic acid from its β-glycosidic union with such compounds as phenolphthalein and sterols (16). However, to the author's knowledge hydrolysis of aldobiuronic acids by this enzyme has never been attempted. As reported in the experimental section no activity could be detected. Levvy (17) has reported that this enzyme is strongly inhibited by compounds having structural similarities to D-glucuronic acid. It is possible therefore that the enzyme was inhibited by the D-xylose portion of the aldobiuronic acid.

## EXPERIMENTAL

### *Isolation of Polysaccharide*

The polysaccharide was extracted by stirring wheat straw holocellulose (1) in 4% aqueous potassium hydroxide (solid: liquid ratio of 1:30) under an atmosphere of nitrogen for 24 hr. The extract was neutralized with acetic acid and evaporated, under diminished pressure, to $\frac{1}{4}$ its volume. Addition of four volumes of 95% ethanol precipitated the polysaccharide as white flocs. The precipitate was suspended in water and dialyzed against running distilled water for 48 hr. After reprecipitation with 95% ethanol and drying through ethanol and ether, the polysaccharide was obtained as a white powder in 22% yield based on the ash-free, moisture-free weight of holocellulose.

### *Analysis of Polysaccharide*

The polysaccharide was analyzed with the results recorded in Table I.

TABLE I
ANALYSIS OF POLYSACCHARIDE*

| | |
|---|---|
| Ash | 3.0 |
| Methoxyl | 1.6 |
| Uronic acid anhydride ($CO_2 \times 4$) | 7.9 |
| D-Xylose | 77.2 |
| L-Arabinose | 6.9 |
| D-Glucose | Trace |
| D-Galactose | Trace |
| Methoxyl/uronic acid anhydride | 1.1** |

**All values are in per cent by weight on an ash-free basis.*
***Molar ratio.*

Ash was determined by incineration at 550° C. and methoxyl by the procedure described by Clarke (7). Uronic acid anhydride was determined by the method of Tracy (23) and individual sugars, liberated by acid hydrolysis to constant reducing power, were determined qualitatively and quantitatively by a combination of chromatographic techniques previously described (4).

### *Hydrolysis of Polysaccharide*

The polysaccharide (50 gm.) was heated at 97° C. with 2.5% (w/w) sul-

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phuric acid (1700 ml.). Hydrolysis was followed by measuring the reducing power of the solution which reached a constant value after nine hours. The hydrolyzate was treated with solid barium carbonate in the usual manner to give a neutral, straw-colored solution (3100 ml.).

*Fermentation of* D-*Xylose*

The neutral hydrolyzate was passed through sterilized Seitz filters, divided into 10 equal portions in Fernbach flasks, and inoculated with *Hansenula suaveolans* (N.R.R.L. No. 838). Yeast extract (0.5%) was added and the flasks were shaken (96 strokes per minute) for 48 hr. at 30° C. Yeast cells were removed by centrifuging and the centrifugate was examined by paper chromatography, using a solvent system of ethyl acetate – pyridine – water (14). Only a trace of D-xylose was found compared with the large quantities present before fermentation. The fermented liquor was acidified (pH 4) with sulphuric acid and proteinaceous material was removed by precipitation with ethanol.

*Isolation of Barium Salt "A"*

Ethanol was removed from the protein-free fermentation liquor by azeotropic distillation with water under diminished pressure. The aqueous residue was made alkaline (pH 10) with saturated barium hydroxide and the mixture stirred vigorously for one and one-half hours at 80° C. in an atmosphere of nitrogen. After neutralizing the mixture with carbon dioxide, insoluble barium salts were removed by centrifuging and were washed three times with hot water. Combined washings and centrifugate were freeze-dried and the residue was taken up in water (70 ml.). When this solution was poured into methanol (500 ml.) the water-soluble barium salt "*A*" was precipitated. Drying through ethanol, ether, and finally over paraffin and anhydrous calcium chloride at 0.1 mm. pressure yielded barium salt "*A*" as a white powder (5.8 gm.). This material contained 3.0% methoxyl and 15.1% uronic acid anhydride, a molar ratio of methoxyl/uronic acid anhydride of 1.1. Theoretical values for these groups in the barium salt of a monomethyl aldobiuronic acid are 7.6% and 43.2%.

A portion of barium salt "*A*" (0.5 gm.) was dissolved in dimethyl sulphate (37.5 ml.) and 30% aqueous sodium hydroxide (90 ml.) was added, drop by drop, while the solution was being stirred in an atmosphere of nitrogen. The mixture was stirred at room temperature for 16 hr., then evaporated to 25 ml. under diminished pressure. Sodium hydroxide (90 ml. of 30%) was added and a second methylation was carried out by the dropwise addition of dimethyl sulphate (37.5 ml.). The reaction was worked up as before and a third methylation was carried out using the same quantities of reagents. The mixture was neutralized with 10% sulphuric acid, care being taken to avoid an excess, and sodium sulphate was removed by centrifuging. The centrifugate was extracted exhaustively with chloroform and, after drying over anhydrous sodium sulphate, the extract was evaporated to a syrup (0.266 gm.). This syrup was dissolved in methyl iodide (15 ml.) and heated under reflux. Silver oxide (12.2 gm.) was added in 1/10th portions every half hour, the mixture being continuously stirred. Silver salts were removed by filtration and washed

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with hot methanol. Washings and filtrate were combined and evaporated to a syrup which was methylated three more times with methyl iodide and silver oxide. The product (0.176 gm.) had a methoxyl content of 37.0%, unchanged by further methylations. Theoretical methoxyl content for a fully methylated aldobiuronic acid is 51.2%.

The methylated syrup was hydrolyzed by heating under reflux with 7% methanolic hydrogen chloride (10 ml.) for 16 hr. Water (10 ml.) was added and hydrolysis continued at 97° C. for 10 hr. The hydrolyzate was worked up with silver carbonate and hydrogen sulphide in the usual manner and the final filtrate evaporated to 5 ml. Examination of this solution by paper chromatography, using a solvent system of butanol: ethanol: water: ammonia in ratios of 40: 10: 50: 1 (5), indicated the presence of trimethyl uronic acid, mono-, di-, and tri-methyl-D-xylose units.

*Isolation of Barium Salt "B"*

Hydrolysis of the polysaccharide was repeated to obtain more barium salt "*A*" which was combined with the first lot to give a total of 10.2 gm. This salt was hydrolyzed by heating at 97° C. for 12 hr. with 5% (w/w) sulphuric acid (70 ml.). The hydrolyzate was worked up with barium carbonate as before and barium salt "*B*" was obtained from the neutral hydrolyzate by precipitation with ethanol. Barium content of barium salt "*B*" was 29.0% but fractionation from water by the gradual addition of 95% ethanol yielded a main fraction having a barium content of 18.1%; calculated for the salt of an aldobiuronic acid, barium = 17.9%. Barium was removed on a column of Nalcite HCR leaving the aldobiuronic acid as a reducing syrup (1.31 gm.) which could not be crystallized. Equivalent weight by titration with 0.107 *N* sodium hydroxide = 305, calculated equivalent weight = 325. $[\alpha]_D^{27} = +18.5$ ($c = 3.28$ in water). Methoxyl = 3.23%, calculated for a monomethyl aldobiuronic acid, methoxyl = 9.1%. Methoxyl/uronic acid anhydride = 0.35 (molar ratio).

*Methylation of Aldobiuronic Acid*

The syrupy aldobiuronic acid (1.3 gm.) was dissolved in water (10 ml.) and 1 *N* thallous hydroxide (20 ml.) was added to the solution. The mixture was evaporated to dryness at 40° C. in a stream of nitrogen and the residue dried for 18 hr. *in vacuo* at 40° C. over anhydrous calcium chloride. The dry solid was powdered (150 mesh) and boiled under reflux with methyl iodide for 58 hr. Thallous salts were removed by centrifuging and extracted three times with boiling absolute ethanol. The extracts and centrifugate were combined and evaporated to dryness under diminished pressure leaving a brown syrup (0.587 gm.) with methoxyl = 30.0%. This syrup was dissolved in methyl iodide (50 ml.) and methylated by the addition of silver oxide (4.0 gm.) in 1/10th portions every half hour. The mixture was stirred and boiled under reflux throughout the reaction. The methylated product was recovered by evaporation of the filtrate and washings after filtration of the silver salts. Three more methylations by the same method gave a product having a constant methoxyl content of 39.1%. This product was dissolved in

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30% sodium hydroxide (30 ml.) and the solution was stirred under nitrogen during the dropwise addition of dimethyl sulphate (15 ml.). The reaction was neutralized with 10% sulphuric acid and exhaustively extracted with chloroform. After the extract had been dried over anhydrous sodium sulphate and evaporated to dryness, a syrup was obtained (0.113 gm.) having methoxyl = 43.4%, unchanged by further methylations, and $[\alpha]_D^{28} = +12.4$ ($c = 2.25$ in chloroform). Calculated for a fully methylated, nonesterified aldobiuronic acid, methoxyl = 45.4%.

*Hydrolysis of Methylated Aldobiuronic Acid*

The methylated aldobiuronic acid was heated under reflux for 16 hr. with 8% methanolic hydrogen chloride (10 ml.). Water (10 ml.) was added and heating was continued for a further nine hours at 97° C. The hydrolyzate was worked up in the usual manner using silver carbonate and hydrogen sulphide. The product was a reducing syrup that was examined by paper chromatography using a solvent system of butanol: ethanol: water: ammonia (5). Only trimethyl uronic acid and a dimethyl-D-xylose could be detected.

*Separation of Trimethyl Uronic Acid and Dimethyl-D-xylose*

The reducing syrup, obtained from the hydrolysis just described, was placed on a column (1.6 × 20 cm.) of powdered cellulose (11). A mixture (40: 60 v/v) of *n*-butanol and 80–100° C. petroleum ether was percolated through the column and the eluate was collected in 5 gm. fractions. Fractions 3–5 inclusive gave positive Molisch tests and, when examined by paper chromatography as before, were found to contain only a dimethyl-D-xylose. The trimethyl uronic acid was washed from the column with water.

*Identification of 2,4-Dimethyl-D-xylose*

Fractions containing dimethyl-D-xylose were evaporated to dryness, leaving a syrup (55 mgm.) with methoxyl = 34.0, 33.7%; calculated = 34.5%. After the syrup had been seeded with a single crystal of 2,4-dimethyl-D-xylose and cooled at 5° C. for a week, a trace of crystal growth was noticed. Because the quantity of crystalline material was too small for isolation, the anilide derivative was made. The dimethyl-D-xylose was boiled under reflux for two hours in a solution of absolute ethanol (5 ml.) containing aniline (1.3 ml.). Ethanol was removed by evaporation under diminished pressure and after the residue had been cooled at 5° C. for a week the crystalline anilide was removed by trituration with cold ether. This compound was recrystallized from ethyl acetate to a constant m.p. of 168–170° C., identical with an authentic sample of the anilide of 2,4-dimethyl-D-xylose.

*Identification of 2,3,4-Trimethyl-D-glucuronic Acid*

The product from the cellulose column was boiled under reflux for eight hours with 5% methanolic hydrogen chloride (10 ml.) to form the methyl ester – methyl glycoside. This compound was a yellow syrup (40.2 mgm.) having a methoxyl content of 56.9, 57.2% and $[\alpha]_D^{27} = +83.2°$ ($c = 2.01$ in water). Calculated methoxyl = 58.7% and reported $[\alpha]_D^{18} = +85°$. The syrup was dissolved in saturated ammoniacal methanol (20 ml.) at 0° C. and

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allowed to stand at room temperature for 48 hr. Evaporation of the solvent under diminished pressure left a semicrystalline residue. Recrystallization from ethanol – petroleum ether yielded the crystalline amide of 2,3,4-trimethyl α-methyl glucuronoside, m.p. and mixed m.p. 182–183° C.

*Preparation of 1,2-3,5-Diacetone-D-xylofuranose*

Anhydrous D-xylose (25 gm.) was converted to its 1,2-3,5-diacetone derivative by shaking with acetone at room temperature in the presence of sulphuric acid (22). The syrupy product (24.2 gm.) was distilled at 85° C. and 0.3 mm. pressure. $[\alpha]_D^{27} = +13.8$ ($c = 4.1$ in water). Reported: $[\alpha]_D^{18} = +14.0$.

*Preparation of 1,2-Monoacetone-D-xylofuranose*

1,2-Monoacetone-D-xylofuranose was prepared from 1,2-3,5-diacetone-D-xylofuranose by hydrolysis with 0.2% aqueous hydrochloric acid (10). The product (20.0 gm.) was a syrup. $[\alpha]_D^{27} = -18.6$ ($c = 6.24$ in water). Reported: $[\alpha]_D^{20} = -19.0$ ($c = 3.0$ in water).

*Preparation of 1,2-Monoacetone-5-trityl-D-xylofuranose*

1,2-Monoacetone-D-xylofuranose was condensed with triphenylchloromethane under conditions described by Levene and Raymond (15). The product (32 gm.) was crystallized from petroleum ether (b.p. 60–90° C.) containing 3% ethyl acetate to a constant m.p. of 118–120° C.; $[\alpha]_D^{27} = +10.2$ ($c = 5.49$ in chloroform). Reported: m.p. = 118–119° C., $[\alpha]_D^{25} = +10.5$.

*Preparation of D-Glucuronic Acid Methyl Ester*

This compound was prepared by boiling D-glucurone in anhydrous methanol under reflux (9). The product (32.3 gm.) was not purified but was immediately acetylated by acetic anhydride and pyridine at room temperature.

*Preparation of α-1,2,3,4-Tetraacetyl-D-glucuronic Acid Methyl Ester*

The mixture of α- and β-tetraacetyl derivatives from the acetylation was isomerized by treatment with sulphuric acid in a mixture of acetic anhydride and acetic acid (3, p. 490). Recrystallization from ethanol (8) yielded α-1,2,3,4-tetraacetyl-D-glucuronic acid methyl ester (30.0 gm.); m.p. 110–111° C., $[\alpha]_D^{20} = +92.1$ ($c = 4.58$ in chloroform). Reported: m.p. 111–112° C., $[\alpha]_D^{24} = +98.0$.

*Preparation of α-Bromo-2,3,4-triacetyl-D-glucuronic Acid Methyl Ester*

α-1,2,3,4-Tetraacetyl-D-glucuronic acid methyl ester (15 gm.) was brominated by hydrogen bromide in acetic anhydride (3, p. 500). The α-bromo-2,3,4-triacetyl-D-glucuronic acid methyl ester (12.5 gm.) was recrystallized from ether to constant melting point and rotation; m.p. 103–105° C., $[\alpha]_D^{20} = +196.5$ ($c = 0.61$ in chloroform). Reported: m.p. 104–105° C., $[\alpha]_D^{24} = +198.0$ ($c = 0.05$ in chloroform).

*Condensation of α-Bromo-2,3,4-triacetyl-D-glucuronic Acid Methyl Ester with 1,2-Monoacetone-5-trityl-D-xylofuranose*

α-Bromo-2,3,4-triacetyl-D-glucuronic acid methyl ester (12.5 gm.) was condensed with 1,3-monoacetone-5-trityl-D-xylofuranose (13.6 gm.) in ether

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solution, in the presence of silver oxide (11.0 gm.) (12). The reaction product (7.2 gm.) was isolated as sticky crystals from ether. The decomposition point of 103–113° C. was not changed by recrystallization or fractional crystallization. $[\alpha]_D^{27} = +94.5$ ($c = 1.18$ in chloroform); saponification equivalent (21, p. 118) = 190, 188; trityl (3, p. 512) = 35.4, 35.3%. Calculated: saponification equivalent = 185, trityl = 35.2%.

*Removal of Trityl and Acetone Groups*

The trityl group was removed from the condensation product (7.0 gm.) in chloroform (150 ml.) by saturating the solution with dry hydrogen chloride and allowing the reaction to proceed to constant rotation at room temperature (3, p. 512).

To remove the acetone group, the chloroform solution was evaporated, under diminished pressure, to a syrup. Ethanol (50 ml.) and 3% sulphuric acid (50 ml.) were added and the solution was heated at 97° C. to constant rotation.

*Removal of Acetyl and Ester Groups*

The alcoholic hydrolyzate from the removal of the acetone group was freed of ethanol by azeotropic distillation with water. The acidic, aqueous solution was made alkaline (pH 10) with saturated, aqueous barium hydroxide and the mixture was stirred at 70° C. under nitrogen for three hours. Saponification was then allowed to continue at room temperature for 18 hr. After neutralization with carbon dioxide all water-insoluble material was removed by filtration and washed three times with hot water. Washings and filtrate were combined, evaporated under diminished pressure to 75 ml., and poured into 600 ml. of methanol. The precipitated barium salt was removed by centrifuging and was dried through ethanol, ether, and finally over phosphoric anhydride at 0.1 mm. This barium salt was fractionally precipitated from water by the gradual addition of ethanol to yield a main fraction with barium = 18.2%, calculated barium = 17.9%. Barium was removed by percolating an aqueous solution of the salt through a column of Nalcite HCR. The eluate from the column was evaporated to dryness yielding the free aldobiuronic acid as a syrup (1.0 gm.), $[\alpha]_D^{27} = -3.97$ ($c = 1.76$ in water).

*Methylation of Synthetic Aldobiuronic Acid*

The synthetic aldobiuronic acid was methylated in exactly the same way as already described for the natural product. The methylated product (0.113 gm.) had a constant methoxyl content of 43.6% and $[\alpha]_D^{28} = 4.79$ ($c = 1.67$ in chloroform). Calculated methoxyl = 45.4%. Hydrolysis of this methylated aldobiuronic acid and separation of the two components were done as described before. The dimethyl-D-xylose (45 mgm.) was crystallized and gave an X-ray diffraction pattern identical with that given by an authentic sample of 2,4-dimethyl-D-xylose. The anilide, prepared as before, had a m.p. 168–170° C.; reported m.p. 170° C. The trimethyl uronic acid (51 mgm.) was identified as 2,3,4-trimethyl-D-glucuronic acid by conversion to the crystalline amide of its $\alpha$-methyl glycoside, m.p. and mixed m.p. 182–183° C.

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*Attempted Enzymatic Hydrolyses of Natural and Synthetic Aldobiuronic Acids*

To each of the aldobiuronic acids (0.5 ml. of a 2.6% solution in water) was added 5 ml. of 0.01 *N* acetate buffer (pH 4.5). These solutions were inoculated with 0.5 ml. of a 1% solution of β-glucuronidase, a commercial preparation (Sigma) of bacterial origin. The solutions were then incubated at 38° C. and samples were removed for examination by paper chromatography at 2, 4, 6, 8, 10, 12, and 24 hr. Blanks containing buffer–enzyme and buffer–aldobiuronic acid were also run. No free D-xylose or D-glucuronic acid could be found on the chromatograms although D-xylose, dissolved in acetate buffer at comparable concentrations, was easily detected by this method.

ACKNOWLEDGMENTS

The author wishes to thank Dr. G. A. Adams who supplied wheat straw holocellulose and who carried out the experiments with β-glucuronidase. The author is also indebted to Dr. J. K. N. Jones, the University, Bristol, England, for a gift of nuclei of 2,4-dimethyl-D-xylose, to Dr. W. H. Barnes, National Research Laboratories, for the X-ray examination, and to Miss M. T. Clement, National Research Laboratories, who assisted with the D-xylose fermentations.

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# MICRODETERMINATION OF COBALT COLORIMETRICALLY AS THE 1-NITROSO-2-NAPHTHOL COMPLEX[1]

By W. E. Nichol

ABSTRACT

An advantage of determining cobalt with 1-nitroso-2-naphthol is that the reagent is relatively stable and forms a very stable cobalt complex. Also this cobalt complex has maximum absorption in the visible spectrum which allows determination visually or with ordinary colorimeters.

The procedure is based on decreasing the iron interference by the removal of part of the iron as phosphate and on a simple purification of the carbon tetrachloride solution of the 1-nitroso-2-naphthol cobalt complex which eliminates traces of palladium, iron, etc.

The method has the same order of accuracy as the *o*-nitrosocresol method but preparation of reagents and the analysis in general require less time.

## INTRODUCTION

Colorimetric determinations of traces of cobalt generally require the elimination of interfering elements. Dithizone extraction (3, 5) of cobalt is often used for separation from iron and from those elements which do not form dithizonates. Interfering elements extracted as dithizonates are then eliminated by other procedures and cobalt is determined by some colorimetric method.

In the method described below the cobalt complex with 1-nitroso-2-naphthol is formed in a pH range where there is a minimum of interference from other metals. It is extracted in carbon tetrachloride. After a rapid purification of this extract, the cobalt in it is determined directly by measuring the intensity of the color of the cobalt complex.

Experiments with pure chemicals showed that ferrous iron interfered through competition for the reagent. The precipitate of ferric phosphate which forms in digests of biological materials at a pH of about 4 also interfered. For general use of the method, elimination of iron interference was desirable.

Willard and Diehl (8) state that the precipitation of iron and some other metals as phosphate is complete at pH 5.0–5.4 in dilute acetic acid – acetate solution but that cobalt forms a double ammonium phosphate which is insufficiently soluble to make possible a separation unless it is present in very small amounts.

North and Wells (6) separated cobalt from iron satisfactorily by precipitating ferric phosphate at pH 3.5. A low pH and the presence of acetic acid tend to keep cobalt in solution (9). It was found that the bulk of the ferric phosphate resulting from constituents of plant ash could be precipitated at an even lower pH—about 2.5—by the method of Willard and his co-workers of gradually and uniformly raising the pH of the solution by the hydrolysis of urea. The precipitate was white and dense. Recoveries of cobalt when using this procedure were good.

In the purification of an extract of the same cobalt complex Paulais (7) removed excess 1-nitroso-2-naphthol by washing with alkali. The rest of his purifi-

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cation process was longer and dissimilar to that outlined below. Boyland (2), using 2-nitroso-1-naphthol, employed acid, alkali, and alcoholic alkali washes. Because of the lessened iron interference and the use of a more selective pH range for the precipitation of cobalt, the purification in this method is shorter than in his.

## METHOD

### *Reagents*

(1) *1-Nitroso-2-naphthol*—Weigh 0.5 gm. of 1-nitroso-2-naphthol recrystallized from hot water. Dissolve in and make to 1 liter with cold $N/10$ sodium hydroxide (1).

(2) *Sodium acetate solution*—Dissolve 100 gm. sodium acetate trihydrate in water and dilute to 200 ml.

(3) *Ethyl alcohol – sodium hydroxide wash*—One volume of 95% alcohol plus one volume $N/10$ sodium hydroxide (2).

(4) *Hydrochloric acid*—Redistill from Pyrex.

### *Procedure*

Weigh into a platinum dish a sample containing 0.2 to 6.0 $\gamma$ cobalt. Ignite in a muffle furnace,* remove silica as fluoride, and prepare a solution according to the Association of Official Agricultural Chemists method (4).

Place the solution, or a suitable aliquot thereof, in a tall 300 ml. beaker. Make to a volume of about 100 ml., add a few drops of 3% hydrogen peroxide. Heat to boiling and add 5 ml. of 50% sodium acetate solution. If any cloudiness develops add a few drops of hydrochloric acid to clear. To the boiling solution add 10 ml. of a freshly prepared 30% solution of urea and continue boiling. A noticeable cloud generally forms at a pH of about 2.5. Continue the hydrolysis until the pH has risen to 3.5 to 3.9 (pH test paper) and filter off the precipitate immediately. Use a Whatman No. 42 paper and collect the filtrate in a wide-stemmed 125 ml. separatory funnel. To the warm filtrate add 5 ml. of 1-nitroso-2-naphthol reagent. Allow to stand for one hour or more. Extract with a constant quantity of carbon tetrachloride by one of the two procedures described below.

Solutions of plant material when prepared as directed generally form no visible precipitate when treated with 1-nitroso-2-naphthol at a pH of 3.5 to 3.9. In this case one extraction with 30 ml. of carbon tetrachloride is satisfactory. Purify the carbon tetrachloride extract by shaking with the quantities of acid, alkali, and water listed below. With intense colors, read directly. For less intense color, evaporate on the water bath and make to a suitable volume.

A slight precipitate is sometimes present. This may contain complexes of copper, iron, or palladium. Extract with one 10 ml. and four 5 ml. portions of carbon tetrachloride. Flush the film which gathers at the interface after each shaking into the hydrochloric acid funnel, using a small portion of the aqueous phase each time for this purpose. The hydrochloric acid is diluted in this way to a concentration of about 2 + 1. Wash each of the five extracts by shaking successively in each of six separatory funnels containing the following:

**Treat liver samples (30 gm. wet weight) with 1 ml. concentrated sulphuric acid before ignition.*

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No. 1 10 ml. concentrated hydrochloric acid,
No. 2 20 ml. water,
No. 3 10 ml. of ethanol – sodium hydroxide reagent,
No. 4 10 ml. of ethanol – sodium hydroxide reagent,
No. 5 20 ml. water,
No. 6 20 ml. water.

Shaking should be vigorous but need not exceed one-half minute by which time the carbon tetrachloride layer clears. After the first two extracts have passed through funnel No. 4, add the wash from this funnel to that in funnel No. 3 and replace it with fresh alcoholic sodium hydroxide. Avoid transfer of the aqueous phase from any one of these funnels to another. Evaporate the combined carbon tetrachloride extracts in a beaker on a water bath to about 2 ml., transfer the remaining liquid to a small volumetric flask, and rinse several times into the flask with carbon tetrachloride.

For examination on the Beckman DU spectrophotometer, make to a volume of 5 ml. and examine at a wave length of 400 mμ. For examination on the Klett-Summerson or Evelyn colorimeters, make to a volume of 10 ml. The weight of sample used for these last two colorimeters should be at least twice that required for the spectrophotometer.

*Blanks*

Run a blank determination covering the entire procedure including the ashing. Run a second blank including that part of the procedure following the elimination of silica. These blanks with reagent-grade chemicals have been found to be the same. If there is a difference, calculate this difference as cobalt and subtract it from the cobalt found.

*Preparation of Standard Curves*

To 100 ml. warm water add the quantities of reagents specified in that part of the procedure following the elimination of silica and known amounts of cobalt, based on a standard cobalt solution containing 0.5 γ of cobalt per ml. as prepared in (4). Carry through as in the procedure.

## APPLICATION OF THE METHOD

The method was designed for the analysis of pastures and grains and the livers of the animals feeding on these materials; but it has also been adapted for the analysis of soils. Plant materials so far examined contained less than 0.05% iron and in general ran below 0.01%. Many analyses indicate that Canadian crops contain in general 0.1 to 0.4% phosphorus. Some special crops such as spinach are higher in both iron and phosphorus. In sheep livers 0.04% of iron and 1.3% of phosphorus (DM) may be expected. Cultivated Canadian soils contain in general 0.05 to 0.13% phosphorus and 0.7 to 6.0% iron. Available information indicates that in plants there is about 1 part of cobalt to 500 parts of iron, in livers 1 part to 1000 parts or more of iron, and in soils 1 part to 5000 parts of iron. More interference might be expected from iron in livers and soils than in plants.

Soils are different in that naturally-occurring phosphorus is not nearly sufficient to precipitate the iron. Rather than adding phosphate it has been found desirable to avoid large precipitates by extracting part of the iron from the hydrochloric

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acid solution of the ash by an ether extraction before application of the procedure outlined above. Ether extraction is desirable for all materials high in iron.

The one-extraction procedure gives the same standard curve and the same analysis of plant materials as the longer five-extraction procedure but is more dependent upon proper manipulation. The recoveries of added cobalt shown in Table I were obtained by the longer method. The quantities of cobalt shown in

TABLE I

| Cobalt added, γ | Total cobalt, γ | Cobalt found, γ | Recovery of added cobalt, % |
|---|---|---|---|
| *Extracted linseed meal*—Size of sample 2.5 gm. Analysis 0.47 p.p.m. | | | |
| 0 | 1.175 | | |
| 0.25 | 1.425 | 1.425 | 100 |
| 0.50 | 1.675 | 1.70 | 105 |
| 0.75 | 1.925 | 1.91 | 98 |
| 1.0 | 2.175 | 2.175 | 100 |
| 1.5 | 2.675 | 2.60 | 95 |
| *Oats*—Size of sample 8.0 gm. Analysis 0.035 p.p.m. | | | |
| 0 | 0.28 | | |
| 0.25 | 0.53 | 0.53 | 100 |
| 0.50 | 0.78 | 0.77 | 98 |
| 1.0 | 1.28 | 1.26 | 98 |
| *Barley*—Size of samples 8.0 and 7.0 gm. Analysis 0.096 p.p.m. | | | |
| 0 | 0.77 | | |
| 0.25 | 1.02 | 1.00 | 92 |
| 0.50 | 1.27 | 1.26 | 98 |
| 0 | 0.67 | | |
| 0.50 | 1.17 | 1.10 | 86 |
| 0.75 | 1.42 | 1.40 | 97 |
| 1.00 | 1.67 | 1.57 | 90 |

the first column were added to samples containing the amount of cobalt shown at the top of column 2. The other figures shown in column 2 are the sum of added and naturally-occurring cobalt. The total cobalt recovered is shown in column 3. The per cent recoveries, column 4, are considered satisfactory for this kind of analysis.

Tables II and III show comparative analyses of livers and soils carried out by the 1-nitroso-2-naphthol method and by the *o*-nitrosocresol method which is generally considered the most accurate method available.

TABLE II
LIVERS

| Sample number | 1-Nitroso-2-naphthol method cobalt, p.p.m.* | *o*-Nitrosocresol method cobalt, p.p.m.* |
|---|---|---|
| 1 | 0.114 | 0.112 |
| 2 | 0.046 | 0.046 |
| 3 | 0.106 | 0.099 |
| 4 | 0.087 | 0.086 |
| 5 | 0.041 | 0.055 |

**Fresh weight basis.*

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TABLE III
SOILS

| Sample number | 1-Nitroso-2-naphthol method cobalt, p.p.m.* | *o*-Nitrosocresol method cobalt, p.p.m.* |
|---|---|---|
| 1 | 8.8 | 9.2 |
| 2 | 16.0 | 18.0 |
| 3 | 2.8 | 2.8 |

**Air-dry basis.*

## DISCUSSION

The procedure outlined eliminates effective competition of iron for the reagent. Variations in materials and ashing procedures may lead to the persistence of ferrous iron in the hydrochloric acid solution of the ash. A treatment with peroxide, more thorough than that specified, is then necessary but a survival of peroxide should be avoided because of its action on the cobalt-1-nitroso-2-naphthol complex. Ferrous iron forms a green complex with 1-nitroso-2-naphthol. The presence of a green color or precipitate may indicate excessive competition and incomplete reaction of the cobalt.

Removal of iron by this method compares favorably in time with its removal by dithizone procedures.

The procedure for purifying the extract of the cobalt complex also compares favorably in time and effectiveness with purification by other methods to which reference has been made.

In comparison with the *o*-nitrosocresol method (4), this method has approximately the same degree of accuracy and is more rapid, particularly where occasional samples are to be tested. All reagents can be prepared in about one hour. The 1-nitroso-2-naphthol reagent is relatively stable. The cobalt complex has maximum absorption in the visible spectrum rather than in the near ultraviolet. It is thus adapted for visual estimation and for use with ordinary colorimeters. A further advantage in the analysis of some materials by this method is the elimination of the interference of traces of palladium.

The cobalt complex with 1-nitroso-2-naphthol is stable and there is no need for immediate examination. This gives the 1-nitroso-2-naphthol an advantage over the nitroso-R-salt–bromine method.

## ACKNOWLEDGMENTS

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# THE DIFFUSION OF POLYISOBUTYLENE IN DIFFERENT SOLVENTS[1]

By C. Luner[2] and C. A. Winkler

## ABSTRACT

The diffusion coefficient of polyisobutylene in *n*-heptane has been found to decrease at first, then to increase with increasing molecular weight.

## INTRODUCTION

In a previous paper (1) it was shown that in methyl ethyl ketone the diffusion coefficient of polystyrene first decreased, then increased slightly with a further increase in molecular weight.

To determine whether a similar behavior might be observed with some other linear polymer the diffusion coefficient – molecular weight relation of polyisobutylene has been investigated in some different solvents.

## APPARATUS AND MATERIALS

The diffusion cells and experimental technique were the same as those used by Adelstein and Winkler (1).

The following unfractionated polymers were used in the study.

| Polymer designation* | Molecular weight** |
|---|---|
| H–300 | 1000 |
| 4227 | 3000 |
| 4186 | 6000 |
| 4224 | 6500 |
| 4184 | 13,500 |
| 4225 | 20,400 |
| 4092 | 24,000 |
| 4116 | 32,700 |
| 4228 | 41,750 |
| 4223 | 110,000 |
| 4222 | 185,000 |
| 4220 | 447,000 |

**Sample H–300 was obtained through the courtesy of Indopol Ltd., while the remaining polymers were kindly supplied by Polymer Corporation, Sarnia.*

***The molecular weight of H–300 was determined by the Rast method (4). Molecular weights of the other polymers were determined by viscosity measurements, using the viscosity – molecular weight equation, $(\eta) = kM^a$, where k and a have the values $3.6 \times 10^5$ and 0.64 respectively.*

The solvents were obtained from Brickman and Co., Montreal, and a middle fraction taken for use.

To prepare solutions of the high molecular weight polyisobutylene, the polymer was cut into small strips and allowed to soften and swell in the solvents. When the polymer appeared to be soft, the mixture was stirred.

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[2] *Holder of Quebec Provincial Scholarship, 1948–52.*

The resulting solutions were filtered since they were turbid and contained some insoluble material. Polymer concentrations were determined by evaporation of an aliquot of the solution to constant weight.

Using samples of H-300, the variation in values of the diffusion coefficient determined in different cells was within the limits of reproducibility of the results (±8%).

## RESULTS AND DISCUSSION

The effect of molecular weight upon the diffusion coefficient was determined in benzene, carbon tetrachloride, and *n*-heptane. The results are plotted in Fig. 1. While the general type of inverse relation predicted by many workers

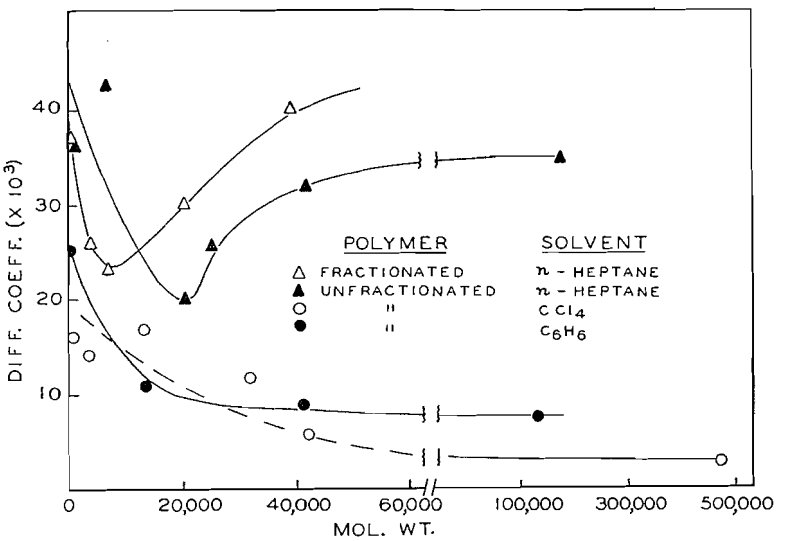



FIG. 1.

was valid for benzene and carbon tetrachloride, the diffusion coefficient – molecular weight relation when *n*-heptane was the solvent was similar to that observed by Adelstein and Winkler for the diffusion of polystyrene in methyl ethyl ketone (1).

To determine whether the distribution of molecular weights in the unfractionated polymers was responsible for the increase in diffusion coefficient with molecular weight, fractions of different molecular weights were obtained from the whole polymer by precipitation with methanol from dilute solutions in benzene. The diffusion coefficients in *n*-heptane are shown in Fig. 1.

Comparison of the behavior of polystyrene and polyisobutylene in different solvents indicates that, whereas viscosity and diffusion data are in agreement as to the relative goodness of solvent for polystyrene, there is a discrepancy between solvent power determined from viscosity and diffusion data for polyisobutylene. According to the present investigation, *n*-heptane is a poorer solvent for polyisobutylene than benzene, whereas viscosity data (2, 3) indicate the reverse to be true. Since the behavior of polyisobutylene in *n*-heptane

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would indicate *n*-heptane to be a poor solvent (higher diffusion rate), the increase in diffusion coefficient with increase in molecular weight might be explained in a manner similar to that proposed for the analogous behavior of polystyrene in methyl ethyl ketone (1).

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# SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

## IV. METHYL-$d_3$ BROMIDE[1]

By B. Nolin and L. C. Leitch

ABSTRACT

Silver acetate-$d_3$ and bromine react readily in the dry state in a sealed tube to give methyl-$d_3$ bromide in high yield. This method is more convenient than the reduction of carbon dioxide to deuterated methyl alcohol with lithium aluminum deuteride, followed by the conversion of the alcohol into the halide, or other methods hitherto reported.

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## INTRODUCTION

As potential sources of deuteromethyl groups, methyl-$d_3$ halides are very valuable compounds in deuterium chemistry. Deuterated methyl halide of high isotopic purity was needed in these laboratories for research on reaction mechanisms, free radicals, and infrared absorption spectra of organic molecules.

Two methods of preparation are available in the chemical literature but both are unsatisfactory in some respects. In 1942, Noether (9) reported the synthesis of two deuterated methyl halides from nitromethane according to the reaction scheme I (X = Cl, or Br).

$$CH_3NO_2 \rightleftharpoons CD_3NO_2 \rightarrow CD_3NH_2.HCl \rightarrow CD_3NHCOC_6H_5 \rightarrow CD_3X \qquad \text{I}$$

This method is inconvenient owing to its length and the low over-all yield.

Beersmans and Jungers later prepared the methyl-$d_3$ halides (2) via methyl-$d_3$ alcohol (1) according to the reaction scheme II (X = Cl, Br, or I).

$$CO + 2D_2 \rightarrow CD_3OD \rightarrow CD_3X \qquad \text{II}$$

The reduction of carbon monoxide was carried out in the presence of a copper–zinc–chromium (49:43:8) catalyst in a specially designed apparatus at 280°C. under a pressure of 3.5 atm. of deuterium gas. The yield of alcohol was very good and the methyl group contained 98 atom % deuterium as determined by infrared absorption. This method, however, requires elaborate apparatus and gives a low daily yield of alcohol (1.5–2.0 ml.). The synthesis of a large amount of alcohol requires many days of continuous operation, while the preparation of a small quantity can hardly justify the use of this process. Moreover, the primary reaction product is the alcohol, whereas in many cases the material required is the halide; the conversion usually gives a yield of 80%.

The reduction of carbon dioxide with lithium aluminum hydride in diethyl carbitol solution was reported to give methanol in 80% yield based on carbon dioxide (11); the yield based on the hydride is however only 40%. Isotopically labeled carbon dioxide was later reduced in a similar way, the yields of methanol and methyl iodide being respectively about 90% and 80% (3, 4); on the basis of the hydride used, they are reduced by half.

In the present work, lithium deuteride was prepared in nearly quantitative

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yield from lithium metal and deuterium gas (99.7 atom % deuterium) in a specially designed reactor at 750°C. The finely ground material was reacted with a diethyl ether solution of aluminum chloride, essentially as described for the preparation of lithium aluminum hydride (5), to give lithium aluminum deuteride in 70% yield, based on lithium deuteride. The compound contained 94.4 atom % deuterium as determined by mass analyses of the deuterium gas evolved on pyrolysis (5).

Carbon dioxide was reduced with lithium aluminum deuteride in diethyl carbitol solution essentially as described for the reduction of isotopically labeled carbon dioxide with lithium aluminum hydride (3), except for the use of a smaller excess (1.33 equivalents) of the reducing agent. The crude deuterated methanol was converted into the iodide by means of a Zeisel reaction in an over-all yield of 40%. This method is tedious and somewhat hazardous. The yield is low and the contamination of the final product with about 5% of normal ethyl iodide is inherent to the use of diethyl carbitol as solvent. This contamination can be reduced to a certain extent by the use of tetrahydrofurfuryloxytetrahydropyran (3, 4), but this solvent is not available commercially and does not improve the yield significantly.

The isotopic purity of the deuterated methyl iodide corresponded to 94.3 atom % deuterium, which is in agreement with the figure found for lithium aluminum deuteride. However, this is lower than that of the deuterium gas used in the preparation of lithium deuteride. No sure explanation is offered for this dilution effect, as precautions were taken during the synthetic process to exclude any obvious source of contamination. The lithium metal might have occluded some hydrogen which eventually diluted the deuterium gas.

In a previous paper from these laboratories (10), one of us mentioned the preparation of deuterated methyl bromide in 25% yield from deuterated silver acetate and bromine in carbon tetrachloride solution; the isotopic content amounted to 90 atom % deuterium. The reaction was not further investigated at the time, but it was felt that a procedure might be developed to give satisfactory yields of pure deuterated methyl bromide of high isotopic purity. This paper describes experiments made in this direction.

Silver salts of monobasic carboxylic acids react with two equivalents of bromine as represented in the simplified scheme III (8).

$$\begin{aligned} \mathrm{RCOOAg} + \mathrm{Br_2} &\rightarrow [\mathrm{RCOOBr}] + \mathrm{AgBr} \\ [\mathrm{RCOOBr}] &\rightarrow \mathrm{RBr} + \mathrm{CO_2} \end{aligned} \qquad \text{III}$$

The reaction is usually carried out in carbon tetrachloride solution. According to Hunsdiecker *et al.* (7) however, methyl bromide was prepared in 80% yield in the absence of solvents in a *suitable vessel*, the nature of which was not specified in the patent.

In the present procedure, silver acetate-$d_3$ is treated in the dry state with a slight excess of bromine in the apparatus illustrated in Fig. 1. This tube permits both reagents to be present under reduced pressure in the same reaction vessel so that their contact may be controlled as desired. Features of the decomposition of the intermediate complex [RCOOBr] are the low temperature at which it

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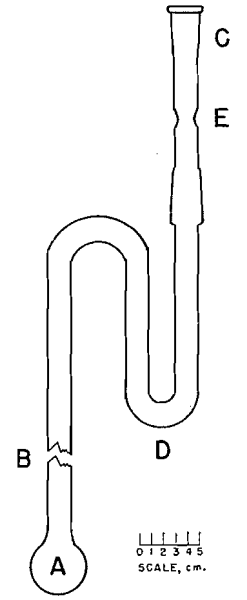



FIG. 1. Apparatus for the reaction of bromine with silver acetate-$d_3$.

occurs, and the fact that as the chain length of the acid is shortened, the decomposition occurs with increasing violence (12, 13). Under the conditions described in the experimental part, the reaction of bromine with silver acetate-$d_3$ is smooth and complete in about half an hour. The crude material is readily purified and 75–82% yields of methyl-$d_3$ bromide are consistently obtained. Its isotopic purity was 99.3 atom % deuterium, which is assumed to be also the deuterium content of its precursors, namely deuterated silver acetate, acetic acid, and malonic acid.

The latter acid was easily prepared on the one-mole scale by repeated exchange of normal malonic acid with deuterium oxide. By decarboxylation, deuterated acetic acid was obtained in nearly quantitative yield. Deuterated malonic acid could also be prepared by direct synthesis from carbon suboxide and heavy water (6, 14).

## EXPERIMENTAL

### *Silver Acetate-$d_3$*

A given weight of deuterated acetic acid is diluted with cold water and the solution neutralized carefully with cold dilute ammonia. On adding silver nitrate deuterated silver acetate is precipitated; it is isolated by filtration, washed with cold water, and dried. The material present in the filtrate is easily recovered by concentration. The yield of the silver salt is practically quantitative. If the silver salt, for some reason, is not free from acetic acid, it is preferably purified by further washing with or crystallization from water, as traces of the acid have been found to reduce the yield of the subsequent preparation.

### *Methyl-$d_3$ Bromide*

The preparation is carried out in the apparatus illustrated in Fig. 1.

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Silver acetate-$d_3$ (0.05 mole, 8.5 gm.) is placed in the 25 ml. flask $A$, which is sealed to an inverted S-shaped tube at $B$, and dried by heating in boiling water under vacuum. Bromine (0.06 mole, 3.1 ml.), dried over phosphorus pentoxide, is distilled from a vacuum line through $C$ and frozen at $D$ with liquid nitrogen (a dry ice – acetone mixture could likely be used). The reactor is then sealed off at $E$. The bromine is melted by plunging $D$ into an acetone bath at room temperature and, by cooling the reaction flask till the bulk of bromine begins to boil, some is frozen above $A$. This portion of bromine is melted and reacted slowly with the silver salt while the tube is being swirled. The process is repeated about ten times and by then the reaction mixture has already yielded some methyl bromide. The reaction is thereafter continued as follows: $A$ is cooled up to $B$ and some bromine* is allowed to run down to the reaction flask and frozen above $A$; the more volatile methyl bromide is frozen at $D$, which facilitates the reaction of the bromine frozen above $A$. The process is repeated till all the liquid at $D$ is used up. The reaction time, as estimated from 10 runs, varies from 30 to 45 min.** The reaction mixture was generally allowed to stand overnight in the dark.

The reaction tube is cooled at $D$, opened, and attached quickly to the evacuated manifold. The system is completely evacuated and all the volatile material is allowed to distill out. The yellow residue in $A$ is heated with a free flame to liberate any remaining methyl bromide from the intermediate complex.

The crude material is passed through a U-tube filled with Ascarite, where carbon dioxide and most of the excess bromine are removed. A similar treatment with Ascarite and Drierite removes the last traces of bromine and any water, the presence of which is however unlikely under the conditions described above. In some runs, a yellow coloration persisted, which disappeared on further treatment with Ascarite. Vapor pressure measurements and mass analyses indicated that the deuterated methyl bromide thus obtained is slightly contaminated with deuterated ethane, acetic acid, and possibly methyl acetate. These by-products are easily removed in the following manner. The material is cooled at − 78°C. and its vapor is allowed to expand four times into a manifold, the fractions being discarded. Four distillations at − 78°C. are then carried out from bulb to bulb to remove the less volatile impurities. Yield, 4.0 gm., 81.7%.

The above treatment yields a product of high chemical purity, as judged by its mass spectrum and its vapor pressure at 0°C., 681.5 mm. This figure is in agreement with that reported by Beersmans and Jungers (2) for pure methyl bromide of comparable deuterium content. Mass analyses have indicated an isotopic purity of 99.3 atom % deuterium (98.0% $CD_3Br$ and 2.0% $CD_2HBr$). This is the equivalent of 2.98 deuterium atoms per methyl group, while the theoretical requirement is 3.

ACKNOWLEDGMENT

The authors wish to thank Dr. F. P. Lossing, Miss F. Gauthier, and Miss J. Fuller for the mass analyses.

*Very small portions of bromine are introduced at first, but larger amounts can be added when the reaction subsides.*

**One must not be anxious to bring about the reaction in a shorter time, even when it seems to proceed smoothly. It is preferable to warm up the reaction flask to room temperature before further addition of bromine; this avoids the accumulation of much undecomposed complex in the reaction mixture.*

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# PHOTOLYSIS OF ACETONE – HYDROGEN CHLORIDE MIXTURES[1]

By R. J. Cvetanović[2] and E. W. R. Steacie

ABSTRACT

The photolysis of acetone – hydrogen chloride mixtures has been investigated at 150° C. and at room temperature. A strong suppression of ethane formation with a corresponding large increase in the formation of methane results from additions of relatively very small amounts of hydrogen chloride to acetone. The importance of the reactions

(1) $CH_3 + HCl \rightarrow CH_4 + Cl$

and

(7) $Cl + CH_3COCH_3 \rightarrow HCl + CH_2COCH_3$

has been demonstrated. The collision yield of reaction (1) at 28° C. is $2 \times 10^{-4}$, and, therefore, the upper limit for $E_1$ is 5.1 kcal. per mole. The effects observed at 150° and 28° indicate that, on the assumption of a zero activation energy and a steric factor of unity for combination of methyl radicals, $E_1 = 2.1 \pm 1$ kcal. per mole, and $P_1$ is approximately $7 \times 10^{-3}$.

## INTRODUCTION

Methyl radicals produced in the photolysis of acetone have been widely used in the investigation of hydrogen abstraction reactions. Recently these investigations have been extended to halide substituted hydrocarbons. Raal and Steacie (12) have determined the activation energies and the steric factors of the reactions of methyl radicals with a number of halogenated methanes in the temperature range 110 to 220° C. The following mechanism of methane and ethane formation is proposed:

(1) $CH_3 + RH \rightarrow CH_4 + R$,
(2) $CH_3 + CH_3 \rightarrow C_2H_6$,
(3) $CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3$.

For experimental conditions where the concentrations of acetone and RH can be regarded constant, and assuming a time independent concentration of methyl radicals, it can be shown that

$$[1] \qquad \frac{k_1}{k_2^{1/2}} = \frac{\dfrac{R_{CH_4}}{(R_{C_2H_6})^{1/2}} - \dfrac{k_3}{k_2^{1/2}}[CH_3COCH_3]}{[RH]}.$$

Experimental measurements of the rates of formation of methane ($R_{CH_4}$) and ethane ($R_{C_2H_6}$) in the absence and presence of RH are used to evaluate $k_3/k_2^{\frac{1}{2}}$ and $k_1/k_2^{\frac{1}{2}}$ respectively. Arrhenius plots of such determinations over a temperature range give the values of $(E_3 - \frac{1}{2}E_2)$ and $(E_1 - \frac{1}{2}E_2)$. Since $E_2$ is approximately zero, these values are to a good approximation identical with the activation energies of the respective elementary reactions (1) and (3).

For the series of reactions of methyl radicals with $CH_3Cl$, $CH_2Cl_2$, and $CHCl_3$, Raal and Steacie thus find a substantial increase in the ease of removal of hydrogen as the number of chlorine atoms in the molecule increases. This

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[2] *National Research Council of Canada Postdoctorate Fellow, 1951–52.*

result is not unexpected in view of the other observations on the reactivity of these compounds. The authors have, however, also observed a very pronounced effect of carbon tetrachloride on the rates of formation of methane and ethane in the photolysis of acetone. The effect is analogous to that produced by chloroform. Relatively small amounts of carbon tetrachloride added to acetone suppress very strongly formation of ethane and the formation of methane is correspondingly increased. While in the case of partially halogenated methanes the increased methane formation is easily explained by hydrogen abstraction, the corresponding effect due to additions of carbon tetrachloride is entirely unexpected. The apparent anomaly introduces, therefore, an element of uncertainty into the above results. The authors' suggestion that the observed anomaly may be due to small amounts of hydrogen chloride, present as an impurity or formed during the photolysis, makes it necessary to obtain some quantitative information on the effect produced by additions of varying amounts of hydrogen chloride to acetone.

In a recent paper A. S. Kenyon (9) reports formation of hydrogen chloride as a product in the photolysis of acetone in the presence of sec-butyl chloride. At the same time ethane formation is completely suppressed even at 25°. The author ascribes the latter fact to a rapid reaction of methyl radicals with sec-butyl chloride. The possibility of an effect of the presence of hydrogen chloride is not considered.

Williams and Ogg (17) have investigated the rate of reaction of methyl radicals, produced by photolysis of methyl iodide, with hydrogen chloride. They find the activation energy of this reaction only about 1.6 kcal. per mole greater than that of the rapidly occurring reaction with hydrogen iodide, although they suggest that in the former case a reaction of "hot" methyl radicals is of importance.

Both in the older and the recent literature a somewhat controversial attitude with respect to the importance of the reaction between methyl radicals and hydrogen chloride is found. At the same time it can be conceived that in the photolysis of acetone in the presence of chlorine containing compounds hydrogen chloride might be formed in the process or could be introduced in varying amounts as an impurity. It was, therefore, considered of interest to investigate separately its effect. A largely qualitative preliminary experiment, conducted in collaboration with Dr. F. A. Raal, showed that the addition of a relatively small amount of hydrogen chloride to acetone photolyzed at 150° suppressed ethane formation almost completely and the amount of methane produced was much increased. A quantitative investigation of this effect necessitated some arrangement for the introduction of known very small quantities of hydrogen chloride into the reaction system. Such an investigation, conducted at 150° and at room temperature, is reported in this paper.

## EXPERIMENTAL

### *Apparatus*

The apparatus was of the same general design as used previously by Raal and Steacie (12). Alterations were made: (1) to allow introduction of known

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small quantities of hydrogen chloride and to ensure thorough mixing with acetone; (2) to eliminate mercury vapor as much as possible from the reaction cell. The former was achieved by a system of calibrated volumes and by ultimately freezing over the two reactants into a 300 ml. calibrated bulb and, on expansion, allowing sufficient time for interdiffusion; the mixed reagents were subsequently expanded into the reaction cell. The latter was accomplished by measuring the pressures of vapors of the reactants contained in large accessory volumes, which were filled simultaneously with the reaction system. The accessory volumes were subsequently isolated from the reaction system and opened to mercury manometers. A correction for the slight increase in volume (amounting to 1 to 2%) was applied to the measured pressure. Repeated calibration and testing of this arrangement ensured satisfactory accuracy.

The light from a Hanovia S-500 medium pressure arc was roughly collimated by a highly polished aluminum cylinder. For most determinations the light beam was passed through a Corning 9–54 filter, and in a few determinations a Corning 0–53 filter was used instead. In the former case the light beam contained the wave lengths greater than about 2200 Å, in the latter greater than about 2800 Å. The light beam filled the cylindrical silica reaction cell 120 ml. in volume.

The reaction cell was contained in an aluminum block furnace. The heating current was supplied from a Sorensen voltage regulator and the temperature was maintained to within about 1°.

The products were analyzed for methane, ethane, and carbon monoxide. The analysis system was of the conventional type. Carbon monoxide was determined by combustion over copper oxide at 215°. In a number of cases simultaneous determinations were made by mass spectrometer analysis as a check. Ethane was separated at −165°. At that temperature no hydrogen chloride was recovered from acetone, as was evident from determinations where large amounts of hydrogen chloride were added to acetone and the ethane fraction was negligibly small.

*Materials*

Acetone was a Mallinckrodt Analytical Reagent product, refluxed over potassium permanganate, dried over Drierite, and distilled. It was degassed in the usual manner by bulb to bulb distillation *in vacuo*. Hydrogen chloride was a Matheson Company product. It was degassed and further purified by several bulb to bulb distillations *in vacuo* (dry ice – acetone to liquid air). The deuterated acetone (87% $d_6$) was made by Dr. L. C. Leitch in this laboratory.

## RESULTS

The photolysis of acetone in the presence of hydrogen chloride was investigated at 150° and at room temperature. Most determinations were carried out with a light beam of wave lengths greater than about 2200 Å and only a few determinations were made with wave lengths greater than about 2800 Å. In all cases addition of hydrogen chloride led to an increase in the amount of

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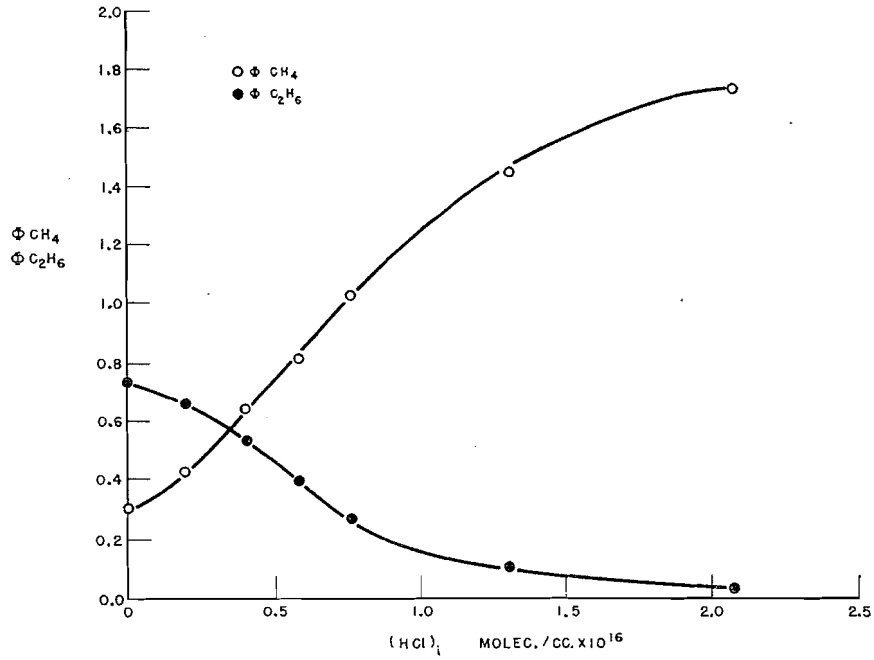



FIG. 1.

methane formed with a corresponding decrease in ethane formation. Fig. 1 shows the quantum yields of methane and ethane at 150° and $\lambda > 2200$ Å for varying initial hydrogen chloride concentrations, the other experimental factors being kept approximately constant.

Relatively small amounts of hydrogen chloride (less than 1 mm. added to 100 mm. of acetone) were sufficient to suppress ethane formation almost completely; the formation of methane was correspondingly increased and approached at 150° a value close to twice the amount of carbon monoxide produced. The yield of carbon monoxide was not or possibly was only slightly affected.

It was found convenient to investigate the influence of different experimental conditions by following trends in the values of $k_1/k_2^{\frac{1}{2}}$ calculated from Equation [1] after substituting in it $[HCl]_i$ for [RH]. It is, therefore, implicitly assumed that hydrogen chloride concentration does not vary with time and is equal to the concentration of the initially introduced hydrogen chloride ($HCl_i$). (In the following the symbol $(k_1/k_2^{\frac{1}{2}})_1$ will denote the values obtained to this approximation.) The reason for this choice may be evident from the following considerations. The amounts of hydrogen chloride added to acetone in these experiments are much too small to account for the increased methane production if it is to be assumed that the additional methane is formed by reaction (1), i.e., hydrogen abstraction from the originally introduced hydrogen chloride. At the same time, as will be seen from the subsequent discussion, there is evidence that reaction (1) is involved in the process. It seems, therefore, to be necessary to assume, as was done previously by Williams and

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Ogg (17), that hydrogen chloride is regenerated, in this case by reaction of chlorine atoms with acetone. If the hydrogen chloride regeneration is complete, and since in all experiments large concentrations of acetone are used and the reactions are carried out to small conversions, the concentrations of hydrogen chloride and acetone remain constant. Equation [1] can then be used for evaluation of $k_1/k_2^{\frac{1}{2}}$. If the hydrogen chloride regeneration is not complete, the effective mean hydrogen chloride concentration will be smaller than the initial hydrogen chloride concentration and the calculated values of $k_1/k_2^{\frac{1}{2}}$ will be too small. A criterion of the completeness of the hydrogen chloride regeneration is, therefore, constancy of $(k_1/k_2^{\frac{1}{2}})_1$ for different experimental conditions.

Typical results of the experiments carried out are presented in Tables I to IV. An attempt was made to investigate trends in the values of $(k_1/k_2^{\frac{1}{2}})_1$ by varying one experimental factor at a time. This, however, was achieved only approximately. For this reason a graphical representation of the results would show a scattering of points not necessarily representative of the actual experimental error. As a result of the necessity of keeping all experimental factors constant but one, in some of the experiments the amounts of the products are very small and may involve a considerable analytical error. They are believed, however, to indicate correctly the trends in the values and have been, therefore, included in the tables.

Table I shows drifts in the values of $(k_1/k_2^{\frac{1}{2}})_1$ with increasing initial hydrogen chloride concentrations for the photolysis of acetone at 150°. Acetone pressure was kept at approximately 100 mm. The first five determinations were carried

TABLE I

PHOTOLYSIS OF ACETONE-HCl MIXTURES AT 150° C.
Effect of HCl concentration

| Run | Temp., ° C. | $[HCl]_i$, molec./cc. $\times 10^{-16}$ | [Ac], molec./cc. $\times 10^{-18}$ | Time, sec. | In molec./cc. sec. $\times 10^{-13}$ | | | $\frac{C_2H_6 + \frac{1}{2}CH_4}{CO}$ | $(k_1/k_2^{\frac{1}{2}})_1 \times 10^9$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | | |
| *Filter 9–54* | | | | | | | | | |
| 23 | 149.5 | .... | 2.33 | 1800 | 6.69 | 1.71 | 5.11 | 0.88 | ... |
| 22 | 151.0 | 0.58 | 2.29 | 1800 | 6.77 | 5.50 | 2.66 | 0.75 | 1.4 |
| 21 | 151.8 | 0.76 | 2.28 | 1800 | 7.00 | 7.19 | 2.28 | 0.76 | 1.9 |
| 20 | 150.4 | 1.31 | 2.28 | 1800 | 7.34 | 10.6 | 0.759 | 0.82 | 2.8 |
| 19 | 148.2 | 2.07 | 2.32 | 1800 | 8.30 | 14.4 | 0.251 | 0.89 | 4.3 |
| 37 | 151.1 | .... | 2.52 | 2400 | 5.92 | 1.77 | 4.28 | 0.87 | ... |
| 34 | 152.6 | 0.19 | 2.30 | 2400 | 6.48 | 2.78 | 4.27 | 0.87 | 0.9 |
| 32 | 151.4 | 0.40 | 2.66 | 2400 | 7.17 | 4.61 | 3.79 | 0.85 | 1.1 |
| 31 | 150.0 | 0.62 | 2.39 | 2400 | 6.92 | 5.68 | 2.80 | 0.85 | 1.3 |
| 35 | 147.0 | 1.50 | 2.14 | 2400 | 5.65 | 9.34 | 0.234 | 0.87 | 3.9 |
| *Filter 0–53* | | | | | | | | | |
| 67 | 150.6 | .... | 2.28 | 10800 | 0.195 | 0.180 | 0.054 | 0.70 | ... |
| 66 | 150.6 | 0.38 | 2.29 | 10800 | 0.199 | 0.326 | 0.005 | 0.84 | 3.1 |
| 65 | 150.5 | 3.14 | 2.31 | 10800 | 0.212 | 0.401 | ..... | 0.96 | ... |

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out under conditions of free access of mercury vapor into the reaction cell from the adjoining mercury manometer. In the case of all the remaining determinations reported mercury vapor was removed from the reaction system. There was no significant difference in the values obtained in the two cases. With increasing hydrogen chloride concentration the values of $(k_1/k_2^{\frac{1}{2}})_1$ become progressively greater. The material balance for the conversion of methyl radicals into methane and ethane, as expressed by the ratio $(C_2H_6 + \frac{1}{2}CH_4)/CO$, remains similar to that of acetone alone. With hydrogen chloride concentrations considerably larger than those reported in Table I ethane was not detected by the analytical procedure used and the amount of methane formed approached a value about twice that of carbon monoxide without exceeding it. The three determinations with $\lambda > 2800$ Å show a similar trend.

Table II shows the analogous experiments at room temperature. It is

TABLE II

PHOTOLYSIS OF ACETONE–HCl MIXTURES AT ROOM TEMPERATURE
Effect of HCl concentration

| Run | Temp., ° C. | $[HCl]_i$, molec./cc. $\times 10^{-16}$ | [Ac], molec./cc. $\times 10^{-18}$ | Time, sec. | In molec./cc. sec. $\times 10^{-13}$ | | | $(k_1/k_2^{\frac{1}{2}})_1$ $\times 10^9$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | |
| *Filter 9–54* | | | | | | | | |
| 49 | 23.1 | .... | 3.28 | 4800 | 0.381 | 0.024 | 0.907 | ... |
| 51 | 26.4 | 0.15 | 3.34 | 3000 | 0.343 | 0.152 | 0.778 | 0.3 |
| 48 | 25.4 | 0.40 | 3.20 | 4800 | 0.215 | 0.603 | 0.357 | 0.8 |
| 47 | 28.8 | 0.71 | 3.30 | 4800 | 0.238 | 1.11 | 0.107 | 1.5 |
| 46 | 26.7 | 3.25 | 3.30 | 4800 | 0.238 | 1.62 | 0.012 | 1.5 |
| *Filter 0–53* | | | | | | | | |
| 62 | 30.1 | .... | 3.23 | 28800 | 0.015 | 0.003 | 0.018 | ... |
| 64 | 28.5 | 0.53 | 3.33 | 50400 | 0.011 | 0.039 | 0.001 | 0.6 |
| 63 | 30.8 | 4.31 | 3.18 | 64800 | 0.011 | 0.043 | ..... | ... |

evident that even at room temperature the effect of small hydrogen chloride concentrations is very pronounced. The general trend in the values of $(k_1/k_2^{\frac{1}{2}})_1$ is similar to that at 150°.

The rates of formation of ethane and methane vary with light intensity, as shown in Table III. It was found that in the photolysis of acetone – hydrogen chloride mixtures at 150° the quantum yield of carbon monoxide formation was close to unity, as in the case of acetone alone. The data on the light absorption in Table III are calculated on the assumption that the quantum yield of carbon monoxide formation is unity. The trend in the ratio of $R_{CH_4}/R_{C_2H_6}$ is qualitatively the same as in the case of acetone alone and the values of $(k_1/k_2^{\frac{1}{2}})_1$ become greater as the amount of light absorbed is reduced. The light intensity in these experiments varied as a result of (*a*) progressive decline in the output of the light source and (*b*) regulation of the current through the mercury arc. The effects in the two cases were approximately the same.

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TABLE III

PHOTOLYSIS OF ACETONE–HCl MIXTURES (150° C., FILTER 9–54)
Effect of light intensity

| Run | Temp., ° C. | $[HCl]_i$, molec./cc. $\times 10^{-16}$ | [Ac], molec./cc. $\times 10^{-18}$ | Light absorbed, quanta/sec. $\times 10^{-15}$ | In molec./cc. sec. $\times 10^{-13}$ | | | $\frac{C_2H_6 + \frac{1}{2} CH_4}{CO}$ | $(k_1/k_2^{\frac{1}{2}})_1 \times 10^9$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | | |
| 32 | 151.4 | 0.40 | 2.66 | 8.60 | 7.17 | 4.61 | 3.78 | 0.85 | 1.1 |
| 42 | 151.2 | 0.34 | 2.29 | 5.60 | 4.67 | 3.44 | 2.11 | 0.82 | 1.5 |
| 36 | 152.3 | 0.36 | 2.23 | 4.33 | 3.61 | 3.37 | 1.16 | 0.80 | 2.1 |
| 70 | 151.5 | 0.36 | 2.39 | 2.87 | 2.39 | 2.67 | 0.417 | 0.73 | 3.0 |
| 38 | 153.3 | 0.34 | 2.17 | 2.03 | 1.69 | 2.11 | 0.262 | 0.78 | 3.1 |

*The time of photolysis in all runs was 2400 sec. The amount of light absorbed was calculated on the assumption that the quantum yield of carbon monoxide formation was unity.*

The effect of varying time of photolysis is shown in Table IV. There is a distinct decrease in the ratio $R_{CH_4}/R_{C_2H_6}$ with increased time of photolysis and the values of $(k_1/k_2^{\frac{1}{2}})_1$ become smaller.

TABLE IV

PHOTOLYSIS OF ACETONE–HCl MIXTURES (FILTER 9–54)
Effect of the time of irradiation

| Run | Temp., ° C. | Time, sec. | $[HCl]_i$, molec./cc. $\times 10^{-16}$ | [Ac], molec./cc. $\times 10^{-18}$ | In molec./cc. sec. $\times 10^{-13}$ | | | $\frac{C_2H_6 + \frac{1}{2} CH_4}{CO}$ | $(k_1/k_2^{\frac{1}{2}})_1 \times 10^9$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | | |
| 51 | 26.4 | 3000 | 0.15 | 3.34 | 0.343 | 0.152 | 0.778 | 2.5 | 0.29 |
| 50 | 26.2 | 5700 | 0.15 | 3.16 | 0.350 | 0.100 | 0.799 | 2.4 | 0.16 |
| 52 | 28.5 | 9000 | 0.14 | 3.16 | 0.386 | 0.076 | 0.835 | 1.9 | 0.11 |
| 42 | 151.2 | 2400 | 0.34 | 2.29 | 4.67 | 3.44 | 2.11 | 0.82 | 1.5 |
| 41 | 149.2 | 5400 | 0.40 | 2.37 | 4.59 | 2.54 | 2.59 | 0.81 | 0.64 |

## DISCUSSION

The experimental results on the photolysis of acetone – hydrogen chloride mixtures can be summarized in the following manner: (*a*) there is a very pronounced effect on addition of relatively small quantities of hydrogen chloride both at 150° and at room temperature: ethane formation is strongly suppressed and the formation of methane is correspondingly increased; (*b*) the effect is approximately the same at $\lambda > 2200$ Å and $\lambda > 2800$ Å; (*c*) the yield of carbon monoxide and the material balance for the conversion of methyl radicals into methane and ethane are approximately the same as in the case of acetone alone; (*d*) the products of the photolysis contain no detectable quantities of hydrogen. There is also a decrease in the values of $(k_1/k_2^{\frac{1}{2}})_1$ with (*e*) time of photolysis, (*f*) decreasing hydrogen chloride concentration, and (*g*) increasing light absorption. At the same time, (*h*) no significant difference in $(k_1/k_2^{\frac{1}{2}})_1$ was observed when acetone pressure was reduced from 100 to 50 mm. (This experiment was performed at 150° and $\lambda > 2200$ Å.)

It can be concluded from (*e*) that hydrogen chloride is at least partially

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consumed in the reaction. At the same time, it is evident from the material balance for methane formation that much less than one molecule of hydrogen chloride is used up whenever an additional molecule of methane is formed. This implies either that for the most part hydrogen chloride participates in the reaction only as a second body and is not itself chemically changed, or, if it does undergo a change, that it must be rapidly regenerated. It is difficult to conceive of a plausible mechanism for the first alternative compatible with all the experimental observations.

The energetically possible quenching reaction

$$(1a)\quad CH_3COCH_3^* + HCl \rightarrow CH_4 + CH_3CO + Cl$$

would have to be followed by $CH_3CO \rightarrow CH_3 + CO$. Evidently, it cannot explain complete suppression of ethane formation unless it is assumed that either of the reactions

$$(1)\quad CH_3 + HCl \rightarrow CH_4 + Cl$$

or

$$(1b)\quad CH_3CO + HCl \rightarrow CH_4 + CO + Cl$$

also takes place and is very fast. Furthermore, no kinetic evidence can be derived from the experimental results that reaction (1*a*) plays an important role. It may, therefore, in the present treatment be disregarded. Since at 150° $CH_3CO$ decomposes rapidly into $CH_3$ and CO, reaction (1) must be of importance. The following scheme of reactions would then seem to be sufficient for a satisfactory explanation of the experimental results:

$$\begin{aligned}
&(I)\quad CH_3COCH_3 + h\nu \rightarrow CH_3 + CH_3CO\\
&(II)\quad CH_3CO \rightarrow CH_3 + CO\\
&(III)\quad CH_3CO + CH_3CO \rightarrow (CH_3CO)_2\\
&\\
&(1)\quad CH_3 + HCl \rightarrow CH_4 + Cl\\
&(2)\quad CH_3 + CH_3 \rightarrow C_2H_6\\
&(3)\quad CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3\\
&(4)\quad CH_3 + CH_2COCH_3 \rightarrow C_2H_5COCH_3\\
&(5)\quad 2\,CH_2COCH_3 \rightarrow (CH_2COCH_3)_2\\
&(6)\quad CH_2COCH_3 \rightarrow CH_3 + CH_2CO\\
&(7)\quad Cl + CH_3COCH_3 \rightarrow HCl + CH_2COCH_3\\
&(8)\quad \begin{cases} HCl + X \rightarrow (HCl.X)\\ Cl + Y \rightarrow (Cl.Y)\end{cases}
\end{aligned}$$

where (8) is some process by which part of the hydrogen chloride is consumed. Reaction (6) is probably not important below 200°.

A proof that hydrogen is abstracted from hydrogen chloride to form methane might be furnished by photolysis of deuterated acetone in the presence of relatively large quantities of hydrogen chloride when the process is carried to a small conversion. We thus find that in the photolysis of 100 mm. of deuterated acetone (87% $d_6$) and 30 mm. of hydrogen chloride the methane produced consists predominantly of $CD_3H$, both at 150° and at room temperature. An eventual spontaneous exchange of H and D between acetone, and hydrogen chloride, even in the case of the most unfavorable redistribution, cannot explain the predominant formation of $CD_3H$.

The possibility of an appreciable direct photolysis of hydrogen chloride

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under conditions of the present experiment seems to be excluded. The long wave length limit of the hydrogen chloride absorption continuum is about 2200 Å (7; 10; 16) and with the filters and the small hydrogen chloride concentrations used no appreciable absorption by hydrogen chloride would be expected. This is substantiated by the lack of hydrogen in the reaction products and the similarity of the observed effects with alternate use of filters 9–54 and 0–53.

The mechanism proposed for the photolysis assumes a partial consumption of hydrogen chloride. A number of chemical processes could explain the decrease in the effective hydrogen chloride concentration, although purely physical phenomena may be also involved to some extent. An assumption that for higher hydrogen chloride concentrations [HCl] = Const. = $[HCl]_i$ should, however, be a good approximation, regardless of the nature of these processes.

An approximate treatment of the mechanism of hydrogen chloride consumption can be attempted by assuming that hydrogen chloride concentration is diminished during the process predominantly through a partial removal of free chlorine atoms. A direct abstraction of a chlorine atom from hydrogen chloride is highly unlikely. Results (*f*) and (*g*), stated in the summary at the beginning of this section, represent a decrease in the values of $(k_1/k_2^{\frac{1}{2}})_1$ with an increase in the methyl radical concentration. For simplicity, therefore, only the following possibilities will be considered:

$$(8a)\quad CH_3 + Cl \rightarrow CH_3Cl$$

$$(8b)\quad CH_3CO + Cl \rightarrow CH_3COCl$$

$$(8c)\quad \begin{cases} CO + Cl \rightarrow COCl \\ COCl \rightarrow CO + Cl \\ CH_3 + COCl \rightarrow CH_3COCl\,. \end{cases}$$

Reactions (8*c*) are suggested as a possibility on the basis of the investigations of photolysis and thermal decomposition of phosgene (3). If (8*c*) plays an important part, additions of relatively small quantities of carbon monoxide should inhibit the reaction very strongly. The analytical accuracy in such experiments is somewhat decreased through the presence of additional quantities of carbon monoxide. Nevertheless, it is evident from Table V that (8*c*) is

TABLE V

PHOTOLYSIS OF ACETONE–HCl MIXTURES (FILTER 9–54)
Effect of carbon monoxide concentration

| Run | Temp., °C. | Time, sec. | $[CO]_i$, molec./cc. $\times 10^{-18}$ | $[HCl]_i$, molec./cc. $\times 10^{-16}$ | [Ac], molec./cc. $\times 10^{-18}$ | In molec./cc. sec. $\times 10^{-13}$ | | | $(k_1/k_2^{\frac{1}{2}})_1$ $\times 10^9$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | |
| 71 | 150.1 | 2400 | 0.206 | .... | 2.20 | (2.36) | 0.878 | 1.28 | ... |
| 73 | 150.8 | 2400 | 0.160 | 0.34 | 2.24 | (2.29) | 2.21 | 0.408 | 2.5 |
| 70 | 151.5 | 2400 | ..... | 0.36 | 2.27 | 2.39 | 2.67 | 0.417 | 3.0 |
| 74 | 28.3 | 7200 | 0.384 | 0.44 | 3.20 | | 0.309 | 0.190 | 0.55 |
| 75 | 27.7 | 7200 | ..... | 0.43 | 3.27 | 0.136 | 0.386 | 0.139 | 0.73 |
| 76 | 27.5 | 7200 | 0.307 | 3.33 | 3.24 | | 0.854 | 0.004 | 1.3 |

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of little or no importance both at 150° and 25° C. The amounts of carbon monoxide added are in excess of the quantities normally produced in the photolysis under conditions where $(k_1/k_2^{\frac{1}{2}})_1$ shows a marked decrease.

An exact mathematical treatment of the proposed mechanism, taking into account reactions (8*a*) and (8*b*), is at present not possible. Chlorine atom and hydrogen chloride concentrations are mutually related in a very complex way. An assumption of a steady state concentration of $CH_3$ and Cl implies that there is a mean hydrogen chloride concentration which is smaller than $HCl_i$ and remains constant during the photolysis. It can be shown that the value of $k_1/k_2^{\frac{1}{2}}$ to this new approximation (denoted by $(k_1/k_2^{\frac{1}{2}})_2$) is

$$\left(\frac{k_1}{k_2^{1/2}}\right)_2 = \frac{\frac{R_{CH_4}}{R_{C_2H_6}^{1/2}} - \frac{k_3}{k_2^{1/2}}[Ac]}{[HCl]_i - \delta} \qquad [2]$$

where

$$\delta = \frac{\left(R_{CH_4} - \frac{k_3}{k_2^{1/2}} R_{C_2H_6}^{1/2}[Ac]\right)\frac{t}{2}}{1 + \frac{1}{k'\frac{R_{C_2H_6}^{1/2}}{[Ac]} + k''\frac{R_{CO}}{[Ac]}}}$$

and

$$k' = \frac{k_{8a}}{k_7 k_2^{1/2}}, \quad k'' = \frac{k_{8b}}{k_7 k_{II}}, \quad Ac = CH_3COCH_3,$$

$t$ is the time of photolysis.

Equation [2] is in qualitative agreement with the experimental observations. At 150° $k_{II}$ is very large and as a further simplification $k''$ can be neglected. A simultaneous plot of quantum yields of methane and ethane formation at 150° and $\lambda > 2200$ Å for varying initial hydrogen chloride concentrations, other experimental factors being approximately constant, is shown in Fig. 1. Acetone pressure in all cases was close to 100 mm. By plotting also the remaining experimental data at 150° and $\lambda > 2200$ Å it is found that all the points either fall on the pair of curves (quantum yields of methane and ethane respectively) or can be brought thereon through a simple shift in hydrogen chloride concentration. Thus there is an indication that $k_1/k_2^{\frac{1}{2}} = f([HCl]_i - \Delta)$. Equation [2] is a very simplified expression of this functional dependence and an accurate agreement with the experimental results cannot be expected. By taking $k' = 4.2 \times 10^{10}$ and $k'' = 0$ the drifts observed at 150° and $\lambda > 2200$ Å largely disappear and the mean value of $(k_1/k_2^{\frac{1}{2}})_2$ is about $4.5 \times 10^{-9}$. However, there remains a large scatter of the values. Also, this treatment fails with the results obtained at room temperature, though the values of $k_1/k_2^{\frac{1}{2}}$ can be mutually approached.

Drifts in the values of $(k_1/k_2^{\frac{1}{2}})_1$ make an accurate evaluation of the activation energy of reaction (1) impossible. On the basis of the proposed mechanism extrapolations to $t = 0$, $Ia = 0$, or to large hydrogen chloride concentrations should supply the true values of $k_1/k_2^{\frac{1}{2}}$. Limitations in the accuracy of the analytical procedure make these extrapolations unreliable. It seems possible,

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however, to obtain an approximate estimate of the activation energy of the reaction from the data in Tables I and II. With increasing hydrogen chloride concentrations $(k_1/k_2^{\frac{1}{2}})_1$ tends to a value of about $4.5 \times 10^{-9}$ at 150° and $1.5 \times 10^{-9}$ at 28° C. From the ratio of the two values, and taking into account the $T^{\frac{1}{2}}$ factor in the pre-exponential term, 2.1 kcal. per mole is obtained for $E_1 - \frac{1}{2}E_2$. Assuming mean collision diameters of 3.5 Å and 1.3 Å for $CH_3$ and hydrogen chloride respectively, $P_1/P_2^{\frac{1}{2}}$ is found to be $6.7 \times 10^{-3}$. With unity as a plausible value for $P_2$ (6), the value of $P_1$ becomes $6.7 \times 10^{-3}$. In view of the uncertainty of the extrapolation to high hydrogen chloride concentrations, an uncertainty of ± 1 kcal. per mole in the above value of $E_1 - \frac{1}{2}E_2$ would seem to be a sufficiently conservative estimate. This introduces a factor of 3.3 as the corresponding uncertainty in the value of $P_1/P_2^{\frac{1}{2}}$.

The present estimate of the activation energy of the reaction (1) is based on the values of rate constants at 150° and 28° C. In the photolysis of acetone alone two distinct values of the activation energy of hydrogen abstraction by methyl radicals have been reported: 9.7 kcal. per mole between approximately 120° and 300° (15) and 6.1 kcal. per mole between 120° and 25° (5). There is still no complete explanation of this apparent anomaly. This discrepancy, however, should not affect the estimated value of the activation energy of reaction (1) because in the extrapolation of $(k_1/k_2^{\frac{1}{2}})_1$ to large hydrogen chloride concentrations the contribution of the reaction (3) becomes negligibly small. At the same time, Equation [1] should be valid regardless of the discrepancy in the value of $E_3 - \frac{1}{2}E_2$ provided methane and ethane are formed by a free radical mechanism. Dorfman and Noyes (5) have shown that the experimental data on photolysis of acetone are fully compatible with the free radical mechanism both at 25° and at higher temperatures. Benson and Falterman (1) have recently investigated the photolysis of equimolecular mixtures of ordinary and deuterated acetone and found that both at 35° and at higher temperatures $C_2D_6$, $CD_3CH_3$, and $C_2H_6$ are formed in the ratio of 1:2:1, as would be expected in the case of a free radical mechanism. In analogous experiments we find that both at 25° and 150° several times as much $CD_3H$ is formed as $CD_4$. It would seem, therefore, that at room temperature as well as at higher temperatures methane and ethane are formed by a free radical mechanism. Nevertheless, it is possible that an eventual explanation of the curvature of the Arrhenius plot for acetone photolysis at lower temperatures may necessitate a revision of the conclusions suggested here.

The value of the steric factor obtained for reaction (1) seems to be in agreement with the values previously observed for similar types of reactions. It is also of interest that from the experimental results of Williams and Ogg (17) a value of 2.4 kcal. per mole is obtained for $E_1$ if it is assumed that the reaction of methyl radicals with molecular iodine requires no activation energy. These authors, however, suggest that under the conditions of their experiments (large hydrogen chloride concentrations) a reaction of "hot" methyl radicals with hydrogen chloride is of importance. On the other hand, in the experiments reported in the present paper, the hydrogen chloride concentrations used were very small and, consequently, any "hot" methyl

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radicals were thermalized by collisions with acetone before reacting with hydrogen chloride, so that a reaction of "hot" methyl radicals is unlikely to be important.

The low value of the activation energy obtained for reaction (1) may appear at first sight somewhat surprising in view of the value of more than 9 kcal. for the reaction of methyl radicals with hydrogen (11). A consideration of bond strengths shows that reaction (1) is nearly thermoneutral or only slightly endothermic. $E_1$ would then be expected to be comparable with the activation energy of the reverse reaction

$$(9) \quad Cl + CH_4 \rightarrow HCl + CH_3.$$

For the comparable set of reactions (which are also approximately thermoneutral)

$$(10) \quad H + HCl \rightarrow H_2 + Cl$$

and

$$(11) \quad Cl + H_2 \rightarrow HCl + H$$

Bodenstein (2) estimates collision yields of the same order of magnitude, $10^{-4}$. Tamura (14), using the method of thermal analysis of reaction velocity (8), has investigated reaction (9) at 19° C. and obtained a collision yield of $2.4 \times 10^{-5}$ and, consequently, $E_9 \leqslant 6.2$ kcal. per mole. The maximum value of 6.2 kcal. per mole corresponds to a steric factor of unity; for a steric factor of $10^{-3}$ $E_9$ reduces to 2.1 kcal. per mole. Taking $E_2 = 0$, $P_2 = 1$, and mean molecular diameters of 3.5 Å and 1.3 Å for $CH_3$ and hydrogen chloride respectively, we obtain for reaction (1) at 28° a collision yield of $2.0 \times 10^{-4}$, which leads to a value of $E_1 \leqslant 5.1$ kcal. per mole. There is, therefore, an approximate agreement between the collision yields of reactions (1) and (9). The consistency of the value obtained for $E_1$ and Tamura's value for $E_9$ is thus seen to be uncertain to the extent of the uncertainty of the steric factor of the latter reaction. Unfortunately, most reactions involving chlorine atoms have been studied at a single temperature. Rodebush and Klingelhoefer (13) have investigated reaction (11) at 25° and 0° C. Chlorine atoms were produced by electrodeless discharge and their concentration measured by a gauge similar to the Wrede gauge. From the experimental measurements reported and the uncertainty suggested by the authors, it would seem that $P_{11}$ is between $10^{-2}$ and unity. However, in view of the relatively small temperature range employed, we do not feel justified in drawing any definite conclusions relevant to the present work.

Reaction between methyl radicals and hydrogen chloride is seen to be fast enough so that the presence of even relatively small quantities of hydrogen chloride may have a pronounced effect on the over-all course of a reaction involving methyl radicals. Actually, $k_2$ is probably about ten thousand times as great as $k_1$ at room temperature and the pronounced catalytic effect of hydrogen chloride is only due to the extremely small $CH_3$ concentrations and to the rapid regeneration of hydrogen chloride. The action of hydrogen chloride may manifest itself in most cases solely in an increased production of methane and almost complete suppression of ethane without affecting in any other way the over-all composition of the products. Under such conditions the $CH_3$ concentration is so much suppressed that only negligible

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quantities of $CH_3Cl$ result from reaction (8*a*) and may not be analytically detectable. Thus, in the photolysis of mixtures of acetone and chlorinated hydrocarbons, hydrogen chloride may be a product of the reaction or could be present as an impurity. The strong suppression of ethane formation could be in such cases predominantly due to a very fast abstraction of hydrogen from the hydrocarbon. At the same time, to a smaller or greater extent, the effect may be due to a fast abstraction of hydrogen via hydrogen chloride. The relative importance of the two possibilities can be ascertained from quantitative considerations when hydrogen chloride concentration is known, or by a suitable selective inhibition of the hydrogen chloride effect (4). The significance of the catalytic effect of hydrogen chloride in the apparent carbon tetrachloride anomaly mentioned in the introduction, and in some other instances, will be discussed elsewhere in this Journal (4) on the basis of additional experiments performed.

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# PHOTOLYSIS OF MIXTURES OF ACETONE AND SOME CHLORINATED METHANES[1]

By R. J. Cvetanović,[2] F. A. Raal,[3] and E. W. R. Steacie

ABSTRACT

Additions of carbon tetrachloride to acetone show in photolysis an apparent anomaly: methane formation is strongly increased and the formation of ethane correspondingly lowered. In this manner a hydrogen abstraction reaction is simulated. The cause of the anomaly and its bearing on the photolysis of acetone with other chlorinated methanes has been investigated.

## INTRODUCTION

The reaction of methyl radicals, formed by the photolysis of acetone, with several partially halogenated methanes has recently been investigated by two of the authors (7). Rates of production of methane, ethane, and carbon monoxide were determined between 110° and 220°C. By analogy with the well investigated photochemical reactions in acetone–hydrocarbon mixtures (11) it was assumed that all ethane was produced by combination of methyl radicals and all methane by hydrogen abstraction from acetone and from the added halogenated methane. With this assumption, and assuming also time independent concentrations of methyl radicals, acetone, and the halogenated methane, it was possible to evaluate the activation energies of the investigated reactions relative to the activation energy of the combination of methyl radicals, as well as their steric factors. In this manner it was shown that the ease of abstraction of a hydrogen atom from a halogenated methane increased as the number of halogen atoms in the compound increased.

In all the investigated reactions the addition of the partially halogenated methane to acetone had the effect of increasing the rate of formation of methane with a corresponding suppression of ethane formation. It seemed reasonable to suppose that the increased methane formation was entirely due to the additional abstraction of hydrogen from the halogenated methane. Thus in the series $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$, the effect became more pronounced as the number of the chlorine atoms in the molecule increased, indicating that the rates of hydrogen abstraction became faster. The last member of the series, carbon tetrachloride, contains no hydrogen atoms and its addition to acetone should not have any effect on the rates of methane production. It was thought, therefore, that the photolysis of a mixture of acetone and carbon tetrachloride would provide a suitable test for the correctness of the assumptions made. Early experiments, however, showed that additions of carbon tetrachloride to acetone produced an effect entirely analogous to that produced by chloroform and possibly even more pronounced. There was, therefore, a continuous increase in the intensity of the

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effect along the series without the expected disappearance in the case of carbon tetrachloride. Since a direct hydrogen abstraction cannot be postulated in the case of carbon tetrachloride, the question of immediate interest is whether the observed effect is of identical nature for all the members of the series, in which case hydrogen abstraction would not suffice to explain it; or otherwise, is the carbon tetrachloride anomaly peculiar to this compound alone without affecting the other members of the series.

Although in all the experiments performed the best available grades of the reagents were used, it was necessary to investigate first the possibility that the anomalous behavior of carbon tetrachloride may be due to the presence of some impurity. Since the effect produced by carbon tetrachloride is at least as pronounced as that of any other member of the series, it is evident that the presence of even large quantities of the other chlorinated methanes cannot explain the observed anomaly. If an impurity is responsible for the large increase in methane production, small additions of it directly to acetone should produce an analogous effect. In a largely qualitative experiment we have observed that additions of relatively small amounts of hydrogen chloride to acetone do suppress strongly ethane formation with a corresponding large increase in the amount of methane formed. In order to be able to draw any unambiguous conclusions regarding the importance of a possible hydrogen chloride impurity in carbon tetrachloride, it was necessary to know how small the quantities of hydrogen chloride are which are still sufficient to produce an appreciable effect. This information is now available (2), and it will be evident from the subsequent discussion, based on a number of experiments performed in order to clarify this point, that a hydrogen chloride impurity alone cannot explain the carbon tetrachloride effect. However, the possibility that certain amounts of hydrogen chloride may be formed during the photolysis itself has been further investigated and the results arrived at seem to offer a satisfactory explanation of the apparent anomaly. In the present paper we wish to report the results of the experiments performed and their bearing on the photolysis of mixtures of acetone and the other members of the series of chlorinated methanes.

## EXPERIMENTAL

### *Apparatus*

The apparatus, the analysis system, and the optical system used have been described before (2), as well as the procedure employed for mixing the reactants. Additional facility was provided for freezing over into sampling traps the condensable fraction of the products without an appreciable contamination with mercury, the latter having been found to obscure to some extent qualitative tests for hydrogen chloride. In order to decrease the solubility of some of the reactants in stopcock grease, a commercial silicone grease was used in the relevant parts of the reaction system.

The light from a Hanovia S-500 medium pressure arc was roughly collimated by a highly polished aluminum cylinder. Two filters were alternately included in the optical system: a Corning 9-54 filter with a cutoff below about 2200 Å and a Corning 0-53 filter with a cutoff below about 2800 Å. The cylindrical silica re-

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action cell had a volume of 120 ml. and during a photolysis was completely filled with the light beam.

The aluminum block furnace used was heated by the current supplied from a Sorensen voltage regulator and its temperature was maintained to within about 1°C.

*Materials*

Acetone was a Mallinckrodt analytical reagent product, refluxed over potassium permanganate, and bulb to bulb distilled *in vacuo*. The same grade acetone, dried over anhydrous sodium sulphate and subjected to repeated bulb to bulb distillation *in vacuo*, without previous permanganate treatment, has also been used without any appreciable difference in the results.

Anachemia and Mallinckrodt reagent grades carbon tetrachloride were alternately used. The methods employed for further purification of carbon tetrachloride will be referred to in the following section.

Chloroform was a reagent grade Anachemia product. It was used alternately (*a*) without drying before the vacuum distillation, (*b*) dried over anhydrous sodium sulphate, and (*c*) dried over phosphorus pentoxide. In all cases it was finally subjected to repeated bulb to bulb distillation *in vacuo*.

Ammonia was a Matheson Company product. Normal pentane was a pure grade Phillips product, 99 mole % minimum. These compounds were further purified before their use by repeated bulb to bulb distillation *in vacuo*.

## RESULTS

In early experiments with acetone and carbon tetrachloride the reagent grade carbon tetrachloride was only subjected to repeated bulb to bulb distillation *in vacuo* prior to its use. In order to test whether a hydrogen chloride impurity was responsible for the observed increased methane production, a sample of the carbon tetrachloride was thoroughly washed 10 times with distilled water, dried over a reagent grade anhydrous sodium sulphate, distilled through a column, and finally bulb to bulb distilled *in vacuo*. This treatment failed to affect the observed rates of methane and ethane formation, although on the basis of the results from photolysis of acetone – hydrogen chloride mixtures (2) the calculated quantities of hydrogen chloride required to produce an analogous effect would have had in some cases to constitute an impurity of several per cent. Evidently, if hydrogen chloride was the cause of the apparent anomaly, it could not have been introduced in such quantities as an impurity but must have been formed subsequently. This is further substantiated by the investigation of the effect of additions of small quantities of ammonia to acetone – carbon tetrachloride mixtures before their photolysis at 150°C. When 1 mm. of hydrogen chloride is added to 100 mm. of acetone and the mixture is photolyzed at 150°, the amount of ethane produced is negligibly small and the amount of methane formed becomes nearly twice the amount of carbon monoxide. On the other hand, if to such a mixture somewhat more than 1 mm. of ammonia is added and all the reactants are condensed together outside the reaction cell and then expanded, the rates of formation of methane and ethane become, in the subsequent photolysis, the same as in the case of pure acetone alone. The pretreatment by ammonia

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removes hydrogen chloride from the gaseous mixture. A similar pretreatment by ammonia of mixtures of acetone and carbon tetrachloride, however, fails to remove the effect due to carbon tetrachloride as is evident from Table I. The

TABLE I

PHOTOLYSIS OF ACETONE–$CCl_4$ MIXTURES AT 150°C.
EFFECT OF ADDITION OF AMMONIA

| Run | Temp., °C. | Time, sec. | In molec./cc. $\times 10^{-18}$ | | | In molec./cc. sec. $\times 10^{-13}$ | | | $\frac{R_{CH_4}}{(R_{C_2H_6})^{\frac{1}{2}} \times 10^{-6}}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | [Ac] | [$CCl_4$] | [$NH_3$] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | |
| *Filter 0-53* | | | | | | | | | |
| 7 | 153 | 7200 | 2.29 | — | — | 0.408 | 0.346 | 0.171 | 2.6 |
| 5 | 153 | 7200 | 2.29 | 0.18 | 0.02 | 0.486 | 0.598 | 0.062 | 7.6 |
| 4 | 153 | 7200 | 2.29 | 0.27 | 0.03 | 0.439 | 0.614 | 0.078 | 7.0 |
| 6 | 153 | 7200 | 2.29 | 0.23 | 0.09 | 0.424 | 0.583 | 0.047 | 8.5 |
| 136 | 151 | 25200 | 2.27 | $0.02_2$ | — | 0.211 | 0.331 | 0.018 | 7.0 |
| *Filter 9-54* | | | | | | | | | |
| 8 | 152 | 3600 | 2.30 | — | — | 4.90 | 1.57 | 3.74 | 2.6 |
| 11 | 152 | 3600 | 2.30 | — | 0.05 | 4.34 | 1.51 | 3.30 | 2.6 |
| 10 | 154 | 3600 | 2.28 | 0.24 | — | 3.84 | 5.78 | 0.405 | 28.7 |
| 9 | 153 | 3600 | 2.31 | 0.20 | 0.18 | 5.03 | 5.81 | 0.816 | 20.3 |

amounts of ammonia added were in all cases in large excess of the calculated quantity of hydrogen chloride corresponding to the observed effect. At the same time, comparable quantities of ammonia had no appreciable effect on the photolysis of acetone alone, as is seen from Expt. 11; this is in agreement with the previous investigation of the photolysis of acetone–ammonia mixtures by Trotman-Dickenson and Steacie (12) who found an activation energy of 10.0 kcal. per mole and a steric factor of $6 \times 10^{-4}$ for the abstraction of hydrogen from ammonia by methyl radicals. In the blank experiments conducted with acetone – carbon tetrachloride mixtures at 150° and differing only in the omission of irradiation, no formation of carbon monoxide, methane, or ethane could be detected; the lack of the usual products shows that under such conditions there are no thermal effects of any importance.

It is evident that the supposition that a hydrogen chloride impurity is solely responsible for the observed anomalous behavior of carbon tetrachloride can be discounted. There remains, however, the possibility that small amounts of hydrogen chloride are formed in the photolysis. The amounts of hydrogen chloride formed would normally be expected to be rather small and their detection in the presence of very large quantities of the reactants and the other products may offer some difficulty. A series of qualitative experiments at 150° has, however, shown that hydrogen chloride is formed when mixtures of acetone and carbon tetrachloride are irradiated, both at $\lambda > 2200$ Å and $\lambda > 2800$ Å. Also at room temperature ($\lambda > 2200$ Å) hydrogen chloride could be detected. In these experiments large quantities of carbon tetrachloride (up to 40 mm.) and 70 to 80 mm.

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of acetone were used and the irradiations extended for periods of 6 to 12 hr. The condensable products and the excess of the reactants were frozen over into a sampling trap containing a small amount of silver nitrate solution. On warming, distinct white precipitates, soluble in ammonia and reprecipitated by nitric acid, were formed. Blank experiments with identical treatment except that the irradiation was omitted showed no silver chloride precipitates. Also, the bulk liquid of the carbon tetrachloride used gave a negative test.

Since hydrogen chloride is a product in the photolysis of acetone – carbon tetrachloride mixtures, it must, in view of its pronounced catalytic action(2), be responsible for at least a part of the observed apparent anomaly. The experiments with addition of ammonia show that at 150° there is at the best only a slight inhibition of the carbon tetrachloride effect. This might be due to a slow removal of hydrogen chloride formed in the reaction because at 150° ammonium chloride would be dissociated to an appreciable extent. On the other hand, small amounts of ammonia added to acetone – carbon tetrachloride mixtures photolyzed at room temperature completely inhibit the anomalous effect and the rates of formation of methane and ethane become the same as in the photolysis of acetone alone.

The effect of additions of carbon tetrachloride to acetone photolyzed at $\lambda > 2200$ Å is summarized in Tables II and III. Variations with carbon tetra-

TABLE II

PHOTOLYSIS OF ACETONE–$CCl_4$ MIXTURES (FILTER 9-54)
EFFECT OF $CCl_4$ CONCENTRATION

| Run | Temp., °C. | Time, sec. | In molec./cc. $\times 10^{-18}$ | | In molec./cc. sec. $\times 10^{-13}$ | | | $\frac{R_{CH_4}}{(R_{C_2H_6})^{\frac{1}{2}} \times 10^{-6}}$ | $\frac{C_2H_6 + \frac{1}{2}CH_4}{CO}$ | $\gamma_{CCl_4} \times 10^{11}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | [Ac] | [$CCl_4$] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | | | |
| *150°C.* | | | | | | | | | | |
| 8 | 152 | 3600 | 2.30 | — | 4.90 | 1.57 | 3.74 | 2.6 | 0.92 | — |
| 13 | 149 | 3600 | 2.29 | 0.023 | 3.88 | 3.28 | 1.55 | 8.4 | 0.82 | 25.2 |
| 89 | 150 | 3000 | 2.41 | 0.030 | 5.61 | 4.52 | 1.70 | 11.0 | 0.80 | 28.3 |
| 88 | 147 | 3000 | 2.32 | 0.078 | 5.60 | 6.10 | 0.979 | 19.5 | 0.72 | 22.0 |
| 87 | 150 | 3000 | 2.41 | 0.086 | 6.26 | 7.44 | 0.860 | 25.4 | 0.73 | 26.6 |
| 12 | 152 | 3600 | 2.32 | 0.18 | 3.99 | 5.17 | 0.536 | 22.3 | 0.78 | 13.7 |
| 10 | 154 | 3600 | 2.28 | 0.24 | 3.84 | 5.78 | 0.405 | 28.7 | 0.86 | 10.9 |
| 24 | 151 | 3600 | 2.41 | 0.39 | 5.43 | 8.22 | 0.252 | 51.8 | 0.80 | 12.6 |
| 86 | 151 | 2400 | 2.44 | 0.55 | 7.73 | 11.2 | 0.551 | 47.8 | 0.80 | 8.2 |
| 14 | 152 | 3600 | 2.37 | 0.75 | 3.22 | 5.84 | 0.093 | 60.5 | 0.94 | 7.7 |
| *Room temperature* | | | | | | | | | | |
| 91 | 26 | 3600 | 3.33 | — | 0.496 | 0.041 | 1.15 | 0.12 | 2.4 | — |
| 90 | 30 | 3600 | 3.32 | 0.12 | 0.474 | 0.316 | 0.910 | 1.0 | 2.3 | 0.8 |
| 96 | 30 | 3390 | 3.24 | 0.45 | 0.368 | 0.946 | 0.371 | 4.9 | 2.3 | 1.1 |
| 95 | 28 | 3600 | 3.06 | 1.24 | 0.295 | 1.32 | 0.161 | 10.4 | 2.8 | 0.8 |

TABLE III

PHOTOLYSIS OF ACETONE–$CCl_4$ MIXTURES (ROOM TEMP., FILTER 9-54)
EFFECT OF TIME OF IRRADIATION

| Run | Temp., °C. | Time, sec. | In molec./cc. $\times 10^{-18}$ | | In molec./cc. sec. $\times 10^{-13}$ | | | $\frac{R_{CH_4}}{(R_{C_2H_6})^{\frac{1}{2}} \times 10^{-6}}$ | $\frac{C_2H_6 + \frac{1}{2}CH_4}{CO}$ | $\gamma_{CCl_4} \times 10^{11}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | [Ac] | [$CCl_4$] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | | | |
| 91 | 26 | 3600 | 3.33 | — | 0.496 | 0.041 | 1.15 | 0.12 | 2.4 | — |
| 93 | 27 | 1800 | 3.24 | 0.122 | 0.496 | 0.365 | 0.941 | 1.2 | 2.3 | 0.9 |
| 90 | 30 | 3600 | 3.32 | 0.120 | 0.474 | 0.316 | 0.910 | 1.0 | 2.3 | 0.8 |
| 92 | 30 | 7200 | 3.27 | 0.125 | 0.458 | 0.414 | 0.732 | 1.5 | 2.1 | 1.1 |
| 94 | 28 | 10800 | 3.18 | 0.130 | 0.388 | 0.366 | 0.621 | 1.4 | 2.1 | 1.0 |

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chloride concentration at 150° and at room temperature are shown in Table II. There is a pronounced increase in the rate of formation of methane and a decrease in production of ethane with increasing carbon tetrachloride concentrations. On the other hand, variation of time of irradiation in the series of experiments in Table III, conducted at room temperature and at $\lambda > 2200$ Å, has little or no effect on rates of methane and ethane formation. At the same time, the rates of carbon monoxide formation remained in all cases approximately the same as in the photolysis of acetone alone under comparable conditions. An eventual slight variation in the carbon monoxide production could, however, remain unnoticed because of a gradual decline in the amount of light absorbed due to decreasing transparency of the reaction cell window.

## DISCUSSION

There seems to be evidence that a halogenated methane molecule can undergo decomposition into a halogen atom and a radical either as a result of direct absorption of a suitable light quantum (4; 5) or by quenching some excited molecule (1) or atom (6). If it can be assumed that in the present experiments carbon tetrachloride undergoes a direct photolysis or an acetone photosensitized decomposition, the formation of hydrogen chloride can be easily explained by subsequent reaction of chlorine atoms with acetone. These processes need take place to only a relatively small extent in order to account for the quantity of hydrogen chloride necessary to explain the carbon tetrachloride effect.

If small amounts of hydrogen atoms appear in acetone photolysis, a hydrogen chloride formation could be attributed to direct abstraction of chlorine from carbon tetrachloride. In the absence of carbon tetrachloride small amounts of hydrogen would thus be formed. While limitations in the mass-spectrometer analysis prevented an unambiguous detection of traces of hydrogen in the products of acetone photolysis, its quantity, if present, would be too small to account for the amounts of hydrogen chloride necessary to explain the carbon tetrachloride effect under conditions of the present experiments.

In order to obtain some insight into the mode of formation of hydrogen chloride a number of experiments were performed with carbon tetrachloride and *n*-pentane, the latter serving only as a supplier of hydrogen. Mixtures of 30 to 40 mm. carbon tetrachloride and about 80 mm. *n*-pentane were irradiated at 150° for 8 to 12 hr. and the products tested qualitatively for hydrogen chloride. Some hydrogen chloride was found when filter 9-54 was used, as was to be expected in view of the characteristics of the filter and the threshold for the long wave length continuous absorption of carbon tetrachloride (5). With filter 0-53, on the other hand, no hydrogen chloride could be detected by the analytical procedure used, although under analogous conditions with mixtures of carbon tetrachloride and acetone, hydrogen chloride was formed. It appears, therefore, that an acetone photosensitized decomposition of carbon tetrachloride does take place and any scheme that may be proposed to explain the carbon tetrachloride effect in acetone photolysis would have to take it into account. It is likely that in the process chlorine atoms are liberated and then abstract hydrogen from acetone to form hydrogen chloride.

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In the photolysis of acetone – hydrogen chloride mixtures (2) methane and ethane are formed by the reactions

(1) $CH_3 + HCl \rightarrow CH_4 + Cl$,

(2) $CH_3 + CH_3 \rightarrow C_2H_6$,

(3) $CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_2COCH_3$.

The following reactions are generally believed also to take place in the photolysis of acetone

(4) $CH_3 + CH_2COCH_3 \rightarrow C_2H_5COCH_3$,

(5) $2\ CH_2COCH_3 \rightarrow (CH_2COCH_3)_2$,

(6) $CH_2COCH_3 \rightarrow CH_2CO + CH_3$,

the last reaction being of importance at temperatures above 200 to 250°. Chlorine atoms liberated in reaction (1) can react with acetone to regenerate hydrogen chloride.

(7) $Cl + CH_3COCH_3 \rightarrow HCl + CH_2COCH_3$.

At the same time, the HCl regeneration is found to be incomplete, probably largely owing to the reaction

(8) $CH_3 + Cl \rightarrow CH_3Cl$.

In the photolysis of acetone – carbon tetrachloride mixtures $CCl_3$ radicals are probably present and may participate in a variety of reactions (10). It is, therefore, possible that chlorine atoms may also be consumed by combination with $CCl_3$ radicals or with some of the products of reactions involving these radicals. This effect would tend to be greater with increasing carbon tetrachloride concentration.

Regardless of the mode of primary formation of hydrogen chloride, its concentration could be expected to reach a steady state, at least under conditions where the primary formation is relatively slow. As a first approximation the hydrogen chloride steady state concentration may be considered proportional to the concentration of carbon tetrachloride. The usual steady state treatment shows then that a quantity

$$[1] \qquad \gamma_{CCl_4} = \frac{\dfrac{R_{CH_4}}{(R_{C_2H_6})^{1/2}} - \dfrac{k_3}{k_2^{1/2}}[Ac]}{[CCl_4]}$$

should be constant at a constant temperature. The values of $\gamma_{CCl_4}$ are given in the last column of Tables II and III and are seen to vary relatively little with time of irradiation (Table III). There is, however, a decrease in $\gamma_{CCl_4}$ by a factor of 3 to 4 with increasing carbon tetrachloride concentrations at 150° and $\lambda > 2200$ Å (Table II).

Equation [1] evidently does not take into account some of the important features of the process considered here. With the available information a more elaborate kinetic treatment could hardly be justifiable, especially in view of the unknown nature of the primary carbon tetrachloride decomposition. It should, however, be mentioned that drift in $\gamma_{CCl_4}$ values in Table II can be explained by an eventual increasing Cl atom consumption with increasing carbon tetrachloride concentration, as indicated previously.

Initial decomposition of carbon tetrachloride may be due to some energy

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transfer process. Alternately, the primary process may be the reaction

(9) $CH_3 + CCl_4 \rightarrow CH_3Cl + CCl_3$,

in which case chlorine atoms would have to result from some secondary reaction of $CCl_3$ radicals, as for example

(10) $CCl_3 + CCl_3 \rightarrow C_2Cl_4 + Cl_2$

followed rapidly by

(11) $CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$.

Schumacher and Wolff (8) failed to detect any $C_2Cl_6$ in the products of the reaction of chlorine atoms with chloroform, although formation of $CCl_3$ radicals seems to be well established. Reaction (9) is analogous to the reaction of hydrogen atoms with carbon tetrachloride, for which Vance and Baumann (13) find an activation energy of 3.5 kcal. per mole and a steric factor of 0.007. In view of the large difference in the bond strengths of the products in the two reactions, reaction (9) would probably be considerably slower. Vance and Baumann find that with the lowest carbon tetrachloride concentrations used in their experiments the number of moles of hydrogen chloride formed is in some cases more than twice the number of moles of carbon tetrachloride originally present. They therefore postulate, besides the chlorine abstraction by hydrogen atoms from carbon tetrachloride, an additional abstraction from $CCl_3$. Smyser and Smallwood (9) and the later workers have observed formation of a solid with high chlorine content, possibly a polymer of $C_2Cl_4$. In the present experiments a slight deposit on the walls of the reaction vessel was also observed, although its nature is not known.

Before additional experimental information is acquired, any attempt to distinguish between different possible mechanisms would be highly speculative, although it is possible on the basis of hypothetical reactions to derive approximate expressions fitting the experimental data reasonably well. It is hoped that as a result of the experiments now in progress with other halogenated methanes, it may become possible to propose, with less ambiguity, an explanation of the mode of hydrogen chloride formation.

Equation [1] is formally identical with the expression generally used for calculating rate constants of hydrogen abstraction reactions. It gives the value of an apparent rate constant (divided by $k_2^{1/2}$) for the hydrogen abstraction reaction, which is, in the case of carbon tetrachloride, meaningless. The approximate constancy of $\gamma$ values obtained for carbon tetrachloride under similar conditions at a single temperature illustrates the danger that such an apparent value could be mistakenly identified with the rate constant of the abstraction reaction in the case of a compound where the abstraction is possible. A question of interest, is, therefore, to what extent the other chlorinated methanes are affected by the anomaly observed in the case of carbon tetrachloride.

Additional experiments were carried out with acetone–chloroform mixtures at 150° and at room temperature. Hydrogen chloride was identified qualitatively as a product in the photolysis at room temperature and with the filter 9-54. Moreover a sample of chloroform purified only by repeated bulb to bulb distillation gave under similar conditions a positive test for hydrogen chloride even in the absence of acetone. In both cases irradiation was essential for hydrogen

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chloride formation. The effect of additions of chloroform to acetone photolyzed at room temperature both at $\lambda > 2200$ Å and $\lambda > 2800$ Å was quite pronounced, comparable in magnitude with that of carbon tetrachloride. The values of $\gamma_{CHCl_3}$, calculated from the expression analogous to Equation [1], showed certain variations with the experimental conditions although the number of determinations was not sufficient to establish definite correlations. At 150° the values of $\gamma_{CHCl_3}$ were found to be considerably larger than previously reported (7), probably partly owing to different light intensities used but mainly owing to an improved mixing of the reactants in the present experiments. The values of $\gamma_{CHCl_3}$ obtained for photolysis at 150° are comparable in magnitude with the corresponding values of $\gamma_{CCl_4}$.

It has been mentioned previously that at room temperature the effect due to carbon tetrachloride can be completely inhibited with relatively very small amounts of ammonia. In the case of chloroform, as shown in Table IV, com-

TABLE IV

PHOTOLYSIS OF ACETONE–$CCl_4$ AND ACETONE–$CHCl_3$ MIXTURES (FILTER 9-54)
EFFECT OF ADDITION OF AMMONIA AT ROOM TEMPERATURE

| Run | Temp., °C. | Time, sec. | In molec./cc. × $10^{-18}$ | | | In molec./cc. sec. × $10^{-12}$ | | | $\frac{R_{CH_4}}{(R_{C_2H_6})^{\frac{1}{2}}\times 10^{-6}}$ | $\gamma \times 10^{11}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | [Ac] | [RCl] | [$NH_3$] | $R_{CO}$ | $R_{CH_4}$ | $R_{C_2H_6}$ | | |
| *Acetone and carbon tetrachloride* | | | | | | | | | | |
| 139 | 28 | 32400 | 3.21 | 0.257 | — | 0.135 | 0.415 | 0.078 | 4.7 | 1.8 |
| 141 | 28 | 27000 | 3.21 | 0.226 | 0.02 | 0.086 | 0.010 | 0.150 | 0.1 | — |
| 140 | 28 | 34200 | 3.20 | 0.217 | 0.28 | 0.118 | 0.017 | 0.220 | 0.1 | — |
| 137 | 26 | 32400 | 3.25 | 0.237 | 0.33 | 0.271 | 0.028 | 0.271 | 0.1 | — |
| 91 | 26 | 3600 | 3.33 | — | — | 0.496 | 0.041 | 1.15 | 0.1 | — |
| *Acetone and chloroform* | | | | | | | | | | |
| 142 | 30 | 3600 | 1.85 | 1.44 | — | 0.438 | 1.61 | 0.274 | 9.8 | 0.67 |
| 145 | 28 | 3600 | 1.81 | 1.36 | 0.03 | 0.315 | 0.679 | 0.479 | 3.1 | 0.22 |
| 143 | 31 | 3600 | 1.71 | 1.36 | 0.27 | 0.462 | 0.935 | 0.654 | 3.7 | 0.26 |
| 144 | 30 | 3600 | 1.91 | 1.34 | 1.22 | 0.407 | 0.804 | 0.545 | 3.4 | 0.25 |

parable amounts of ammonia suppress only partly the additional formation of methane and further additions of ammonia, up to relatively large concentrations, fail to produce any further inhibition. It may be justifiable to assume that under these conditions the part of the effect due to the presence of hydrogen chloride is completely inhibited. The residual effect can then be ascribed to the reaction

$$(12)\quad CH_3 + CHCl_3 \rightarrow CH_4 + CCl_3,$$

and the approximately constant value of $\gamma_{CHCl_3} = 0.24 \times 10^{-11}$ can be identified with $k_{12}/k_2^{1/2}$. Assuming as plausible values (3) $P_2 = 1$ and $E_2 = 0$ and taking mean collision diameters of 3.5 Å and 5 Å for $CH_3$ and $CHCl_3$ respectively, a collision yield of $10^{-7}$ is obtained for reaction (12) at 30°C. The upper limit for $E_{12}$ is then found to be 9.6 kcal. per mole corresponding to a steric factor of unity, or $E_{12} = 6.8$ kcal. per mole if $P_{12} = 10^{-2}$. Since at 150° $k_{12}/k_2^{1/2} \leqslant \gamma_{CHCl_3}$, a comparison of the total effect observed at 150° and the inhibited effect at 30° shows that $E_{12}$ is smaller than about 8 kcal. per mole. It is thus evident that the previously reported (7) trend in the values of activation energies for hydrogen abstraction reactions for the series of chlorinated methanes is at least quali-

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tatively correct. A hydrogen atom is more easily abstracted as the number of chlorine atoms substituted in the molecule of methane increases.

Further experiments are in progress with methyl chloride and other halogenated methanes.

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# THE PAPILIONACEOUS ALKALOIDS
## XVIII. *LUPINUS SERICEUS* PURSH.[1]

By Léo Marion, Nelson J. Leonard, and Barry P. Moore[2]

ABSTRACT

The plant investigated has been found to contain at least five alkaloids, three of which, *l*-sparteine, *d*-lupanine, and *d*-α-isolupanine, are of known structure. The remaining two are both isomeric with hydroxylupanine. One of these, lupilaxine, was identical with a base previously reported as occurring in *Lupinus laxus*. The other, lupanoline, appeared to be new. Both these alkaloids were shown by their infrared absorption spectra to contain, like hydroxylupanine, one hydroxyl group and one carbonyl.

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It has been reported by Couch (3) that *Lupinus sericeus* Pursh. contains the alkaloids spathulatine and nonalupine. These, however, have since been shown to be identical and to consist of the monohydrate of pusilline monohydrochloride (4). In order to investigate the structure of pusilline a quantity of plant material tentatively identified as *L. sericeus* Pursh. was obtained through the courtesy of S. B. Penick and Company. Some doubt was raised concerning the identity of this plant when it was found to contain no pusilline. Couch had also investigated a closely related plant, *L. sericeus* var. *flexuosus* C. P. Smith, in which he found octalupine (2) later shown to be identical with hydroxylupanine (5). This base did not occur in the plant under investigation in which five different alkaloids have now been isolated. Owing to the impossibility so far of procuring more of this plant, and to the importance of the alkaloids found in it, the work is reported without further delay in spite of its uncertain identity.

Of the alkaloids isolated from this plant there are two (*l*-sparteine and *d*-lupanine) which are well known, one (*d*-α-isolupanine) which has been reported for the first time recently (7), and two which are isomeric with hydroxylupanine but not identical with it. It is noteworthy that *d*-α-isolupanine and matrine, which are isomeric, show a striking similarity in their properties and those of their salts, although the latter is now known to possess a quite different structure (8). One of the two isomers of hydroxylupanine has been shown by direct comparison (melting points and X-ray powder patterns) with an authentic sample to be identical with the "isomer of hydroxylupanine" previously isolated by Couch[3] from *Lupinus laxus* (1); it is therefore proposed to designate it as lupilaxine. Its infrared absorption spectrum showed absorption peaks at 3623 cm.$^{-1}$ and 1628 cm.$^{-1}$ indicative respectively of a hydroxyl group and a lactam carbonyl. Attempts to form an anhydro-base or a benzoyl derivative both failed.

The second isomer of hydroxylupanine found in this plant appears to be new and it is proposed to designate it as lupanoline. The bulk of it crystallized readily from an acetone solution of the crude mixture of alkaloids. It gave rise to a monohydrochloride and a methiodide. Although the melting points of the base

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[2] *National Research Council of Canada Postdoctorate Fellow (1950-51).*
[3] *The alkaloid isolated from L. laxus was generously given to us by Dr. James F. Couch not long before his death, together with all his samples of lupine alkaloids.*

and its monohydrochloride were practically the same as those of hydroxylupanine and its corresponding salt, admixture caused strong depressions. Furthermore, the infrared absorption spectra of the two bases were quite different although they offered some points of similarity. The spectrum of lupanoline showed absorption peaks at frequencies indicative of the presence of both a lactam carbonyl and a hydroxyl group. No functional derivative involving the hydroxyl group could be prepared.

Lupanoline is a derivative of $\beta$-isosparteine[4] and therefore the plant investigated affords the first example of one containing alkaloids derived from all three stereoisomers of the sparteine structure (6).

## EXPERIMENTAL[5]

The plant was collected in the late blooming stage in the northern part of the State of Washington. Dried and ground it weighed 9308 gm. It was extracted with methanol and the extract concentrated on the steam bath. The concentrated extract was diluted with twice its volume of water, made acid to Congo red with hydrochloric acid, and heated on the steam bath for one hour. The mixture was cooled first to room temperature, then in the refrigerator, and filtered with suction. The insoluble cake was heated with dilute hydrochloric acid for one hour, cooled as before, and filtered. Both filtrates were combined and diluted with water; this caused the precipitation of a gum which was removed by filtration through filter-cel. This last filtrate was extracted repeatedly with large volumes of ether, alkalized with ammonia, and thoroughly extracted with chloroform. To the aqueous liquor was added a concentrated potassium hydroxide solution and the strongly basic liquor was again extracted with chloroform. The chloroform extracts were combined and the solvent distilled off under reduced pressure. To remove the last of the chloroform, a little methanol was added to the residue which was heated on the steam bath under reduced pressure. There was left a thick basic syrup (wt. 92.3 gm.) consisting of the crude alkaloids.

### *Lupanoline*

The crude alkaloid syrup was dissolved in acetone and the solution allowed to stand in the refrigerator for several days during which a crystalline deposit gradually formed. The crystalline substance was filtered and recrystallized repeatedly from acetone from which it separated as colorless stout prisms, m.p. 174–176°. $[\alpha]_D^{23}+ 31° \pm 1$ ($c$, 0.726 in ethanol), $+ 64.4° \pm 0.8$ ($c$, 0.88 in water). Calcd. for $C_{15}H_{24}O_2N_2$: C, 68.14; H, 9.15; N, 10.60. Found: C, 69.06, 68.93; H, 8.94, 8.75; N, 10.86, 10.78% (dried *in vacuo* at 100°). Sublimation did not alter the analytical results. When exposed to a moist atmosphere it formed a hydrate. In admixture with hydroxylupanine the melting point was markedly decreased. Wt. 6 gm.

A small quantity of lupanoline was dissolved in methanol and the solution made just acid to Congo red with methanolic hydrochloric acid. The solution was evaporated to dryness and the residue dissolved in boiling acetone from which the hydrochloride separated in beautiful colorless prisms. After one recrystallization

[4] *Moore, B. P. and Marion, L. Can. J. Chem. 31: 187-92. 1953.*
[5] *All melting points are corrected.*

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from acetone–methanol it melted at 275–276°. Calcd. for $C_{15}H_{24}O_2N_2.HCl$: C, 59.90; H, 8.38; N, 9.32. Found: C, 60.49, 60.64; H, 8.27, 8.31; N, 9.42, 9.39%.

The methiodide, prepared by boiling the base with acetone and methyl iodide, was recrystallized from methanol. It consisted of long colorless needles, m.p. 230–231°. Calcd. for $C_{15}H_{24}O_2N_2.CH_3I$: C, 47.30; H, 6.70; N, 6.90. Found: C, 47.37, 47.21; H, 6.31, 6.43; N, 7.78, 7.74%.

The acetone mother liquor from which lupanoline had crystallized was evaporated to dryness and the residue dissolved in dilute hydrochloric acid. The acid solution was thoroughly extracted with ether, alkalized with strong aqueous potassium hydroxide, and extracted with chloroform, first in a separatory funnel and then in a continuous liquid–liquid extractor. The extracts were combined except for a quantity of the first separatory funnel extract which was evaporated to dryness and used for chromatographic separation. The bulk of the extract was distilled on the steam bath to remove most of the solvent while the last traces were removed by azeotropic distillation with methanol.

A quantity (3 gm.) of the crude base reserved for chromatography was dissolved in benzene (200 ml.) and the solution passed through a column of 60 gm. of alumina. The elution was made with (*a*) 200 ml. of benzene (10 fractions), (*b*) 300 ml. of 50–50 benzene–ether (7 fractions), (*c*) 200 ml. of ether (3 fractions), (*d*) 300 ml. of 95–5 ether–methanol (3 fractions), and (*e*) 200 ml. of 90–10 ether–methanol (3 fractions). Twenty-six fractions were thus collected. The first four fractions contained negligible quantities of base and were discarded. Fractions 5, 6, and 7 were combined (582 mgm.) and fractionated by distillation *in vacuo* into: fraction (*a*), b.p. 117–126° at 0.1 mm., faintly yellow oil; fraction (*b*), b.p. 125–145° at 0.1 mm., faintly yellow oil, and a residual reddish resin.

*l-Sparteine*

Fraction (*a*) was divided into two portions. One of these was added to methanolic picric acid and the crystalline picrate that separated was recrystallized from methanol. It consisted of fine yellow needles, m.p. 207–208° either alone or in admixture with *l*-sparteine dipicrate.

The second portion of fraction (*a*) was dissolved in methanol and perchloric acid was added dropwise to a phenolphthalein end point. A crystalline perchlorate separated which after two recrystallizations from methanol–ether consisted of colorless needles melting at 173° either alone or in admixture with *l*-sparteine perchlorate. In admixture with *d*-sparteine perchlorate it began to soften at 133° and melted over a wide range. *l*-Sparteine constitutes about 15% of the alkaloid mixture after removal of lupanoline.

*d-α-Isolupanine*

Fraction (*b*) from the distillation proved to consist of the same alkaloid, although less pure, as that obtained from fraction 8 of the chromatogram. The latter yielded a crystalline base which after two recrystallizations from petroleum ether consisted of colorless needles, m.p. 70–72°, unchanged when mixed with *d*-α-isolupanine (7). After purification through the perchlorate the base melted at 75–76°. $[\alpha]_D^{26} + 39° \pm 1$ (*c*, 0.774 in water). The infrared absorption spectrum of the purified base was exactly superposable on that of *d*-α-isolupanine (7).

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The perchlorate of the base was prepared in methanol by the dropwise addition of 72% perchloric acid to a Congo red end point. Ether was then added to incipient cloudiness and the solution cooled in the refrigerator. The perchlorate after two recrystallizations from methanol–ether consisted of colorless elongated prisms, m.p. 239° (uncorr.) alone or in admixture with *d*-α-isolupanine perchlorate (6, 7).

A small quantity of the base was dissolved in ethanol–ether and the solution neutralized by the dropwise addition of concentrated hydrochloric acid. The solution was evaporated to dryness and the residue dissolved in ethanol–ether from which the hydrochloride separated as very small colorless prisms which softened at 148° and melted over a range.

The picrate of the base was prepared as previously described (7). It melted at 196–198° either alone or in admixture with *d*-α-isolupanine picrate.

To a solution of the base in absolute ethanol was added a solution of auric chloride in absolute ethanol containing a few drops of concentrated hydrochloric acid. On standing overnight the solution deposited the chloroaurate in clusters of elongated prisms which after two recrystallizations from absolute ethanol containing a few drops of hydrochloric acid melted at 195.5–196.5° when immersed at 175°.

The chloroplatinate was prepared from a solution of the base in absolute ethanol containing a few drops of hydrochloric acid by the addition of chloroplatinic acid. It consisted of short orange prisms, m.p. 241–243°.

Fractions 9 to 15 of the chromatogram also contained *d*-α-isolupanine. It was found that the alkaloid could be obtained pure when the base recovered from the chromatogram fractions was first washed with ether which dissolved the α-isolupanine while a gummy impurity remained undissolved. The base recovered from the ether solution, after recrystallization from petroleum ether, consisted of pure *d*-α-isolupanine.

Fraction 22, eluted with ether containing 5% methanol, consisted after evaporation of the solvent of sticky crystals which crystallized from acetone as colorless stout prisms, m.p. 169–170°. In admixture with lupanoline (m.p. 174–176°) the melting point was unchanged. This fraction (500 mgm.) consisted mostly of lupanoline.

*d-Lupanine*

A quantity of the crude base was warmed with shaking with petroleum ether and the mixture allowed to settle. The clear solution was poured off and the residue warmed again repeatedly with fresh portions of petroleum ether until the residue left by evaporation of the solvent was negligible. The base recovered by evaporation of the combined petroleum ether extracts will be designated crude base *A* and the residue insoluble in petroleum ether, crude base *B*.

Crude base *A* was fractionated *in vacuo* into fraction I, b.p. 90°–100° at 0.15 mm., fraction II, b.p. 110°–140° at 0.15 mm., and a small undistilled residue. Fraction I consisted of *l*-sparteine. It was converted to the dipicrate, m.p. 208°, and to the perchlorate, m.p. 173°.

Fraction II was dissolved in methanol and the solution neutralized to Congo red by the dropwise addition of 72% perchloric acid. The perchlorate which

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crystallized was filtered and recrystallized twice from methanol–ether, m.p. 197–198°. It was dissolved in water, the solution alkalized with ammonia and exhaustively extracted with chloroform. The oily base recovered from the extract by evaporation of the solvent was redistilled; it boiled at 125–138° at 0.2 mm. Part of the distillate was dissolved in methanol and converted to the perchlorate as before. The crystalline perchlorate was filtered and recrystallized from methanol–ether from which it separated as colorless feathery aggregates, m.p. 211° either alone or in admixture with *d*-lupanine perchlorate.

The remainder of the distilled base was dissolved in water and a stoichiometrical proportion of ammonium thiocyanate in water was added. The resulting solution was evaporated to dryness and the residue crystallized from boiling acetone. When immersed in a bath at 155° the base thiocyanate liquefied but immediately resolidified and melted at 183°. When heated slowly from about 100°, it melted at 180°. Admixture with *d*-lupanine thiocyanate did not alter the melting point behavior.

The original mother liquor from the crystallization of *d*-lupanine perchlorate when allowed to evaporate slowly at room temperature deposited crystals which after two recrystallizations from methanol consisted of colorless prisms, m.p. 231–233°, unaltered by admixture with *d*-α-isolupanine perchlorate.

*Lupilaxine*

Crude alkaloid *B* which was insoluble in petroleum ether was distilled *in vacuo*. About two-thirds of the material distilled at 140–180° at 0.3 mm., as a pale yellow oil while the residue consisted of a dark resin. Since the distillate failed to crystallize from acetone it was dissolved in benzene and chromatographed on alumina. It was eluted with benzene, benzene–ether, ether, and finally ether containing 5% of methanol. The base obtained by evaporation of the ether–methanol eluate crystallized; that obtained from the ether fraction partly crystallized on seeding with the first crystals but consisted in part of an oily product. The oily base when distilled *in vacuo* afforded a fraction, b.p. 170–175° at 0.4 mm., which soon crystallized. The benzene eluate also yielded a quantity of this crystalline base. The various portions of crystalline base were combined and recrystallized from acetone from which it separated as colorless prisms, m.p. 175° (wt. 0.85 gm.). This base gave large depressions in melting point when mixed with lupanoline or with hydroxylupanine. However, the melting point was unaltered when the base was mixed with a sample of the isomer of hydroxylupanine isolated by Couch (1) from *Lupinus laxus* Rydb. The infrared absorption spectrum of the base showed the presence of a hydroxyl group and a carbonyl group (absorption bands at 3623 cm.$^{-1}$ and 1628 cm.$^{-1}$). The X-ray powder patterns of lupilaxine and of the "isomer of hydroxylupanine" isolated by Couch were exactly superposable.

ACKNOWLEDGMENT

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Division of these laboratories for the X-ray powder patterns.

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# THE PAPILIONACEOUS ALKALOIDS
## XIX. THE STRUCTURE OF LUPANOLINE[1]

By Barry P. Moore[2] and Léo Marion

ABSTRACT

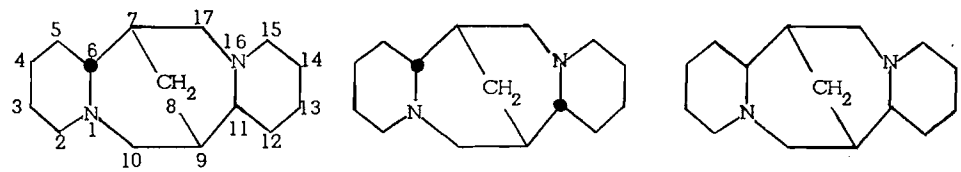
Lupanoline which contains both a carbonyl and a hydroxyl group was reduced by lithium aluminum hydride to β-isosparteine. The identity of β-isosparteine was established by its conversion into sparteine by dehydrogenation and subsequent rehydrogenation. Attempts to acylate lupanoline resulted in the formation of anhydrolupanoline which was hydrogenated to dihydroanhydrolupanoline, a compound also obtained by the direct oxidation of β-isosparteine. It is concluded that lupanoline is 2-hydroxy-17-oxo-β-isosparteine.

The alkaloid lupanoline, the occurrence of which has been reported recently (4), is an isomer of hydroxylupanine, $C_{15}H_{24}O_2N_2$. It behaves as a monoacidic base, giving rise to a monohydrochloride and a monomethiodide so that one of its two nitrogens is neutral. The infrared absorption spectrum of lupanoline shows absorption peaks at 3591 cm.$^{-1}$ and 1624 cm.$^{-1}$ corresponding to a hydroxyl group and a carbonyl respectively, and thus accounting for both oxygen atoms.

The carbonyl group of lupanoline is inert towards the usual ketone reagents and is apparently lactamic in character. The presence of a nonbasic nitrogen in the molecule and the location of the carbonyl absorption band in the infrared spectrum support this conclusion. The hydroxyl group could not be acylated. Under the wide variety of conditions investigated, the group was invariably eliminated with the formation of anhydrolupanoline, $C_{15}H_{22}ON_2$, a substance which regenerated lupanoline on treatment with mineral acids. This characteristic behavior of the hydroxyl group of lupanoline is noteworthy.

Reduction of lupanoline with lithium aluminum hydride in dioxane proceeded smoothly, leading to the complete removal of oxygen from the molecule with the production of an oily base, $C_{15}H_{26}N_2$. Hence the reaction involved not only the conversion of the carbonyl to a methylene group thus confirming its lactamic nature, but also involved the reductive elimination of the hydroxyl. The reduction product was identical neither with sparteine nor with α-isosparteine although isomeric with them, and it appeared possible that it might be the so far unknown β-isosparteine.

It has already been shown (2, 3) that of the three possible stereoisomeric forms I, II, and III of the sparteine structure two represent sparteine and




I II III

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[2] *National Research Council of Canada Postdoctorate Fellow, 1950–1951.*

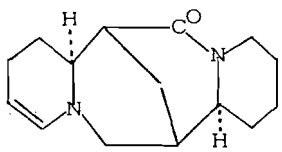
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$\alpha$-isosparteine. In formula I which represents sparteine the $C_6$-hydrogen is *cis* to the 7,9-methylene bridge whereas the $C_{11}$-hydrogen is *trans*. In $\alpha$-isosparteine (II) both the $C_6$-hydrogen and the $C_{11}$-hydrogen are *cis* to the 7,9-methylene bridge (3). This structure which was assigned to $\alpha$-isosparteine on the basis of hydrogenation results (3) has since been confirmed by a detailed X-ray crystallographic examination (5). $\beta$-Isosparteine should then be represented by III in which both the $C_6$-hydrogen and the $C_{11}$-hydrogen are *trans* to the 7,9-methylene bridge. Winterfeld and Rauch (6) converted sparteine into $\alpha$-isosparteine by dehydrogenation with mercuric acetate, which removed two moles of hydrogen, and subsequent rehydrogenation. This conversion must therefore have resulted from the elimination of the *cis* $C_6$-hydrogen and the *trans* $C_{11}$-hydrogen, and their replacement both in the *cis* position. The same reaction should convert $\beta$-isosparteine to $\alpha$-isosparteine if it removed two moles of hydrogen, or to sparteine if it removed only one mole. The reduction product of lupanoline was therefore oxidized with mercuric acetate and immediately rehydrogenated catalytically. The quantity of precipitated mercurous acetate corresponded to one mole of hydrogen, and the base obtained after rehydrogenation was identical with *l*-sparteine. Hence, the reduction product is $\beta$-isosparteine and lupanoline is an hydroxy-oxo-$\beta$-isosparteine.

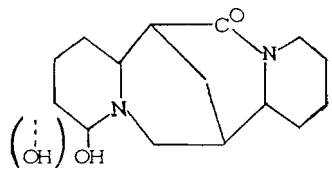
Information as to the positions of the substituents in lupanoline has been derived from a study of anhydrolupanoline and its derivatives. Anhydrolupanoline was readily hydrogenated over Adams' catalyst to yield the saturated dihydroanhydrolupanoline, $C_{15}H_{24}ON_2$, which had the composition of an oxosparteine, and could be prepared by the direct oxidation of $\beta$-isosparteine with alkaline potassium ferricyanide. By analogy with the similar oxidation of sparteine to oxosparteine, it is reasonable to assume oxidation to have occurred at the 17-position (or equivalent 10-position) in $\beta$-isosparteine (III). Dihydroanhydrolupanoline could also be obtained directly from lupanoline by catalytic hydrogenation in acid solution. The failure of the carbonyl to reduce under these conditions also militates in favor of its occupying the 17-position.

On reduction with lithium aluminum hydride, anhydrolupanoline afforded an unstable oily dehydro-base which was readily converted to $\beta$-isosparteine on catalytic hydrogenation. No stereochemical inversion, therefore, is involved in the series: lupanoline $\rightarrow$ anhydrolupanoline $\rightarrow$ dehydro-$\beta$-isosparteine $\rightarrow$ $\beta$-isosparteine. Thus it is clear that, if the possibility of migration be discounted, the double bond of anhydrolupanoline and the hydroxyl group of lupanoline itself cannot involve an angular position. The characteristic properties of the hydroxyl group (ready elimination and reduction) suggest association with a basic center in the form of an aldehyde-ammonia. The reductive elimination of the hydroxyl by lithium aluminum hydride particularly is indicative of such a grouping. The formulation of lupanoline as an aldehyde-ammonia is supported by the facile rehydration of anhydrolupanoline to the parent alkaloid under the influence of mineral acid. Thus anhydrolupanoline would appear to be best formulated as IV and lupanoline as 2-hydroxy-17-oxo-$\beta$-

isosparteine (V). An alternative formulation with a 10-hydroxyl group is



IV



V

considered unlikely as the preparation of an anhydro-base from such a system would require the formation of a double bond at a bridge head, in violation of Bredt's rule. Whether the hydroxyl group at the 2-position is *cis* or *trans* is not yet known.

Lupanoline is thus the first alkaloid known to be derived from β-isosparteine. The hitherto unknown β-isosparteine prepared from it is an oil which like sparteine discolors on standing in air. It has not yet been possible to induce its picrate to crystallize, but like its two other stereoisomers it forms a crystalline perchlorate. For the infrared absorption spectrum of β-isosparteine and the spectra of its two stereoisomers see Fig. 3, Ref. (1).

Anhydrolupanoline and its hydrogenation product are isomers of monspessulanine and dihydromonspessulanine, and their melting points are about the same. However, admixture with authentic samples of these two bases caused depressions in the melting points, and the infrared absorption spectra were quite distinct from those of the two derivatives of lupanoline. The sample of monspessulanine was kindly given to us by Dr. E. P. White.

## EXPERIMENTAL[3]

Lupanoline has been described previously (4). It melts at 174–176° and has $[\alpha]_D^{26} + 64.4° \pm 0.8$ (*c*, 0.88 in water). It forms a monohydrochloride, m.p. 275–276°, and a methiodide, $C_{15}H_{24}O_2N_2.CH_3I$, m.p. 230–231°. Its infrared absorption spectrum showed absorption peaks at 1624 cm.$^{-1}$ and 3593 cm.$^{-1}$ indicating the presence of a lactam carbonyl and a hydroxyl group respectively.

### *Reduction of Lupanoline with Lithium Aluminum Hydride*

A solution of lupanoline (250 mgm.) in pure, dry dioxane (5 ml.) was treated with an ethereal solution of lithium aluminum hydride (3 ml., 0.016 gm. per mole, 1.3 moles) and the mixture refluxed in an atmosphere of nitrogen for four hours (the ether being allowed to escape). The mixture was cooled, treated with a little ethanol to destroy excess hydride, and then acidified with dilute hydrochloric acid. The solution was freed from nonbasic impurities by extraction with ether and alkalized with aqueous potassium hydroxide. The liberated base was extracted with ether and after evaporation of the extract was distilled *in vacuo*. The main fraction afforded β-isosparteine as a colorless oil, b.p. 110–120° (air bath) at 1 mm., which gave a crystalline diperchlorate crystallizing from methanol as colorless prisms, m.p. 255° (dec.). Calcd. for

[3] *All melting points are corrected.*

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$C_{15}H_{26}N_2.2HClO_4$: C, 41.38; H, 6.48; N, 6.43. Found: C, 41.36, 41.22; H, 6.28, 6.55; N, 5.95%.

*Conversion of β-Isosparteine to Sparteine*

A mixture of β-isosparteine (234 mgm., 1 mM.), 5% aqueous acetic acid (35 ml.), and mercuric acetate (2.5 gm., 8 mM.) was stirred under an atmosphere of nitrogen and heated on a water bath for three hours. The mixture was cooled and the crystalline mercurous acetate collected by filtration (1 mM. obtained ≡ 2H). The clear aqueous solution was saturated with hydrogen sulphide and the precipitated mercuric sulphide filtered off. The aqueous filtrate was evaporated *in vacuo* to a small bulk, diluted with water, and evaporated again in order to ensure complete removal of hydrogen sulphide. The concentrated liquor was alkalized with aqueous sodium hydroxide and extracted with chloroform. The washed chloroform extract was dried rapidly over anhydrous potassium carbonate, filtered, added to glacial acetic acid (7 ml.), and the resulting solution heated on a steam bath until all the chloroform had evaporated. Since the dehydro-base thus obtained was not stable it was not isolated from the acetic acid concentrate, but was hydrogenated directly over fresh Adams' catalyst for 12 hr. The hydrogen uptake (ca. 40 ml.) corresponded approximately to 2H. After filtration the solution was alkalized with aqueous sodium hydroxide and extracted with chloroform. Evaporation of the chloroform extract yielded a base which was distilled; it consisted of a colorless oil (80 mgm.), boiling at 0.4 mm. at an air bath temperature of 95–105°, which did not crystallize. The dipicrate of this base, which crystallized from a solution of the components in methanol, was recrystallized from methanol. It consisted of bright yellow needles, m.p. 209°, undepressed in admixture with authentic *l*-sparteine dipicrate. The infrared absorption spectrum taken as a Nujol mull was identical with that of *l*-sparteine dipicrate measured under the same conditions.

*Anhydrolupanoline*

A solution of lupanoline (500 mgm.) in purified acetic anhydride (3 ml.) was refluxed for one hour, cooled, and treated with cold water. It was extracted twice with ether and alkalized with aqueous sodium hydroxide. The liberated base was extracted with ether, recovered from the extract by evaporation of the solvent, and distilled *in vacuo*. Anhydrolupanoline was thus obtained as a colorless oil, b.p. 145–150° at 0.1 mm., which crystallized readily from ligroin (60–80°) in colorless prisms, m.p. 94–95°, yield 315 mgm. Recrystallization did not alter the melting point. $[\alpha]_D^{24} - 43.1° \pm 1$ (*c*, 0.58 in water). Calcd. for $C_{15}H_{22}ON_2$: C, 73.13; H, 9.01. Found: C, 73.15, 73.30; H, 9.03, 8.85%. In admixture with monspessulanine (m.p. 100°) of which it is an isomer it melted at 65–70°. Admixture with aphyllidine also caused a depression.

Anhydrolupanoline formed a perchlorate in the usual way which separated from methanol as colorless, elongated prisms, m.p. 252–253° (dec.). $[\alpha]_D^{26} - 57° \pm 1$ (*c*, 0.912 in water). Calcd. for $C_{15}H_{22}ON_2.HClO_4$: C, 51.94; H, 6.68; N, 8.08. Found: C, 51.77; H, 6.68; N, 7.71%.

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*Dihydroanhydrolupanoline*

Anhydrolupanoline (100 mgm.) was hydrogenated in ethanol (10 ml.) at room temperature and atmospheric pressure in the presence of freshly prepared Adams' catalyst (50 mgm.). Hydrogenation proceeded rapidly and was essentially complete within 15 min. After one hour (hydrogen uptake ca. 15 ml.) the mixture was filtered and the filtrate evaporated on a steam bath. The residual dihydroanhydrolupanoline crystallized readily from ligroin (60–80°) in colorless sheaves, m.p. 103–104° (yield 70 mgm.). Calcd. for $C_{15}H_{24}ON_2$: C, 72.51; H, 9.74; N, 11.28. Found: C, 72.56, 72.78; H, 9.59, 9.58; N, 11.15%. The infrared absorption spectrum of the base was not identical with that of the isomeric dihydromonspessulanine.[4]

A small quantity of the base was dissolved in methanol and the solution made just acid to Congo red by the dropwise addition of 67% perchloric acid. On standing the solution deposited a crystalline perchlorate which after several recrystallizations from methanol consisted of colorless prisms, m.p. 224–225°. Calcd. for $C_{15}H_{24}ON_2.HClO_4$: C, 51.65; H, 7.17. Found: C, 51.61, 51.72; H, 6.84, 6.75%.

*Action of Mineral Acid on Anhydrolupanoline*

A solution of anhydrolupanoline (100 mgm.) in *N* hydrochloric acid was heated to 100° for two hours, then cooled and alkalized with aqueous sodium hydroxide. The product, isolated by extraction with chloroform, crystallized from ligroin (60–80°) in colorless rhombs, m.p. 163–167° (65 mgm.). Two recrystallizations raised the melting point to 169–170° (with previous shrinking). The material gave no depression in melting point on admixture with pure lupanoline. Calcd. for $C_{15}H_{24}O_2N_2$: C, 68.14; H, 9.15; N, 10.60. Found: C, 67.53, 67.83; H, 9.27, 8.91; N, 10.50%. This base was converted by the action of lithium aluminum hydride into β-isosparteine which was identified as its perchlorate. It is thus identical with lupanoline but probably contains a trace of an isomer sufficient to cause the unsharp melting point behavior.

*Reduction of Anhydrolupanoline with Lithium Aluminum Hydride*

Anhydrolupanoline (100 mgm.) in dry ether (10 ml.) was treated with ethereal lithium aluminum hydride (1 ml., 0.015 gm. per ml.) and the mixture refluxed for four hours. Water was then added cautiously, followed by aqueous sodium hydroxide, and the product isolated with ether. A portion of the oily base thus obtained decomposed on attempted distillation *in vacuo* and formed an oily perchlorate. The remainder of the product was hydrogenated in acetic acid solution over fresh Adams' catalyst for 12 hr. The basic product, isolated in the usual way, distilled as an oil, b.p.110–120° (air bath) at 0.2 mm. The diperchlorate, m.p. 255° (dec.), proved to be identical with that of β-isosparteine.

*Oxo-β-isosparteine*

β-Isosparteine (freshly distilled, 130 mgm.) was shaken vigorously with

[4] *Dihydroanhydrolupanoline is also obtainable directly by catalytic hydrogenation of lupanoline. This experiment as well as the comparison with dihydromonspessulanine was carried out by Dr. Bryce Douglas.*

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cold water (25 ml.), the resulting suspension treated with a solution of potassium ferricyanide (660 mgm.) and potassium hydroxide (60 mgm.) in water (10 ml.) and shaken mechanically for one hour. The resulting straw-colored solution was allowed to stand overnight at room temperature, and then extracted with chloroform. The crude base obtained by evaporation of the chloroform extract was distilled *in vacuo* and afforded a pale yellow oil (35 mgm.), b.p. 135–140° (air bath) at 0.5 mm., together with a considerable nonvolatile residue. The distillate was dissolved in ligroin (60–80°), the solution filtered, evaporated to a small bulk, and allowed to stand. Oxo-β-sparteine crystallized which after recrystallization from ligroin (60–80°) consisted of colorless sheaves, m.p. 103–104°, undepressed on admixture with a specimen of dihydroanhydrolupanoline.

ACKNOWLEDGMENT

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# THE ESSENTIAL OIL OF *ABIES BALSAMEA* (L.) MILL.[1]

By A. C. Shaw

ABSTRACT

Foliage of *Abies balsamea* yielded 0.591% of an essential oil comprised of *l*-β-pinene, *l*-bornyl acetate, *d*-$\Delta^3$-carene, *l*-limonene, *l*-α-pinene, *l*-camphene, myrcene, santene, tricyclene, *l*-camphor, *l*-borneol, *d*-canadene, bisabolene, terpinolene, and a compound related to S-guiaiazulene.

## INTRODUCTION

*Abies balsamea* (L.) Mill., or balsam fir, is one of the most prolific species in Eastern and Central Canada. It ranges from the Atlantic coast of Canada westward and northward to northeastern Alberta, and is cut extensively for both pulp and lumber. The essential oil of *A. balsamea* has been reported (4) to contain 17.6% bornyl acetate, and probably *l*-α-pinene. More recently an essential oil prepared from Canada balsam (12) was reported to contain *l*-α-pinene, *l*-β-pinene, and *l*-β-phellandrene. However it is probable that this latter oil, since it had an ester value of only 2.24, was actually a turpentine oil of balsam fir, and that the needle oil of *A. balsamea* has not previously been examined in detail.

## EXPERIMENTAL

### *Preparation of the Essential Oil*

Steam at 90 p.s.i. was admitted at the rate of 10 lb. per min. for six hours, to a cylindrical wooden still at atmospheric pressure containing 2960 lb. of foliage and terminal branches of *A. balsamea* which were collected and distilled in April, 1948. Because of heat losses and the large heat capacity of the charge, effluent steam from the still was in general saturated, and heat-sensitive compounds were not exposed to temperatures much in excess of 100°. The oil, obtained in a yield of 0.591%, had the following properties: $\eta_D^{20}$ 1.4737, $d_{20}^{20}$ 0.8825, $\alpha_D^{30}$ − 18.8°, acid value 0.23, ester value 52.4, ester value after acetylation 77.2, aldehyde and ketone value, nil.

### *Fractional Distillation of the Oil*

The oil was fractionated according to the scheme shown in Fig. 1. The preliminary distillation, yielding the hydrocarbon, oxygen compound, and sesquiterpene fractions, was carried out without reflux through an unpacked column. The sesquiterpenes and higher boiling compounds were fractionated through a 1-ft., 25 mm. I.D. Podbielniak column at 10 mm. pressure, 3 mm. back pressure, and reflux ratio 15/1. For all other distillations a 6-ft., 25 mm. I.D. Podbielniak column was employed at a reflux ratio of 20/1, and 20 mm. back pressure. The properties of the fractions obtained are shown in Figs. 2 and 3. In Fig. 2 the fractions judged to be most nearly homogeneous were assigned letters *a* to *m*.

### *Identification of Constituents*[2]

The oil was found to be qualitatively very similar in composition to oil of *Picea*

[1] *Manuscript received in original form December 21, 1951 and, as revised, November 17, 1952. Contribution from Ontario Research Foundation, 43 Queen's Park, Toronto 5, Ontario.*

[2] *Except where otherwise noted, melting points were determined with a Kofler micro hot stage. The identification of all solid derivatives was confirmed by determination of their melting points in admixture with authentic samples.*

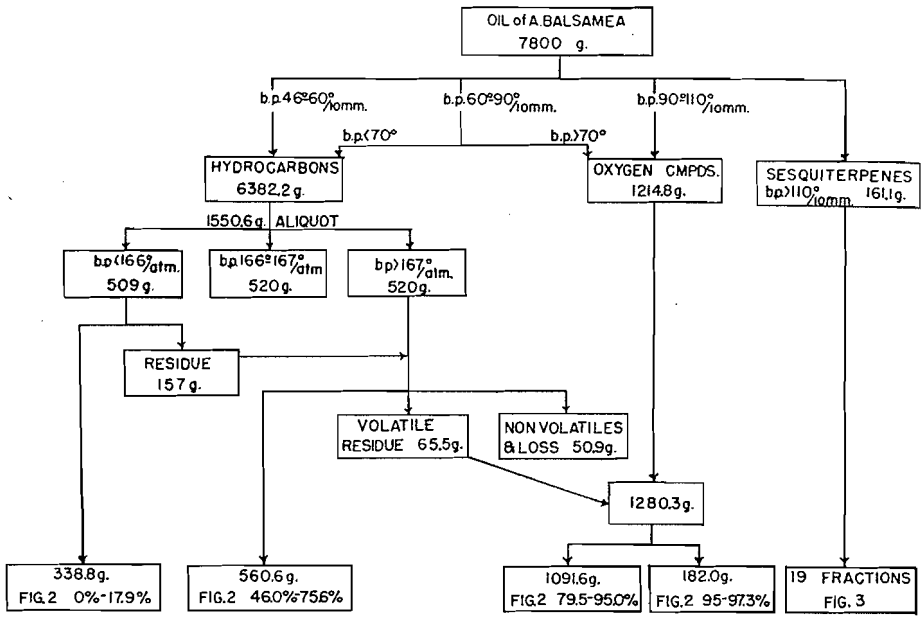



FIG. 1. Fractional distillation of the oil.

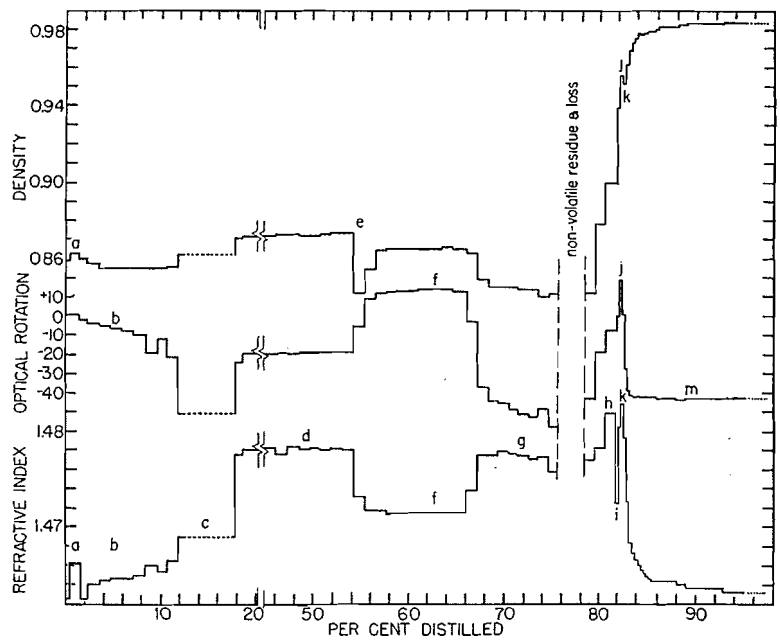



FIG. 2. Properties of fractions boiling below 110°C. at 10 mm.

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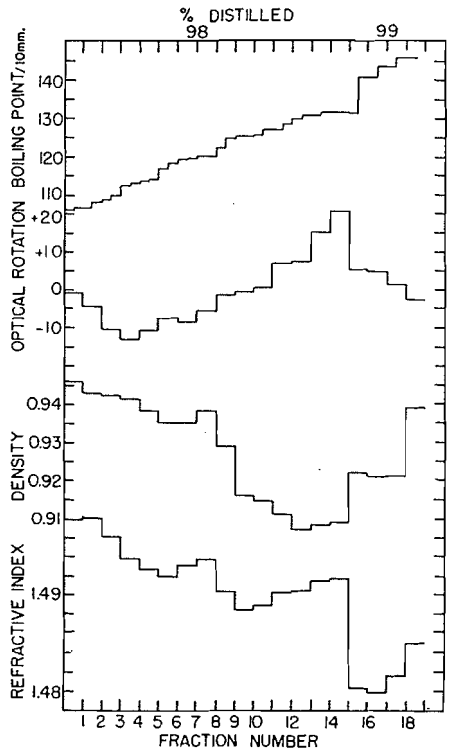



FIG. 3. Properties of fractions boiling above 110°C. at 10 mm.

*mariana* (Mill.) B.S.P. With the exception of the sesquiterpene compounds all constituents were identified by methods described in a previous communication (9) dealing with oil of *P. mariana*.

*Santene and Tricyclene*

Fraction *a* was redistilled at atmospheric pressure, 0.5 mm. back pressure, and reflux ratio 40/1, through the 1-ft. Podbielniak column, to separate two optically inactive compounds, b.p. 139.5°C., $\eta_D^{20}$ 1.4664, $d_4^{20}$ 0.862, and b.p. 151.5–153.0°, $\eta_D^{20}$ 1.4610, $d_4^{20}$ 0.866. The former, when treated with nitrous acid according to Müller (7), gave santene nitrosite m.p. 123–125°C. in 30.9% of theoretical yield. The latter compound was treated for one hour with 10 volumes of 10% aqueous permanganate at 100°C. to remove unsaturated impurities. Unchanged tricyclene, recovered in a current of steam, melted at 65°C. after crystallization from methanol and sublimation from sodium.

*dl-α-Pinene*

By permanganate oxidation (2) of 39.5 gm. of fraction *b* ($\eta_D^{20}$ 1.4648, $d_4^{20}$ 0.855, $\alpha_D$ − 6.03°) 15.02 gm. of crude acids were obtained from which, by repeated crystallization from benzene–hexane mixtures, *dl*-pinonic acid m.p. 104–106°C., $(\alpha)_D^{25}$ − 0.18° ($c$ = 10.88, chloroform) was separated.

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*l-Camphene*

Fraction *c* was a solid, m.p. 43°C., b.p. 160.5°C., $(\alpha)_D$ − 91.3° (*c* = 10.33, benzene). Hydration of 5.0 gm. of this material with Bertram–Walbaum reagent (1) yielded 5.56 gm. of isoborneol, which after crystallization from hexane, melted at 210–213°C. in a sealed capillary.

*l-β-Pinene*

Twenty grams of fraction *d* (b.p. 166.9°C. (758 mm.), $\eta_D^{20}$ 1.4783, $d_4^{20}$ 0.870, $\alpha_D$ − 19.54°) in 200 ml. of acetone was cooled in a freezing mixture, and 48 gm. of powdered potassium permanganate added with mechanical stirring over 16 hr. The manganese dioxide was removed, washed with acetone, and finally extracted six times with 100 ml. volumes of boiling water. When concentrated under reduced pressure to a volume of 75 ml., the aqueous extracts deposited 2.60 gm. of a sparingly soluble potassium salt. The salt was recrystallized from water, and the free acid extracted from an acidified aqueous solution with ether. By crystallization from benzene–hexane mixtures, small needles of *l*-nopinic acid m.p. 126–127°C., $(\alpha)_D^{25}$ − 15.2° (*c* = 6.12, ether) were obtained.

*Myrcene*

Refractionation of fraction *e* gave a liquid b.p. 167.5–168°C. (751 mm.), $\eta_D^{20}$ 1.4720, $d_4^{20}$ 0.820, $\alpha_D$ − 4.60° which reacted with maleic anhydride to give in 39% yield an adduct, m.p. 34–35°C., b.p. 145–155°C. (0.4 mm.). *cis*-4-Isohexenyl-$\Delta^4$-tetrahydrophthalic acid m.p. 123–125°C. was obtained by saponification of the adduct.

*d-$\Delta^3$-Carene*

Five grams of fraction *f* (b.p. 172.0°, $\eta_D^{20}$ 1.4715, $d_4^{20}$ 0.865, $\alpha_D$ + 14.00) was mixed with amyl nitrite (4 gm.) and glacial acetic acid (2 ml.), and to this mixture 3.5 ml. of concentrated nitric acid was added dropwise with ice cooling. After 15 min. the product was precipitated with 10 ml. of methanol. After several precipitations from warm chloroform with methanol, *d*-$\Delta^3$-carene nitrosate (0.45 gm.), m.p. 146°C. with decomposition, was obtained.

*l-Limonene*

Bromination of 10 gm. of fraction *g* (b.p. 177.9°C., $\eta_D^{20}$ 1.4775, $d_4^{20}$ 0.844, $\alpha_D$ − 51.33) in isoamyl alcohol – ether solution yielded 7.2 gm. of solid bromides, which were crystallized from ethanol to give 1.6 gm. of *dl*-limonene tetrabromide. The mother liquors, after concentration and removal of a further quantity of racemate, deposited at − 70°C. 150 mgm. of *l*-limonene tetrabromide m.p. 102–104°C.

*Examination of Fractions h and i*

Fraction *h* (10 gm.) was allowed to stand for one week in an ethanol solution containing excess semicarbazide hydrochloride and sodium acetate. Nonketonic compounds (4.6 gm.) were separated from the crude semicarbazones (2.9 gm.) by steam distillation. The crude semicarbazones deposited 0.69 gm. of crystalline material m.p. 231–233°C. from ethanol, which when mixed with an equal weight of oxalic acid and steam distilled was decomposed to yield 0.02 gm. of *dl*-camphor

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m.p. 178–179°C.; 2,4-dinitrophenyl hydrazone m.p. 167–169°C.

The nonketonic portion was treated with *n*-butyl borate as previously described (9), and liberated *n*-butyl alcohol and nonalcoholic compounds separated from the borate esters (0.65 mgm.) by distillation. By bromination of this distillate 0.11 gm. of terpinolene tetrabromide m.p. 115–116°C. was obtained.

Fraction *i* (15.5 gm.) treated in an analogous manner gave 6.45 gm. of crude semicarbazones yielding camphor with $(\alpha)_D$ — 24.0° ($c$ = 4.99, ethanol) on hydrolysis, and 10.2 gm. of nonketonic compounds from which 4.5 gm. of borate esters were prepared. The alcohol, regenerated by saponification of the combined borate esters of fractions *h* and *i*, boiled at 82–83°C. (10 mm.), $\eta_D^{20}$ 1.4743, and formed a *p*-nitrobenzoate (0.05 gm. from 0.6 gm.) m.p. 105–107°C., $(\alpha)_D$ + 21.02 ($c$ = 0.76, ethanol).

*Examination of Fractions j and k*

Fraction *j* (10.4 gm.) yielded 1.9 gm. of semicarbazone and 8.7 gm. of nonketonic oil. From fraction *k* (13.7 gm.), 4.10 gm. of semicarbazone and 9.6 gm. of nonketonic compounds were obtained. The semicarbazones did not crystallize well from common solvents. Fraction *k* semicarbazones were crystallized from acetonitrile to give 0.43 gm. of a crystalline compound m.p. 205–212°C. The acetonitrile insoluble semicarbazones were crystallized from nitromethane, and 0.36 gm. of a compound m.p. 214–219°C. obtained. Too little material was available to allow crystallization to constant melting point. As the semicarbazones were not hydrolyzed by the action of 1*N* sulphuric acid or oxalic acid at 100°C., the ketone was not isolated or identified.

The combined alcohols of fractions *j* and *k* (9.66 gm.), isolated by means of their borate esters, deposited 0.86 gm. of solid borneol when cooled. The liquid portion, b.p. 91.5–96°C. (12 mm.), $\eta_D^{20}$ 1.4848, $d_4^{20}$ 0.952, $\alpha_D$ — 12.34°, yielded only derivatives of borneol when treated with *p*-nitrobenzoyl chloride, α-naphthyl isocyanate, or phenylisocyanate, and failed to form a solid hydrochloride. This fraction then consists of a mixture of borneol, and an unidentified tertiary alcohol.

*Bornyl Acetate*

Forty grams of fraction *m* ($\eta_D^{20}$ 1.4649, $d_4^{20}$ 0.980, $\alpha_D$ — 43.98) were saponified as previously described (10); and 33.5 gm. of borneol, m.p. 206–207°C., $(\alpha)_D$ — 39.02° ($c$ = 10.89, toluene), and 15 gm. of crude potassium salts obtained. A 20% aqueous solution of 5 gm. of the salts was allowed to percolate through 50 gm. of Amberlite resin IR-120, (hydrogen cycle) and the eluate refluxed briefly to remove carbon dioxide. The Duclaux constants of this solution were 7.0, 7.3, and 7.7, indicating the absence of significant amounts of volatile acids other than acetic. From 4.0 gm. of the salt, 0.5 gm. of acetanilide m.p. 114–115°C. was prepared.

*Dehydrogenation of the Sesquiterpene Fractions*

Only those fractions which appeared to contain a maximum concentration of one constituent were examined. Fractions 4, 6, 9, 10, 15, 17, and 18 were dehydrogenated as follows: A mixture of 1.0 gm. of the oil and 0.10 gm. of palladium–charcoal catalyst (6) was heated under nitrogen, at 200°C. for two hours, then at 245°C. for six hours. The reaction mixture was diluted with

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hexane, filtered, and the filtrate extracted with 5% aqueous sodium hydroxide. Hexane was removed from the extracted filtrate and the residue in 10 ml. of ethanol was refluxed for 15 min. with 1.0 gm. of picric acid. Cadalene – picric acid addition compound m.p. 116–117°C. was obtained in a yield of 700 mgm. from fraction 15, 296 mgm. from fraction 10, and a few crystals from fraction 9. Fraction 17 gave a black product which apparently decomposed during recrystallization as only picric acid m.p. 121°C. was recovered. No picrate forming substances were obtained from fractions 4, 6, or 18.

A further quantity of fraction 17 dehydrogenation product in six volumes of hexane was extracted with two 1-ml. volumes of 85% phosphoric acid at 0°C. as described by Sherndal (11). The phosphoric acid was exhaustively extracted with hexane, diluted with ice water, and extracted with ether. Steam distillation of the ether extract gave 23 mgm. of an intensely blue oil, which when refluxed with 0.5 ml. of ethanol and the calculated weight of *sym*-trinitrobenzene formed black silky needles of S-guiaiazulene-trinitrobenzene addition compound m.p. 145–147°C. The authentic sample of S-guiaiazulene was prepared by dehydrogenation of the fraction b.p. 120°–130°C. (10 mm.) of gurjun balsam oil.

*Sesquiterpene Hydrochlorides*

A solution of 2.4 gm. of fraction 14 in 2.5 ml. of ethyl ether was saturated with dry hydrogen chloride at 0°C., and refrigerated overnight. After evaporation of the ether and removal of oily products on a cold porous tile, 1.1 gm. of hydrochlorides remained. The hydrochloride mixture was separated by crystallization from ethanol, and by mechanical means, into long needles of *l*-cadinene hydrochloride m.p. 138–139°C., and small platelets of bisabolene hydrochloride m.p. 80–81°C. We are indebted to Dr. E. Guenther for the gift of the distilled lime oil residues from which an authentic sample of bisabolene was isolated.

## RESULTS AND DISCUSSION

The approximate composition of oil of *A. balsamea*, as estimated from the distillation data, is as follows:

| Terpenes | | Oxygen compounds | |
|---|---|---|---|
| *l*-β-Pinene | 36.1% | *l*-Bornyl acetate | 14.6% |
| *d*-Δ³-Carene | 11.1% | *l*-Camphor | 0.2% |
| *l*-Limonene | 11.1% | *l*-Borneol | 0.1% |
| *l*-α-Pinene | 8.4% | Alcohol, b.p. 91.5–96°C. (12 mm.) | 0.3% |
| *l*-Camphene | 6.8% | Alcohol, b.p. 82–83°C. (10 mm.) | 0.1% |
| Myrcene | 2.3% | Unidentified ketones | 0.2% |
| Santene | 1.3% | | |
| Tricyclene | 1.3% | Sesquiterpenes | |
| Terpinolene | 0.05% | *d*-Canadene | 0.1% |
| Residue and loss | 3.4% | Bisabolene | 0.1% |
| Unaccounted for | 2.3% | Compound related to S-guiaiazulene | Trace |

The β-pinene content of 36.1% is among the highest recorded for any oil.

Tricyclene has now been identified in the needle oils of *P. mariana* (9), *Tsuga canadensis* (10), and *A. balsamea*. Its place as a normal constituent of coniferous oils appears well established.

If β-phellandrene were present as might be expected from the work of Smith and West (12), it would be found in fraction *f*. This fraction, however, failed to give a solid nitrosite with cold nitrous acid, indicating the absence of significant amounts of α- or β-phellandrene.

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In the absence of a reliable estimate of homogeneity it might be concluded that fraction 15 contains bisabolene, *l*-cadinene, and a third compound responsible for the dextrorotation of the fraction. However, cadalene was obtained in 32.5% yield from fraction 15. Linstead and co-workers (5) obtained cadalene in 50% yield by dehydrogenation of pure *l*-cadinene under comparable conditions. *l*-Cadinene hydrochloride, and a small amount of bisabolene hydrochloride, was obtained in 33.7% of the theoretical yield from fraction 15. Under the same conditions a 64.7% yield of hydrochloride was obtained from a pure *l*-cadinene regenerated from the hydrochloride. Thus if *l*-cadinene were present it would constitute, at a minimum, 60% of the fraction. Since bisabolene, which is optically inactive, is present in detectable quantities, the third constituent responsible for the dextrorotation of the fraction could not amount to more than about 30% of the fraction. Accepting the value of $(\alpha)_D$ — 113.0° for *l*-cadinene, the specific rotation of this third constituent would have to be about + 300° to account for the observed rotation, $(\alpha)_D$ + 22.8°, of fraction 15. Although a compound with this high rotation should be easily recognized, no sesquiterpene with a rotation approaching + 300° is known. More probably the dextrorotation is associated with the precursor of the cadalene and *l*-cadinene hydrochloride. Deussen (3) was first to isolate a dextrorotatory sesquiterpene which gave the hydrochloride of *l*-cadinene. He assigned the misleading name "*d*-cadinene" to this compound. Other workers who have isolated similar fractions have generally referred to the constituent as simply "cadinene" (8). Since the compound is actually a structural isomer of *l*-cadinene (the product of dehydrohalogenation of *l*-cadinene hydrochloride), this nomenclature is not satisfactory. The name "*d*-canadene" was suggested for the dextro sesquiterpene of oil of *Tsuga canadensis* and *P. mariana* (10). The sesquiterpene of *A. balsamea* is probably identical with that of these two latter species.

## ACKNOWLEDGMENT

This investigation was undertaken at the suggestion of Mr. R. N. Johnston, Chief, Division of Research, Department of Lands and Forests, Province of Ontario, and his colleagues, to whom we are also indebted for supplies of plant material. The essential oil was prepared by Mr. J. N. Brown and Dr. T. F. West. The investigation was supported by a grant from the Research Council of Ontario.

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# STUDIES ON RDX AND RELATED COMPOUNDS

## IX. DETERMINATION OF NITRIC ACID AND ACETIC ANHYDRIDE IN BACHMANN LIQUORS[1]

BY R. H. BETTS, R. S. STUART, AND C. A. WINKLER

ABSTRACT

An electrometric method for determination of nitric acid in RDX(*B*) liquors has been developed. The method is not largely affected by ammonium nitrate and acetic anhydride. A precision of ±0.5% may be readily obtained. Acetic anhydride in RDX(*B*) liquors may be determined by direct titration with standard aniline–toluene solution at 0° C., using calcium hypochlorite as an external indicator. In routine analysis, a precision of ±2% may be obtained.

### DETERMINATION OF NITRIC ACID

When equivalent amounts of nitric acid (0.3*M*) and sodium hydroxide (0.3*M*) were added to known volumes of aqueous acetic acid, it was observed that the dilution so effected caused a shift in the pH of the solution of approximately 0.01 unit for each 7 ml. water added. This observation was applied to the estimation of nitric acid in Bachmann RDX liquors as follows:

A 25.0 ml. sample was pipetted from the supernatant liquid of the RDX(*B*) slurry, and added to 100 ml. of water in a 250 ml. beaker. The solution was titrated with standard alkali (0.3*N*) using a suitable glass electrode assembly (Beckmann pH meter). Alkali was added until a pH of 2.07 was reached. The appropriate dilution correction of +0.01 pH units per 7.0 ml. alkali used was then added to the value 2.07, and the titration completed to this final pH. Determinations of known amounts of nitric acid added to RDX(*B*) filtrates could be made by this method with considerable precision, as indicated by the following typical results:

| Original $HNO_3$, gm., in RDX(*B*) liquor | $HNO_3$ added, gm. | Total $HNO_3$ present, gm. | $HNO_3$ analysis, gm. |
|---|---|---|---|
| 0.579 | 0.446 | 1.025 | 1.034 |
| 0.579 | 0.445 | 1.024 | 1.025 |
| 0.734 | 0.758 | 1.492 | 1.500 |

The concentrations of acetic anhydride and ammonium nitrate were varied over limits wider than those encountered in practice without affecting the precision of the nitric acid determination by more than 2 to 3%.

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*Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council.*



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## DETERMINATION OF ACETIC ANHYDRIDE

Ivanov (1) has described a method for the estimation of aniline by a titration with acetic anhydride, using ground pulp paper as external indicator. The reverse of this, an estimation of acetic anhydride by titration with a toluene solution of aniline, has been mentioned by Zavarov (3). Preliminary experiments indicated that a similar method might be applicable to the analysis of acetic anhydride in RDX(*B*) liquors, but that a more satisfactory indicator than that of Ivanov was necessary. An adaptation of the calcium hypochlorite spot test for aniline (2) has been made for the purpose. The reagents and procedure were as follows:

Dry aniline (1.0 mole) is dissolved in dry toluene and made up to 1.0 liter. The indicator, a triturated mixture of calcium hypochlorite and water, is used externally.

A 20.0 ml. sample of Bachmann filtrate is pipetted into 25 ml. of toluene in a 250 ml. Erlenmeyer flask. This sample is kept in an ice-water bath during titration. Addition of toluene to the sample promotes the acetylation reaction. Aniline–toluene solution from a burette is added slowly, with continuous agitation of the flask. A precipitate of acetanilide is formed during the titration but does not interfere. The end point has been reached when a drop of titrated liquid in the flask produces an immediate intensely colored ring on the surface of the indicator, the color varying from reddish-orange to purple. A secondary orange color develops gradually, but should not be confused with the true end point. Near the end point of the titration, one minute should be allowed before testing for excess aniline in titrated material. This permits completion of the acetylation reaction between aniline and anhydride.

The aniline–toluene solution was standardized against weighed amounts of pure acetic anhydride dissolved in toluene, using the technique outlined above.

The method was checked under various conditions. Determination of known amounts of acetic anhydride added to RDX(*B*) liquors may be made with a precision of ±2%, as shown by the following results.

| Original $Ac_2O$ in 20.0 ml. RDX(*B*) filtrate, gm. | $Ac_2O$ added, gm. | Total $Ac_2O$, gm. | $Ac_2O$ by analysis, gm. | % Error |
|---|---|---|---|---|
| 3.331 | 1.000 | 4.331 | 4.251 | −1.8 |
| 1.912 | 1.505 | 3.417 | 3.458 | +1.2 |
| 2.041 | 2.860 | 4.901 | 4.846 | −1.2 |
| 2.175 | 2.124 | 4.299 | 4.220 | −1.8 |

Deviations of ±2% are also encountered in duplicate determinations of anhydride in RDX(*B*) liquors and represent the precision of the method.

There was a possibility of reaction between nitric acid present and the aniline added. Such a reaction would of course give high values for anhydride. Addition of 0.75 gm. of 98% nitric acid to a 20.0 ml. sample of RDX(*B*) liquor destroyed the specificity of the indicator for aniline. Since this effect did not exist if both nitric acid and ammonium nitrate in a molar ratio of 1:1

were added to a sample of normal RDX(*B*) mother liquor, it would appear that all the nitric acid in anhydrous RDX(*B*) liquor is present as a complex with ammonium nitrate or as acetyl nitrate. Experience has shown that if nitric acid is present in excessive amounts, as in a partially completed Bachmann reaction, the end point is difficult to establish. The limited solubility of ammonium nitrate in such reaction liquors may make it impossible to nullify the effect of the higher nitric acid concentration. However, with liquors corresponding to completed Bachmann reactions, no such interference has been encountered. It may be concluded that free nitric acid interferes with the indicator and that ammonium nitrate – nitric acid complexes do not. The method has the advantage that it measures only the acetic anhydride present in the Bachmann liquor.

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# THERMAL NEUTRON CAPTURE CROSS-SECTION OF $Na^{23}$ AND $Mn^{55}$[1]

By Rosalie M. Bartholomew, R. C. Hawkings, W. F. Merritt, and L. Yaffe[2]

ABSTRACT

The thermal neutron capture cross sections of $Na^{23}$ and $Mn^{55}$ have been determined using the activation method. The values are $0.53 \pm 0.03$ and $12.7 \pm 0.3$ barns respectively with respect to $\sigma_{Au197} = 93$ barns. These agree well with recent pile oscillator results. The half-life for $Mn^{56}$ is found to be $2.576 \pm 0.002$ hr.

A very complete survey of the thermal neutron capture cross section of a number of nuclides has recently been made by Pomerance (5) using the "pile oscillator" technique. If one compares this with results obtained by Seren, Friedlander, and Turkel (6) using the activation method, discrepancies are found in certain cases. If the pile oscillator value is higher than that obtained by the activation method, then a possible short-lived isomer of the nuclide in question may exist which the latter method has been unable to detect.

We have previously reported the re-determination of the capture cross section of $Co^{59}$ (8) where some difference existed in the values obtained by the two methods. This paper deals with determination of the activation cross sections of $Na^{23}$ and $Mn^{55}$. As a reference standard the cross section for $Au^{197}$, $\sigma = 93$ barns (3), at a neutron velocity of 2200 meters per second has been used in this work. This appears to be the best value if one makes sure that no contribution from the 5 ev. resonance in Au capture appears. Any change in the accepted value will of course cause a change in the experimentally determined cross sections as quoted here.

## EXPERIMENTAL

### (*a*) *Irradiation*

#### (*i*) *Sodium*

The sodium was irradiated as anhydrous 'spec-pure' sodium carbonate in a small silica capsule. The gold used was the highest quality obtainable (> 99.97%). In some cases gold leaf was used. Circular pieces were punched out of a sheet. The diameter of the circles was measured under a microscope. The area and weight of the original sheet were determined and thus the weight of gold used obtained. In other cases .001 in. thick gold foil was used and an amount weighed out such that the error in weighing was less than 1%.

The samples of sodium carbonate and gold were placed together in a polythene capsule so that they were very close together and received essentially the same neutron flux. Self-shielding of the gold was calculated to be of the order of 1% and appropriate corrections made.

The samples were irradiated in a 'self-serve' position where the neutron spectrum was predominantly thermal. Irradiations were also made with the entire sample

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wrapped in cadmium. The results of these latter irradiations enabled correction factors to be computed to allow for epicadmium capture (1.79% in the case of $Au^{197}$ and 0.35% for $Na^{23}$). After irradiation the sodium carbonate was dissolved in dilute nitric acid and made to a standard volume. The gold was dissolved in a minimum amount of aqua regia, heated to prevent aggregate formation and made to a standard volume.

(*ii*) *Manganese*

The manganese was irradiated as 'spec-pure' manganese oxide ($Mn_3O_4$) sealed in a small silica tube along with the gold. The gold used was the .001 in. thickness as described in the previous section. Again the epicadmium contribution was determined. After irradiation the manganese oxide was dissolved in concentrated hydrochloric acid and made up to a standard volume. The gold was treated as described above. The epicadmium correction was 0.50%.

(*b*) *Measurements*

All measurements of disintegration rates were made using the $4\pi$ counter described by Borkowski (2) and Hawkings, Merritt, and Craven (4). Sources were deposited on thin (100 $\mu$gm. per cm.$^2$) zapon-formvar laminated films which had a coating of 25 $\mu$gm. per cm.$^2$ gold sputtered on each side to make the film conducting.

The aliquots were removed from the solution using calibrated micropipettes and represented essentially weightless sources. Small corrections, of the order of one per cent, were made for absorption of the $\beta$-particles in the film (4) and for coincidence losses.

The disintegration rates were corrected for decay and lack of saturation of bombardment.

The decay corrections on $Na^{24}$ were made using a half-life of 15.04 $\pm$ 0.06 hr. (7). The decay of $Mn^{56}$ from the first two cross-section experiments was followed for 11 half-lives with a $4\pi$ proportional counter. The result of a least squares fit to the data is 2.576 hr. with a standard deviation of $\pm$ 0.002 hr. This figure, which is slightly less than the value of 2.586 $\pm$ 0.005 hr. given by Bishop, Wilson, and Halban (1), was used to make the decay corrections on $Mn^{56}$.

## RESULTS

The results for the determination of the sodium cross-section are given in Table I.

TABLE I

| Experiment No. | Corrected dis./sec./mgm. | | Cross section of Na ($\times 10^{24}$ cm.$^2$) |
|---|---|---|---|
| | Na $\times 10^{-7}$ | Au $\times 10^{-8}$ | |
| 1 | 1.56 | 3.03 | 0.565 |
| 2 | 1.64 | 3.60 | 0.495 |
| 3 | 1.73 | 3.46 | 0.543 |
| 4 | 1.69 | 3.14 | 0.594 |
| 5 | 1.55 | 3.17 | 0.529 |
| 6 | 1.50 | 3.28 | 0.497 |
| 7 | 1.73 | 3.32 | 0.564 |
| 8 | 1.96 | 4.05 | 0.525 |
| 9 | 1.60 | 3.55 | 0.488 |
| 10 | 1.74 | 3.73 | 0.506 |
| | | | Average 0.53 $\pm$ .03 |

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The average obtained is 0.53 ± 0.03 barns where the error quoted is the standard deviation. The value obtained by Pomerance (5) was 0.47 ± .02 barns by the pile oscillator method, while the activation method used by Seren, Friedlander, and Turkel (6) gave 0.63 ± 0.19 barns.

The results for the manganese cross section are given in Table II.

TABLE II

| Experiment No. | Corrected dis./sec./mgm. | | Cross section of Mn ($\times 10^{24}$ cm.$^2$) |
|---|---|---|---|
| | Mn $\times 10^{-8}$ | Au $\times 10^{-8}$ | |
| 1 | 1.96 | 4.03 | 12.8 |
| 2 | 1.72 | 3.50 | 12.7 |
| 3 | 1.83 | 3.65 | 13.2 |
| 4 | 1.81 | 3.85 | 12.4 |
| 5 | 1.74 | 3.62 | 12.6 |
| 6 | 2.07 | 4.40 | 12.4 |
| | | | Average 12.7 ± 0.3 |

The average obtained is 12.7 ± 0.3 barns where the error shown is the standard deviation. The value obtained by Pomerance was 12.8 ± 0.6 barns using the pile oscillator method, and 10.7 ± 3.3 barns by Seren, Friedlander, and Turkel using the activation method.

Our values for both the $Na^{23}$ and $Mn^{55}$ cross sections agree with the pile oscillator value and fall within the wide limits given by the activation value of Seren *et al.*

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# STUDIES OF LIGNIN BIOSYNTHESIS USING ISOTOPIC CARBON

## I. LONG-TERM EXPERIMENT WITH $C^{14}O_2$[1]

By J. E. Stone

ABSTRACT

Wheat plants were fed with $C^{14}O_2$ at the stage of growth corresponding to rapid lignification. Thereafter, plants were harvested every few days until maturity. The specific and total activity of the plants, and the specific and total activity in some lignin degradation products were determined. Results indicated that (i) $C^{14}O_2$ was still being respired from the plants at maturity, (ii) all the $C^{14}$ which gets into the lignin does so within 24 hr. from the administering of $C^{14}O_2$, (iii) the total activity originally acquired by the syringaldehyde portion of the lignin remains constant throughout the growth of the plant, that is, the lignin (as represented by syringaldehyde) is a final end product of the plant and is not a part of the respiratory system, (iv) the total activity originally acquired by the vanillin suffers an initial drop for about two weeks after activation and then becomes constant, (v) the *p*-hydroxybenzaldehyde activity drops continuously throughout the life of the plant.

### INTRODUCTION

When considering the mechanism of lignin biosynthesis it is usual to postulate a precursor which might by its structure and known reactions lead to lignin. There must be many intermediates between carbon dioxide and lignin but it is very probable that a simple aromatic compound, or to be more explicit, a phenol substituted in the para position, lies somewhere along the route. Klason (2) suggested that coniferyl alcohol or aldehyde might be a lignin precursor, and Freudenberg's recent work (1) on the polymerization of coniferyl alcohol to a lignin-like substance by polyphenol oxidase seems to support this contention.

It is probable that much light can be shed on this problem by the feeding of suspected precursors, labelled with $C^{14}$, to plants which are actively synthesizing lignin. Activity should appear in the lignin if the added compound is a precursor. One disadvantage to this method however is that carbon dioxide is the only precursor which can be added without risking some disturbance of the normal metabolism of the plant. A more serious difficulty arises owing to the fact that lignin is not a well-defined crystalline compound which can be obtained in a pure state. Because of this it would be rather difficult to decide whether activity which appeared in the isolated lignin was due to a true incorporation of the precursor into a normal lignin molecule or whether it was due to the copolymerization of the actual precursor and the supposed one which had been added. Polyphenol oxidases are present in many plants and the mere isolation of a radioactive lignin-like substance from a plant which had been fed a radioactive phenol would need interpreting with caution.

The difficulty goes even further than this because the lignin as isolated from the majority of plants is highly contaminated with complexes of the humic acid type which are definitely not lignin-like from the chemical point of view. Regardless of the precursor used, from $C^{14}O_2$ to $C^{14}$ labelled coniferyl alcohol, the

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total activity acquired by the isolated "lignin" fraction would be meaningless.

It appeared necessary, therefore, to study the activity acquired by the crystalline degradation products of lignin, i.e. vanillin, syringaldehyde, and possibly *p*-hydroxybenzaldehyde, rather than lignin itself. It was decided to use $C^{14}O_2$ for activating the plants because, although it has the disadvantage of causing the majority of plant components to become radioactive after a few seconds, continuing growth in an atmosphere of normal carbon dioxide should distinguish between those which were intermediates and those which were stable end products. The former should become depleted in activity with time while the latter should increase in total activity.

It was hoped that the present work would provide answers to the following questions. After wheat plants are given a fixed dose of $C^{14}O_2$ and their growth is continued in carbon dioxide,

(1) How long does it take for the lignin, as represented by the three phenolic aldehydes, to acquire its maximum activity?

(2) Is lignin a stable end product of plant metabolism or is it part of a dynamic system with a consequent gradual loss of activity?

(3) What percentage of the activity originally administered to the plant shows up in the phenolic aldehydes? If an appreciable amount, this could be a convenient biological method for preparing $C^{14}$ labelled aromatic compounds.

Future papers in this series will deal with the conversion of $C^{14}O_2$ to aldehydes during the first few minutes and hours of photosynthesis, and the feeding of multicarbon plant metabolites labelled with $C^{14}$.

## EXPERIMENTAL

### *Apparatus*

A dual purpose chamber was constructed for growing the plants in an enclosed atmosphere and for carrying out subsequent large sheet paper chromatography.

The dimensions of the chamber were 27 in. × 16 in. and 30 in. high, constructed of plate glass cemented into an angle iron frame and provided with casters for easy moving. The cover, also made of plate glass, was ground to fit the top of the chamber. This cover contained three $\frac{1}{2}$ in. holes for (*a*) the carbon dioxide generator, (*b*) a thermometer, (*c*) a tube for watering the plants. When the chamber was used for chromatography these holes were used for adding the solvent to the three stainless steel troughs after equilibration of the paper. Air was drawn through a 2 in. hole in the bottom of the chamber and exhausted outside the greenhouse by means of a blower connected to a side hole. Illumination was provided by daylight supplemented by artificial light to give a total of 17 hr. of light and 7 hr. of darkness per day.

### *Procedure*

Thatcher wheat was grown (three plants per 5 in. pot) under normal conditions until alkaline nitrobenzene oxidations indicated that the plants were reaching the stage when rapid lignification was about to set in (4). Nine pots containing 27 plants of similar size were selected and placed in the growing chamber. The latter was sealed and 1 millicurie of $C^{14}O_2$ added. Illumination was maintained for 24 hr. and then the blower started in order to sweep out any

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remaining $C^{14}O_2$. After air had been drawn through the chamber and exhausted outside the greenhouse for one hour, a single plant was removed for analysis. Thereafter, a plant was removed at intervals of a few days up to the cessation of growth. As much as possible of the root was retained by carefully washing away the earth clinging to it.

The plants were dried in a rapid current of air at 35°C. and ground to pass a 40-mesh screen. Samples of about 10 mgm. weight were burnt to carbon dioxide in a normal combustion train and the carbon dioxide trapped as sodium carbonate and converted to barium carbonate. The barium carbonate was filtered and its "specific activity" at infinite thickness determined using a Simpson gas flow counting chamber and an RCL scaler. The residue remaining in the crucible after the combustion gives the percentage ash in the plant material and all results were calculated on an ash-free basis.

The nitrobenzene oxidations and determination of *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde were carried out by the micromethod of Stone and Blundell (3). About 60-80 mgm. samples were used and after the oxidation, one half of the liquor (0.5 ml.) was placed on a paper chromatogram sheet 18 in. × 22 in. and developed with the organic layer of petroleum ether – *n*-butyl ether – water 6:1:1. The pure phenolic aldehydes which separated on the paper were extracted with ethanol, the solutions evaporated to small volume (about 5 ml.), made alkaline with alcoholic potassium hydroxide, and aliquots removed for the determination of (*a*) percentage aldehyde, (*b*) specific activity of aldehyde. The latter was carried out by evaporating 1.0 ml. on to an aluminum disk and measuring the counts per minute obtained. The very small weight of material on each disk gave an "infinitely thin" sample so that the specific activity of the aldehydes recorded as counts per minute per mgm. should be interpreted on this basis.

## RESULTS AND DISCUSSION

The results are shown graphically in Figs. 1 to 5 and are almost self-explanatory. Fig. 1 demonstrates the fall in specific activity of the total plant carbon

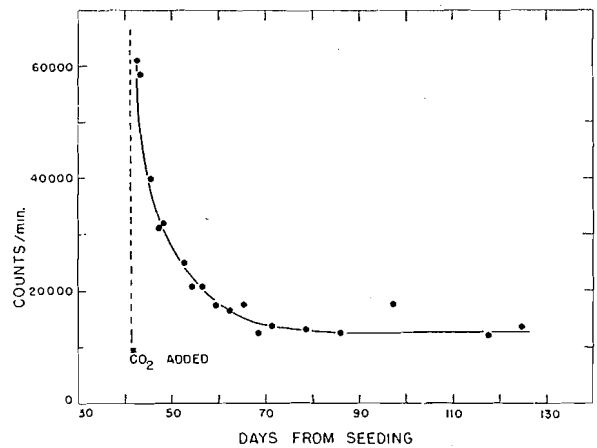



FIG. 1. Specific activity of total plant carbon (measured as barium carbonate, infinitely thick). $C^{14}O_2$ added on 41st day from seeding. First active plant removed for analysis 25 hr. later.

with time, this fall being due to two causes. One is the continuing growth of the plant in inactive carbon dioxide with a consequent dilution of activity. The other cause is the loss of $C^{14}O_2$ through respiration. This latter is demonstrated in Fig. 2

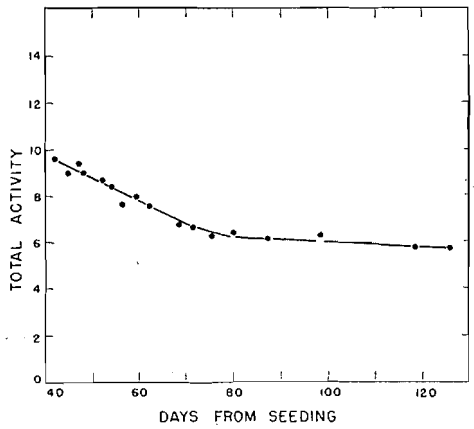



FIG. 2. Total activity of wheat plants. Weight (ash free) × specific activity.

where the total activity of the plant (specific activity × weight of plant) is seen to fall with time.

Figs. 3, 4, and 5 refer to the results of the alkaline nitrobenzene oxidation of the plants. Fig. 3 shows the change in the percentage of vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde and indicates the age of the plants at the time of activation and at subsequent harvests. (In the other figures a number of points have been omitted for the sake of clarity.) It will be noted that the vanillin and syringaldehyde percentages are increasing quite rapidly during the course of the experiment, whereas *p*-hydroxybenzaldehyde rises only slightly.

The specific activities of the three aldehydes fall as the plant matures, this being demonstrated in Fig. 4. This fall is only to be expected since inactive lignin

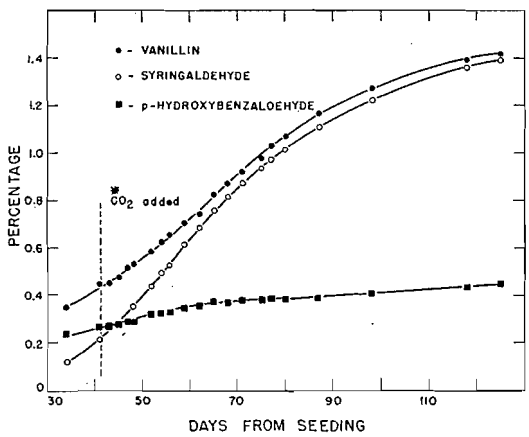



FIG. 3. Percentage of aldehydes based on whole plant.

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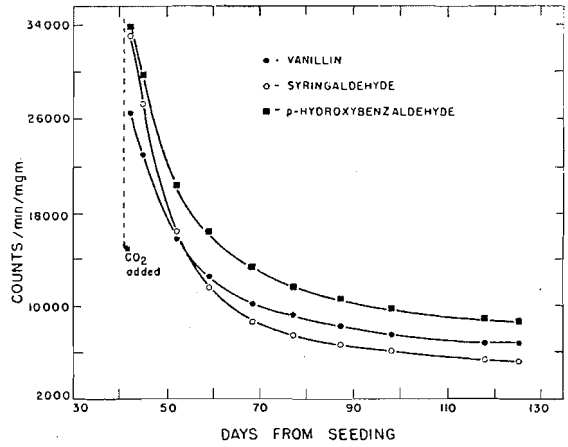



FIG. 4. Specific activity of aldehydes.

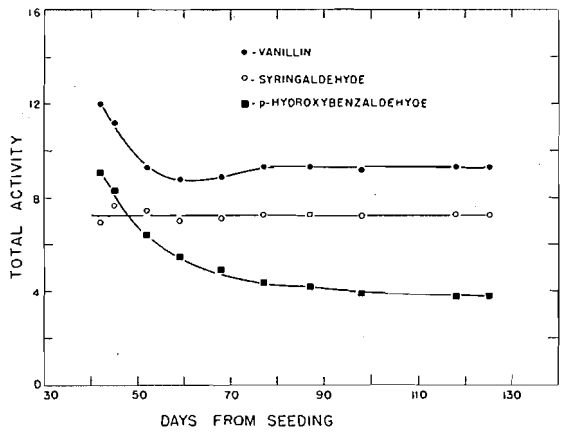



FIG. 5. Total activity of aldehydes (percentage × specific activity).

is being synthesized by the plant the whole time and is diluting the activity of the material formed immediately after the addition of $C^{14}O_2$.

Of more interest are the curves shown in Fig. 5 where the total activity of each aldehyde is given. The total activity is the specific activity (see Fig. 4) in counts per min. per mgm. multiplied by the percentage of aldehyde (see Fig. 3) and represents the total amount of activity acquired by that portion of the lignin molecule. The units of total activity are arbitrary ones and have not been calculated as microcuries since it is unnecessary for comparative purposes.

The curves of Fig. 5 are interesting in that each of the three aldehydes appears to behave differently. The activity of the *p*-hydroxybenzaldehyde drops continuously throughout the life of the plant and supports the contention put forward in a previous paper (4), that this aldehyde is derived from tyrosine present in plant protein and not from the lignin fraction of the plant. Tyrosine can lose active carbon in a number of ways as it is part of a dynamic system so that loss

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of activity from its oxidation product, *p*-hydroxybenzaldehyde, is not surprising.

Syringaldehyde, on the other hand, is apparently derived from an irreversible system since it loses no activity over a period of two to three months and cannot therefore be involved in respiration unless its loss of activity is exactly compensated for by a gain in activity from other active plant components. This latter is very unlikely. It will also be noted that there is no gain in total activity after the first 25 hr. from administering $C^{14}O_2$ so that evidently the path from $C^{14}O_2$ to the parent substance of syringaldehyde is complete in less than this time. This implies that it would be necessary to study the changes taking place in the first 25 hr. in order to obtain information regarding intermediates in lignin formation, and the results of such a study will be reported in later papers of this series.

Considering the total activity in the vanillin fraction (Fig. 5) it is seen to be between *p*-hydroxybenzaldehyde and syringaldehyde in its behavior. An initial drop in total activity is followed by a levelling out to constant activity. The most probable explanation for this is that the young plants contain guaiacyl-type lignans which give rise to higher percentages of vanillin than does lignin. As the plant matures these lignans are polymerized or condensed in some way to form lignin which is less susceptible to oxidation. There is evidence (4) that young wheat plants contain guaiacyl-type lignans which disappear during the early stages of lignification so this explanation is not unlikely.

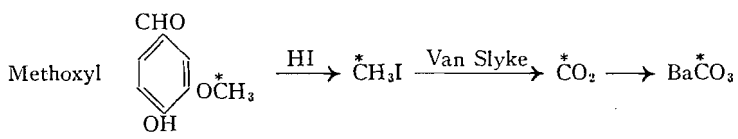
A separate experiment was conducted to find out what percentage of the activity which had been added to the plant appeared in the form of active aldehydes.

Five wheat plants (taken just prior to heading out) were kept in the dark for 18 hr. and then activated with 0.2 mc. of $C^{14}O_2$ in the light for a period of 24 hr. The plants weighed 6 gm. when dry and had absorbed 96% of the $C^{14}$ added. The finely ground material was oxidized with alkaline nitrobenzene and the three aldehydes separated by chromatography. The results are shown in the table.

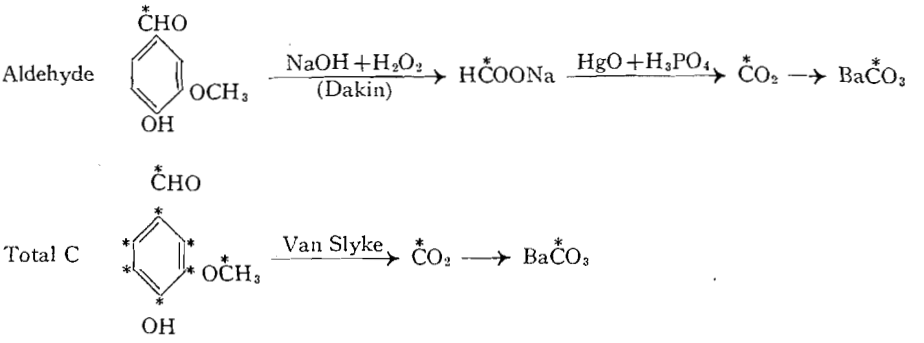
TABLE I

| | Wt. of aldehyde, mgm. | Specific activity, μc. per gm. of carbon | Percentage of $C^{14}$ added |
|---|---|---|---|
| *p*-Hydroxybenzaldehyde | 10 | 60 | 0.3 |
| Vanillin | 49 | 40 | 1.0 |
| Syringaldehyde | 60 | 45 | 1.3 |

It would be expected that under the conditions of activation and growth used here, the carbon atoms in the compounds under consideration would have equal activity. This was shown to be the case. Taking vanillin as the example the reactions used for the degradations were:—




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It is possible that for certain purposes this could be a convenient method for obtaining $C^{14}$ labelled phenolic aldehydes if the uniform labelling were not a disadvantage.

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# STUDIES ON RDX AND RELATED COMPOUNDS

## X. ANALYSIS FOR NITRIC ACID IN ACETIC ACID – ACETIC ANHYDRIDE MEDIA[1]

By R. A. Marcus[2] and C. A. Winkler

ABSTRACT

An analytical method has been developed for the estimation of nitric acid in acetic acid – acetic anhydride media, with a precision of 0.3%. The procedure involves the addition of a solution of potassium acetate in acetic acid to the sample. The excess is back-titrated conductometrically with a standard solution of nitric acid in acetic acid.

## INTRODUCTION

A study of the formation of 1,9-diacetoxypentamethylene-2,4,6,8-tetranitramine (AcAn) from 2-acetoxymethyl-4,6,8-trinitrocyclotetramethylene tetramine (PHX), nitric acid, and acetic anhydride, the results of which are presented in a later paper, required a knowledge of the rate of nitric acid disappearance during the reaction. To this end, it was necessary to develop a method for analyzing nitric acid in an acetic acid – acetic anhydride medium, as outlined below.

## EXPERIMENTAL

Potassium acetate dissolved in glacial acetic acid was added to the acetic acid – acetic anhydride reaction mixture containing the nitric acid to be analyzed. The addition was accompanied by precipitation of potassium nitrate, owing to its insolubility in the anhydride-medium. The mixture was then back titrated with a dilute acetic acid solution of nitric acid, and the titration followed conductometrically. During the course of the titration, potassium nitrate was again precipitated and a decrease in conductivity was observed.

When reaction of nitric acid with the excess alkali acetate was complete, further addition of reagent caused the conductivity to increase, unless the reagent

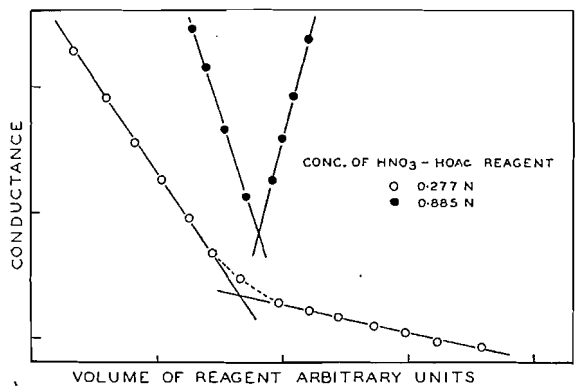



Fig. 1. Change of conductance with addition of analytical reagent.

[1] *Manuscript received October 14, 1952.*
*Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Que. with financial assistance from the National Research Council of Canada.*
[2] *Holder of National Research Council Studentship. Present address: Assistant Professor, Polytechnic Institute of Brooklyn, N.Y.*

was sufficiently dilute, in which case the conductivity continued to decrease but at a smaller rate than before. An example of both types of curves is given in Fig. 1.

Using the same acetic acid solutions of potassium acetate and nitric acid, several titrations of acetic acid – acetic anhydride mixtures containing known amounts of nitric acid, permitted a linear calibration curve to be established with the aid of which solutions of unknown nitric acid content could be analyzed with a precision better than 0.3%. This calibration method was adopted in preference to direct titration with potassium acetate – acetic acid solution for two reasons. First, unless there are a large number of nuclei of the nitrate present, the direct titration is very slow and tedious. Secondly, the addition of an excess of potassium acetate was effective in quenching immediately the nitrolysis reaction that was under investigation.

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# THE NONSPECIFIC PRECIPITATION OF PROTEINS BY POLYHAPTENIC DYES[1]

By J. L. Morrison

ABSTRACT

The serum proteins albumin and γ-globulin were precipitated by two polyhaptenic azobenzenearsonic acid dyes, at pH values in the region of or below the isoelectric points of the proteins. The occurrence of an optimum zone of precipitation suggests either a colloidal precipitation or the formation of a framework of dye and protein. The molecular ratios of dye to protein in the precipitate suggest increasing aggregation of the dye with lowering pH. The aggregation appears to be an acid constant effect. An estimate of the number of protein combining groups for one of the dyes is 22 for albumin, and 44 for γ-globulin. At pH values between 5.0 and 5.4, at which albumin is not precipitated, the precipitation of γ-globulin by the dyes is dramatically reduced by the presence of albumin. Apparently albumin forms soluble complexes with either the dye or γ-globulin or with both these substances.

In immunochemistry, the reactions between antisera and antigens are well characterized by their specificity (7). On the other hand, recently much study has been made of the nonspecific binding of simple substances by proteins (4, 5, 6). That nonspecific binding is a complicating factor in the reaction of simple antigens and antisera has been shown by Pardee and Pauling (9) who found that the reaction of polyhaptenic substances with purified hapten-homologous antibody is considerably different from that of the same substances with antiserum. They interpreted the differences as resulting from the combination of the polyhaptenic substances (which were azo dyes) with the serum albumin present in the antiserum, this combination serving to keep the dye monomer concentration low, and thus to prevent the formation of polymeric aggregates of dye molecules. It is well known that many dyes form aggregates in solution, and the formation of these aggregates has been verified for some of the dyes used in serological work (1, 10). Serum albumin is known to have a significant binding power for azo dyes (4, 5, 6).

The nonspecific binding of dyes and proteins is also of importance in connection with attempts to produce antibodies *in vitro* by controlled denaturation of serum protein in the presence of certain dyes (12).

Thus, experiments were carried out to discover nonspecific interactions between some polyhaptenic dyes used in serological reactions and some normal serum proteins. It is well known that these polyhaptenic dyes do not give precipitates with normal serum proteins in the usual pH range, around 8, of the serological precipitin reaction. However, by lowering the pH to around or below the isoelectric points of the serum proteins, the author found that precipitates could be obtained. Precipitation of proteins below their isoelectric points has been observed by Putnam and Neurath (15, 16) for horse serum albumin and the anionic detergent, sodium dodecylsulphate.

[1] *Manuscript received October 6, 1952.*
*Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. Presented at the Western Regional Conference, Chemical Institute of Canada, Saskatoon, Sask., October 25, 1952.*



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## EXPERIMENTAL METHODS

### *Haptenic Compounds*

The two polyhaptenic compounds used in the present investigation, 2-methyl-4,6-di(*p*-azobenzenearsonic acid)phenol (compound III) and 1,3-dihydroxy-2,4,6-tri(*p*-azobenzenearsonic acid)benzene (compound VI), were from preparations that have been previously described (13). Compound III had been shown by chromatographic tests to contain a small amount of an unidentified impurity. Solutions of the compounds were made in water and adjusted to pH 7 and to concentrations of about 0.57 and 0.80% respectively (in each case approximately 0.01 molar).

Some other haptenic substances used in single experiments are described later.

### *Proteins*

The bovine γ-globulin that was used was kindly supplied by Armour and Co., with the label "Fraction II from bovine plasma". The serum albumin, provided through the courtesy of the Department of Physical Chemistry, Harvard Medical School, was labeled "Human albumin, run 35, fract. V, crystals". The proteins were dissolved in sodium acetate – acetic acid buffers between pH 3.72 and 5.72 and ionic strengths of 0.20 from pH 3.72 to 4.83 and 0.10 from pH 5.00 to 5.72, and were dialyzed against large volumes of these buffers before use.

### *Experimental Procedure*

Either 0.5 or 1.0 ml. of protein solution was added to 0.5 or 1.0 ml. of each of a series of serially diluted dye solutions, the dilutions being made with buffer of the same pH and ionic strength as the protein solution. Protein concentrations were varied from 0.1 to 1.0%, so as to give a convenient amount of precipitate for analysis. The samples were immediately shaken by hand after mixing, and the sample tubes were stoppered with cork. The samples were refrigerated for two days and then were centrifuged. Then, without disturbing the precipitate a few milliliters of the same buffer were added to wash out extraneous solution, the tubes were centrifuged again, and were allowed to drain dry. The precipitate was dissolved in a few drops of 2*N* sodium carbonate solution and was analyzed with a Klett photoelectric colorimeter for the dye concentration, and with Nessler reagent for total nitrogen. It was found that the dyes did not yield their total nitrogen in a Nessler analysis; however, each dye gave a consistently constant percentage of its nitrogen in this analysis, 72.5 and 46% for compounds III and VI, respectively. In the calculations reported below the molecular weights of the proteins were taken to be 68,000 for serum albumin and 160,000 for γ-globulin.

## EXPERIMENTAL RESULTS AND DISCUSSION

### *General Description of the Precipitations*

It was found that each of the two dyes gave precipitates with each of the proteins in the lower part of the pH range investigated, the amount of precipitate falling off rapidly in the region of the isoelectric points of the protein (these are 4.8 for human serum albumin (3) and 6.5 for bovine γ-globulin (2)). Quan-

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titative studies were made for each of the four systems γ-globulin – compound VI, albumin–compound VI, γ-globulin–compound III, and albumin–compound III, at 11 pH values nearly equally spaced in the range 3.72 to 5.72, in each case with the use of eight different amounts of dye differing by successive factors ½. A typical set of data is reported in Table I. Dye solutions of 0.5 ml. volume,

TABLE I

TYPICAL PRECIPITATION REACTION OF γ-GLOBULIN AND COMPOUND VI AT pH 4.62

| Tube Number | Amount of dye added, mgm. | Composition of precipitate | | |
|---|---|---|---|---|
| | | Dye, mgm. | Protein, mgm. | Molar ratio of dye to protein |
| 1 | 4.02 | 0.069 | 0.378 | 36.8 |
| 2 | 2.01 | 0.0756 | 0.387 | 39.3 |
| 3 | 1.00 | 0.0725 | 0.390 | 37.5 |
| 4 | 0.50 | 0.0597 | 0.342 | 35.1 |
| 5 | 0.25 | 0.0526 | 0.330 | 32.3 |
| 6 | 0.125 | 0.0392 | 0.237 | 33.3 |
| 7 | 0.062 | 0.0142 | 0.090 | 31.8 |
| 8 | 0.031 | 0.0074 | 0.042 | 35.4 |

containing varying amounts of compound VI in acetate buffer at pH 4.62 and ionic strength 0.20, were mixed with 0.5 ml. of similarly buffered γ-globulin containing 0.412 mgm. protein. The amount of compound VI varied from 4.02 mgm. to 0.031 mgm. by successive factors ½. The precipitates were analyzed for dye and protein. It is seen from the table that in the first three tubes over 90% of the protein was precipitated, and that the amount of precipitated protein then decreased. The molecular ratio of dye to protein in the precipitate remained essentially constant through the series, the average value being 35.2.

The change in ionic strength from 0.20 to 0.10 at pH 5.00 was necessary in order to secure precipitates above this pH. The dye–protein ratio of the γ-globulin – compound VI precipitate at pH 4.83 was determined at both ionic strengths and showed no difference.

With both compound III and compound VI, over 90% of the γ-globulin was precipitated in the optimum zone throughout the pH range 3.72 to 4.83. The amount precipitated then began to decrease, reaching about 50% at pH 5.25, 25% at 5.5, and 2% at 5.7. With both compounds the amount of albumin precipitated was over 90% of the amount present to pH 4.5, dropping to about 50% at 4.8, and about 20% at pH 5.0.

*Colloidal Hypothesis*

In general, in experiments at any one pH value, it was found that the amount of protein precipitated was a maximum in about the second or third tube—occasionally the fourth or fifth. The optimum zone of precipitation in the dye–protein systems appears to be similar to the equivalence zone of precipitation observed for a detergent–protein system (15, 16). Putnam and Neurath account for their results in terms of a mutual precipitation of oppositely charged colloidal particles, *as well as* a stoichiometric combination of detergent and protein.

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However, certain important differences exist between the present dye–protein and the detergent–protein systems.

(*a*) Both the amount and composition of the dye–protein precipitates are dependent on pH. The optimum zone is not sharply defined (see Figs. 2-5). In the optimum zone, except for a few cases below pH 4.27, only part of the protein is precipitated by dye. In the $\gamma$-globulin systems in particular, for all dye concentrations at a pH greater than 4.27, more than 50% of the dye is still in solution (e.g. Table I). Thus, at a pH greater than 4.27, there is always both unprecipitated dye and protein in the supernatant liquid.

In contrast, both the amount and composition of the detergent–protein precipitates are independent of pH up to the isoelectric point of the protein. The equivalence zone is sharply defined. Practically all the detergent is in the precipitate below the region of detergent excess, and in the equivalence zone, all the protein is precipitated. Thus, within the equivalence zone, there is no detergent or protein in the supernatant liquid. To explain their observations, Putnam and Neurath suggest that the anionic detergent not only neutralizes the opposite net charge of the protein, but also combines with *all* the cationic groups in the protein, limited only by the amount of detergent present.

The ratios of dye to protein in their precipitates are largely dependent on pH for compound VI and on both pH and dye concentration for compound III. For example, in the $\gamma$-globulin – compound VI system, the dye–protein ratios for the precipitates are practically independent of dye concentration and completely dependent on pH at pH values above 4.27. In contrast, the ratio of detergent to protein in their precipitates is dependent on the ratio of substances before mixing, and independent of pH up to the isoelectric point of the protein.

(*b*) The dye–protein systems show a *decrease*, whereas the detergent–protein system shows an *increase* in precipitation with an increase in ionic strength. The latter is the expected behavior of a colloidal precipitation, whereas the former is similar to the behavior of a pure protein.

It would appear that the application of the colloidal hypothesis to account for the precipitations in the dye–protein systems is not as satisfactory as it is for the precipitations in the detergent–protein system.

*Framework Hypothesis*

The occurrence of a zone of optimum precipitation for the dye–protein system may also be compared with similar observations made for serological precipitations. To account for the latter, Pauling (11) and others have suggested a framework hypothesis. Without assuming the same *kind* of interaction as in specific serological reactions, the framework hypothesis may be applied to account for the present results. Then the decreased amount of precipitation in the dye-excess region can be explained by the formation of soluble complexes in which all the combining regions are saturated with separate dye molecules. The effect would be similar to the antigen-excess effect (solution of the specific precipitate in excess antigen). The decrease in the amount of precipitate in the low-dye region might be attributed simply to the presence of a smaller amount of dye. However, it is to be noticed in Table I (and this is typical) that the amount

of dye contained in the precipitate is only a fraction (about one-quarter) of the total amount of dye present, even in the last tube, in which only 1/10th of the protein is precipitated. This suggests that the dye remaining in solution is present in the form of small soluble complexes with protein molecules, and that this may be a phenomenon similar to that of solubility of a serological precipitate in excess of antibody, which is observed in some serological systems, and in particular those in which the precipitating antigen is a simple substance (13).

To further test the hypothesis that the precipitate is a framework of dye and protein molecules, some monohaptenic dyes and arsanilic acid were mixed with the proteins. Solutions of *p*-(*p*-azobenzenearsonic acid)phenol (pH 4.7), its 2-methyl derivative (pH 4.5) and a saturated solution of arsanilic acid were separately added to each of the two proteins (pH 4.45). The absence of precipitates in every case supports this application of the framework hypothesis.*

*Dye Aggregation*

Values of the molecular ratio of dye to protein in the precipitate as a function of pH are shown for the four systems in Fig. 1. Each point represents the average of the three largest values obtained with the eight tubes in a set. For either γ-globulin or albumin with compound VI the values in a set showed good consistency whereas the values for compound III were very sensitive to dye concentration, being larger for the higher concentrations.

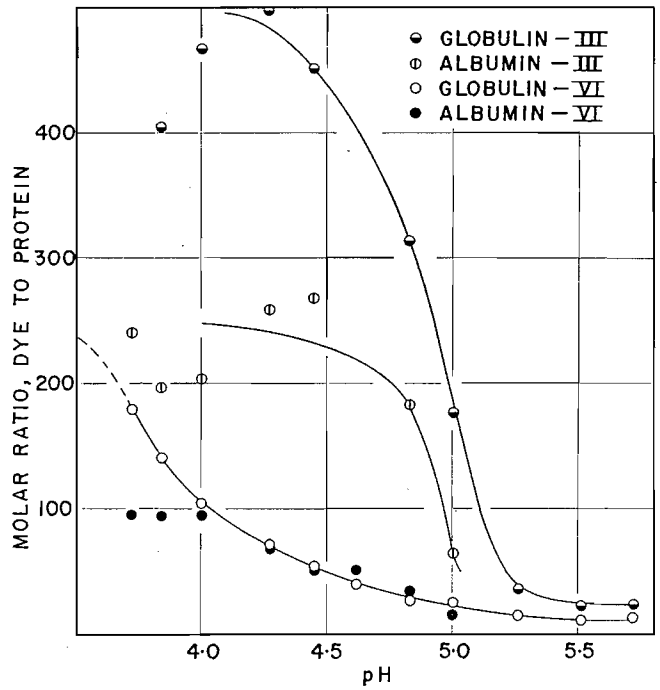



FIG. 1. The dependence of the molecular ratio of polyhaptenic dye to protein on pH.

**The referee suggests that this does not rule out the colloidal hypothesis, in that the monohaptenic dyes may be too small for aggregation. McMeekin (8) points out that sulphate and sulphonate detergent molecules containing more than eight carbon atoms are excellent protein precipitants.*

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For γ-globulin and compound III the molecular ratio changes from a maximum of about 500 at low pH values to a lower asymptote of 22 for pH values 5.5 and 5.7. A similar course is shown by albumin and compound III, the values of the ratio being at each pH about 50% as great as for globulin and compound III.

The large increase in the dye–protein ratio with decreasing pH may be a result of either an increase in dye aggregation or an increase in the protein net charge or both these effects. It may be noted that in the case of the detergent–protein precipitations (15, 16) the net charge does *not* determine the amount of bound detergent. Its only role is to ensure that precipitation will occur. Thus, the bonding between the detergent and protein is not a net charge effect. Similarly in the present case, there are no theoretical grounds for assuming that the net charge of the protein should determine the amount of bound dye. Then, consider the case of γ-globulin and compound III at pH 4.62, in which the dye–protein ratio changes 13-fold in the first five tubes, yet, except for one tube, at least 40% of the dye remains in solution and in all five tubes more than 84% of the protein is precipitated. It is difficult to account for these facts by any means other than dye aggregation.

Thus, the *same* assumption as for the detergent–protein system is made, namely, that the protein combines with all the dye available up to a limit set by the number of dye-receptive groups in the protein. Since in all cases down to pH 4.27 and for most at a lower pH, there is some dye and protein in the supernatant liquid, it is considered that the increase in dye–protein ratio with decrease in pH is the result of an increase in the degree of aggregation of the dye molecules. It might well be expected that the tendency to aggregation would be small at high pH values because of the electrostatic repulsion of the negative ions, and would increase at low pH values as the benzene arsonate ions combine with hydrogen ions to form uncharged benzene arsonic acid groups. In other words, the dye aggregation may be an acid-constant effect.

The pH at half maximum for both curves for compound III is about 4.9; this value is close to $pK_2$ for compound III. The pK values of compound III were determined by titration, and found to be $pK_1 = 3.65$ and $pK_2 = 5.15$. The points for γ-globulin and compound VI lie on a smooth curve with asymptotic value 12 at pH values above 5.5, increasing to 180 at pH 3.7. The points for albumin and compound VI lie near those for γ-globulin and this compound but show a greater scatter. If the curve for γ-globulin and compound VI is assumed to be similar in form to those for compound III and to be approaching an asymptote of about 250, the characteristic pH value for compound VI can be estimated as 3.9. This value is close to $pK_2$ for this compound; by titration, it was found that $pK_1 = 3.26$, $pK_2 = 4.10$, and $pK_3 = 5.32$.

*Protein Combining Groups*

On the assumptions that the framework hypothesis applies, that at pH 5.5 to 5.7 the dye molecules combine with the proteins as monomeric molecules, and that the haptenic groups (two for compound III, three for compound VI) interact with separate combining groups of the proteins, the number of combining groups per γ-globulin molecule is calculated to be 44 from the asymptotic ratio 22 for compound III and 36 from the asymptotic ratio for compound VI.

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There is some question, however, as to whether compound VI can use all three of its haptenic groups in combining with proteins; in specific serological precipitation compound VI has been found to have an effective valence of about 2.35, rather than 3, the decrease below 3 being attributed to steric hindrance (14). There are no independent determinations of the number of combining groups possessed by $\gamma$-globulin.

The curve for albumin with compound III in Fig. 1 is similar to that for $\gamma$-globulin for this compound, with the ordinate only about one-half as great. If the factor $\frac{1}{2}$ is assumed to hold into the region with larger pH, the asymptotic value with albumin would be 11, and, with consideration of the bivalence of this hapten, the corresponding number of combining groups would be 22. This value happens to coincide with the value found by Karush for the number of combining groups of bovine serum albumin with an azobenzoate ion (4).

*Suppression of Precipitation by Albumin*

It was found that at pH values of 5.0 and above, at which neither compound III nor compound VI produce a precipitate with albumin, the presence of albumin in the solution decreases the amount of precipitation of these compounds and $\gamma$-globulin. Measurements were made on a series in which the albumin concentration was varied and the pH kept at 5.26. The dye to protein molar ratios of the precipitates are given in Table II for globulin and for one of the

TABLE II

DYE–PROTEIN MOLAR RATIOS IN SOME ALBUMIN SUPPRESSION EXPERIMENTS AT pH 5.26*

| Compd. III, mgm. | Compd. VI, mgm. | Molar ratio of dye to protein. $\gamma$-Globulin with: | | | |
|---|---|---|---|---|---|
| | | Compd. III | Albumin and Compd. III | Compd. VI | Albumin and Compd. VI |
| 2.79 | 4.02 | 118 | 89 | 17.5 | 22.2 |
| 1.39 | 2.01 | 68 | 47 | 16.9 | 15.4 |
| 0.69 | 1.00 | 36 | 28 | 15.8 | 15.1 |
| 0.35 | 0.50 | 22 | 28 | 15.9 | 12.5 |
| 0.175 | 0.25 | 22 | 55 | 14.8 | 21.0 |
| 0.085 | 0.125 | 25 | | 10.1 | |
| | 0.062 | | | 5.4 | |

**In these experiments, 1 ml. dye solution containing 2.79 mgm. III or 4.02 mgm. VI was serially diluted with acetate buffer, and 0.5 ml. protein solution added, containing either 2.05 mgm. $\gamma$-globulin or 2.05 mgm. $\gamma$-globulin + 0.68 mgm. albumin. The protein solutions were buffered in acetate buffer of 0.10 ionic strength.*

globulin–albumin mixtures with each of the dyes. The amounts of precipitated protein for all the mixtures at pH 5.26 are shown in Figs. 2 and 3. Measurements of the suppression effect in which the protein concentrations were kept approximately constant and the pH varied from 5.00 to 5.40 are shown in Figs. 4 and 5. In all of the experiments 1 ml. dye solution and 0.5 ml. protein solution, at 0.10 ionic strength, were mixed.

The results may be comparable with the observation of Pardee and Pauling (9) at the somewhat higher pH of 6.2 in which serum albumin suppressed the precipitation of an antibody protein by its homologous polyhaptenic dye antigen.

No attempt was made to determine whether the protein in the precipitates

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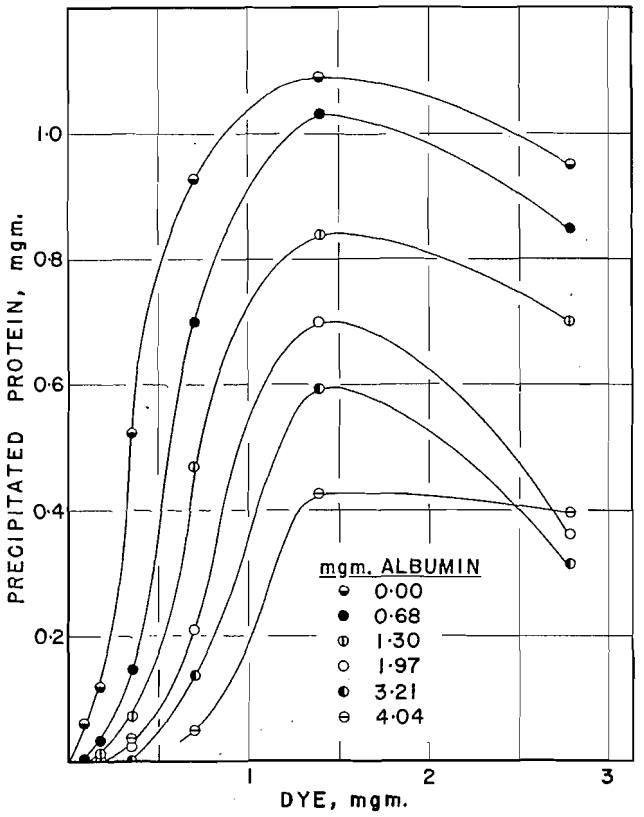



FIG. 2. The effect of albumin concentration on the precipitation of γ-globulin with compound III.

of the albumin suppression experiments was γ-globulin or a mixture of the two proteins. However, the dye–protein molar ratios of the precipitates of the systems dye–albumin–γ-globulin did not differ essentially from those for dye and γ-globulin alone (Table II), suggesting that the protein in the precipitates was probably γ-globulin. The reduction in the molar ratios of compound III in the presence of albumin, compared with its absence, is not inconsistent with the behavior of this compound. It has already been noted that the degree of aggregation of compound III, as indicated by the dye–protein molar ratios, depends on both pH and concentration, whereas the degree of aggregation of compound VI depends only on pH. In Table II, the smaller molar ratio in the presence of albumin could be a consequence of a reduction in dye concentration.

The results reported in this part are difficult to interpret because of the possible alternatives of the formation of soluble complexes of either dye–albumin, dye–albumin–globulin, or even albumin–globulin.

Nevertheless, one may speculate as to why the amount of precipitate formed in the presence of albumin is less than in its absence. It is seen in Figs. 2 to 5 that the effect of the presence of albumin is especially pronounced in the region where the amount of dye is small. This suggests that the effect is due to

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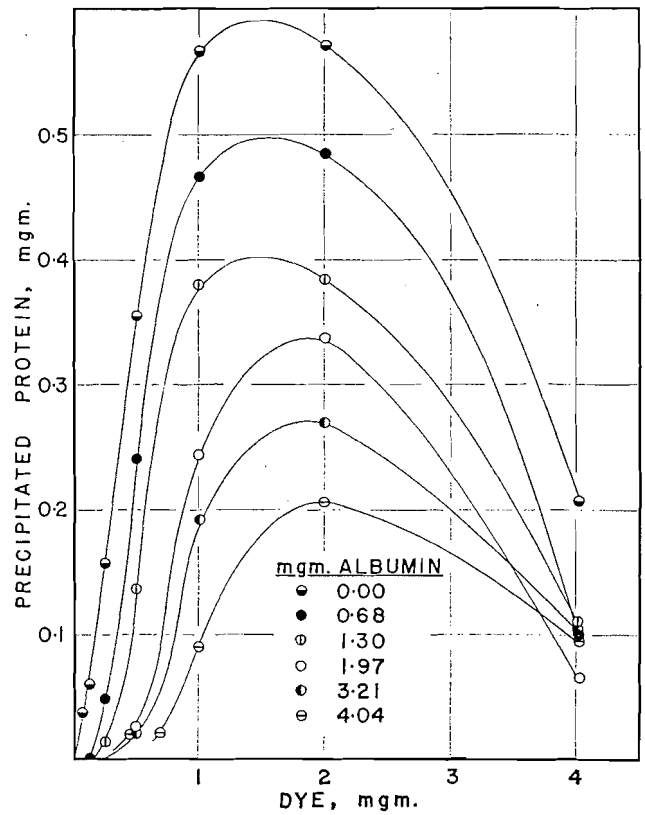



FIG. 3. The effect of albumin concentration on the precipitation of γ-globulin with compound VI.

the combination of the dye with albumin to form a soluble complex, kept in solution by the electrostatic repulsion of the strongly negatively charged molecules at these pH values, which are considerably greater than the isoelectric point of albumin. However, it is clear that the removal of the dye from solution by combination with albumin would alone not change the amount of precipitate at the maximum, but would only shift the position of the maximum. If, on the other hand, some globulin molecules are incorporated into soluble complexes with albumin, with the dye compound serving as a bond between them, this also would decrease the amount of precipitate. Inasmuch as at pH values greater than 5.0 and in the absence of albumin, only a part of the globulin is precipitated, some presumably being present as soluble complexes even at the optimum ratio of dye and protein, this explanation of the effect of albumin might be better given by saying that a larger amount of globulin is retained in solution in complexes because of the incorporation of albumin.

*Production of Antibodies in Vitro*

Pauling and Campbell (12) reported the production of antibodies *in vitro* by controlled denaturations of serum protein. *One* of their methods was to

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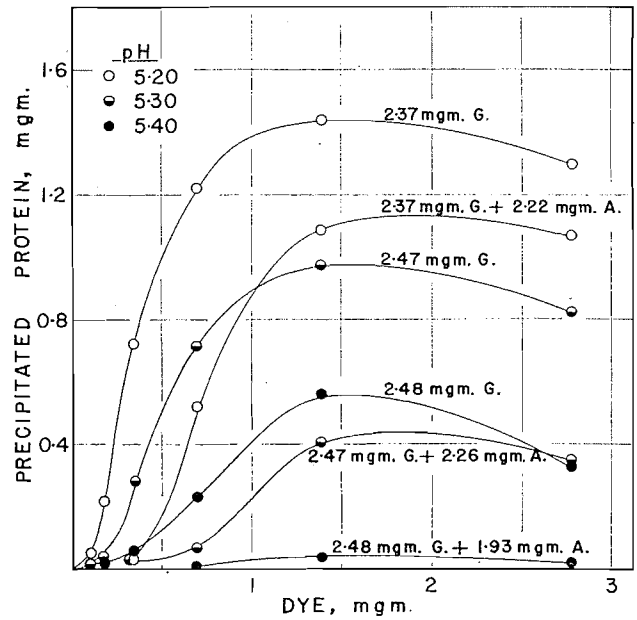



FIG. 4. The effect of pH on the suppression by albumin of the precipitation of γ-globulin with compound III.

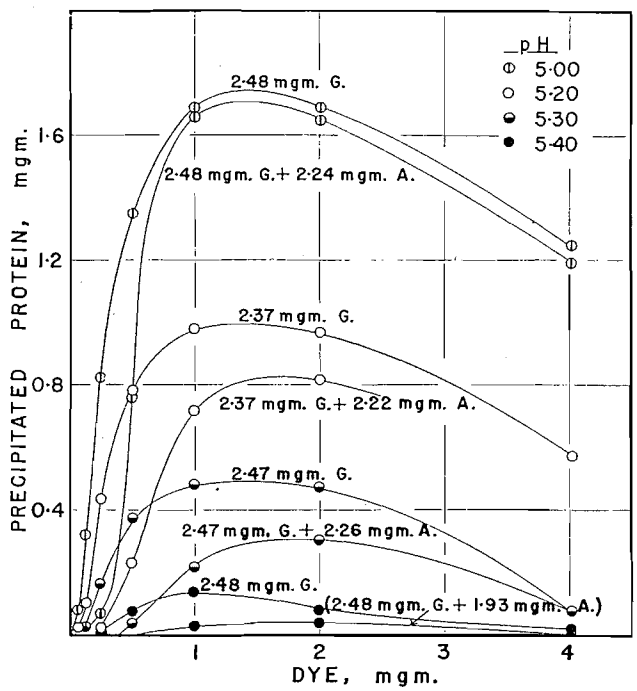



FIG. 5. The effect of pH on the suppression by albumin of the precipitation of γ-globulin with compound VI.

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maintain γ-globulin at 57°C. in the presence of compound VI, for several days; then the dye was removed from the protein by dialysis. The modified protein was found to behave like natural antibody in forming specific precipitates with the same dye compound. Typical precipitin curves were formed, but at pH values of 5.0 and 5.5 which are well below the pH values of the specific precipitation of natural antibodies (pH 7 to 9).

The results in the present paper suggest that this particular method of producing antibodies *in vitro* would be difficult to validate because any specific precipitates would be masked by nonspecific precipitation of the protein by the same dye at the same pH values.

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# KILIANI'S REDUCTION OF GLUCOSE AND FRUCTOSE CYANOHYDRINS TO THE CORRESPONDING HEPTANOIC ACIDS AND LACTONES[1]

By A. S. Perlin[2] and C. B. Purves

## ABSTRACT

Kiliani's classic reduction of α-glucoheptonic (D-gluco-D-guloheptonic) lactone led to small, variable yields of *n*-heptanoic acid and varying amounts of the lactone of a hydroxy-*n*-heptanoic acid. A repetition of this work showed that the combined yields of these two products reached a maximum near 70% of theory when the reduction with constant-boiling hydriodic acid (b.p. 127° C.) and phosphorus was limited to two hours. Under these conditions up to 9/10ths of the product consisted of the lactone. After purification through the hydrazide, m.p. 89° C., the fragrant smelling lactone boiled at 61° to 62° C. at 10 mm. pressure, had a density of 0.9948, and a refractive index of $n_D$, 1.4405, both at 20° C. The supposition that this lactone referred to 4-hydroxy-*n*-heptanoic acid was confirmed by preparing it from the known 4-keto-*n*-heptanoic acid, which in turn was synthesized by an improved method.

The optimum time for reducing an uncrystallized mixture of α- and β-fructoheptonic acids under similar conditions was three to four hours, and the optimum yield of product was again near 70% of theory. This product consisted almost exclusively of the lactone of 2-methyl-4-hydroxyhexanoic acid. After purification through the crystalline hydrazide, m.p. 122° C., the lactone was recovered as a fragrant oil boiling at 48° to 49° C. at 2 mm. pressure, with density 0.9806 and refractive index $n_D$ 1.4332 at 25° C. The structure of this lactone was not in doubt.

These lactones, prepared in good yield and with well defined hydrazides, were more readily characterized than the fully reduced heptanoic acids upon which Kiliani relied.

## INTRODUCTION

While considering possible ways of locating carbonyl groups in oxystarches and oxycelluloses, it appeared that the method Kiliani used in 1885 to 1888 to solve the same problem for reducing sugars might be capable of development. In the case of fructose (structure I), for example, the addition of the elements of hydrogen cyanide gave the cyanohydrin which was hydrolyzed to the α,β-mixture of the corresponding fructoheptonic acids (II). Reduction of these acids with red phosphorus and hot hydriodic acid then yielded methyl-*n*-butyl acetic acid (III), and the result clearly showed that the ketone group occupied the second position in the fructose. Application of the same sequence to glucose first gave the lactone of glucoheptonic acid and then *n*-heptanoic acid. Mowry (29) reviewed the general applications of the cyanohydrin synthesis, and its value

| | | | |
|---|---|---|---|
| $H_2COH$ | $H_2COH$ | $CH_3$ | $CH_3$ |
| CO | HOC — R | HC — COOH | HC — CO |
| HOCH | HOCH | $CH_2$ | $CH_2$ \| |
| HCOH | HCOH | $CH_2$ | CH—O |
| HCOH | HCOH | $CH_2$ | $CH_2$ |
| $H_2COH$ | $H_2COH$ | $CH_3$ | $CH_2$ |
| I | II R = CN → $CONH_2$ → COOH | III | IV |

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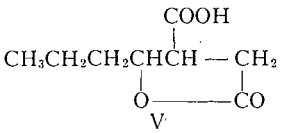
for the preparation of higher sugars was discussed in detail by Hudson (12); others (3, 13, 32) studied the preparation and hydrolysis of the sugar cyanohydrins, and the synthesis has been recently used to estimate carbonyl groups in hydrocelluloses and reducing sugars (11, 39), as well as to obtain sugars containing radioactive carbon (14). The reduction of the sugar acids to hydrocarbon acids, on the other hand, has received little attention since the time of Kiliani.

As early as 1860, Lautemann (24) employed concentrated hydriodic acid at 140° C., or "phosphorus di-iodide" and a little water near 100° C., to reduce lactic to propionic acid. Wislicenus (37) extended the work to pyruvic acid, and noted that the presence of phosphorus made possible a great economy in hydriodic acid. Benzylic acid was economically reduced to diphenylacetic acid in this way (26), and the general utility of the process was discussed by Miescher and Billeter (27). According to Kehrer and Tollens (15), the reduction of levulinic acid was preferably carried out for 12 hr. at 150° C. followed by eight hours at 200° C., but cyclic $C_{10}$ to $C_{15}$ hydrocarbons and tar were formed as by-products. The first application of the method to sugar acids was by Kiliani and Kleeman (23), who heated 1 part of gluconolactone under reflux with 10 parts of constant-boiling hydriodic acid and 0.4 parts of red phosphorus for seven hours. The relevant portion of the product, a red oil containing 2% of combined iodine, was de-iodinated with zinc and boiling hydrochloric acid, and the lactone of 4-hydroxyhexanoic acid (caprolactone) remained in a yield of 40% at most. This lactone gave caproic acid in small but unstated amount when the reduction was repeated at 160° instead of 127° C., but much of the starting material was recovered unchanged.

Kiliani's similar reduction of fructoheptonic acids (16) at reflux temperature gave about 60% of the theoretical yield of a heptanoic lactone, which was further reduced at 180°C. for 7.5 hr. to neutral substances and an unstated yield of an acid later proved to be 2-methyl hexanoic acid (17). The same acid was obtained in about 30% yield by Spoehr and Strain (36) who reduced a mixture of nonfermentable sugars, called "glutose", prepared by the action of alkaline phosphate solution on glucose or fructose. A temperature of 150° to 170° C. was employed for two hours in this reduction. Kiliani's experiments on the reduction of $\alpha$-glucoheptonic (D-gluco-D-guloheptonic) lactone (18, 19) showed that only traces of *n*-heptanoic acid survived when similar temperatures were used, and that hydrocarbons were the major product. At reflux temperature, however, about half of the starting material was reduced to *n*-heptanoic acid in five hours, and more was recovered as the crude lactone of a hydroxy-*n*-heptanoic acid. The ready decomposition of the straight chain 7-carbon acid led to the adoption of reflux conditions in later reductions; galaheptonic acid after 1.5 hr. gave an unstated yield of heptonic lactone and an extremely small amount of a fatty acid (21); barium mannoheptonate yielded 15% of a lactone and 30% of *n*-heptanoic acid after five hours (8); and mannolactone (from L-arabinose) gave after five hours a large yield of caprolactone and *n*-hexanoic acid in smaller amount (20). Although the quantitative aspects of all the above work were unsatisfactory, they suggested that high and reproducible yields might be obtained if proper conditions were found for the reduction. The discovery of such conditions was the primary object of the present research.

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Kiliani (19, 21) encountered difficulties in obtaining the *n*-heptanoic lactone in a pure condition, although the samples from the reduction of gluco- and galactoheptonic acids gave crystalline barium salts that seemed to be identical. This identity was extended by Fittig and Schmidt (10) to a barium salt corresponding to a lactone obtained by the destructive distillation, at 250° to 260° C., of propyl paraconic acid (V), which had been synthesized from bu-



V

tyraldehyde, sodium succinate, and acetic anhydride. The yield of lactone from this distillation was small (5%), and the major product was an unsaturated heptanoic acid, from which more of the lactone could be prepared by adding and then removing the elements of hydrogen bromide. Rupe, Ronus, and Lotz (31) also obtained the lactone by the action of sulphuric acid on a mixture of unsaturated acids prepared by heating α-bromoheptanoic acid with quinoline, and Bagard (1) by the destructive distillation of α-hydroxyheptanoic acid. In all three cases the carbon and hydrogen analyses were satisfactory. Since these observations hardly sufficed for the claim that the lactone was that of 4-hydroxyheptanoic acid, their reliability was incidentally confirmed by an independent synthesis during the present research. The lactone from fructoheptonic acid was certainly that of 2-methyl-4-hydroxyhexanoic acid, because Blaise and Luttringer (2) obtained it by reducing the corresponding 4-keto acid, which was synthesized from ethyl sodio-*n*-propionyl acetate and ethyl 2-bromopropionate. Another synthesis was carried out by Lukeš (25).

## RESULTS AND DISCUSSION

Pure α-glucoheptonic lactone was heated under reflux for varying times with red phosphorus and constant-boiling hydriodic acid, and the resulting dark syrup was freed from combined iodine either by high pressure hydrogenation or, more conveniently, by nickel–aluminum alloy and caustic soda, according to Schwenck, Papa, and Ginsberg (34). Kiliani's use of zinc and hydrochloric acid for this purpose was found to be tedious and uncertain. After recovery, the product distilled almost completely between 97° and 113° C. at 20 mm. pressure as a pale yellow, acidic oil with a somewhat variable refractive index. This oil was accepted as the crude lactone of 4-hydroxyheptanoic acid, and the yields given in Table I were calculated on this basis.

When the de-iodinated products from the reduction period of 0.75 hr. were recovered in ether, a small amount of insoluble material remained. The reason that the yield in Experiment 2 exceeded that in Experiment 1 was perhaps because in the former case the above fraction was redissolved in alkali, reprecipitated by acid, and re-extracted with ether. This fraction was absent when the reduction was more prolonged. The table clearly shows that reduction for 1.75 to 2 hr. gave the highest yields of about 70% of theory (Experiments 3, 4, and 5) and that times of three and four hours were definitely less advantageous. Although the rate of the reduction was considerably lessened when the temperature was reduced from 127° to 100° C. (Experiment 9), a time much longer than 5.5

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TABLE I

REDUCTION OF α-GLUCOHEPTONIC LACTONE[a]

| Expt. | Hours | Yield,[b] % | Refractive index | |
|---|---|---|---|---|
| | | | $n_D$ | °C. |
| 1 | 0.75 | 54 | 1.4360 | 24 |
| 2 | 0.75 | 62 | 1.4355[c] | 27 |
| 3 | 1.75 | 72 | 1.4360[d] | 24 |
| 4 | 2 | 70 | 1.4365 | 25 |
| 5[e] | 2 | 72 | 1.4370 | 25 |
| 6 | 3 | 60 | 1.4390 | 20 |
| 7[f] | 3 | 53 | (I)[g] 1.4390 | 25 |
| | | | (II) 1.4390 | 25 |
| 8 | 4 | 47 | (I) 1.4265[h] | 19 |
| | | | (II) 1.4400 | 19 |
| 9 | 5.5[k] | 48 | 1.4380 | 24 |

[a] *Five grams of the lactone, 2 gm. of red phosphorus, and 70 gm. of hydriodic acid under reflux at 127° C.*
[b] *After de-iodination by hydrogenation and after a single distillation. Calcd. as % of the theoretical amount of heptonic lactone, 3.08 gm. from 5 gm. of the glucoheptonic lactone.*
[c] *Neutralization equivalent 128. Theory, 128.*
[d] *Neutralization equivalent 130.*
[e] *De-iodination with nickel-aluminum alloy.*
[f] *Double the quantities noted in (a) were used.*
[g] *Successive fractions of the single distillation denoted by (I) and (II).*
[h] *Neutralization equivalent, 202, 193. Theory 128.*
[k] *Reduction at 100° C. instead of 127° C.*

hr. might have given the highest over-all yield. A shorter period of 3.5 hr. at 100° C. gave too small a yield of de-iodinated product to warrant further investigation. The same result was encountered when the large excess of hydriodic acid employed in the reduction was replaced by a small amount of potassium iodide in presence of 90% phosphoric or 20% hydrochloric acid, and a considerable amount of charring occurred in the former mixture. Since redistillation of the crude lactone, even into a receiver cooled by solid carbon dioxide, occasioned a 10% loss, the yields in Table I were low by at least this amount.

In order to study the properties of the crude lactone in greater detail, that from Experiment 8 was fractionally distilled. The first fraction, roughly corresponding to (I) in Table I, boiled at 46° to 48° C. at 12 mm. pressure and had a low refractive index, $n_D^{19}$, 1.4130, and the high neutralization equivalent of 342, 351 (theory 128). These properties suggested that some decarboxylation occurred during the reduction, but the higher boiling fraction (b.p. 88° to 94° C.) was almost pure lactone. In Experiments 2 and 3, however, the neutralization equivalents were correct, and in these cases the somewhat low refractive indices pointed to contamination with heptanoic acid, $n_D^{20}$, 1.4234 (28). A 7% yield of this acid was isolated as the crystalline *p*-bromophenacyl derivative by oxidizing the crude lactone with nitric acid and distilling the liquor in steam. The crude lactone deposited Bagard's (1) "hydrazino-lactone" in high yield when warmed with hydrazine hydrate, and Darapsky and his collaborators (7) later showed that such compounds were true hydrazides. Hydrolysis of the pure, crystalline hydrazide, m.p. 89° C., made it possible to regenerate the pure lactone as a fragrant, colorless, neutral oil with a refractive index of $n_D^{20}$, 1.4405. In addition

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to being rather stable to constant-boiling hydriodic acid under reflux, the lactone was recovered without change from an attempt to reduce it with Raney nickel catalyst and hydrogen at 110° C. and 2000 p.s.i. for 2.5 hr.

The early view that the lactone was derived from 4-hydroxyheptanoic acid was supported by the recovery of succinic acid in 35% yield from a sample oxidized with boiling nitric acid. Confirmation was obtained when the hydrazide of the lactone from the Kiliani reduction failed to depress the melting point of the hydrazide of the hydroxy acid prepared by reducing crystalline 4-keto-*n*-heptanoic acid with aluminum isopropylate, or by hydrogenation over a platinum oxide catalyst. Bouveault and Bongert (4) synthesized the keto acid by a standard method that established its structure, but they failed to record a yield. The sample used on the present occasion was obtained in 27% yield by condensing succinic anhydride with di-*n*-propyl cadmium in isopropyl ether, or by the general method of Cason and Prout (6).

Since the separation and crystallization of the isomeric α- and β-fructoheptonic lactones was difficult and gave poor yields (22, 33), the reductions with hydriodic acid and red phosphorus were carried out on the crude α,β-mixture obtained when the cyanohydration of fructose, and the subsequent hydrolysis of the cyanohydrin, were known to be at least 96% complete. After the reductions at 127° C., which were standardized except for time, the products were freed of combined iodine and once distilled as already described. The colorless, neutral oils boiled at 50° to 55° C. and 1 mm. pressure and were more uniform as regards refractive index than those from α-glucoheptonic lactone. When condensed with hydrazine hydrate, they yielded the crystalline hydrazide, melting at 123° to 124° C., characteristic of the hydrazide of 2-methyl-4-hydroxyhexanoic acid (IV) (2). Acid hydrolysis of the purified hydrazide then gave the pure lactone as a fragrant oil. The yield of this oil in the crude state was not very sensitive to the time of reduction over the period two to five hours (Table II) but the optimum was probably near four hours.

Although fructoheptonic was somewhat less easily reduced than α-glucoheptonic acid to the lactone of the corresponding 4-hydroxy fatty acid, in both cases the crude yield was at least 70%, and the lactones were readily characterized as crystalline hydrazides. Kiliani's further reduction of these lactones, in much poorer yield, to the unsubstituted fatty acids therefore appeared to be unnecessary in a modern repetition of his research.

## EXPERIMENTAL

All melting points were uncorrected.

### *Reduction of α-Glucoheptonic Lactone*

Following Kiliani's (18) method, 5 gm. samples of the pure, crystalline lactone (13) were heated under reflux with 70 gm. of constant-boiling hydriodic acid (sp. gr. 1.7) and 1.7 to 2.0 gm. of red phosphorus. In other experiments which used potassium iodide in place of the hydriodic acid (26, 27), 5 gm. of the lactone was heated under reflux with 35 cc. of 90% phosphoric acid, 3 gm. of red phosphorus, and 1 gm. of potassium iodide; or with 50 cc. of 20% hydrochloric acid, 5 gm. of red phosphorus, and 3.5 gm. of potassium iodide. After the heating

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period, which varied from 45 min. to six hours, the reaction mixture was cooled, diluted with 150 cc. to 200 cc. of water, and extracted continuously with ether for 12 hr. A more rapid procedure was to saturate the liquor with ammonium sulphate and to extract three or four times with ether in a separatory funnel. The ether extract was filtered through glass wool to remove any phosphorus and was carefully concentrated at atmospheric pressure to a syrup.

In the earlier runs the removal of combined iodine from this syrup was accomplished by solution in 110 cc. of *N* sodium hydroxide and hydrogenation for two hours with hydrogen at 2000 p.s.i. and 110° C. over 2 gm. of Raney nickel catalyst (30). The liquid, originally turbid, changed to a clear yellow solution from which nickel was removed by filtration; acidification to pH 1 with 10% sulphuric acid followed, and then continuous extraction for three hours with ether. An alternative, and more convenient, method of de-iodination (34) consisted of dissolving the syrup in 80 cc. of 2 *N* sodium hydroxide contained in a tall, narrow, 500 cc. beaker covered with a watch glass. Six grams of Raney nickel–aluminum alloy powder was gradually and cautiously added during 10 min., and after the foaming subsided the mixture was kept at 90° to 95° C. for about 75 min. with occasional stirring. Sulphuric acid, 10%, was then added until the aluminum hydroxide initially precipitated was redissolved, and the extraction with ether was carried out for three hours.

The residue from the dried ether extract gave a pale yellow oil when distilled, preferably at 20 mm. pressure and into a receiver cooled in acetone – solid carbon dioxide; b.p. 109° to 113° C. (20 mm.), 88° to 94° C. (11 mm.), and 68° to 70° C. (1 mm.). Yields were recorded in Table I. Although the still-pot retained traces of charred material, decomposition caused by any entrained sulphuric acid probably did not occur during the distillation, because charring was not increased by the prior addition of a few milligrams of this acid. Kiliani's conclusion that the oil was impure heptonic lactone was supported by the low (0.8%) and variable results of combustion analyses.

*Hydrazide of 4-Hydroxy-n-heptanoic Acid*

The crude lactone, 0.5 gm., was heated upon the steam bath for two hours with 0.2 gm. of hydrazine hydrate (2). Upon cooling, the liquid solidified and the mass was twice recrystallized from ethyl acetate. The light white crystals (0.2 gm.) melted correctly at 88° to 89° C. (1) and a mixed melting point with an authentic sample (see below) was not depressed.

*Lactone of 4-Hydroxy-n-heptanoic Acid*

A 0.8 gm. sample of the pure hydrazide, dissolved in a small amount of water, was made strongly acid with dilute sulphuric acid and was heated for two to three minutes on the steam bath. The ether extract was filtered through glass wool, was dried, and the residue was distilled through a semimicro Cooke–Bower column (5). Three fractions were collected at 61° to 62° C. and 2 mm. pressure, and a fourth at 62° to 67° C., the total yield being 0.4 gm. The colorless oil had a density $d_{20}^{20}$, 0.9948, a refractive index, $n_D^{20}$, 1.4405, was neutral toward aqueous sodium carbonate, and gave a negative test for the hydroxyl group with phenyl and α-naphthyl isocyanate. Calcd. for a lactone $C_7H_{12}O_2$: mol. refraction, $M_D$,

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34.08; neutralization equivalent, 128. Found: $M_D$, 33.92, neutralization equivalent, 128. Molecular refractions were calculated as described in the book by Shriner and Fuson (35), and neutralization equivalents after saponifying 15 to 20 mgm. samples in aqueous ethanolic alkali by warming for 15 to 20 min. on the steam bath.

*Oxidations of 4-Hydroxy-n-heptanoic Lactone*

The procedure used by Fittig and Messerschmidt (9) for valerolactone was followed.

(*a*). A pure sample, 2.3 gm. from a Kiliani reduction, was heated under reflux with 82 cc. of aqueous nitric acid (1 vol. : 1 vol.) for one hour, after which time the evolution of oxides of nitrogen had almost ceased. The liquid was then steam-distilled into a receiver cooled to − 10° C., but ether extracted from the 400 cc. of distillate no acid that gave a crystalline *p*-bromophenacyl derivative. Nevertheless, propionic, butyric, and acetic acid (from malonic acid) were probably present. Concentration of the still residue *in vacuo* yielded 0.74 gm. (35%) of succinic acid melting at 165° to 171° C., and at 170° to 175° C. when mixed with an authentic sample, m.p. 185° C. Recrystallization raised the m.p. to 180° C., and the mixed m.p. to 181° to 183° C.

(*b*). The once distilled, but still crude, acidic lactone from a Kiliani reduction, 1.53 gm., was oxidized with nitric acid, 54 cc., and the liquor steam distilled as just described. The distillate, 200 cc., was strongly acidified with sulphuric acid and was extracted four times with ether. Distilled water, 3 to 4 cc., was added to the extract and after evaporation of the ether the aqueous residue was nearly but not quite neutralized with dilute sodium hydroxide. The solution was then heated under reflux with 1 gm. of *p*-bromophenacyl bromide and 10 cc. of ethanol for one hour (35), and the crystals deposited when the solution cooled were twice recrystallized from 50% ethanol. The first crop, 0.18 gm., melted at 70° to 71° C., unchanged by admixture with the *p*-bromophenacyl derivative of authentic *n*-heptanoic acid (28). The melting point of the second crop, 0.09 gm., was increased from 63° to 65° C. to 68° to 70° C. by a similar admixture. These yields corresponded to one of 0.11 gm. of free heptanoic acid, or to about 7% of the original crude lactone.

*Improved Synthesis of 4-Hydroxy-n-heptanoic Lactone*

Di-*n*-propyl cadmium, when prepared by a general procedure (6), proved too volatile to be readily isolated from the ether–benzene used as a solvent. Magnesium turnings, 8.8 gm. (0.37 mole), were suspended in 200 cc. of anhydrous, peroxide-free isopropyl ether and 29 gm. (0.37 mole) of dry 1-chloropropane was slowly added under an atmosphere of nitrogen. After gentle heating to dissolve the magnesium completely, the solution was cooled in an ice bath and 34.8 gm. (0.19 mole) of anhydrous cadmium chloride was added in one portion. Thirty grams (0.3 mole) of pure succinic anhydride was added in one portion, the mixture was heated under reflux for four hours and was kept at room temperature for a further 12 hr. before being slowly poured into an excess of ice and dilute sulphuric acid. The aqueous phase was extracted with isopropyl ether and the extract combined with the upper layer. Acids were removed from the upper layer by

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four extractions with 5% sodium carbonate, and were recovered by extracting the acidified sodium carbonate solution for 12 hr. with ether.

The residue from the ether, 21.7 gm. of a yellow oil, when distilled at 1 mm. pressure yielded 12.5 gm. (27%) of a clear colorless oil that boiled at 95° to 105° C. and crystallized readily in the receiver. Two recrystallizations raised the melting point to 48.5° to 49.5° C., in agreement with that quoted for *n*-4-ketoheptanoic acid (4, 25). The analyses and neutralization equivalent were also correct. In one experiment employing 15 gm. of succinic anhydride, the ether extract yielded 6.6 gm. of succinic acid in addition to the main product.

One gram of the pure keto acid was reduced by boiling under gentle reflux for 90 min. with 1 gm. of aluminum isopropoxide and 7 cc. of toluene, according to the procedure of Young and co-workers (38). Toluene was then allowed to distill slowly from the solution through a Widmer column, and was replaced at intervals by fresh toluene until the distillate amounted to 20 cc. three hours later. A slurry made from 30 cc. of 6 *N* sulphuric acid and crushed ice was added to the still residue, and the mixture was extracted six times with ethyl ether until the gel originally present had disappeared. Distillation of the oil recovered from the ether–toluene yielded 0.64 gm. (65%) of 4-hydroxy-*n*-heptanoic lactone with the correct neutralization equivalent and refractive index. The hydrazide melted correctly at 88° to 89° C. (1). As others observed (31), the lactone had a strong odor reminiscent of clover.

*Reduction of α,β-Fructoheptonic Acid*

Five grams of pure fructose, dissolved in 75 cc. of water, was mixed with 25 cc. of a solution containing 2.4 gm. of sodium cyanide (75% excess) and buffered to pH 9.5 with acetic acid. A preliminary experiment showed that the condensation was about 96% complete after 60 hr. at room temperature. At the end of this time, the mixture was diluted to 300 cc. and 150 cc. were distilled *in vacuo*. The still residue was again diluted to 300 cc. and the distillation repeated in order to complete the hydrolysis of the cyanohydrin and the expulsion of the ammonia. After acidification to pH 3 with hydrochloric acid, the still-residue was evaporated *in vacuo* to expel hydrogen cyanide and to recover the sodium salts of α- and β-fructoheptonic acid as a thick, yellow-brown syrup contaminated with sodium chloride.

A mixture of the syrup with 55 cc. of constant-boiling hydriodic acid was gently warmed until complete solution occurred without charring, and 2.5 gm. of red phosphorus was then added. The flask was connected to a small Liebig condenser and a slow distillation was carried out until the vapor temperature reached 125° to 127°C., or that of constant-boiling hydriodic acid; thereafter heating was continued under gentle reflux for two to five hours. At the end of this period the distillate was combined with the reaction mixture, and the products were isolated by extraction with ether followed by de-iodination with nickel–aluminum alloy, as already described for the reduction of glucoheptonic lactone. The final product, when distilled at 50° to 55° C. and 1 mm. pressure, was a clear, colorless oil with a refractive index near $n_D^{25}$ 1.4330. Yields were recorded in Table II.

Condensation of this oil with hydrazine yielded a hydrazide whose nitrogen

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TABLE II

REDUCTION OF THE α,β-FRUCTOHEPTONIC ACID MIXTURE[a]

| Expt. | Hours | Yield[b], % | Refractive index | |
|---|---|---|---|---|
| | | | $n_D$ | °C. |
| 1 | 2 | 59 | 1.4340 | 25[c] |
| 2 | 2 | 57 | 1.4335 | 27[d] |
| 3 | 3 | 62 | 1.4340 | 24 |
| 4 | 4 | 72 | 1.4320 | 25 |
| 5 | 4 | 64 | 1.4345 | 25 |
| 6 | 4 | 74 | 1.4330 | 24 |
| 8 | 5 | 68 | 1.4320 | 28 |

[a] *Five grams of fructose converted to the heptonic acids and reduced with 2.5 gm. of red phosphorus and 55 cc. of constant-boiling hydriodic acid at 127°C.*
[b] *Based on the theoretical yield, 3.55 gm., of 2-methyl-4-hydroxyhexanoic lactone from 5 gm. of fructose.*
[c] *Neutralization equivalent 128. Theory 128.*
[d] *Neutralization equivalent 129.*

content of 17.5% and melting point of 123° to 124° C., after two recrystallizations from chloroform, were those of the hydrazide of 2-methyl-4-hydroxy-4-ethyl butyric acid (2). The hydrazide was hydrolyzed with sulphuric acid as previously described and the product was distilled at 2 mm. pressure in the Cooke–Bower (5) column. Three fractions were collected at 48° to 49° C. and a fourth at 48° to 54° C. The product, 2-methyl-4-ethyl butyrolactone (structure IV), was a colorless oil with a delicate odor, with $n_D^{25}$ 1.4332 and a density, $d_{20}^{25}$, 0.9806. Found: neut. equiv. 127, 128; $M_D$ 33.94. Calcd. for a lactone $C_7H_{12}O_2$: neut. equiv. 128; $M_D$ 33.99.

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# AN ELECTRON-MICROGRAPH STUDY OF OXIDE FILMS ON ELECTROPOLISHED SURFACES OF IRON[1]

By E. J. Caule and M. Cohen

ABSTRACT

An electron micrographic study has been made of iron surfaces subjected to electropolishing. It has been found that although electropolishing produces a relatively smooth surface, the iron is covered with a film. The strengthening of this film by oxidation and its disruption by reduction with hydrogen have been followed. The film is assumed to be oxide and its thickness has been estimated to be approximately 100 Angstrom units. The effect of reduction of the film on surface area and thus on initial oxidation rates of the reduced specimen has been considered.

## INTRODUCTION

For some time electropolishing has been advocated as a method of preparation of metal surfaces for studies of oxidation rates. This has arisen from the fact that metallographic grinding and polishing produces a surface which is distorted and is not representative of the metal. It has also been shown (4, 14) that in some cases oxide films and inclusions are formed by mechanical polishing.

For most common metals and alloys, the proper electropolish treatment, once found by trial and error, will give a high degree of polish. This is assumed to be associated with a low specific area (or low "roughness factor"), a desirable feature for quantitative oxidation study since a surface of low specific area will be more invariable, as oxidation proceeds, than one of high specific area. In discussing the cleanliness and lack of disturbance in the structures of electropolished surfaces, Jacquet (7) showed that electrodeposits of copper on electropolished copper electrodes will follow the crystal pattern of the electrode, while on mechanically polished electrodes they will set up their own grain structure and orientation. His conclusion that electropolishing gives a clean surface was supported by Allen (1) who by two independent methods found no oxide on electropolished copper. On the other hand, Raether (12) used electron diffraction on copper and aluminum surfaces and concluded that there was a film produced by electropolishing which affected the rate of subsequent oxidation of the specimens in air. Hoar and Farthing (6) by an indirect method detected a film on brass while it was being electropolished. Cohen (3) has detected an oxide film on electropolished iron by the use of electron diffraction. Wilms (15) has produced micrographic evidence for the existence of a film on electropolished aluminum. Furthermore, it will be noticed in any collection of technical or scientific formulae for electropolishing baths that a great number of such successful formulae contain oxidizing agents, of which the most common is perchloric acid. There is therefore sufficient evidence to suspect that electropolished metal surfaces may be covered by very thin films whose thickness may be controlled by variables not yet appreciated.

The work to be described below is a study, with the aid of the electron microscope, of the topography of the surfaces produced by the electropolishing of one

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particular batch of iron in one successful bath liquid. Since it was not a comparative study of formulae or metals, care must be exercised in drawing general conclusions from the results. Gulbransen and his co-workers (10) have employed the electron microscope in oxidation experiments to examine oxide films which had been stripped from the substrate metal; since these were examined by transmission they could give little information about the topography of the surfaces. The same is true of the work of Mahla and Nielsen (8). In the present research plastic replicas of iron surfaces were made and shadow cast with chromium. Changes in surface structure due to oxidation and reduction were used to determine the normal features of the electropolished metal surface.

## EXPERIMENTAL

The iron used was a sample obtained through Dr. U. R. Evans of Cambridge University from the British Iron and Steel Research Association. Its analysis was: C—0.005, Si—0.0075, S—0.013, P—0.003, Mn—0.007, Ni—0.018, Cr—0.02, Cu—0.003, O—0.12, N—0.008, H—0.00009%. As supplied, it was in sheets 15 cm. × 30 cm. × 0.003 cm. From these sheets specimens were cut to a size of 1 cm. × 1½ cm. and were degreased in benzene. A soft iron wire was spotwelded to the middle of one edge to provide a lead for the electropolishing current.

The conditions necessary for electropolishing this particular type of iron were determined by trial and error. The composition of the electropolish bath is based on that used by Radanovich and Wert (11), i.e., 850 cc. ethyl alcohol, 70 cc. water, and 50 cc. concentrated perchloric acid, but was modified by the addition of 23 cc. concentrated hydrochloric acid. The current density used was 1.0 ampere per sq. cm. and the temperature of the bath was kept below 18° C. by surrounding the bath with copper cooling coils. After having been polished for 30 sec. the specimen was rapidly washed in distilled water, then in alcohol, then in distilled water, and finally again in alcohol, after which it was allowed to dry. Drying was hastened by waving the specimen in the air.

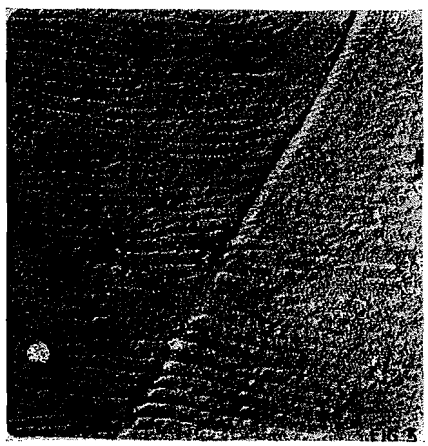
The replicas of the metal surface were made as follows. A drop of a solution of ½% Formvar in 1,4-dioxane was placed on the specimen and the excess drained off the lower edge onto filter paper. The specimen was then held at a 45° angle until the solvent had evaporated, usually in three minutes. It was heavily scored with a razor blade in squares about 3 mm. on an edge. Double-sided "Scotch tape" was pressed down on the plastic after the plastic had been moistened by heavily breathing on it and the tape was then removed smoothly from the metal surface. The replica, now on the "Scotch tape", was shadow cast with chromium at an angle whose tangent was ⅕, after which it was removed from the tape by gentle agitation in amyl acetate. Sections were picked up on portions of 250 mesh screen, washed in fresh amyl acetate, and finally picked up on the 200 mesh grids used in the electron microscope. The instrument used in obtaining the pictures was an R.C.A. model EMU.

Oxidations and reductions were performed in the infrared furnace previously described (2). Specimens to be treated were spotwelded at one corner to a chromel–alumel thermocouple and supported in the furnace. They were then heated in a vacuum after which appropriate pressures of air or of hydrogen were

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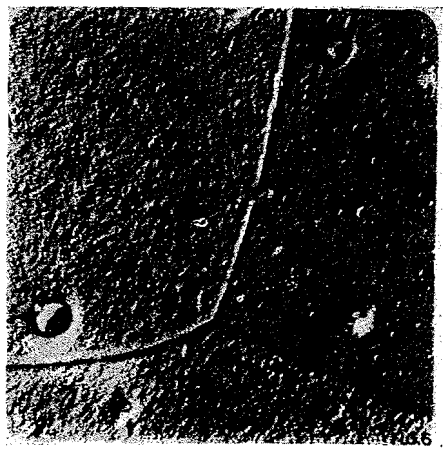






1. Mechanical polish. ×16,000
2. Electropolished. ×6,000
3. Electropolished, reduced in 0.05 mm. $H_2$ at 360°C. for 20 min. ×6,000
4. Electropolished, reduced in 0.05 mm. $H_2$ at 440°C. for 45 min. ×8,000

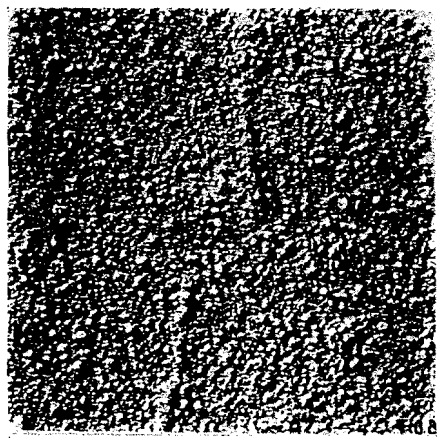
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5. Same specimen as 4. ×11,000
6. Electropolished, oxidized in 0.01 mm. air at 310°C. for 0.5 minute to purple brown color. ×6,000
7. Electropolished, oxidized to blue temper color. ×11,000
8. Electropolished, reduced in 0.05 mm. $H_2$ at 550°C. for 62 min., then oxidized in 0.01 mm. air at 250°C. for 1 min. ×16,000

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admitted. As mentioned in the description of the furnace, good control of the duration of heating was possible. After removal from the furnace, the test pieces were covered with plastic solution within a few minutes.

## RESULTS

Electron micrographs were made of replicas of specimens which had been treated as follows:

(*a*) As electropolished.
(*b*) Reduced after electropolishing.
(*c*) Oxidized after electropolishing.
(*d*) Reduced and re-oxidized after electropolishing.

For comparison, a specimen which had been given a metallographic mechanical polish is shown. The exact treatments are given in the captions of the photographs. The photographs are "reverse prints" and have the same appearance as the negatives.

Photograph 1 is typical of a mechanically polished specimen, while photograph 2 is typical of an electropolished specimen and it is evident that the electropolishing treatment produces a relatively smooth surface. Photographs 3, 4, and 5 are of electropolished specimens which have been reduced in hydrogen, with 4 and 5 having been reduced at a higher temperature for a longer time. The reduction in hydrogen leads to a furrowed surface with patches of film and some distortion of the surface lifting the film. There is also a decrease in the sharpness and depth of the boundary. Photographs 6 and 7 are of electropolished surfaces which have been oxidized to a purple brown and a blue color respectively. The main features of the pictures are the change in texture on oxidation and the filling in of the grain boundaries with increasing oxidation. Photograph 8 is of an originally electropolished surface which was reduced and then oxidized to a light golden color. This treatment results in a very rough surface, which, according to Evans (5) is necessary for the production of temper colors. A close examination shows traces of what appears to be an old boundary.

## DISCUSSION

A comparison of the electronographs of the mechanically polished and electropolished surfaces of iron (Figs. 1 and 2) shows that the electropolished surface is much the smoother. This has also been observed with electron micrographs of copper (13).

On treatment of an electropolished surface with hydrogen there is a shrinking and breaking effect on it. This film is most probably an oxide film. Examination of photographs 3, 4, and 5 shows that light reduction furrows the surface and that further reduction results in small patches of oxide being left as islands on a reduced surface. In some cases, as in photograph 4, there is a comparatively large area of unreduced oxide (in the center of the photograph) with probably some curling at the edges. The shadowing on photographs 4 and 5 is sufficiently sharp to allow an estimate to be made of the thickness of the film. From a consideration of the shadowing angle, the width of the dark areas, and the magnification, the thickness of the oxide is estimated to be about 100 Angstrom units.

The film grows on the iron during the electropolishing and drying process,

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since the specimen of Fig. 2, which was covered with plastic as soon as it was dry, still appears to have a film. From the data in this study it is not possible to determine whether the oxide is formed during the polishing process or during the drying. Such a decision would be of value to the electrochemist since there is at present no adequate theory of electropolishing. The view that an oxide film arises in the polishing process would be in accord with that of some authors who believe that the presence of a film is necessary before polishing, as distinct from etching, begins (9).

A second feature of the photographs is the presence of what would appear to be grain boundaries. The boundary in Fig. 2 is very sharp and separates regions of different texture. The inability of the electron microscope to give more than a surface view makes it difficult to decide whether or not the grains in the oxide are based on those in the metal.

The oxidation of an electropolished surface lends to further oxide growth on top of the oxide formed by electropolishing. The surface retains its relatively smooth character. This is shown in photographs 6 and 7. However, the reduction of an electropolished surface forms a roughened surface as shown in photographs 3, 4, and 5 and re-oxidation of this surface leads to a relatively bumpy oxide film. This should lead to a higher initial oxidation rate with a reduced surface than with an electropolished surface although the final oxidation rate may be the same in both cases. This large increase in initial oxidation rate on a reduced surface has been shown to exist by microbalance measurements which will be published at a later date. The effect of the film due to electropolishing on the oxidation rate will depend on the severity of the oxidizing conditions and will be most marked when these conditions are mild. Once the thickness of oxide has been increased to the point at which further growth takes place by a diffusional mechanism, the effect of the original surface condition will be minimized. The effect of surface area will also be most apparent in the early stages of oxidation.

It is again emphasized that the results found here are connected with one type of iron and with one formula of electropolish bath. Yet the view is held that film formation nearly always accompanies electropolishing and that in those cases where its absence has been noted, the fault lies with the means of detection.

ACKNOWLEDGMENT

The authors wish to express their indebtedness to Dr. Boswell of the Mines Branch, Department of Mines and Technical Surveys, Ottawa, for his assistance and advice in developing a method of making replicas. Thanks are due to Mr. R. I. Spearman for his aid in the experimental work of this study. The electron micrographs were made by Dr. W. Barnes and Mr. W. Forsythe of the Physics Division, National Research Council of Canada, and we wish to thank them for their willing cooperation and careful examination of specimens.

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# THE INDEPENDENT YIELD OF $Xe^{135}$ PRODUCED IN THE FISSION OF NATURAL URANIUM BY PILE NEUTRONS[1]

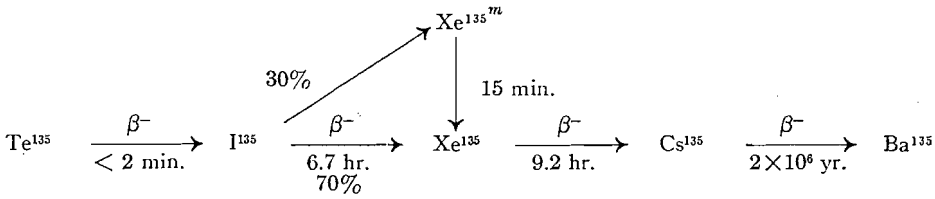
By F. Brown and L. Yaffe[2]

ABSTRACT

Fission of uranium yields $Xe^{135}$ by two routes: direct production and production by the $\beta$-decay of $I^{135}$. The amount produced directly (independent yield) has been measured by comparison with the amount produced from $I^{135}$. The independent fission yield of $Xe^{135}$ is found to be $2.7 \pm 1.0\%$ of the cumulative yield of $I^{135}$. Assuming this latter quantity to be 5.6% of all fissions, the independent yield of $Xe^{135}$ is $\backsim 0.15\%$. The half-life of $Xe^{135}$ has been measured as $9.13 \pm .05$ hr.

## INTRODUCTION

The fission product chain with which these experiments are concerned is the following:




The independent yield of $Xe^{135}$ has been measured by Hoagland and Sugarman (5) who found it to be about 5% of the mass 135 chain. The cumulative fission yield of the chain up to and including $I^{135}$ was taken as 5.6% (4, 7) so that the primary yield of $Xe^{135}$ was $\sim 0.3\%$. Adding this to the cumulative yield of $I^{135}$, one obtains the cumulative yield of the mass 135 chain up to and including Xe as 5.9% of fissions. The value for the independent yield of $Xe^{135}$ obtained by Hoagland and Sugarman would not be significantly changed by making a correction for the removal of $Xe^{135}$ by neutron capture during irradiation since the time of irradiation was short (two minutes).

The cumulative yield of the mass 135 chain up to and including $Cs^{135}$ has been measured by Thode (9) and found to be 2.15 times that of $Xe^{131}$. Corrections were made for the loss of $Xe^{135}$ by neutron capture during the irradiation.

Recent work in these laboratories (1) has given a value of 3.1% for the cumulative fission yield of $I^{131}$. Assuming therefore that the cumulative yield of $Xe^{131}$ is 3.1%, we obtain the cumulative yield of $Cs^{135}$ as 6.67%. The value of 3.1% for the cumulative yield of $I^{131}$ is based upon the yield of $Ba^{140}$ taken as 6.1%. The value of 5.6% for the cumulative yield of $I^{135}$ (4, 7) is also based upon a value of 6.1% for $Ba^{140}$.

Thus we have the data for the mass 135 chain reduced to one single comparison substance ($Ba^{140}$) and the following values result: cumulative yield of $I^{135}$ — 5.6%, cumulative yield of $Xe^{135}$ — 5.9%, cumulative yield of $Cs^{135}$ — 6.67%. If

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correct, these figures demand that the primary fission yield of $Cs^{135}$ be very much higher than that allowed by any reasonable charge distribution in fission theory (3). An investigation has been undertaken of both the cumulative yield of $I^{135}$ and the primary yield of $Xe^{135}$. Since the fission yield of $Ba^{140}$ is the standard for all these determinations, this quantity has also been redetermined (2).

## EXPERIMENTAL

The principle of the experimental method is as follows. A sample of uranium is irradiated for a short time with reactor neutrons. The $Xe^{135}$ is extracted as soon as possible after the end of the irradiation and its activity measured.This xenon consists of that formed directly in fission (independent) and some formed by the radioactive decay of $I^{135}$. After an interval of several hours a second extraction of xenon is made and counted. This xenon was formed only by iodine decay. From the ratio of the two amounts extracted, knowing the necessary times, half-lives, etc., one can calculate the ratio of the primary yield of $Xe^{135}$ to the cumulative yield of $I^{135}$.

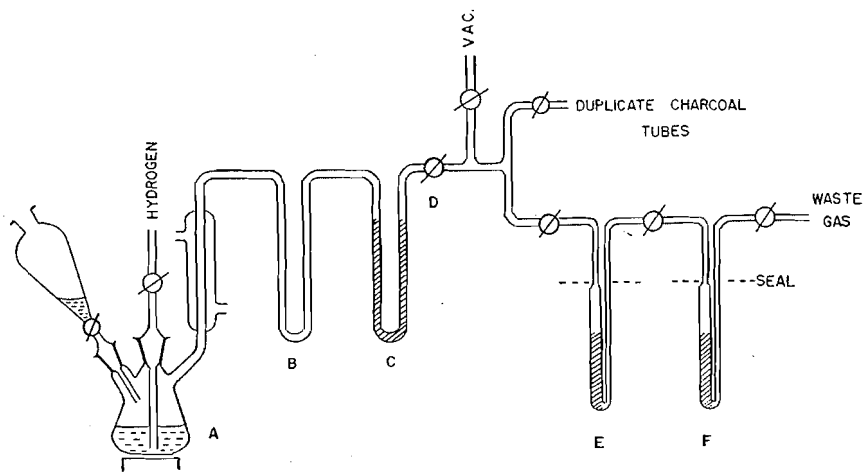



FIG. 1. Xenon extraction apparatus.

The apparatus used to dissolve the uranium or uranium compound and to collect the xenon is shown in Fig. 1. The final technique chosen for irradiation was to seal uranium oxide or uranyl nitrate in a small very thin-walled aluminum capsule. This capsule was irradiated in a high flux position ($5 \times 10^{13}$ neutrons/cm.$^2$/sec.) in the Chalk River N.R.X. reactor for five minutes and returned immediately to the laboratory by pneumatic conveyor. The aluminum capsule was dropped into the dissolving flask *A*, which contained about 50 mgm. of potassium iodide as "hold back carrier", and the whole apparatus was evacuated. (The charcoal traps *E* and *F* were thoroughly pumped out prior to the experiment.) Hydrogen was then admitted, followed by hot 1:1 sulphuric acid into the flask *A*. The acid rapidly dissolved the capsule and contents. The uranium solution was boiled gently while a stream of hydrogen was passed through. The effluent gas was dried by a reflux water condenser and by a trap *B* cooled in

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solid carbon dioxide, after which it passed over solid sodium hydroxide in the trap $C$ and thus into the collecting tubes $E$ and $F$. These tubes contained activated charcoal and were cooled in a mixture of solid carbon dioxide and acetone. They were so arranged that $F$ acted as guard tube for $E$. Hydrogen was passed through until the time elapsed from the end of irradiation was 30 min., the stopcock $D$ was then closed, and the hydrogen and heat turned off. The tubes $E$ and $F$ were evacuated to a pressure of less than 5 microns mercury and then, with coolant not yet removed, they were sealed off on both sides by a flame as shown in Fig. 1. The sealed tubes containing the first gas sweep were now ready for counting as described below. After an interval of about three and one-half hours the hydrogen sweep was restarted, the solution boiled, and the gases swept into the duplicate charcoal tubes. When the time elapsed since the end of irradiation was just four and one-half hours, the stopcock $D$ was again closed, and the tubes were evacuated and sealed as before.

The $Xe^{135}$ was counted in a Shonka type ionization chamber (8). In this instrument the sample is placed inside a tube so that it is at the center of the sensitive volume. Thus the counting rate is not sensitive to small changes in the position of the sample. This was checked experimentally and no detectable change in counting rate resulted when the sample was moved through the maximum amount permitted by the counter construction. The output from the ionization chamber was amplified by a vibrating reed instrument (Applied Physics Corporation, Model 30) and this output fed on to a Speedomax recorder. Shunts were provided which could be varied so as to make the instrument cover a wide range of disintegration rates. The walls of the central tube containing the sample were of iron, approximately $\frac{1}{4}$ in. thick, so that the instrument counted almost entirely $\gamma$-rays from the sources. Background counts were taken at frequent intervals during the counting and the necessary corrections made.

The gases swept from irradiated uranium by the method employed consist of various krypton and xenon isotopes. Under the circumstances of the irradiation and counting technique used, the decay curve of the gases shows three components; a short lived one of three to four hours associated with $Kr^{85}$ and perhaps traces of other nuclides, the $Xe^{135}$ component with half-life about nine hours (see below for discussion of this half-life), and a long-lived component of 5.3 days half-life due to $Xe^{133}$. A typical example of the decay curves obtained is shown in Fig. 2. The curves obtained for each sweep of gas were analyzed in the usual manner and the $Xe^{135}$ activity extrapolated back to the time at which that particular sweep ended. The average value for the half-life of $Xe^{135}$ in all experiments was 9.13 hr. (see also under Results), and this value was used to extrapolate in the final analysis of results.

With regard to the gas sweeping technique the following points were established. The activity in the charcoal tubes rises very rapidly when the sweep is commenced and then reaches an almost constant value. This indicates that the sweeping technique is rapid and efficient. The slow rise in activity which continues after the bulk of xenon has been swept through is due to continuing production of xenon from iodine. The guard tubes were found to contain short-lived activity, probably $Kr^{85}$, but no trace of either $Xe^{135}$ or $Xe^{133}$,

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thus showing complete absorption of xenon in the first charcoal tube.

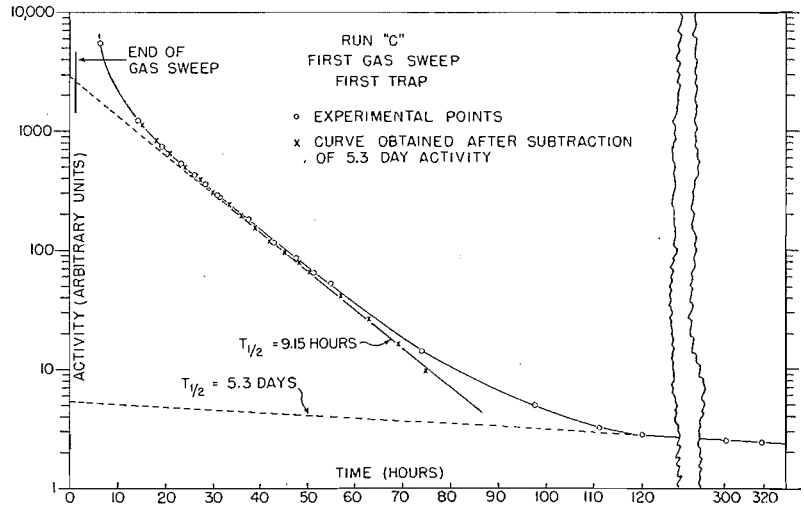



FIG. 2. Curve showing decay of first gas sample.

## RESULTS

The experimental value measured is the ratio $R$ of the $Xe^{135}$ activity in the first gas sweep to that in the second sweep, both measured at the times of completing their respective sweeps. The first sweep contains $Xe^{135}$ produced by decay of $I^{135}$ and also that produced directly in fission. The second sweep contains only $Xe^{135}$ produced from $I^{135}$. From this ratio $R$ one can calculate the ratio of the primary fission yield of $Xe^{135}$ to the cumulative fission yield of $I^{135}$. The method of calculation is shown below.

Let $t_0$ = time of the irradiation
$t_1$ = time elapsed between the end of the irradiation and the end of the first gas sweep
$t_2$ = time elapsed between the end of the first gas sweep and the end of the second gas sweep
$\lambda_1$ = decay constant for $I^{135}$
$\lambda_2$ = decay constant for $Xe^{135}$
$Y$ = cumulative fission yield of $I^{135}$
$Y_p$ = primary fission yield of $Xe^{135}$
$N$ = number of fissions occurring per unit time
$I_0$ = amount of $I^{135}$ present at the end of irradiation
$Xe_0$ = amount of $Xe^{135}$ present at the end of irradiation
$I_1$ = amount of $I^{135}$ present at the end of the first gas sweep
$Xe_1$ = amount of $Xe^{135}$ present in the first gas sweep
$Xe_2$ = amount of $Xe^{135}$ present in the second gas sweep.

*During Irradiation*

Note that during irradiation the rate of disappearance of $Xe^{135}$ is greater than expected from its decay constant, $\lambda_2$, because a considerable quantity is con-

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sumed by the reaction $Xe^{135}(n, \gamma)Xe^{136}$. The *effective* decay constant, $\lambda_2^*$, is given by

$$\lambda_2^* = \lambda_2 + \sigma\rho v$$

where $\sigma$ is the neutron capture cross section of $Xe^{135}$ and $\rho v$ is the neutron flux.

The resulting correction to the yield for a five minute irradiation is small even for the very high neutron capture cross section of $Xe^{135}$. It is quite negligible in the case of $I^{135}$.

If $I$ is the amount of $I^{135}$ present at any time, $t$, the net rate of production of $I^{135}$ is

$$\frac{dI}{dt} = YN - \lambda_1 I$$

and the amount present after a time of irradiation $t_0$ is

$$I_0 = \frac{YN}{\lambda_1}(1 - e^{-\lambda_1 t_0}). \qquad [1]$$

If $Xe$ is the amount of $Xe^{135}$ present at any time, $t$, the net rate of production of $Xe^{135}$ *from* $I^{135}$ is

$$\frac{dXe}{dt} = YN(1 - e^{-\lambda_1 t}) - \lambda_2^* Xe.$$

The net rate of production by direct fission is

$$\frac{dXe}{dt} = Y_p N - \lambda_2^* Xe.$$

The total net rate of production during irradiation is

$$\frac{dXe}{dt} = YN(1 - e^{-\lambda_1 t}) - \lambda_2^* Xe + Y_p N$$

and the amount present at the end of irradiation $t_0$ is

$$Xe_0 = \frac{N(Y + Y_p)}{\lambda_2^*}(1 - e^{-\lambda_2^* t_0}) - \frac{YN(e^{-\lambda_1 t_0} - e^{-\lambda_2^* t_0})}{\lambda_2^* - \lambda_1}. \qquad [2]$$

*During the Interval between the End of Irradiation and the End of the First Gas Sweep*

The amount of $Xe^{135}$ growing from an initial amount of iodine, $I_0$, in time $t_1$ is

$$\frac{\lambda_1 I_0}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}).$$

The amount of $Xe^{135}$ remaining from an original amount of $Xe^{135}$, $Xe_0$, after time $t$, is

$$Xe_0 e^{-\lambda_2 t_1}.$$

So that the amount of $Xe^{135}$ present at the end of the first gas sweep is

$$Xe_1 = \frac{\lambda_1 I_0}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}) + Xe_0 e^{-\lambda_2 t_1}.$$

Substituting for $I_0$ and $Xe_0$ from [1] and [2] we have

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$$Xe = Y\left\{\frac{N}{\lambda_2 - \lambda_1}(1 - e^{-\lambda_1 t_0})(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1}) - \frac{N}{\lambda_2^* - \lambda_1}(e^{-\lambda_1 t_0} - e^{-\lambda_2^* t_0})e^{-\lambda_2 t_1}\right\}$$
$$+ (Y + Y_p)\left\{\frac{N}{\lambda_2^*}(1 - e^{-\lambda_2^* t_0})(e^{-\lambda_2 t_1})\right\}.$$

*During the Interval between the End of the First Gas Sweep and the End of the Second Gas Sweep*

The amount of iodine remaining at the end of the first gas sweep (beginning of second) is

[3] $$I_1 = I_0 e^{-\lambda_1 t_1}.$$

The amount of xenon present at this time is nil. Considering therefore the growth of $Xe^{135}$ from the $I^{135}$, $I_1$, during $t_2$, we have the amount of $Xe^{135}$ at the end of the second sweep given by

$$Xe_2 = \frac{\lambda_1 I_1}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t_2} - e^{-\lambda_2 t_2})$$

and substituting for $I_1$ as in [3] and for $I_0$ as in [1] we have

$$Xe_2 = \frac{YN}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t_1} - e^{-\lambda_1(t_0+t_1)})(e^{-\lambda_1 t_2} - e^{-\lambda_2 t_2}).$$

Therefore if $R$ is the ratio of $Xe^{135}$ in the first gas sweep to that in the second, we have

$$R = \frac{Xe_1}{Xe_2} \text{ and thus}$$

$$R = \frac{Y\left\{\frac{(1 - e^{-\lambda_1 t_0})(e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1})}{\lambda_2 - \lambda_1} - \frac{(e^{-\lambda_1 t_0} - e^{-\lambda_2^* t_0})e^{-\lambda_2 t_1}}{\lambda_2^* - \lambda_1}\right\}}{Y\left\{\frac{(e^{-\lambda_1 t_1} - e^{-\lambda_1(t_0+t_1)})(e^{-\lambda_1 t_2} - e^{-\lambda_2 t_2})}{\lambda_2 - \lambda_1}\right\}}$$
$$+ \frac{(Y + Y_p)\left\{\frac{(1 - e^{-\lambda_2^* t_0})e^{-\lambda_2 t_1}}{\lambda_2^*}\right\}}{Y\left\{\frac{(e^{-\lambda_1 t_1} - e^{-\lambda_1(t_0+t_1)})(e^{-\lambda_1 t_2} - e^{-\lambda_2 t_2})}{\lambda_2 - \lambda_1}\right\}}$$

$$R = 0.2063 + 3.385\frac{Y_p}{Y}$$

if one uses the following values:

$t_0 =$ 5 min. half-life $I^{135} = 6.7$ hr.
$t_1 =$ 30 min. half-life $Xe^{135} = 9.15$ hr.
$t_2 =$ 240 min. $\sigma$ for $Xe^{135} = 3.5 \times 10^{-18}$ cm.$^2$
$\rho v = 5 \times 10^{13}$ neutron/cm.$^2$/sec.

Four runs were made using the standard procedure outlined above.
*Run A* employed 260 mgm. of uranium metal in three pieces, not sealed.

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*Run B* employed 260 mgm. of uranium oxide, $UO_3$, sealed in a small aluminum capsule.

*Run C* employed 250 mgm. of uranium oxide as in Run *B*.

*Run D* employed 250 mgm. of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, also sealed in an aluminum capsule.

The following Table I gives the measured values of $R$, the ratio of activities as defined above and also the values of $Y_p/Y$ calculated from them, where $Y_p$ is the primary fission yield of $Xe^{135}$ and $Y$ is the cumulative fission yield of $I^{135}$.

TABLE I

| Run | $R$ | $\frac{Y_p}{Y} \times 100$ | $t_{1/2}$ $Xe^{135}$ (hr.) |
|---|---|---|---|
| *A* | 0.251 | 1.33 | 9.12<br>9.11 |
| *B* | 0.366 | 4.72 | 9.18<br>9.06 |
| *C* | 0.234 | 0.82 | 9.15<br>9.09 |
| *D* | 0.340 | 2.70 | 9.23<br>9.10 |
| Average | 0.298 | 2.7 | 9.13 |

The average value for $R$ is 0.298 with a standard deviation of 0.033. The corresponding value for $Y_p/Y$ is $2.7 \pm 1.0\%$. Assuming $Y = 5.6\%$ of fissions (4, 7) the primary fission yield of $Xe^{135}$ would be $0.15 \pm 0.06\%$ of fissions. It is important to note, however, that the value for $Y_p/Y$ is very sensitive to small changes in the experimental quantity $R$ when $Y_p$ is very small compared to $Y$. In fact, the primary yield of $Xe^{135}$ is too small to be measured satisfactorily by the method used. One is essentially measuring a small difference between two large quantities which can not themselves be measured with high accuracy. The results therefore should be taken to indicate that the primary fission yield of $Xe^{135}$ is very small but finite.

Each of the four runs yielded two values for the half-life of $Xe^{135}$ making eight values in all (Table I). The average value is 9.13 hr. with a standard deviation of $\pm$ 0.02 hr. The value given by Hoagland and Sugarman (6) is 9.2 hr., being based upon measurements with a Geiger tube which gave 9.3 hr. and measurements with an ion chamber which gave $9.15 \pm .05$ hr. A value of 9.1 hr. was obtained by Thulin, Bergström, and Hedgran (10) using a mass spectrometer. All these results are in satisfactory agreement and one should perhaps assume a value of $9.15 \pm .05$ hr.

## DISCUSSION

This result is in general agreement with that of Hoagland and Sugarman (5). The independent yield of $Xe^{135}$ is too small to account for the difference in the cumulative yields of $I^{135}$ and $Cs^{135}$ as measured (4, 7, 9). The reason for this discrepancy has yet to be found.

The independent yield of $Xe^{135}$ is one of the points used by Glendenin, Coryell,

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and Edwards (3) to fix the position of the curve showing the variation of fission yield with nuclear charge. Since this is plotted on a logarithmic scale, the use of our value, which is lower than the Hoagland and Sugarman one, will not have much effect. It is in the direction of giving even better agreement with the equal charge displacement theory than before.

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# BETATRON IRRADIATION OF AQUEOUS FERROUS SULPHATE SOLUTIONS[1]

By R. W. Hummel and J. W. T. Spinks

ABSTRACT

The oxidation of aerated aqueous solutions of ferrous ammonium sulphate has been studied using radium gamma rays and X rays of 24.5 Mev. peak energy from a betatron. The behavior at high photon energies has been shown to be closely similar to that at lower photon energies.

## INTRODUCTION

In recent years the study of radiation chemistry has acquired a new importance. The effects of new radiations have been investigated and in some cases the range of older observations has been extended. In the present paper, the oxidation of ferrous sulphate solutions by the X rays from a betatron is reported.

## DOSIMETRY

The dose unit universally adopted is the roentgen which is officially defined as "that quantity of X- or gamma radiation such that the associated corpuscular emission for 0.001293 gram of air produces, in air, ions carrying one electrostatic unit of quantity of electricity of either sign." The mass of air referred to is 1 cc. of dry air at 0°C. and 760 mm. Hg.

Special techniques have been developed in order that radiation dosages may be measured in compliance with the requirements of the definition. In this work, the Victoreen thimble chamber was used for dosimetry.

The original idea underlying the thimble chamber method was supplied by Bragg (3), but the first experimental application was apparently that of Fricke and Glasser (6). Gray (9, 10) is generally credited with developing the theory on which the air-wall chamber is based and has suggested (11) that accuracies of better than 5% are attainable. A recent discussion of the theory and of the factors affecting accuracy has been given by Wang (24).

With high energy photons from the betatron a very thick-walled chamber is necessary in order to satisfy the equilibrium conditions demanded by the Bragg–Gray relation. For instance, the depth–dose curve for water indicates that for 25 Mev. X rays the dose is greatest at a depth of about 4 cm. (17). In contrast, when using a gamma ray source and an air-filled chamber, a wall thickness of about 4 mm. of graphite is sufficient (19). The effective atomic number of Lucite is not very different from that of water, and consequently a thickness of 4 cm. of Lucite has been used in dosage determinations with betatron X rays (4). A roentgen measured with a Lucite wall chamber is sometimes called a "Lucite roentgen."

An expression for the value of a roentgen in terms of a "Lucite roentgen" can be derived from the Bragg–Gray relationship, $E_v = J_v W \rho$, where $E_v$ = energy

[1] *Manuscript received October 2, 1952.*
*Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*

absorbed per cm.$^3$ by the medium, $J_v$ = number of ionizations per unit volume of air, $W$ = energy required to form an ion pair, taken as 32.5 ev. (18), and $\rho$ = ratio of the stopping power of the medium to that of air. It is found that:

$$\frac{\text{energy giving a roentgen}}{\text{energy giving a Lucite roentgen}} = \frac{({}_e\tau_a + {}_e\sigma_a + {}_e\pi_a)_{\text{Lucite}}}{({}_e\tau_a + {}_e\sigma_a + {}_e\pi_a)_{\text{air}}} \cdot \frac{{}_eS_{\text{air}}}{{}_eS_{\text{Lucite}}}$$

where ${}_eS_{\text{air}}/{}_eS_{\text{Lucite}}$ = ratio of electronic stopping powers of air and Lucite and ${}_e\tau_a$, ${}_e\sigma_a$, and ${}_e\pi_a$ are the real electronic absorption coefficients for the photoelectric, Compton, and pair production processes, respectively.

The "Lucite roentgen" is measured by having the Victoreen thimble chamber in a Lucite block. The ratio of the "Lucite roentgen" to the true roentgen has been calculated for the energy range, 0.1 to 25.5 Mev., by the betatron group at this University. The variation with energy of this ratio makes it necessary to calculate an average value weighted according to the relative intensity of the X rays at different energy levels. The spectral distribution of photon energies of the X rays coming from the betatron, at a maximum energy of 24.5 Mev., is shown in Fig. 2, and the relative intensities at several energy levels are estimated from curve $B$ of this figure. The values obtained are given in Table I.

TABLE I

| Energy level (Mev.) | Relative intensity |
|---|---|
| 24 | 6.3 |
| 20 | 16.9 |
| 16 | 21.9 |
| 12 | 25.0 |
| 8 | 28.8 |
| 4 | 31.9 |
| 2 | 32.2 |
| 1 | 30.6 |

TABLE II

RELATIONSHIP BETWEEN A "LUCITE ROENTGEN" AND A TRUE ROENTGEN FOR 24.5 MEV. PEAK ENERGY BETATRON RAYS

| (1) Energy region, Mev. | (2) Fraction of bremsstrahlung in each region | (3) Energy giving a roentgen / Energy giving a "Lucite roentgen" | (4) (2) × (3) |
|---|---|---|---|
| 0.1- 1 | 0.051 | 0.95 | 0.0485 |
| 1 - 2 | 0.103 | 0.979 | 0.101 |
| 2 - 4 | 0.106 | 0.972 | 0.103 |
| 4 - 6 | 0.103 | 0.956 | 0.0985 |
| 6 - 8 | 0.098 | 0.938 | 0.0919 |
| 8 -10 | 0.092 | 0.923 | 0.0849 |
| 10 -12 | 0.085 | 0.912 | 0.0775 |
| 12 -14 | 0.080 | 0.904 | 0.0723 |
| 14 -16 | 0.075 | 0.896 | 0.0672 |
| 16 -18 | 0.068 | 0.888 | 0.0604 |
| 18 -20 | 0.060 | 0.881 | 0.0529 |
| 20 -22 | 0.047 | 0.875 | 0.0411 |
| 22 -24 | 0.031 | 0.870 | 0.0270 |

$\sum$ (2) × (3) = 0.926  1/0.926 = 1.08 true roentgens/"Lucite roentgen"

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From a plot of these points, the average intensity of the bremsstrahlung in energy regions 2 Mev. or less in width was estimated. By dividing the values thus obtained by their sum, the fraction in each region was obtained. The sum of the products of these values and the values giving a "Lucite roentgen" in the same energy regions gave an average value for the ratio weighted in the desired manner. The results of the calculations are given in Table II.

Dosage measurements made with the Victoreen thimble chamber in the Lucite block at 24.5 Mev. peak energy were therefore increased by 8% in order to obtain the dose received in air roentgens.

## EQUIPMENT

### *The Betatron*

Fig. 1 shows the general arrangement existing during experiments with the

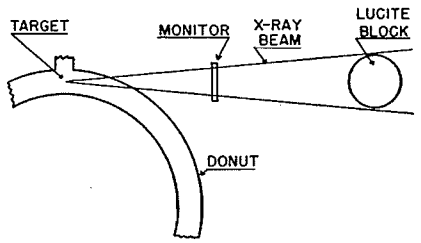



FIG. 1. Experimental arrangement for betatron irradiations.

betatron. Electrons accelerated in the donut are allowed to strike a tungsten target. The *bremsstrahlung* produced by deceleration of the electrons has a continuous spectrum of energies ranging from 25 Mev., the maximum kinetic energy of the electrons—less 0.5 Mev. rest energy—to zero energy. The shape of the spectrum at a given maximum energy may be calculated from a formula due to Schiff (22).

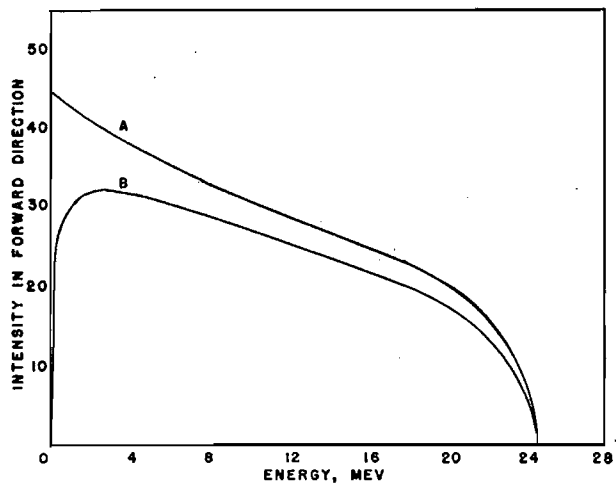



FIG. 2. Effect of absorption on photon distribution.
A. Theoretical Schiff distribution for the maximum photon energy of 24.5 Mev.
B. Curve *A* modified by absorption of donut, monitor, and Lucite block using real absorption coefficients.

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The spectral distribution as obtained is modified by absorption due to the walls of the donut, the monitor, and the Lucite block used to hold samples being irradiated. This is illustrated in Fig. 2, where curve *A* is the theoretical Schiff distribution for a maximum photon energy of 24.5 Mev. and curve *B* is curve *A* modified by absorption due to donut, monitor, and Lucite block, and is a fairly close approximation to the distribution to which the Victoreen responds. Curve *B* was calculated for an 8 cm. cube of Lucite with a 1.8 cm. hole drilled to a depth of 5 cm. in the center of one face. The circular Lucite block in which the ferrous iron solutions were irradiated in this study is described later and will, of course, give a slightly different distribution.

On operating the betatron an ionization current is induced in the monitor through which the photon beam passes. The current charges a condenser which operates a counter and relay when its potential reaches a predetermined value. The relay operates a shorting circuit which discharges the condenser. Each count or "click", therefore, represents a definite amount of radiation which has passed through the monitor. The number of "Lucite roentgens" per click can be determined by placing a Victoreen r-meter in the sample position and taking the average of several measurements. The dose rate is obtained by timing the click rate with a stop watch.

*Apparatus for Betatron X-Ray Irradiations*

Irradiations with betatron X rays were carried out in 13 × 100 mm. Pyrex test tubes inserted in the Lucite block illustrated in Fig. 3. The block was almost

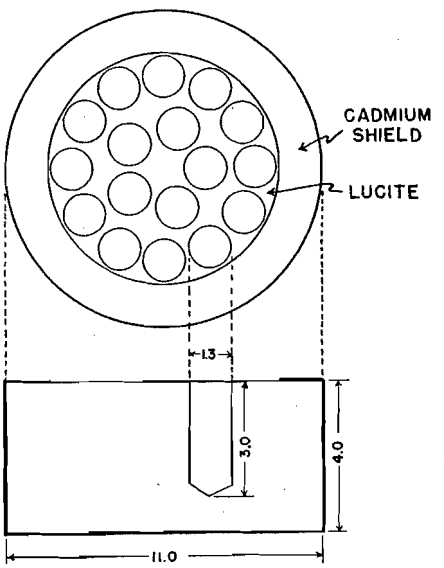



FIG. 3. Apparatus for irradiations with the betatron. Dimensions in centimeters.

completely covered with sheet cadmium* about 0.4 mm. thick, a space being left uncovered at the top to allow insertion of the sample tubes. A wooden pulley wheel was fastened to the bottom of the block, a smaller pulley wheel was

**The cadmium was intended to stop the slow neutrons present in both γ-ray and betatron X-ray beams.*

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mounted on a synchronous motor whose rate of rotation was 240 r.p.m., and the two were connected by a cord. The pulley wheels were made so that the Lucite block would rotate at about 30 r.p.m. The mountings for the Lucite block and the synchronous motor were clamped to an ordinary laboratory stand. The stand was placed on a platform fastened to the betatron, and the block adjusted as closely as possible to the center of the aperture from which the X rays emerged. A clamp held the stand rigidly to the platform during an irradiation so that the position of the block relative to the beam would not be altered. This method of positioning the block was not completely reproducible, but, since a dose determination was carried out at the beginning of each run, no error resulted thereby.

A rotating block for the betatron experiments was chosen because the X-ray intensity was not constant across the beam, and hence a stationary block would receive different dosages at different points. In addition, the direction of the beam has been known to shift slightly during operation of the betatron, whence the dose rate at any point in a stationary block would change as often as the beam changed direction. With the rotating system, variations in intensity across the beam, or changes in beam direction, or attenuation due to varying thicknesses

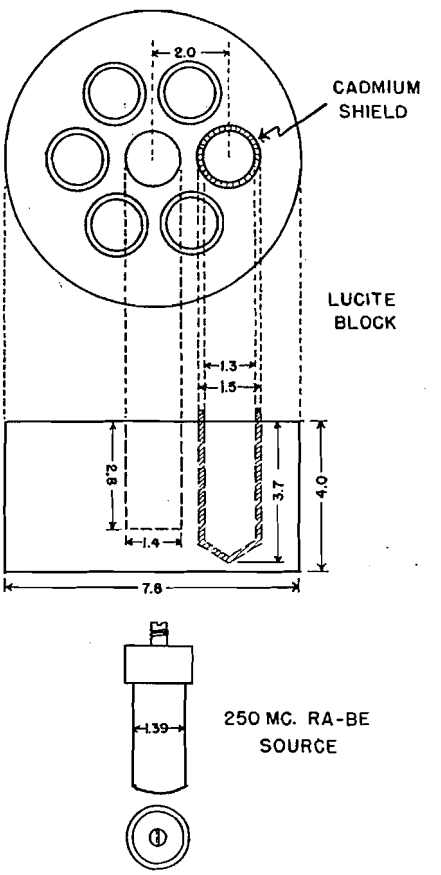



FIG. 4. Apparatus for irradiations with gamma-ray source. Dimensions in centimeters.

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of Lucite traversed by the beam, did not have to be allowed for and each sample in a given circle received the same dose.

*Gamma-ray Source*

The gamma-ray source available to us was a 250 mc. Ra–Be mixture. This source was also a neutron emitter. The possible effect of these neutrons was investigated by carrying out several experiments in which some of the sample tubes were placed in cadmium shields and others in Lucite shields of identical geometry. The results showed no significant differences, and it was assumed that oxidation due to slow neutron bombardment was comparatively unimportant. However, cadmium shields were used in all subsequent experiments as a precautionary measure.

*Apparatus for Gamma-ray Irradiations*

Irradiations with the 250 mc. gamma-ray source were carried out in 13 × 100 mm. Pyrex test tubes inserted in the Lucite block illustrated in Fig. 4. The gamma-ray source was inserted in the central hole and the tubes placed in the cadmium shields in the six surrounding positions.

## ANALYTICAL METHOD

Ferrous ion concentrations were determined colorimetrically using orthophenanthroline (2). To develop the color, orthophenanthroline solution was added to the iron solution, and finally enough sodium citrate solution was added to bring the pH to about 4. The pale yellow ferric citrate complex did not interfere with the analyses since the iron solutions were not irradiated enough to oxidize more than three-quarters of the ferrous ions. Sodium acetate buffer was found to be unsatisfactory in this respect (15).

A calibration curve was established for ferrous–orthophenanthroline systems buffered with sodium citrate at about pH 4. The extinction coefficient at 510 mμ was 11,550 ± 30, using a Beckman model D.U. spectrophotometer.

Laboratory distilled water was redistilled first from alkaline permanganate solution and then from alkaline manganous hydroxide suspension. Pyrex glass was used throughout.

The analytical procedure was carried out as follows. To aliquots of the iron solution were pipetted first a slight excess of 0.1% orthophenanthroline solution and then sufficient sodium citrate solution to buffer at a pH of about 4. Dilution in a volumetric flask was effected when necessary. The importance of adding the indicator before the buffer has been pointed out by Bandemer and Schaible (1). The optical density was determined at 510 mμ, and the concentration found from the calibration curve.

For an irradiation, 3- or 2-ml. aliquots, depending on whether radium or the betatron, respectively, was used as the radiation source, were transferred with a calibrated pipette to 13 × 100 mm. Pyrex test tubes which had been thoroughly cleaned with hot chromic acid solution and rinsed at least three times each with tap water, distilled water, and triple distilled water and then air-dried.

After irradiation, the ferrous ion concentration was determined in the same manner as before.

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## EXPERIMENTAL RESULTS

### *Dosage Determinations*

Victoreen condenser thimble chambers were used to determine dosages in roentgens. With the gamma-ray source a 25 r. chamber was used, while with the betatron a 100 r. chamber was found necessary.

To determine dosages obtained from the gamma-ray source, the source was placed in the center hole of the Lucite block shown in Fig. 4. The 25 r. thimble chamber was placed in turn in each of the six surrounding holes, and the dose received in three minutes read off the scale on the Victoreen charging unit. It was possible to take two sets of readings in the above manner, the first set with the sensitive volume of the chamber in the upper half of the hole, and the second set with the sensitive portion in the lower half. The average of these two sets of dose determinations was taken as the average dose received throughout the hole, and consequently, since the 3-ml. portions of ferrous sulphate solution used in this study almost completely filled the space in which the dose determinations were made, as the dose received by the irradiated solutions.

The Victoreen reading was corrected for temperature and pressure, for the change in calibration of the chamber as determined independently using a set of radium needles, and for the fact that the measurements were made in a Lucite block. The latter correction factor was + 2% and was estimated from Table II by assuming that the important gamma rays from radium have energies between 0.3 and 2 Mev. The corrected dose rate was 430 r. per hr.

To determine dosages with the betatron source of X rays, the 100 r. chamber was used. By experiment, this chamber gave 3% higher values at 23 Mev. than did the 25 r. chamber. The dosages obtained with the 100 r. chamber were therefore reduced by 3% so that all the results reported in this work could be based on dosages determined with the 25 r. chamber. Dosages were determined at the start of an experiment by inserting an empty test tube into one of the positions in the Lucite block (Fig. 3), the tube being shortened considerably in order to accommodate the thimble chamber. Tubes containing 2 ml. of water were placed in the other positions. The block was rotated at about 30 r.p.m., five or more clicks at a known maximum X-ray energy were given, and the dose read off the Victoreen unit. Several measurements were made at any one position in both the inner and outer circles of holes, and it was assumed that the dose received at each of the positions in a circle was the same. The average value of the dose per click for each circle was corrected for temperature and pressure, decreased by 3% to obtain the value which would have been recorded by the 25 r. chamber, and increased by 8% to convert from "Lucite roentgens" to true roentgens.

### *Irradiation of Ferrous Ion Solutions with Radium Gamma Rays*

A series of runs at different initial ferrous ammonium sulphate concentrations, all in 0.8 *N* sulphuric acid, confirmed the results obtained by other workers in this field. A typical result is shown in Fig. 5. The over-all reaction obeyed zero order rate equations throughout the concentration range studied. The oxidation rate was independent of concentration at initial $Fe^{++}$ concentrations greater than $5 \times 10^{-5}$ molar, but decreased at lower initial concentrations. The variation of oxidation rate with initial $Fe^{++}$ concentration is shown in Fig. 6.

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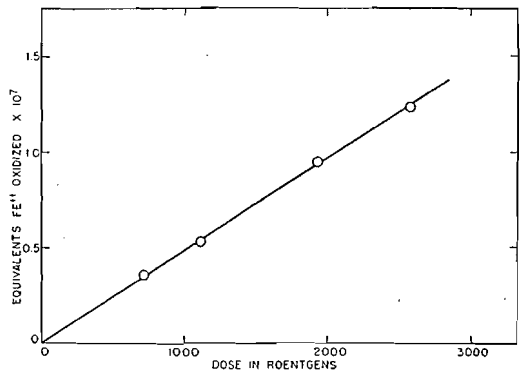



FIG. 5. Oxidation yield as a function of roentgen dose; typical result obtained with the gamma-ray source. Initial ferrous concentration = $5.48 \times 10^{-5}$ *M*.

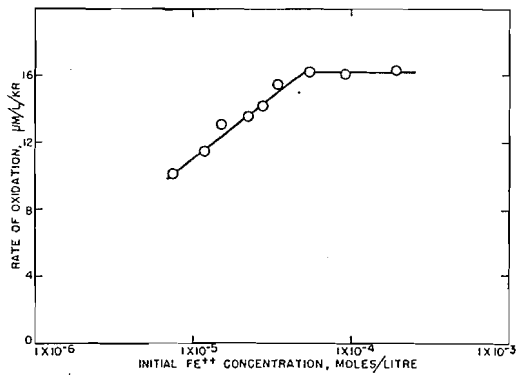



FIG. 6. Variation of oxidation rate with initial ferrous ion concentration using radium gamma rays.

The rates are expressed in terms of micromoles ferrous ion oxidized per liter of solution per 1000 roentgens. The oxidation yields are also often expressed in terms of the number of ions oxidized per 100 electron volts absorbed in the solution and are represented by the letter *G*. The average value of *G* in the concentration independent region = 16.8 ions oxidized per 100 ev. at 23°C. The temperature coefficient is very low in the concentration independent region but increases when the initial concentration is less than $5 \times 10^{-5}$ molar. Some results at low concentrations are given in Table III. The change in the oxidation rate at 25°C. was about 0.2 μM./l./kr./°C. for the $1.32 \times 10^{-5}$ *M* solution. Minder and Liechti (21) did not find a variation in the rate from 4°C. to 54°C., owing to their use of a 2 *M* solution. The average rate in the concentration independent region is compared with the rates obtained using the betatron and with values obtained by other workers, in Table V (see below).

*Irradiation of Ferrous Ion Solutions with Betatron X Rays*

The dependence of oxidation rate on initial ferrous ion concentration was investigated in the same manner with the betatron as with the radium source. Two-milliliter aliquots of each solution were irradiated.

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TABLE III

EFFECT OF TEMPERATURE ON OXIDATION RATE

| Initial $Fe^{++}$ concentration, $M$ | Temperature, °C. | Oxidation rate, $\mu$M./l./kr. |
|---|---|---|
| $1.32 \times 10^{-5}$ | 84 | 16.2 |
| " | 61 | 16.2 |
| " | 27 | 12.9 |
| " | 12.5 | 9.0 |
| $1.19 \times 10^{-5}$ | 2 | 8.1 |

After determining the number of roentgens per click, the ferrous ion solutions, in Pyrex test tubes, were placed in the Lucite block, the block was rotated, and a known number of clicks given to each sample tube. As each tube was removed, a similar tube containing 2 ml. of water was put in its place. Since the number of clicks for each sample as well as the number of roentgens per click were known, the dosage was readily calculated. The dose per click at the end of the run was checked on several occasions, but no change from the initial value was observed.

At 24.5 Mev. peak energy the dose rate at the inner circle of sample holes in the Lucite block was about 400 r. per min. while at the outer circle the dose rate approximated 280 r. per min. These rates were not constant throughout a run, the number of clicks per minute being determined by manual setting of the betatron controls. At 18 Mev. peak energy the dose rate dropped to about 110 r. per minute and 120 r. per minute at the outer and inner circles, respectively.

A number of ferrous solutions of different initial concentrations were irradiated with 24.5 Mev. peak energy X rays. The results were very similar to those obtained with radium gamma rays. The results of a typical run are shown in Fig. 7.

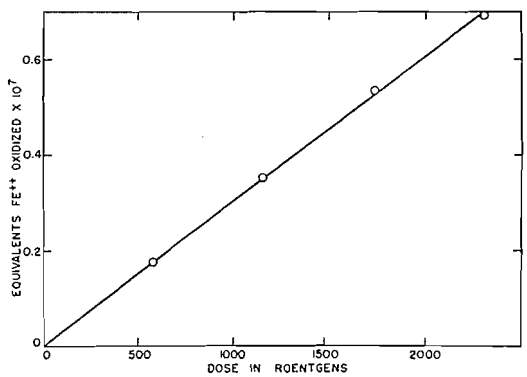



FIG. 7. Oxidation yield as a function of roentgen dose; typical result obtained with betatron X rays at 24.5 Mev. peak energy. Initial ferrous ion concentration = $5.38 \times 10^{-5}$ $M$.

At every initial concentration a zero order rate equation was obeyed. The rates of oxidation were expressed in the usual way and are plotted in Fig. 8 against the initial ferrous ion concentrations. A comparison with Fig. 6 shows that the behavior of these solutions at 24.5 Mev. peak X-ray energy is very similar to their behavior at much lower energies. For example, in both cases the rate is constant above initial ferrous ion concentrations of about $4 \times 10^{-5}$ $M$ and decreases as

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the concentration is decreased below that value. There appeared to be no difference in rate of ferrous ion oxidation between samples irradiated in the inner or outer holes.

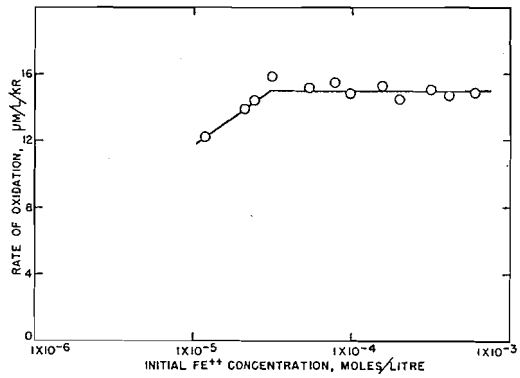



FIG. 8. Variation of oxidation rate with initial ferrous ion concentration using betatron X rays at 24.5 Mev. peak energy.

Several experiments at different initial concentrations were carried out at 18 Mev. peak X-ray energy. The rates of oxidation are essentially the same as were found with 24.5 Mev. X rays. The results of the betatron experiments are tabulated in Table IV.

TABLE IV

RATE OF OXIDATION AS A FUNCTION OF INITIAL CONCENTRATION (BETATRON X RAYS)

| Initial ferrous ion concentration, *M* | Peak energy, Mev. | Oxidation rate, μM./l./kr. |
|---|---|---|
| $6.00 \times 10^{-4}$ | 24.5 | 14.9 |
| $4.10 \times$ | 24.5 | 14.7 |
| $3.15 \times$ | 24.5 | 15.1 |
| $2.00 \times$ | 24.5 | 14.5 |
| $1.55 \times$ | 24.5 | 15.3 |
| $9.90 \times 10^{-5}$ | 24.5 | 14.9 |
| $7.90 \times$ | 24.5 | 15.5 |
| $5.38 \times$ | 24.5 | 15.2 |
| $3.16 \times$ | 24.5 | 15.9 |
| $2.44 \times$ | 24.5 | 14.4 |
| $2.11 \times$ | 24.5 | 13.9 |
| $1.19 \times$ | 24.5 | 12.3 |
| $2 \times 10^{-4}$ | 18.0 | 15.3 |
| $7.90 \times 10^{-5}$ | 18.0 | 15.5 |
| $3.16 \times$ | 18.0 | 15.1 |

They are compared with gamma-ray results obtained in the present experiments and by other workers, in Table V.

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TABLE V

COMPARISON OF $G$ VALUES FOR DIFFERENT WORKERS

| Workers | Type of radiation | Oxidation rate, $G$ |
|---|---|---|
| Fricke *et al.* (7, 8) | X rays | 18.0 |
| Shishacow (23) | X rays | 15.9 |
| Miller (Polystyrene cells) (20) | Radium gamma rays | 20.4 |
| Miller (Pyrex cells) (20) | Radium gamma rays | 18.2 |
| Johnson (16) | 2 Mev. X rays | 17.3 |
| Hardwick (Polystyrene cells)* (12) | $Co^{60}$ gamma rays | 20.8 |
| Hardwick (13) | Beta rays, $P^{32}$ | 21.1 |
| Hardwick (13) | Beta rays, $S^{35}$ | 20.2 |
| Hochanadel and Ghormley (14) | $Co^{60}$ gamma rays | 15.7 |
| Freeman *et al.* (5) | $Co^{60}$ gamma rays | 17.4 |
| Present work | Radium gamma rays | 16.8 |
| Present work | Betatron X rays 24.5 Mev. peak energy | 15.8 |

**Using essentially the same equipment as Miller.*

## DISCUSSION

The primary purpose of this study was to extend the field of radiation chemistry, in particular the radiation chemistry of aqueous ferrous ammonium sulphate solutions, to high energy X-ray regions which heretofore have not been reported in the literature.

The behavior of aerated aqueous ferrous ammonium sulphate solutions made 0.8 $N$ to sulphuric acid has been shown here to be similar at high photon energies to that found at the low photon energies associated with X-ray machines and gamma-ray sources. That is, in the concentration range above $5 \times 10^{-5}$ $M$ and for temperatures at or above room temperatures, the rate of oxidation is independent of concentration and in a given experiment the amount of ferrous ion oxidized is proportional to the energy absorbed. In addition, the yield per ion pair is nearly the same at both low and high photon energies. Hence, the mechanism whereby X rays cause oxidation of ferrous ion in aqueous sulphuric acid solutions is probably the same with the 24.5 Mev. peak X-ray beam as at low X-ray or gamma-ray photon energies ($< 3$ Mev.). Since the mechanism at low photon energies is thought to involve oxidizing intermediates formed by disruption of water molecules and does not result from "direct hits" by X-ray photons on the ferrous ions, then the same oxidizing intermediates may be postulated at these higher energies. The behavior of the solutions at concentrations below $5 \times 10^{-5}$ $M$ has been shown to be parallel to the behavior found at lower energies in that with both the 24.5 Mev. peak energy X-ray beam and radium gamma rays the rate of oxidation decreases with decreasing initial concentration.

The slightly lower yield obtained with betatron radiations at initial ferrous ion concentrations greater than $10^{-4}$ $M$, compared with the yield obtained with radium gamma rays, may be due to the pulsed nature of the betatron beam. The pulses are of about 4 $\mu$sec. duration and occur 180 times each second. Thus for a measured dose rate of $10^4$ r. per hr. the dose rate in a pulse is about $14 \times 10^6$ r. per hr. In this connection, Miller (20) has indicated that the ferrous ion system is dose-rate dependent above $0.36 \times 10^6$ r. per hr. while Hochanadel and Ghormley

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(14) found the system dose-rate independent from $18 \times 10^3$ r. per hr. to $0.81 \times 10^6$ r. per hr. with initial ferrous ion concentrations greater than $10^{-4}$ *M*. Thus the situation with respect to dose rate is still ambiguous and in addition the highest dose rate reported is much lower than is obtained during a betatron pulse.

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# REACTIONS IN DISSOCIATED PEROXIDE VAPOR[1]

By J. S. Batzold,[2] C. Luner,[3] and C. A. Winkler

## ABSTRACT

The products of the electrical discharge through hydrogen peroxide vapor were hydrogen peroxide, water, oxygen, and hydrogen, in amounts which depended upon the arrangement and temperature of the trap, reaction time, and surface to volume ratio of the reaction vessel. Water, hydrogen, and oxygen resulted from the gas phase reactions of the dissociated hydrogen peroxide, with hydrogen peroxide produced only in a trap cooled below − 120°C. Products trapped below − 150°C. evolved oxygen on warming to room temperature. The decomposition products of the electrical discharge through hydrogen peroxide correspond closely with products obtainable both from a similar discharge through water vapor and from the interaction of hydrogen atoms with oxygen molecules in a cold trap. A mechanism which accounts for their correspondence is included. Water was the only product when molecular hydrogen peroxide was caused to react with hydrogen atoms, dissociated hydrogen peroxide vapor, or dissociated water vapor in the presence or absence of molecular hydrogen. A chain mechanism is postulated for these reactions.

## INTRODUCTION

When water vapor is dissociated in an electrical discharge, the yields of products depend upon experimental conditions such as trap temperature, reaction time, and ratio of surface to volume in the reaction chamber, in the manner outlined in a previous paper from this laboratory (5). The product trapped at liquid nitrogen temperature was found to evolve oxygen when warmed above − 120°C. In this respect, the product of the discharge through water vapor showed the same behavior as products obtained by Geib and Harteck from the reaction of hydrogen atoms with oxygen molecules in a cold trap (3). To account for the similar behavior in the two systems, a mechanism was suggested involving an unstable collision complex [HOOH]*, formed either from two OH radicals, or from two hydrogen atoms and an oxygen molecule, similar to the activated complex proposed by Badin for the low temperature hydrogen atom – oxygen molecule reaction (1).

Since production of hydroxyl radicals by an electrical discharge through water vapor (6, 7) involves the simultaneous production of hydrogen atoms, while the similar dissociation of hydrogen peroxide vapor yields only hydroxyl radicals (2), a study has been made of the reactions in dissociated hydrogen peroxide vapor to enable comparison to be made with the reactions in dissociated water vapor studied previously. The results are summarized in the present paper together with the results of some studies on reactions of hydrogen peroxide vapor with hydrogen atoms and with dissociated water and peroxide vapors.

## EXPERIMENTAL

The apparatus was a conventional flow system essentially identical with that described by Jones and Winkler (5). Commercial 90% hydrogen peroxide

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[2] *Holder of National Research Council Fellowship.*
[3] *Holder of a Scholarship under the Bureau of Scientific Research of the Province of Quebec.*

(Buffalo Electro-chemical Co.)* was distilled twice *in vacuo* to obtain a product better than 99% hydrogen peroxide by weight, (analyzed by permanganate titration). A constant pressure of hydrogen peroxide vapor (about 4 mm. Hg) was obtained at the inlet side of the flow meter by maintaining a reservoir of liquid peroxide in a water bath at 34.2°C. The flow meter was heated to 35°C. in an air bath to prevent condensation of peroxide vapor.

In most of the experiments, the rate of flow into the discharge tube was 7.4 mM. of hydrogen peroxide per hour, together with 1.4 mM. of water vapor per hour originating from the unavoidable presence of small amounts of water in the liquid peroxide. The discharge potential varied from 900 to 1200 volts at 200 milliamperes, depending on the pressure in the discharge tube, which was usually close to 0.1 mm. of Hg.

## RESULTS

### *Influence of Trap Temperature*

Preliminary experiments showed that no molecular hydrogen peroxide survived the discharge, since a trap cooled in dry ice collected only water at all the flow rates used. Thus, all hydrogen peroxide collected at lower trap temperatures could be attributed to reactions in the cold trap itself. Experiments were made at intervals of 10°C. over the range of trap temperatures between − 195°C. (liquid nitrogen) and − 78°C. (dry ice − acetone). Liquid oxygen provided a trap temperature of − 183°C., while other temperatures were obtained, and regulated to within 0.2°C. of the desired temperature, by addition of small amounts of liquid nitrogen to a test tube immersed in liquid propane. After each experiment the product was warmed to 0°C. and the evolved oxygen determined manometrically. After the trap and its contents were weighed, the yield of hydrogen peroxide was determined by permanganate titration. The water yield was calculated by difference. The yields of molecular oxygen and hydrogen were also obtained by difference, from the known input of hydrogen peroxide and water. The results are shown Fig. 1, which also includes the results obtained by Jones and Winkler with a discharge through water vapor. Their experimental values have been adjusted to the production of OH radicals (16.2 mM. per hr.) in the discharge through hydrogen peroxide vapor.

The products of both systems collected at the same trap temperature evolved the same amounts of oxygen. The yields of hydrogen peroxide were essentially the same at trap temperatures between − 120°C. and − 170°C., below which temperature the peroxide yield from the water system became noticeably larger. The amount of water obtained from each system was roughly equivalent at trap temperatures between − 78°C. and − 120°C., but at lower temperatures the yield from dissociated water vapor increased rapidly. Between − 160°C. and − 195°C., the yields of water were sensibly constant from both systems, with the yield from the water system about 30% larger than that from dissociated peroxide vapor.

### *Influence of Reaction Chamber*

In a series of experiments, the dissociated hydrogen peroxide was allowed to

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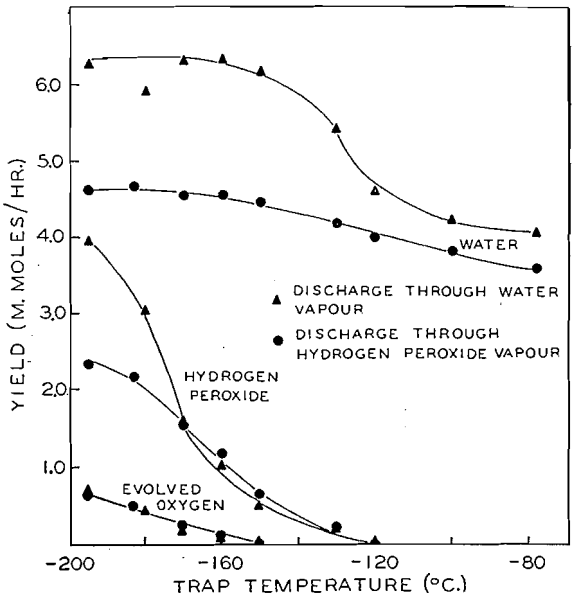



FIG. 1. Variation in the yields of product trapped with changing trap temperature for the discharge through water vapor and hydrogen peroxide vapor.

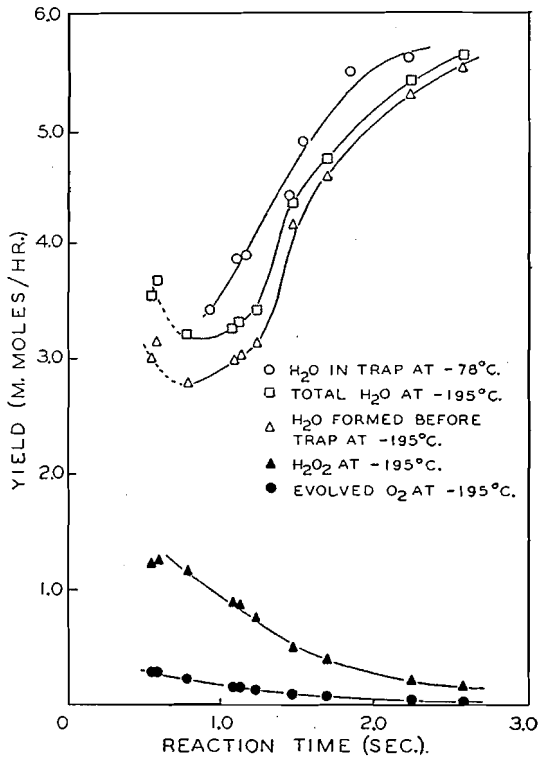



FIG. 2. Variation in yields of products with changing time in the small reaction flask for the discharge through hydrogen peroxide vapor.

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react at room temperature for lengths of time which depended upon the pressure in the reaction chamber (volume = 1024 ml.) situated between the discharge tube and trap. The pressure varied linearly from 0.049 mm. for the shortest reaction time (0.57 sec.) to 0.22 mm. for the longest reaction time (2.57 sec.) with a trap temperature of − 195°C., and from 0.080 mm. to 0.182 mm. as the reaction time increased from 0.93 sec. to 2.22 sec., with a trap temperature of − 78°C.

Fig. 2 shows that the amount of water obtained in a trap cooled in dry ice was larger than the amount collected in a trap cooled in liquid nitrogen at all reaction times. The yields of hydrogen peroxide and evolved oxygen at a trap temperature of − 195°C. decreased steadily with increasing reaction time, while the yield of water increased, both at − 78°C. and − 195°C. Similar experiments with a larger reaction chamber (5400 ml.) exhibited the same behavior.

Two experiments were made at constant pressure, one with each reaction vessel, in which the surface to volume ratios of the vessels were made approximately equal (0.66 $cm.^{-1}$) by the addition of the required number of Pyrex glass rods (Table I). The results of these experiments, in which the only experimental variable was the reaction time, again showed that the yields of hydrogen peroxide and evolved oxygen were decreased, and the yield of water increased, with increased reaction time.

TABLE I

EFFECT OF REACTION TIME ON YIELDS OF PRODUCTS
TRAP TEMPERATURE: −196°C.

| Volume of reaction chamber (ml.) | Reaction time (sec.) | Yields—mM. per hour | | | | |
|---|---|---|---|---|---|---|
| | | $H_2O_2$ | $H_2O$ | Evolved $O_2$ | $H_2$ | $O_2$ |
| 1024 | 1.21 | 0.43 | 3.78 | 0.07 | 4.59 | 5.71 |
| 5400 | 6.19 | 0.12 | 5.50 | 0.02 | 3.18 | 5.21 |

The effect of the surface area to which the dissociated hydrogen peroxide was exposed was investigated by loosely filling the small reaction chamber with 0.175 gm. of glass wool (Table II). At a trap temperature of − 195°C., the yields of hydrogen peroxide and evolved oxygen were drastically reduced, corresponding to an increase in the yield of gaseous oxygen and hydrogen. At − 78°C., the yield of water (the sole condensed product) was reduced, again with a corresponding increase in the amount of hydrogen and oxygen.

*Discharge Through a Mixture of Hydrogen and Hydrogen Peroxide*

The differences between the yields obtained from the hydrogen peroxide and water systems could have been caused by differences in the concentration of hydrogen atoms present in the two systems. A discharge through a mixture of hydrogen gas and hydrogen peroxide might be expected to yield products more

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TABLE II

EFFECT OF SURFACE: VOLUME RATIO ON YIELDS OF PRODUCTS

| | Yields: mM. per hour | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Trap temp.: −196°C. | | | | | Trap temp.: −78°C. | | |
| | $H_2O_2$ | $H_2O$ | Evolved $O_2$ | $H_2$ | $O_2$ | $H_2O$ | $H_2$ | $O_2$ |
| Unpacked vessel | 0.87 | 3.26 | 0.14 | 4.67 | 5.46 | 3.86 | 4.94 | 6.17 |
| Packed vessel | 0.24 | 3.18 | 0.04 | 5.38 | 6.23 | 3.22 | 5.58 | 6.49 |

closely resembling those obtained with a discharge through water vapor. Hydrogen gas was passed at a steady rate through a conventional flow system and mixed with hydrogen peroxide vapor before entering the discharge tube. The input of hydrogen gas was within 5% of 16 mM. per hour in each experiment. Products were trapped at − 195°C., − 150°C., and − 78°C. in individual experiments.

In general, the results followed the expected trend (Table III). The proportions of products were closer to those obtained from the discharge through

TABLE III

YIELDS OF PRODUCTS FROM DISCHARGE THROUGH HYDROGEN PEROXIDE–HYDROGEN MIXTURES

| Trap temperature (°C.) | $H_2$ input (mM./hr.) | Yields: mM. per hour | | | | |
|---|---|---|---|---|---|---|
| | | $H_2O_2$ | $H_2O$ | Evolved $O_2$ | $H_2$ | $O_2$ |
| − 195° | 16.30 | 3.70 | 7.02 | 0.56 | 15.05 | 0.33 |
| − 150 | 15.9 | 1.06 | 6.33 | 0.04 | 18.00 | 3.86 |
| − 78 | 15.8 | | 5.00 | | 20.35 | 5.54 |

water vapor than to those from dissociated hydrogen peroxide alone. Exact correspondence would not be expected; not only was the concentration of hydrogen atoms much lower than that present in dissociated water vapor but there was probably some reaction between hydrogen atoms and hydrogen peroxide (see later).

*Reactions in Systems of Significance to the Formulation of a Mechanism*

The dissociation products of an electrical discharge through hydrogen peroxide or water vapor may be composed of a number of chemical species, both molecules (e.g. hydrogen peroxide, water, hydrogen, and oxygen) and fragments of molecules, (e.g. hydroxyl radicals, hydrogen atoms, oxygen atoms, and perhydroxyl radicals). This large number of possible primary and secondary

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products of the discharge could lead to many reactions, some of which might occur in the gas stream, others on the walls of the tubing between the discharge tube and trap, and still others in the cold trap itself. The investigation of certain reactions between some of these species is described below.

*Addition of Molecular Hydrogen to Dissociated Peroxide*

The reactants in this experiment were mixed in the large spherical reaction chamber (volume 5400 ml.). The hydrogen gas was supplied to this chamber at a steady rate (not through the discharge tube as in the previous experiment) and the products were collected in a trap cooled in liquid nitrogen. The input to the discharge was 7.4 mM. of hydrogen peroxide and 1.4 mM. of water per hour, while 16.4 mM. of hydrogen per hour was passed into the reaction chamber. The pressure in the discharge tube and reaction chamber was approximately 0.1 mm.

The products obtained when hydrogen gas was added to the dissociated peroxide vapor were identical with those from the dissociated peroxide itself. Therefore, the dissociation products of hydrogen peroxide must be unreactive toward molecular hydrogen.

*Reactions of Dissociated Hydrogen Peroxide and Dissociated Water with Molecular Peroxide*

In one series of experiments, the dissociated hydrogen peroxide vapor was mixed in a reaction vessel with molecular hydrogen peroxide and the products collected in a trap at − 195°C. The flow of molecular hydrogen peroxide into the reaction vessel was varied from 3.4 mM. per hour to 14.9 mM. per hour with a flow of 1.16 mM. of hydrogen peroxide and 0.64 mM. of water through the discharge tube. Sufficient helium gas was passed into the discharge to increase the operating pressure to about 0.2 mm. and to prevent back diffusion of molecular hydrogen peroxide into the discharge. Experiments were made at temperatures of 26°C. and 100°C. in the reaction chamber.

At low molecular peroxide flow rates, the amount of water produced in the reaction at 26°C. was directly proportional to the molecular hydrogen peroxide flow rate (Curve 2, Fig. 3), while at higher flow rates, the production of water became constant. In these experiments the peroxide found in the trap was assumed to be unreacted, an assumption supported by the absence of any oxygen evolution from the product. No significant change was found in the products of the reaction at 100°C.

The reaction observed between the dissociated hydrogen peroxide and molecular hydrogen peroxide could have been due, in part at least, to hydrogen atoms produced from the decomposition of the water which entered the discharge along with the peroxide. Since it was impractical to remove this water before the discharge, experiments similar to those outlined above were made by passing dissociated water vapor into molecular hydrogen peroxide to determine the relative effect of hydrogen atoms in the presence of hydroxyl radicals.

The input of water vapor to the discharge was 3.0 mM. per hour, which provided about the same theoretical production of OH radicals (3.0 mM. per hour) as before, with a fivefold increase in the production of H atoms (3.0 mM.

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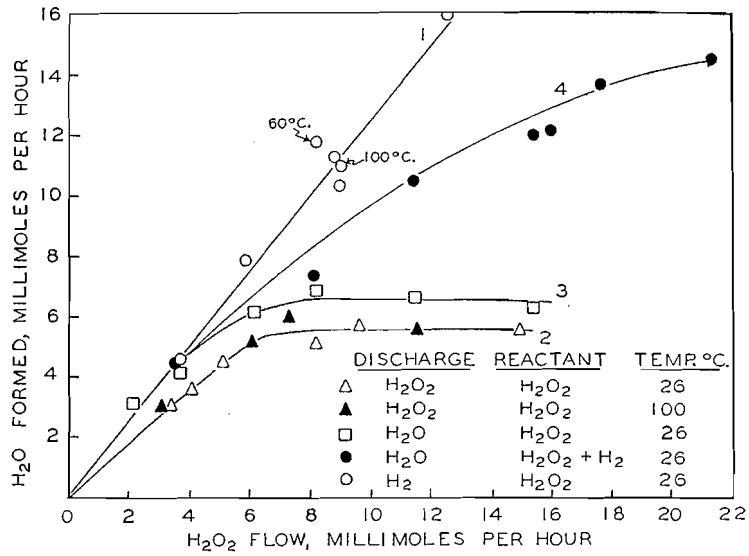



FIG. 3. Rate of production of water as a function of hydrogen peroxide flow.

as against 0.6 mM. per hour). Helium was again added to the discharge, for the reasons given previously. The temperature of the reaction vessel was 26°C. The input of molecular peroxide to the reaction vessel was varied from 2.15 to 15.42 mM. per hour.

The results obtained were similar to those obtained from the reaction of dissociated peroxide vapor with molecular peroxide. (Curve 3, Fig. 3). Again, the water production was a linear function of the amount of peroxide introduced at low flow rates, but became constant at higher flow rates. The yield became constant at about the same peroxide flow rate (6 mM. per hour), but was about 20% larger than the yield obtained from the reaction of dissociated hydrogen peroxide vapor at comparable flow rates.

*Reaction of Hydrogen Atoms with Molecular Peroxide*

Although only a relatively small effect of hydrogen atoms on molecular peroxide in the presence of a constant concentration of hydroxyl radicals was revealed in these experiments, the actual extent to which hydrogen atoms might attack peroxide was not evident. Experiments were therefore made in which molecular peroxide was subjected to the action of hydrogen atoms in the range of flow rates concerned.

Molecular hydrogen was introduced to the discharge tube which was operated at 1220 v. and 200 ma. at a pressure of about 0.25 mm. Wrede and thermocouple gauges were used to measure the hydrogen atom concentration, which was found to be about 10%. Since the molecular hydrogen flow into the discharge was about 16 mM. per hour, the production of hydrogen atoms was 1.8 mM. per hour. In two experiments, the reaction chamber was heated to 60°C. and 100°C.

The production of water from this reaction was a linear function of the

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peroxide input at all flow rates studied (Curve 1, Fig. 3), in contrast to the constant value reached at high flow rates in both the dissociated water and dissociated peroxide reactions. In a study of the hydrogen atom – peroxide reaction at higher flow rates (12.0 to 37 mM./hr.) Geib (3) also found a linear relation between water formed and peroxide introduced.

At the higher reaction temperatures, no appreciable change in the product yield was observed.

The different behavior shown by this reaction could be the result of either the absence of hydroxyl radicals or the presence of excess molecular hydrogen. Experiments were therefore made to determine the effect of molecular hydrogen on the reaction of dissociated water vapor with molecular peroxide.

*Reactions of Dissociated Water with Molecular Hydrogen and Peroxide*

In these experiments molecular hydrogen was introduced into the reaction chamber at a rate of 18 mM. per hour, together with molecular hydrogen peroxide, while helium gas and 3.0 mM. per hour of water vapor entered the discharge tube. As before, the products of the reaction were collected in a trap cooled in liquid nitrogen.

Water formation from this reaction (Curve 4, Fig. 3) was intermediate between that from attack of peroxide by hydrogen atoms and that from the reactions of peroxide with dissociated peroxide or water vapors. An increase in temperature of the glass tubing at the entrance of the hydrogen peroxide and hydrogen mixture to the reaction vessel was observed, an effect found in the hydrogen atom, but not in the dissociated water and peroxide reactions with molecular peroxide.

## DISCUSSION

The products obtained from dissociated hydrogen peroxide and dissociated water vapors exhibit much the same dependence on experimental conditions. The most obvious similarity, shown in Fig. 1, is the effect of trap temperature on the proportions of products. Both systems are capable of yielding products which evolve the same amount of oxygen on warming. Formation of hydrogen peroxide is observed in both systems at trap temperatures below − 120°C., and the temperature dependence of its formation is the same down to a trap temperature of − 170°C. The final products of the gas phase reactions in both systems are water, hydrogen, and oxygen. Further, an increase in the surface area to which the dissociated products are exposed leads to an increase in the amounts of oxygen and hydrogen from both systems.

It seems reasonable to assume that the close similarity in the behavior of the two systems is due to the presence of hydroxyl radicals in the dissociation products from both peroxide and water molecules. However it is unlikely that the similar behavior observed in the hydrogen atom – oxygen molecule reaction can be attributed to primary formation of hydroxyl radicals in that reaction. The mechanism postulated by Jones and Winkler as an adaptation of one proposed by Badin (1) appears to afford a satisfactory explanation of the experimental observations with all three systems. This mechanism assumes the formation of an unstable collision complex from either two OH radicals, or two H

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atoms and an $O_2$ molecule. Stabilization of the complex by collision with a cold wall is assumed to produce either normal hydrogen peroxide or the abnormal form of peroxide postulated by Geib and Harteck, which is unstable above − 115°C., and decomposes into water and oxygen. If the complex is not stabilized, it may decompose either reversibly to the original reactants, or irreversibly to water and atomic oxygen. (The present authors have confirmed the report of Harteck and Kopsch (4), that oxygen atoms do not react with water vapor at room temperature or 100°C.)

On the other hand, Bawn has reported* thermochemical measurements made during oxygen evolution from the warmed products, and has expressed the opinion that the relatively small heat effect observed (*ca.* 300 cal.) is not consistent with decomposition of a molecular entity.

Fig. 1 shows that the yield of water below a trap temperature of − 120°C. and the yield of hydrogen peroxide below − 170°C. from dissociated water vapor were larger than the corresponding yields from dissociated hydrogen peroxide vapor. This behavior suggests that the following trap reactions occurred in the water vapor system where excess H atoms were present.

$$H + HO_2 \rightarrow H_2O_2 \text{ below } -170°C.$$
$$H + OH \rightarrow H_2O \text{ below } -120°C.$$

The products of the discharge through hydrogen – hydrogen peroxide mixture (Table III) showed the influence of these reactions.

If decomposition of an abnormal hydrogen peroxide is assumed to produce water, the amount of water so formed can be calculated from the amount of oxygen evolved. However, another source of water is apparent from the results in Fig. 2. In these experiments, a trap cooled in dry ice collected more water than a trap cooled in liquid nitrogen. Further, the difference in the yields was greatest at shorter reaction times. This suggests that formation of water occurred at a trap temperature of − 78°C., which possibly accounts for the rather large amount of water formed from dissociated hydrogen peroxide at − 78°C. with no reaction chamber (Fig. 1). This amount of water continued to be formed as the trap temperature was lowered, until formation of hydrogen peroxide became appreciable, after which a decrease in the amount of water produced by this means must have occurred. This behavior is readily explained on the basis of a complex which decomposes at trap temperatures down to those where it becomes stabilized to peroxide.

The surface reaction by which hydrogen and oxygen were formed is postulated to involve hydroxyl radicals as follows

$$OH + OH + M \rightarrow H_2 + O_2 + M.$$

The gas phase reactions of molecular peroxide with hydrogen atoms, (System I), dissociated peroxide, i.e. OH radicals (System II), and dissociated water, i.e. mixture of H atoms and OH radicals, in the presence (System III) and absence (System IV) of excess hydrogen are prohibited, in dissociated water vapor itself, by the absence of any molecular hydrogen peroxide. In view of the correspondence between the products of dissociated water vapor and hydrogen peroxide vapor (Fig. 1) these reactions are presumably unimportant in dissoci-

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ated hydrogen peroxide vapor also. The decomposition of hydrogen peroxide in the discharge may then be considered to be fast compared with the reaction between hydroxyl and peroxide.

The results with Systems I to IV above can be explained on the basis of a chain mechanism, involving reactions of hydrogen atoms and hydroxyl radicals as follows:

$$H + H_2O_2 \rightarrow H_2O + OH \quad (1)$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad (2)$$
$$HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH \quad (3)$$

This series of reactions is adequate to explain the mole for mole relation between water formed and hydrogen peroxide reacted in Systems II and III (Curves 2 and 3, Fig. 3) at all flow rates. To explain the constant amount of water formed at higher flow rates in these experiments, chain breaking reactions involving hydrogen peroxide as a third body appear to be necessary, viz.

$$OH + OH + [H_2O_2] \rightarrow H_2O_2 + [H_2O_2] \quad (4)$$
$$H + OH + [H_2O_2] \rightarrow H_2O + [H_2O_2] \quad (5)$$

Of all the species, $H_2O_2$ is apparently the most effective in accommodating the energy liberated in these reactions.

Curve 3 (Fig. 3) lies above Curve 2, presumably because of the relatively larger concentration of hydrogen atoms present, capable of initiating more chains by reaction 1. However the fact that a fivefold increase in the hydrogen atom concentration in this reaction over that which prevailed in System II caused an increase in water production of only 20% would seem to indicate that reaction 2 predominates. In the hydrogen atom reaction (Curve 1, Fig. 3) an additional step involving molecular hydrogen is possible

$$H_2 + HO_2 \rightarrow H_2O + OH \quad (6)$$

This reaction may explain the linear relation between water formed and input over the range of flow rates studied.

In addition to increasing the chain length, this reaction should lead to production of water in excess of the mole for mole amounts predicted by reactions 1, 2, and 3. The observed ratio in the hydrogen atom reaction was 1.3.

Reaction 6 also appears to be operative in the reaction between peroxide and dissociated water vapor in the presence of hydrogen (Curve 4). However the effect of reactions 4 and 5 is noticeable at higher flow rates.

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# THE ALKALOIDS OF *LYCOPODIUM* SPECIES

## XII. RELATIONSHIP BETWEEN SOME OF THE MINOR ALKALOIDS AND LYCOPODINE[1]

By Bryce Douglas,[2] D. G. Lewis,[2] and Léo Marion

ABSTRACT

Reduction of the carbonyl group of lycopodine with lithium aluminum hydride gives rise to dihydrolycopodine which contains a secondary alcoholic group. The new base can be dehydrated to form anhydrodihydrolycopodine and this is identical with alkaloid L14($C_{16}H_{25}N$). Acetylation of dihydrolycopodine produces O-acetyldihydrolycopodine which is identical with alkaloid L2($C_{18}H_{29}O_2N$). On distillation at atmospheric pressure alkaloid L2 is pyrolyzed and gives rise to 7-methylquinoline. Alkaloids L8 and L30 which had been reported previously as different have now been found to be identical.

Lycopodine ($C_{16}H_{25}ON$), the most widely distributed alkaloid in the *Lycopodium* species, contains a carbonyl group as indicated in its infrared absorption spectrum, and confirmed by the formation of a hydrazone and by conversion to a tertiary carbinol via the action of phenyl-lithium (5). It has now been possible also to prepare an oxime of lycopodine. The Beckmann rearrangement of this oxime, however, failed to take place under the usual conditions. Attempted condensation of lycopodine with benzaldehyde failed to give a benzylidene derivative. As previously reported the reduction of lycopodine with the aid of lithium aluminum hydride converted the carbonyl group to a secondary alcoholic group giving rise to dihydrolycopodine (5), a base which could be oxidized with chromic acid back to lycopodine.

Through the action of phosphorus pentachloride it was possible to remove the elements of water from dihydrolycopodine. The product of the reaction, anhydrodihydrolycopodine ($C_{16}H_{25}N$), was an oily base forming a crystalline perchlorate. Whereas the infrared absorption spectrum of dihydrolycopodine showed an absorption band at 3625 cm.$^{-1}$ indicative of a hydroxyl group, that band was absent in the spectrum of anhydrodihydrolycopodine. Alkaloid L14 which occurs in *L. tristachyum* (9) is isomeric with this base and gives rise to a perchlorate having the same optical rotation and the same melting point as anhydrodihydrolycopodine perchlorate. Admixture failed to alter the melting point and the X-ray diffraction patterns of both salts were superimposable. It can therefore be concluded that alkaloid L14 is anhydrodihydrolycopodine.

Dihydrolycopodine could be acetylated readily to O-acetyldihydrolycopodine, $C_{18}H_{29}O_2N$, which was crystalline and formed a crystalline perchlorate. The acetylated base was isomeric with alkaloid L2 occurring in *L. flabelliforme* (6). The infrared absorption spectrum of alkaloid L2 showed no absorption in the OH region, but contained a sharp absorption peak in the carbonyl region at 1730 cm.$^{-1}$ Further, the spectrum showed absorption in the region

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near 1239 cm.$^{-1}$ normally displayed by acetates. This absorption consisted of a double peak at 1228 and 1241 cm.$^{-1}$ The occurrence of a single maximum near 1239 cm.$^{-1}$ or of multiple peaks in this region has been related to cis–trans configuration (1, 4) or to the equatorial or polar orientation of the acetoxy group (2, 3). When the structure of lycopodine becomes better known this observation may prove useful. Both O-acetyldihydrolycopodine and its perchlorate had the same respective melting points as alkaloid L2 and its perchlorate, and admixture of the two bases and the two salts failed to alter these melting points. X-ray powder diagrams of the two perchlorates were exactly identical. Hence, alkaloid L2 is naturally occurring O-acetyldihydrolycopodine. Distillation of the acetylated base at atmospheric pressure brought about partial decomposition, the distillate consisting mostly of the unchanged material and a small quantity of an oily base which proved to be 7-methylquinoline. This supplied further evidence of the readiness with which lycopodine gives rise to 7-methylquinoline.

Alkaloid L8, $C_{15}H_{25}O_2N$, m.p. 180° (perchlorate, m.p. 318°), has been reported as occurring in *L. annotinum* (7). Later, alkaloid L30, m.p. 178°, forming a perchlorate melting at 311°, was found in *L. annotinum* var. *acrifolium* (8). On closer examination it has now been established that alkaloids L8 and L30 are identical, admixture of the bases and of their perchlorates failing to depress the respective melting points.

## EXPERIMENTAL[3]

### *Lycopodine*

Lycopodine had $[\alpha]_D^{26} -24.5°$ (*c*, 1.10 in absolute ethanol). Its pK, 7.44 (pH at half titration), was obtained by titration of the perchlorate in 50% methanol. The equivalent of the salt thus found was 347 (calcd. 347.4).

### *Lycopodine Oxime*

Lycopodine (620 mgm.) dissolved in aqueous ethanol (20 ml.) was treated with molar hydroxylamine solution (2.5 ml.) and molar sodium acetate solution (3 ml.). The mixture was heated on the steam bath for three hours, cooled, and a drop of 10 *N* sodium hydroxide added. A solid was precipitated which was filtered and dried (307 mgm.), m.p. 220–230°. Recrystallization from aqueous ethanol gave colorless prismatic needles, m.p. 262–264°. Calcd. for $C_{16}H_{26}ON_2$: C, 73.25; H, 9.99; N, 10.68. Found: C, 72.74, 72.82; H, 9.77, 9.85; N, 11.02, 10.94%. The mother liquors yielded unchanged lycopodine (80 mgm.).

### *Dihydrolycopodine*

This was prepared by the action of lithium aluminum hydride on lycopodine as previously described (5). It crystallized from ether as colorless prisms, m.p. 168°. Calcd. for one active hydrogen, 0.40; found, 0.44% (Zerewitinow). Its pK was 9.2 (value of pH at half titration of the perchlorate in 50% aqueous methanol), and the equivalent weight of the salt was 349 (calcd. 349.5). The infrared absorption spectrum of dihydrolycopodine contained no absorp-

[3] *All melting points are corrected.*

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tion in the carbonyl region, but contained an absorption band at 3625 cm.$^{-1}$ indicative of a hydroxyl group.

*Oxidation of Dihydrolycopodine*

The base (94 mgm.) and chromic oxide (180 mgm.) were dissolved in purified glacial acetic acid (20 ml.) and the mixture maintained at 25° for six days. The brown solution was diluted with water (5 ml.), made slightly alkaline with sodium hydroxide, and extracted exhaustively with chloroform. The chloroform extract was washed repeatedly with 2*N* hydrochloric acid and the combined aqueous washings made alkaline with sodium hydroxide and extracted repeatedly with chloroform. This final combined chloroform solution was dried over anhydrous sodium sulphate and concentrated to yield an oil which solidified on seeding with a minute crystal of lycopodine (72 mgm.). After recrystallization the product melted at 116° either alone or after admixture with an authentic sample of lycopodine.

*Anhydrodihydrolycopodine*

Dihydrolycopodine (122 mgm.) and phosphorus pentachloride (200 mgm.) were dissolved in hot dry xylene (20 ml.) and heated under reflux in an atmosphere of nitrogen for six hours, during which time a considerable volume of hydrogen chloride was liberated. Water (20 ml.) was added to the cooled solution and the mixture shaken vigorously. The aqueous layer was separated and the xylene solution further extracted with three 20 ml. portions of 2 *N* hydrochloric acid. The combined acid extract was extracted once with a little chloroform, made slightly alkaline with sodium hydroxide, and extracted exhaustively with chloroform. This extract was dried and evaporated, leaving a brown syrup (103 mgm.) which was distilled *in vacuo*. A colorless oil was thus obtained, b.p. 125–130° at 1 mm., which slowly became yellow on standing. The infrared absorption spectrum of anhydrodihydrolycopodine in chloroform showed no hydroxyl absorption.

The bulk of the distilled oil was converted to the perchlorate in methanol by the usual procedure. The crystalline perchlorate separated from aqueous methanol as plates, m.p. 234–237°. Two recrystallizations from acetone yielded colorless prisms, m.p. 238–239°. Calcd. for $C_{16}H_{25}N.HClO_4$: C, 57.91; H, 7.90. Found: C, 57.94; H, 7.85%. $[\alpha]_D^{26} -107°$ (*c*, 1.10 in methanol). In admixture with the perchlorate of alkaloid L14 (m.p. 238°) the melting point of anhydrodihydrolycopodine perchlorate was unchanged. Alkaloid L14 perchlorate has $[\alpha]_D^{26} -105.5°$ (*c*, 1.86 in methanol). The X-ray diffraction patterns of both perchlorates were superimposable.

*Acetyldihydrolycopodine*

Dihydrolycopodine (200 mgm.), trifluoracetic anhydride (0.16 ml.), and acetic acid (0.1 ml.) were mixed and maintained at 25° overnight. The solution was poured into excess sodium bicarbonate solution, extracted exhaustively with ether, and the dried (anhydrous sodium sulphate) extract evaporated down to a pale yellow oil which solidified on scratching, m.p. 90–95°. This product was dissolved in methanol and converted to a perchlorate in the usual

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way (yield 140 mgm., m.p. 240–242°). Recrystallization three times from methanol yielded colorless prisms, m.p. 246–247° when immersed at 205°. The melting point, however, varies with the rate of heating and the temperature of immersion. When heated from room temperature the melting point can be as low as 230°. Calcd. for $C_{18}H_{29}O_2N.HClO_4$: C, 55.15; H, 7.71; N, 3.57. Found: C, 55.10, 55.27; H, 7.72, 7.71; N, 3.37, 3.53%. The pK of the base determined by titration of the perchlorate in 50% methanol with 0.063 *N* sodium hydroxide was 8.4 (value of pH at half titration) and the equivalent weight of the salt was 390 (calcd. 392). Alkaloid L2 perchlorate (m.p. 231°) was isomeric with the perchlorate of acetyldihydrolycopodine and in admixture with it melted at 246–247° when immersed at 205°. X-ray diffraction patterns of the two perchlorates were superimposable.

Acetyldihydrolycopodine perchlorate was dissolved in the minimum volume of water, the solution made alkaline with ammonia and the precipitated white needles collected, washed with water, and dried, m.p. 95–96°. In admixture with alkaloid L2 (m.p. 97°) the base melted at 95–96°. The acetylated base was also obtained by the action of acetic anhydride on dihydrolycopodine. The infrared absorption spectrum of acetyldihydrolycopodine shows absorption bands at 1730 $cm.^{-1}$ in the carbonyl region and at 1238 and 1241 $cm.^{-1}$ in the "acetyl region."

A 5 *N* solution of sodium hydroxide in 50% methanol (2 ml.) was added to acetyldihydrolycopodine (50 mgm.) dissolved in methanol (3 ml.) and the solution maintained at 40–50° overnight. The bulk of the solvent evaporated during this time. The aqueous solution was cooled and the separated oil which solidified was collected, washed, and dried (43 mgm.), m.p. 160–163°. In admixture with an authentic specimen of dihydrolycopodine (m.p. 168°) it melted at 164–165°.

*Thermal Decomposition of Acetyldihydrolycopodine*

Acetyldihydrolycopodine (700 mgm.) was heated in a stream of nitrogen under the vacuum of a water-pump in a small distilling flask. Almost all of the compound distilled unchanged. The distillate was redistilled at atmospheric pressure. A first fraction was obtained which was slightly yellow (480 mgm.) and a second high boiling fraction (155 mgm.) consisted of a colorless oil with a strong quinoline-like odor. The first fraction was converted to a perchlorate in acetone–ether, m.p. 216–220°. Recrystallization from methanol gave colorless rhombs, m.p. 246–247° (immersed at 205°) which showed no depression when mixed with acetyldihydrolycopodine perchlorate. The high boiling fraction was dissolved in dilute hydrochloric acid and extracted with ether. The ether extract yielded only a small trace of oil which was discarded. The acidic solution was made alkaline with sodium hydroxide and extracted exhaustively with chloroform. The extract was dried over anhydrous sodium sulphate and distilled on the steam bath to remove the solvent. There was left an oil (20 mgm.) which was converted to a picrate in methanol. After recrystallization from methanol the picrate consisted of lemon-yellow needles, m.p. 235–236° either alone or in admixture with an authentic specimen of 7-methylquinoline picrate.

*Alkaloids L8 and L30*

Alkaloid L8 ($C_{16}H_{25}O_2N$) was reported as having m.p. 180° and forming a perchlorate, m.p. 318° (4). Alkaloid L30 ($C_{16}H_{25}O_2N$), m.p. 178°, formed a perchlorate, m.p. 311°. In admixture, the two bases had the same melting point and so had the two perchlorates.

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# THE ESSENTIAL OIL OF *THUJA OCCIDENTALIS* L.[1]

By A. C. Shaw

ABSTRACT

Foliage of *Thuja occidentalis* yielded 0.269% of an essential oil containing *l*-thujone, *d*-isothujone, *l*-fenchone, *l*-bornyl acetate, *dl*-limonene, *d*-sabinene, *l*-β-pinene, *d*-terpinen-4-ol, *dl*-α-pinene, *l*-camphor, *l*-camphene, myrcene, *l*-α-thujene, and an unidentified ester.

## INTRODUCTION

*Thuja occidentalis* or eastern white cedar ranges from the maritime provinces westward as far as Lake Winnipeg, and northward to the southern end of James Bay. The essential oil of *T. occidentalis* was examined by Wallach (8, 9) who reported it to contain *d*-α-pinene, *l*-fenchone, *d*-thujone, esters of acetic acid, and carvatanacetone. It was noted that, at elevated temperatures, thujone is isomerized to carvatanacetone (5), and that the latter might not have been present in the oil prior to fractional distillation. The presence of esters of valeric acid has also been reported (3).

The present contribution is the last of a series describing the oils which are obtainable in acceptable yield from coniferous species which are cut commercially in Canada.

## EXPERIMENTAL

### *Preparation of the Oil*

Leaves and terminal branches of *T. occidentalis*, collected in April 1948, were distilled for six hours with steam from a boiler at 90 lb. pressure. The oil, obtained in a yield of 0.269%, had the following properties: $\eta_D^{20}$ 1.4612, $d_{20}^{20}$ 0.9168, $\alpha_D^{30}$ −7.8°, acid number 0.53, ester number 33.7, ester number after acetylation 72.7, aldehydes as citral 1.4%, ketones as carvone 50.7%.

### *Fractional Distillation of the Oil*

The oil was distilled through a 6-ft., 25-mm. I. D. Podbielniak column using a reflux ratio of 20/1, and a pressure drop across the column of 20 mm. The properties of the fractions obtained are listed in Table I.

### *Identification of Constituents*

Melting points were measured with a Kofler micro hot stage apparatus. Optical rotations were measured in a 1-dcm. tube.

#### *l-α-Thujene*

An unidentified, low-boiling fraction, b.p. 96–133°C., $\eta_D^{20}$ 1.4265, $\alpha_D$ +1.60°, and a levo compound, b.p. 150.5–152.5°C., $\eta_D^{20}$ 1.4559, $\alpha_D$ −14.76°, were separated by redistillation of fraction 1. The latter compound (0.5 gm.) when treated with hydrogen chloride in ether solution at 0° yielded 0.09 gm. of terpinene hydrochloride, m.p. 50–51°C.; mixed with dipentene hydrochloride, m.p.

[1] *Manuscript received in original form February 1, 1952, and, as revised, November 27, 1952. Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto, Canada.*



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TABLE I

| Fraction | $\eta_D^{20}$ | $d_4^{20}$ | $\alpha_D$ | B.p. | % Distilled |
|---|---|---|---|---|---|
| 1 | 1.4484 | 0.846 | − 1.55° | 140.8°/760 mm. | 0.55 |
| 2 | 1.4600 | 0.842 | − 10.79 | 155.0 | 1.17 |
| 3 | 1.4623 | 0.849 | − 7.36 | 156.0 | 1.80 |
| 4 | 1.4641 | 0.850 | − 5.47 | 156.5 | 2.43 |
| 5 | 1.4655 | 0.855 | − 5.95 | 156.9 | 3.05 |
| 6 | 1.4676 | 0.855 | − 10.04 | 157.7 | 3.68 |
| 7 | 1.4692 | 0.857 | − 17.45 | 148.3 | 4.31 |
| 8 | 1.4708 | 0.860 | − 28.95 | 159.2 | 4.92 |
| 9 | 1.4713 | 0.863 | − 40.86 | 159.6 | 5.42 |
| 10 | 1.4709 | 0.857 | − 6.88 | 161.7 | 6.05 |
| 11 | 1.4703 | 0.846 | + 55.53 | 164.5 | 6.75 |
| 12 | 1.4705 | 0.845 | + 55.47 | 165.2 | 7.36 |
| 13 | 1.4710 | 0.848 | + 51.25 | 165.3 | 7.98 |
| 14 | 1.4717 | 0.848 | + 43.95 | 165.5 | 8.69 |
| 15 | 1.4722 | 0.844 | + 31.07 | 165.8 | 9.32 |
| 16 | 1.4703 | 0.810 | + 6.83 | 168.0 | 9.89 |
| 17 | 1.4705 | 0.816 | + 5.14 | 170.5 | 10.46 |
| 18 | 1.4730 | 0.837 | + 3.54 | 171.5 | 11.02 |
| 19 | 1.4773 | 0.838 | + 4.51 | 176.0 | 11.65 |
| 20 | 1.4781 | 0.840 | − 9.72 | 177.4 | 12.24 |
| 21 | 1.4785 | 0.840 | − 11.34 | 177.8 | 12.75 |
| 22 | 1.4698 | 0.884 | − 22.43 | 178.0 | 14.72 |
| Nonvolatile residue | | | | | 14.95 |
| Loss | | | | | 15.03 |
| 23 | 1.4556 | 0.922 | − 32.44° | 105.5°/50 mm. | 38.54 |
| 24 | 1.4535 | 0.923 | − 32.74 | 106 | 39.18 |
| 25 | 1.4511 | 0.918 | − 26.01 | 109 | 41.82 |
| 26 | 1.4505 | 0.916 | − 22.62 | 109 | 42.55 |
| 27 | 1.4503 | 0.915 | − 21.78 | 109 | 45.18 |
| 28 | 1.4497 | 0.914 | − 18.26 | | 45.87 |
| 29 | 1.4493 | 0.913 | − 16.89 | 90°/20 mm. | 46.60 |
| 30 | 1.4493 | 0.912 | − 17.27 | | 49.24 |
| 31 | 1.4490 | 0.912 | − 16.67 | | 54.22 |
| 32 | 1.4488 | 0.912 | − 14.09 | | 62.14 |
| 33 | 1.4490 | 0.913 | − 7.23 | | 62.81 |
| 34 | 1.4490 | 0.913 | − 6.33 | | 63.45 |
| 35 | 1.4490 | — | — 6.33 | | 64.12 |
| 36 | 1.4486 | 0.912 | − 5.46 | | 64.81 |
| 37 | 1.4489 | 0.913 | − 9.12 | 90°/20 mm. | 65.49 |
| 38 | 1.4488 | 0.913 | − 10.00 | | 66.14 |
| 39 | 1.4487 | — | − 6.97 | | 66.81 |
| 40 | 1.4488 | 0.914 | − 2.86 | | 67.45 |
| 41 | 1.4490 | — | + 1.51 | | 68.12 |
| 42 | 1.4490 | — | + 4.53 | | 68.75 |
| 43 | 1.4490 | 0.914 | + 6.89 | | 69.42 |
| 44 | 1.4490 | — | + 9.94 | | 70.07 |
| 45 | 1.4490 | — | + 13.58 | | 70.74 |
| 46 | 1.4490 | 0.914 | + 17.03 | | 71.38 |
| 47 | 1.4490 | 0.915 | + 10.44 | | 72.08 |
| 48 | 1.4492 | 0.915 | + 19.23 | | 72.73 |
| 49 | 1.4494 | — | + 29.07 | | 73.42 |
| 50 | 1.4494 | 0.914 | + 33.81 | | 74.13 |
| 51 | 1.4494 | — | + 40.14 | | 74.77 |
| 52 | 1.4494 | — | + 44.68 | | 75.41 |
| 53 | 1.4496 | 0.915 | + 48.81 | | 76.10 |
| 54 | 1.4495 | 0.914 | + 32.78 | | 76.76 |
| 55 | 1.4495 | 0.917 | + 55.45 | | 77.40 |
| 56 | 1.4495 | 0.917 | + 61.85 | | 78.06 |
| 57 | 1.4494 | 0.916 | + 65.00 | | 78.70 |
| 58 | 1.4504 | 0.913 | + 65.52 | 91°/20 mm. | 79.37 |
| 59 | 1.4568 | 0.934 | + 22.70 | | 79.95 |

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TABLE I (Concluded)

| Fraction | $\eta_D^{20}$ | $d_4^{20}$ | $\alpha_D$ | B.p. | % Distilled |
|---|---|---|---|---|---|
| 60 | Solid, m.p. 90–110° | | | | 81.78 |
| 61 | 1.4726 | 0.949 | + 5.51° | 102°/20 mm. | 82.44 |
| 62 | 1.4740 | 0.940 | + 22.91 | 102 | 83.12 |
| 63 | 1.4750 | 0.939 | + 19.40 | 102 | 83.69 |
| 64 | 1.4760 | 0.944 | + 8.39 | 108.5 | 84.42 |
| 65 | 1.4693 | 0.958 | − 3.30 | 110 | 85.08 |
| 66 | 1.4634 | 0.967 | − 11.83 | 110 | 85.79 |
| 67 | 1.4634 | 0.967 | − 18.02 | 110 | 86.43 |
| 68 | 1.4632 | 0.968 | − 22.32 | 110 | 87.13 |
| 69 | 1.4632 | 0.969 | − 27.38 | 110 | 87.81 |
| 70 | 1.4650 | 0.961 | − 26.44 | 98°/10 mm. | 88.52 |
| 71 | 1.4650 | 0.960 | − 26.34 | 102 | 89.27 |
| 72 | 1.4659 | 0.958 | − 25.71 | 104 | 89.95 |
| Nonvolatile residue | | | | | 90.52 |
| Sesquiterpenes and high boiling compounds | | | | | 98.42 |

40°C.; mixed with terpinene hydrochloride prepared from an authentic sample of sabinene from oil of savin, m.p. 50–51°C.

A mixture of 1.0 gm. of the levo compound and 2.35 gm. of potassium permanganate in 100 ml. of ice water was shaken for 24 hr., the manganese dioxide was separated and washed, and the combined aqueous liquors extracted with ether, acidified, saturated with salt, and again extracted with ether. From the latter extract was obtained 1.1 gm. of a noncrystallizing oil. This oil on standing for several days with an ethanolic solution of semicarbazide formed a semicarbazone which crystallized from ethanol in short needles, m.p. 198–199° C., alone, or in admixture with an authentic sample of *l*-α-thujaketonic acid semicarbazone.

*dl-α-Pinene*

Fraction 5 (17 gm.) when oxidized with permanganate by the method of Delepine (2) yielded 11.2 gm. of crude acids. After two crystallizations from a benzene–hexane mixture, the product melted at 103–104° C., undepressed by a known specimen of *dl*-pinonic acid.

*l-Camphene*

Although no solid terpene was isolated, the high negative rotation of fraction 9 suggested the presence of a small amount of camphene. Five grams of the fraction was hydrated with Bertram–Walbaum reagent (1). The resultant ester was saponified with ethanolic caustic, and poured into water. The oily paste which separated, when triturated with cold hexane, yielded 2.1 gm. of crude isoborneol, identified as the *p*-nitrobenzoate m.p. 131–133° C. undepressed by a known specimen.

*d-Sabinene and l-β-Pinene*

Fraction 11 (5.0 gm.) in 10 ml. of ether was saturated with hydrogen chloride at 0° C., refrigerated overnight, freed of ether, and refrigerated for several days. Oils were removed from the partially crystalline product on a cold porous tile, leaving 1.6 gm. of a hydrochloride, m.p. 50–51° C., after three crystallizations

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from ethanol. The melting point of a mixture of this derivative and the terpinene hydrochloride prepared from α-thujene was not depressed. Terpinene hydrochloride may be formed by the action of hydrogen chloride on α-thujene, sabinene, α-, β-, or γ-terpinene, or β-phellandrene, as well as terpinen-4-ol and terpinen-1-ol.

Fraction 11 (24.1 gm.) was shaken for one hour with 57 gm. of potassium permanganate and 12 gm. of sodium hydroxide in 400 ml. of water containing 400 gm. of crushed ice. The solution was freed from manganese dioxide in the centrifuge, once extracted with chloroform, concentrated to 300 ml., and refrigerated. The product (1.7 gm.)—a sparingly soluble sodium salt—was recrystallized from water. From an acidified solution of the salt, the free acid was extracted with ether, and crystallized from hexane. Surprisingly *l*-nopinic acid, m.p. 125–126° C., m.p. with a known sample 126–127° C., derived from *l*-β-pinene, was obtained. The terpinene hydrochloride could not have been formed from β-pinene.

The aqueous oxidation liquors were therefore acidified, and extracted with chloroform. The noncrystallizing oil thus obtained, when treated with 5 ml. of 10% aqueous sodium hydroxide, yielded a crystalline salt (0.08 gm. of white platelets after two crystallizations from water). The free acid, isolated as before and crystallized from hexane and then from water, gave a few milligrams of sabinenic acid, m.p. 56–57° C. alone, or in admixture with an authentic sample prepared from oil of savin sabinene.

*Myrcene*

Fraction 16 (2.7 gm.) reacted violently when warmed with 2.0 gm. of maleic anhydride. Crude adduct (2.6 gm., b.p. 190–200° C. at 10 mm.) was separated by distillation, and crystallized from hexane. The product melted at 35–36° C. alone, or in mixture with *cis*-4-isohexenyl-$\Delta^4$-tetrahydrophthalic anhydride.

*dl-Limonene*

Bromine (ca. 7 ml.) was added dropwise to an ice-cold solution of 10 gm. of fraction 21 in 10 ml. of isoamyl alcohol and 20 ml. of absolute ethyl ether. On evaporation of the ether 8.7 gm. of bromide separated and was recrystallized from ethanol. *dl*-Limonene tetrabromide, m.p. 125–126°C., undepressed by an authentic sample, was obtained.

*l-Fenchone*

Fraction 23 was redistilled and a compound with optimum properties, $\eta_D^{20}$ 1.4620, $d_4^{20}$ 0.9406, $\alpha_D$ − 55.66°, b.p. 103° at 50 mm., comprising 7.8% of the oil obtained. A part of this material was heated with three volumes of nitric acid until brown fumes were no longer evolved, washed, steam distilled, dried, and made to solidify in dry ice. The melting point, measured with an immersed thermometer, was 5.0°C. Fenchone melts at 5–6°C. and is stable to nitric acid.

A solution of 5.0 gm. of the fraction with 11 gm. of hydroxylamine hydrochloride and 6 gm. of potassium hydroxide in 80 ml. of ethanol in 10 days at room temperature deposited 1.21 gm. of beautifully crystalline oxime, m.p. 165–167° C., $[\alpha]_D$ − 44.0° ($c$ = 3.03, ethanol). Hückel and Sachs (4) for *d*-fenchone-α-oxime reported m.p. 167°C., $[\alpha]_D$ + 46.5° (96% ethanol).

*l-Thujone and d-Isothujone*

Fractions 26 to 58 were mixtures of two compounds difficultly separable by

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distillation. From fraction 32 was prepared a semicarbazone, m.p. 197–199° C., $[\alpha]_D$ + 53.7° ($c$ = 1.02, ethanol), which must have been *l*-thujone semicarbazone, since it was decomposed by the action of oxalic acid and steam to yield an oil $\eta_D^{20}$ 1.4490. This oil (0.4 gm.) was oxidized by 40 ml. of cold aqueous 2% potassium permanganate to α-thujaketonic acid (0.19 gm.) m.p. 74.5–75.5° C., $[\alpha]_D$ + 173.4° ($c$ = 1.04, ether).

Fraction 53 semicarbazone melted at 170–175° C., $[\alpha]_D$ + 180° ($c$ = 2.49, chloroform). For *d*-isothujone semicarbazone Short and Read (6) reported m.p. 172° C., $[\alpha]_D$ + 222° ($c$ = 1, methanol). The ketone, regenerated from the semicarbazone as before, had $\eta_D^{20}$ 1.4494, $d_4^{20}$ 0.916, $\alpha_D$ + 66.3°, and was oxidized by permanganate to α-thujaketonic acid.

*l-Camphor*

The solid from fraction 60 melted at 90–110° C., $[\alpha]_D$ − 35.5° ($c$ = 2.3, ethanol). It formed a 2,4-dinitrophenyl hydrazone (0.37 gm. from 0.5 gm.), m.p. 175–176° C., undepressed by *l*-camphor 2,4-dinitrophenyl hydrazone.

*d-Terpinen-4-ol*

When fraction 62 was treated with hydrogen chloride as previously described, a small amount of terpinene hydrochloride, m.p. 50–51°, was obtained. This derivative could have been formed from terpinen-1-ol, terpinen-4-ol, or possibly γ-terpineol. The oil (3.75 gm.) was shaken with an ice-cold solution of 2.55 gm. of permanganate in 200 ml. of water, and refrigerated overnight. The aqueous liquors were freed of manganese dioxide, neutralized with carbon dioxide, extracted with a small volume of ether, and finally evaporated to dryness. The residue was exhaustively extracted with ethanol, the ethanol removed in a vacuum desiccator, and the ethanol-soluble residue exhaustively extracted with benzene. On cooling, the glycerol separated as a gelatinous precipitate, which was purified by repeated crystallization from chloroform. The product did not melt sharply, but rectangular anisotropic needles melting up to 128° C. were obtained. *p*-Menthane 1,2,4-triol melts at 128–129° C. The glycerols derived from terpinen-1-ol and γ-terpineol melt at 120–121° C. and 110–112° C. respectively.

*Bornyl Acetate*

Fraction 69 was saponified, the alcohol fragment identified as the *p*-nitrobenzoate, and the acid fragment converted to the anilide, as previously described (7). *l*-Borneol, m.p. 204–206° C., *p*-nitrobenzoate, m.p. 135–136° C., $[\alpha]_D$ − 37.8° ($c$ = 4.53, chloroform), and acetanilide m.p. 114° C., undepressed by an authentic sample, were obtained.

*Fractions 18 and 19*

The dextrorotation of these fractions cannot be due to contamination with *d*-sabinene, since their boiling points differ from that of *d*-sabinene by more than 6° C. Fraction 19 (1.0 gm.) in 2 ml. of ether, when treated with hydrogen chloride, gave 0.13 gm. of *dl*-limonene hydrochloride m.p. 50° C. Fraction 18, treated in the same manner, gave 0.06 gm. of a hydrochloride, m.p. 71.5–72° C., which may have been sylvestrene hydrochloride. No authentic specimen was available. Both fractions failed to form crystalline nitrosites or nitrosates, indicating the absence

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of $\Delta^3$-carene, $\alpha$- or $\beta$-phellandrene. These fractions may contain $\Delta^4$-carene.

*Higher-boiling Compounds*

The fraction of cedar oil boiling above 110° C. at 10 mm. (7.9% of the oil) was fractionally distilled through a 1-ft., 25-mm. I.D. Podbielniak column at 10 mm. pressure, 3 mm. back pressure, and reflux ratio 15/1. Sixty fractions were collected. The plot of properties against weight distilled indicated that at least 10 constituents were present but only five had been isolated in a state of approximate purity. The properties of these fractions are listed in Table II.

TABLE II

| Fraction | $\eta_D^{20}$ | $d_4^{20}$ | $\alpha_D$ | Boiling range, °C. | % of original oil |
|---|---|---|---|---|---|
| *A* | 1.4655 | 0.962 | − 21.84° | 96.4–98.2° (10 mm.) | 0.5 |
| *B* | 1.4645 | 0.962 | − 38.91 | 105.8–109.4 (10 mm.) | 0.6 |
| *C* | 1.4955 | 0.968 | + 17.7 | 116–124 (10 mm.) | 0.4 |
| *D* | 1.4888 | 0.983 | − 35.4 | 115.3–116.2 (2 mm.) | 0.1 |
| *E* | 1.5033 | 1.026 | — | 159.3–161.0 (1 mm.) | 0.1 |

Fraction *A* was *l*-bornyl acetate. Fraction *B* was an ester which on saponification yielded acetic acid; *s*-benzyl thiuronium salt m.p. 133° C.; Ducleaux constants 6.8, 7.1, and 7.4. The alcohol portion ($\eta_D^{20}$ 1.4748, $d_4^{20}$ 0.935, $\alpha_D$ − 49.62°) formed a *p*-nitrobenzoate (0.29 gm. from 0.75 gm.), m.p. 140–141.3° C., $[\alpha]_D$ − 38.1° ($c$ = 5.67, chloroform), but was dehydrated by phenyl isocyanate, and gave only oily products with hydrogen chloride.

Fraction *C* (0.7 gm.) when dehydrogenated with palladium–charcoal and treated with picric acid gave 0.08 gm. of cadalene picrate m.p. 115–117° C., but yielded no crystalline derivatives with *p*-nitrobenzoyl chloride or phenyl isocyanate. At 100° C. it reacted violently with sodium, but below 70° C. the reaction proceeded sluggishly or not at all. Fraction *C* may have contained an oxygenated derivative of a sesquiterpene related to cadalene. However, the yield of cadalene was low and the purity of the fraction questionable.

Fractions *D* and *E* yielded no aromatic products on dehydrogenation. Too little material was available to permit more detailed examination of these fractions.

## RESULTS

From the data of Table I, a plot of properties against per cent distilled was made, and inflection points in the curve representing each property were marked. The per cent occurrence of each compound was given by the distance between the inflection points of the corresponding plateau. The percentage composition of the oil is as follows.

| Terpenes | | Oxygen compounds | |
|---|---|---|---|
| *dl*-Limonene | 3.6% | *l*-Thujone | 47.5% |
| *d*-Sabinene and *l*-$\beta$-pinene | 3.5% | *d*-Isothujone | 9.2% |
| *dl*-$\alpha$-Pinene | 2.6% | *l*-Fenchone | 7.8% |
| *l*-Camphene | 2.0% | *l*-Bornyl acetate | 5.9% |
| $\Delta^4$-Carene ? | 1.3% | *d*-Terpinen-4-ol | 2.7% |
| Myrcene | 0.9% | *l*-Camphor | 2.5% |
| *l*-$\alpha$-Thujene | 0.8% | Unidentified ester b.p. 105.8–109.4° C. at 10 mm. | 0.6% |
| Unidentified liquid b.p. 96–133° C. at 760 mm. | 0.4% | | |
| Sesquiterpenes and higher-boiling compounds | 6.8% | | |

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## ACKNOWLEDGMENTS

This investigation was undertaken at the suggestion of Mr. R. N. Johnston, Chief, Division of Research, Department of Lands and Forests, Province of Ontario, and his colleagues, to whom we are also indebted for supplies of plant material. The essential oil was prepared by Mr. J. N. Brown and Dr. T. F. West. The investigation was supported by a grant from the Research Council of Ontario.

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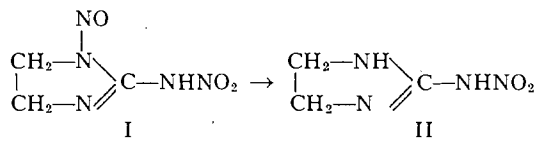
# REACTION OF METHYLAMINE WITH 1-NITROSO-2-NITRAMINO-2-IMIDAZOLINE[1]

By A. F. McKay

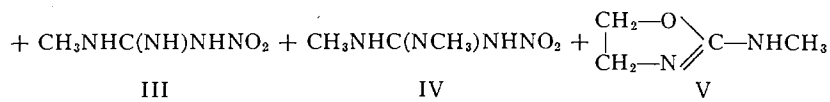
ABSTRACT

On the addition of methylamine to 1-nitroso-2-nitramino-2-imidazoline, 2-nitramino-2-imidazoline, N-methyl-N′-nitroguanidine, N,N′-dimethyl-N″-nitroguanidine, and 2-methylamino-2-oxazolidine were obtained. This reaction is discussed briefly.

In a continuation of the studies (3, 4, 6) of the reactions of amines with 1-nitroso-2-nitramino-2-imidazoline (I) (6) methylamine was used. The order of addition in the latter reaction was reversed. This resulted in the denitrosation of part of the 1-nitroso-2-nitramino-2-imidazoline to give 2-nitramino-2-imidazoline (II) (7). The other products obtained, which are normal (4) to this type of reaction, were N-methyl-N′-nitroguanidine (III) (1), N,N′-dimethyl-N″-nitroguanidine (IV), and 2-methylamino-2-oxazolidine (V). The formation of these products and similar types of products from the reaction



I II



III IV V

of other amines with nitrosamides can be explained by the assumption of a carbonium ion intermediate (3, 5). However it should be emphasized that the mechanisms suggested (3, 5) are only offered as a method of describing a course for these reactions and predicting the reaction products from any given reaction in this series.

The structure of 2-methylamino-2-oxazolidine (V) was established by the cyclization of N-β-chloroethyl-N′-methylurea to this same compound by the method of Gabriel and Stelzner (2).

## EXPERIMENTAL[2]

*Reaction of Methylamine with 1-Nitroso-2-nitramino-2-imidazoline*

Thirty grams (0.177 mole) of 1-nitroso-2-nitramino-2-imidazoline were suspended in 61 cc. of water and the mixture was maintained at 5–7° C. while 44 cc. of a 25% aqueous methylamine solution was added over a period of five minutes. After gas evolution had ceased, which required two hours and ten minutes, the solid was removed by filtration, yield 3.1 gm. (12.6%).

[1] *Manuscript received October 20, 1952.*
*Contribution from Defence Research Chemical Laboratories, Ottawa, Ontario. Issued as D.R.C.L. Report No. 112.*

[2] *All melting points are uncorrected. Microanalyses by Mr. C. W. Beazley, Skokie, Illinois.*



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This solid melted at 220–221° C. with decomposition alone and on admixture with an authentic sample of 2-nitramino-2-imidazoline (7).

The filtrate was transferred to a crystallizing dish and on evaporation deposited a second crop of crystals (m.p. 143–151° C.), yield 2.82 gm. After several fractional crystallizations from 95% ethanol, these crystals were divided into the previously known N-methyl-N′-nitroguanidine (1) (380 mgm.) and N,N′-dimethyl-N″-nitroguanidine (100 mgm.). The remaining crystals appeared as a constant melting mixture (m.p. 147.5–148° C., hazy 145° C.). N-Methyl-N′-nitroguanidine (m.p. 160–160.8° C.) was identified by a mixed melting point determination with a known sample of methylnitroguanidine (m.p. 160–161° C.). The pure N,N′-dimethyl-N″-nitroguanidine melted at 170.5–171° C.

Anal. Calcd. for $C_3H_8N_4O_2$: C, 27.28; H, 6.06; N, 42.42%.
Found: C, 27.54; H, 6.28; N, 42.60%.

The filtrate from the second crop of crystals was treated with an aqueous saturated picric acid solution. The crystalline picrate melted at 149–157° C., yield 5.28 gm. (8.8%). Several crystallizations from 95% ethanol raised the melting point to 167° C. This picrate was identified as 2-methylamino-2-oxazolidine picrate by analysis and synthesis.

Anal. Calcd. for $C_{10}H_{11}N_5O_8$: C, 36.48; H, 3.34; N,21.29%.
Found: C, 36.58; H, 3.60; N, 21.44%.

*Methyl Isocyanate*

Methyl isocyanate (b.p. 34–36° C.) was prepared in 48% yield by the method of Slotta and Lorenz (8).

*N-β-Chloroethyl-N′-methylurea*

β-Chloroethylamine hydrochloride (15.90 gm.) was converted to the free amine in benzene solution as previously described (3). To this benzene solution, 5.45 gm. (0.096 mole) of methyl isocyanate was added under cooling. The benzene solution was cooled in the refrigerator until precipitation appeared complete. The solid (m.p. 65–70.0° C.) was recovered by filtration and washed with petroleum ether (b.p. 30–60° C.). Yield 13.1 gm. (99.8%). Several crystallizations from benzene – petroleum ether were required to obtain a constant melting point of 95–96° C.

Anal. Calcd. for $C_4H_9ClN_2O$: C, 35.19; H, 6.61; N, 20.52; Cl, 25.95%.
Found: C, 34.90; H, 6.63; N, 20.40; Cl, 25.30%.

*2-Methylamino-2-oxazolidine Picrate*

One gram (0.007 mole) of N-β-chloroethyl-N′-methylurea was refluxed with 10 cc. of water for 10 min. The homogeneous solution on addition of an aqueous solution of triethanolamine picrate solution gave 2.06 gm. (88.0%) of picrate (m.p. 164–166° C.). Two crystallizations from water did not alter the melting point. This compound did not depress the picrate (m.p. 166–167° C.) obtained from the reaction of methylamine with 1-nitroso-2-nitramino-2-imidazoline.

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# ELECTROPHORESIS OF RESIN EMULSIONS

## I. THE EFFECT OF EMULSIFYING AGENTS[1]

By L. A. Munro and F. H. Sexsmith

ABSTRACT

A modified Briggs electrophoretic glass cell was used to measure the mobility of over 2500 particles of vinyl acetate latices prepared with different emulsifying agents. Although anionic and cationic agents conferred negative and positive mobilities respectively, nonionic agents invariably resulted in negatively charged particles. This is attributed to partial chemical change to anionic materials or to hydrogen bonding and polarization processes. The nature of the emulsifying agent and electrolyte concentration rather than concentrations of the latex or particle size were the most significant variables affecting the mobility of any latex.

During the past ten years there has been rapid progress in the manufacture and use of aqueous suspensions of synthetic polymers (14). The dispersion of monomers to be polymerized in the emulsion state is effected by the use of surface-active agents. The latter are numerous, of a variety of structures and types, and are used either singly or in combinations. Variation in wetting agent or protective colloid in latex formulation alters the electrical charge on the disperse phase. Current commercial latices of good stability are cited as being negatively or positively charged. Some are described as neutral, although as will be shown, emulsions fitting this category are probably nonexistent. No quantitative data on particle charge or stability are available.

The following paper reports electrophoretic studies of polyvinyl acetate latices emulsified in the presence of various cationic and nonionic wetting agents and with combinations of these.

## APPARATUS AND METHODS

Electrophoresis was measured using the microscope technique. Abramson has cited several advantages of this method (1).

Various microcells for electrophoresis have been described. Rectangular or flat cells have been used by several workers (4, 5, 6, 7, 8). Cells of cylindrical cross section have been preferred by others (2, 11, 12). Both types have inherent advantages and disadvantages.

The apparatus used for these studies embodied features of different cells described in the literature (2, 5, 6).

Pyrex capillary tubing was ground flat on both sides to within as small a distance from the actual bore as was possible (about 0.1 mm.). Four grades of abrasive on rotary-powered plates served to accomplish this grinding:

Carborundum F,
Emery 5 or Alundum 500,
Alundum 600,
Chrome oxide.

A micrometer was used to keep the sides as closely parallel as possible during this operation. Several capillary sections of varying radii were ground and polished.

[1] *Manuscript received October 23, 1952.*
*Contribution from Department of Chemistry, Queen's University, Kingston, Ontario.*



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They were checked with the microscope to enable the tube of proper radius to be selected.

The ground and polished mid-section which was ultimately chosen was fused onto capillary tubing of approximately the same internal radius. The unground capillary was notched first to receive the thin cell, and very fine Pyrex rod was laid on either side of this recess (Fig. 1). The fine rod was fused and sealed into

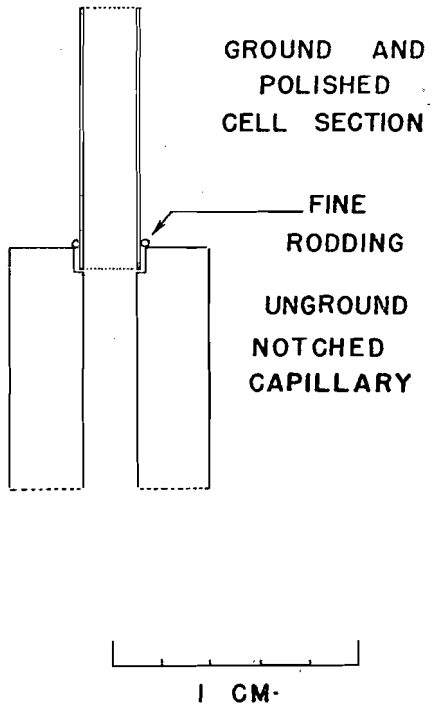



FIG. 1. Method of joining flat mid-section of cell to capillary tubing.

the recess with a small, cool flame, then stronger heating around the unground capillary end completed the operation. The complete cell is shown in Fig. 2.

The capillary used for the central optical section was of radius 1.087 mm. When a microscope equipped with a 47× air objective and 20× hyperplane eyepiece was focused on this central section, polyvinyl acetate emulsion particles contained therein were suitably magnified with a minimum of image distortion. Sufficient working distance was available for particles to be brought into focus anywhere from the roof of the bore to within half of the distance between the top and the axis. The cell itself could be completely cleaned by passage of liquid through it without removing it from the permanent microscope stand.

A potential across the cell of at least 200 v. was necessary to give the emulsion particles measurable electrophoretic velocities. A power pack, enabling 110 v. a-c. to be converted to 360 v. d-c., was used in conjunction with potentiometers and resistances for varying the potential down to zero. As shown in Fig. 3, the selective sensitivity of the potentiometers was increased for the upper voltage

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range by inserting the 25,000 ohm resistance into the circuit. Under conditions of low salt concentration (less than 0.01 *M* as sodium chloride) the mercury electrodes were completely reversible. Currents through the cell never exceeded 1000 microamperes and generally were less than 50.

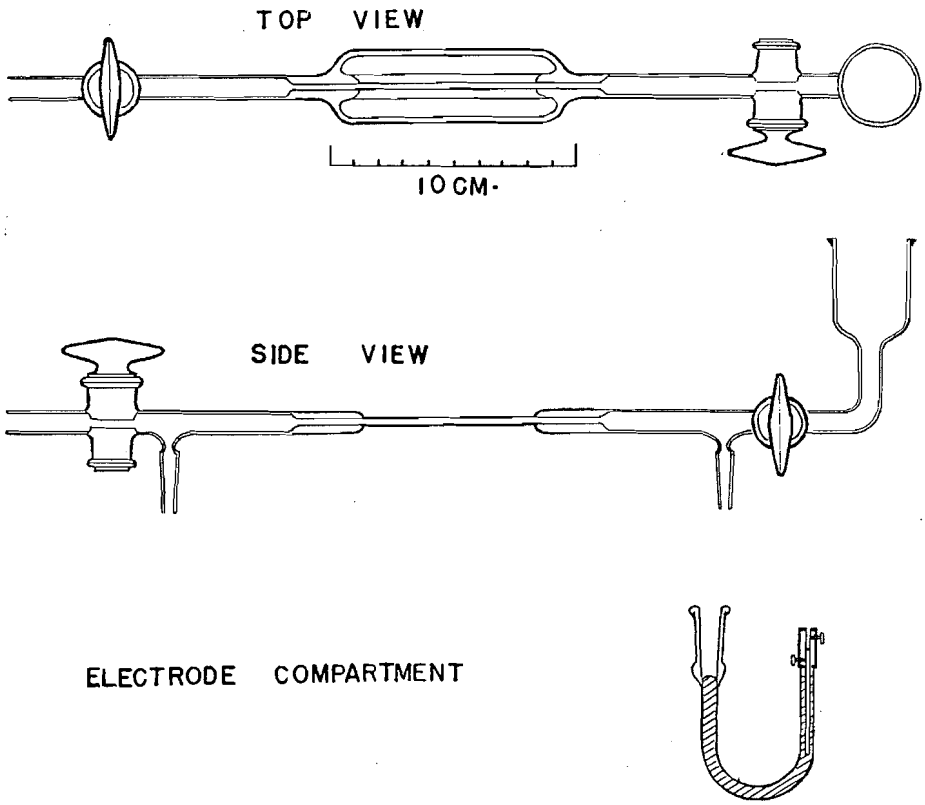



FIG. 2. Completed cell and an electrode compartment.

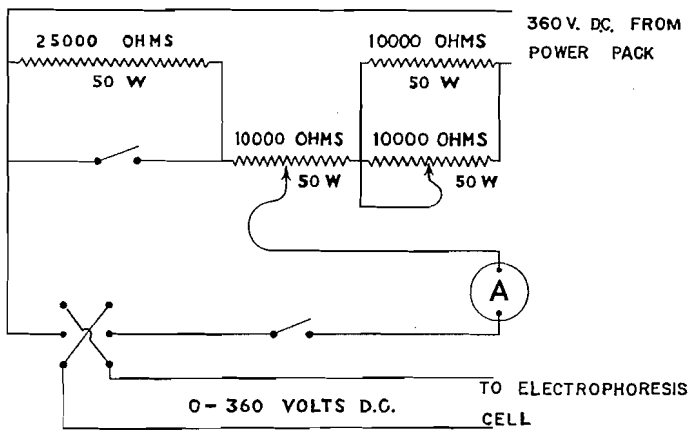



FIG. 3. Wiring diagram for the apparatus.

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The use of reversible mercury electrodes offers advantages over electrode compartments previously designed for microelectrophoresis cells (2, 5, 6). These have combined reversible systems such as $Hg–Hg(NO_3)_2$, Ag–AgCl, and $Cu–CuSO_4$ with plugs of plaster or glass wool for hindering diffusion. With such arrangements it seems quite probable that minute changes in electrolyte concentration must take place in the sample for investigation once it is placed in the cell. Any small variation in salt concentration would introduce error into mobility measurements, especially when electrophoresis is being conducted at provisionally low ionic strengths. Data and discussion of this field will appear in a subsequent paper.

The stage of the microscope was removed to accommodate the central section of the cell. The complete cell was clamped securely to three small retort stands. By means of two screw pinions attached to the bench and pressing down and in from either side against the base of the microscope, the latter was made movable with respect to the cell. Turning these screws a fraction of a revolution made it possible to shift the entire microscope through a few thousandths of a centimeter across the bench top. The layout of the optical bench is shown in Fig. 4*A*.

The lighting arrangement was composed of a parabolic microscope light as source with a plane mirror inclined at 45°. Vertical reflected light thus struck the cell perpendicular to the flat sides. To determine the location of a particle in the cell visible through the microscope, the following correction was applied:

$$r = r_0 - n_w d.$$

$r$ = vertical distance from cell bore to particle level.
$r_0$ = radius of capillary.
$n_w$ = index of refraction of dispersion medium (water).
$d$ = vertical displacement (air) from internal cell roof to particle level.

The fine adjustment of the microscope was calibrated into fiftieths of a turn to enable accurate measurement of $d$. One division = $4.82 \times 10^{-3}$ mm. A graticule was sealed into the 20× hyperplane eyepiece. A particle traversing the full scale length moved through 140.3 microns.

The field strength (volts per cm.) in the center chamber

$$E = \frac{I}{q\sigma}.$$

$E$ = field strength, $\sigma$ = specific conductance of suspension,
$I$ = current, $q$ = cell constant.

Then:

$$\text{Electrophoretic mobility} = \frac{\text{particle velocity}}{E} \text{ (microns per sec. per volt per cm.)}$$

It has been established that with cells of this type, a considerable change of field strength occurs in experiments carried out over a wide range of ionic strengths, even though the applied voltage is constant (3). Hence it is not sufficient to measure the applied voltage alone and to assume that the drop in the cell is a constant fraction of the total drop. This important factor often has been ignored in earlier published work (13). With the apparatus as shown in Fig. 3 the current was conveniently kept constant during mobility measurements.

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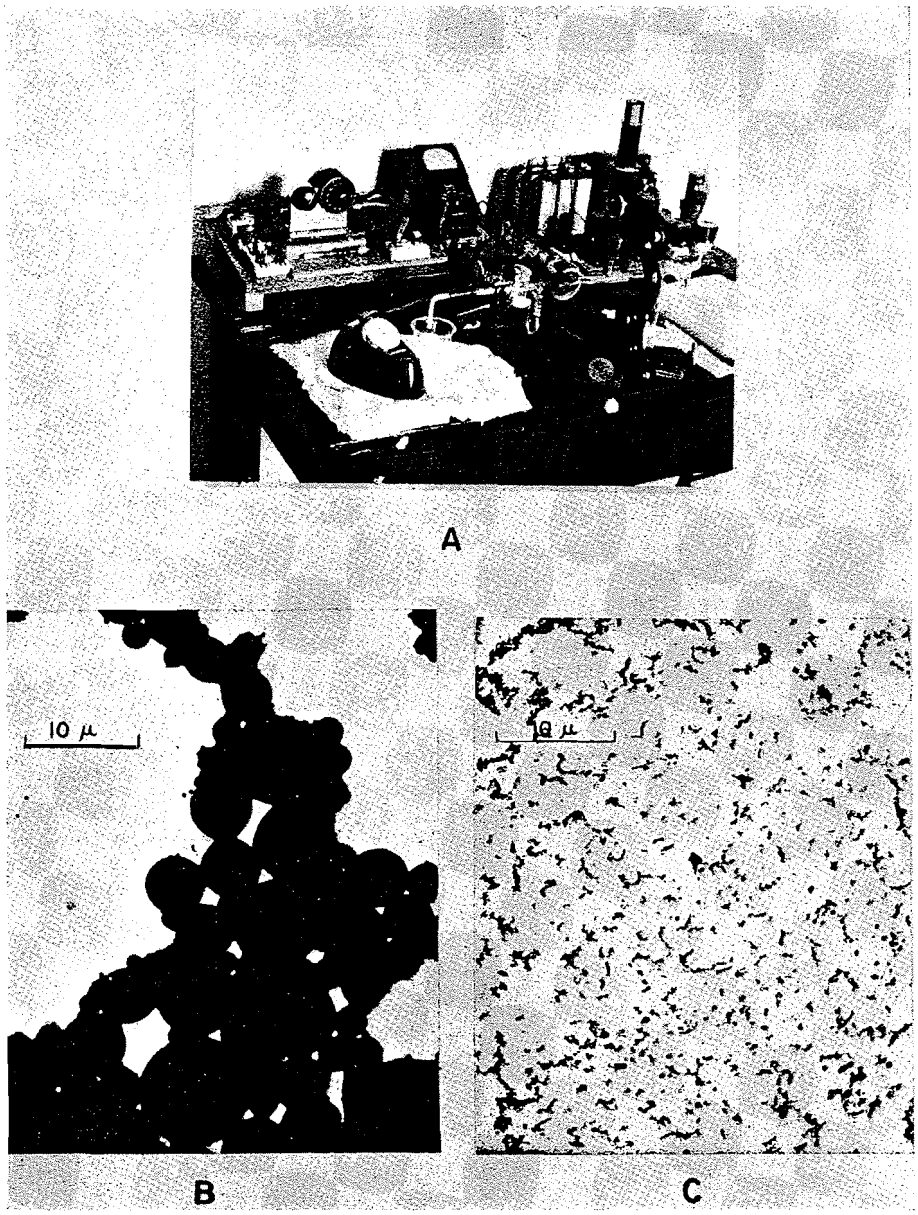



FIG. 4. *A*. General view of the apparatus.
*B*. Electron micrograph of latex (5CN) having the largest particle size of emulsions studied.
*C*. Electron micrograph of latex (17A) having the smallest particle size.

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The actual cross-sectional area of the central capillary may be used as $q$, the cell constant, provided it is very small in comparison with the cross-sectional area of the end electrode compartments. Since this proviso did not hold for the cell in Fig. 2, calibration was carried out according to the quartz powder method of Smith and Lisse (12). This gave a value of 0.058.

The accuracy of this standardization method leaves much to be desired. Any trace of electrolyte present in the quartz suspension drastically affects the apparent electrophoretic mobility. However the experimental results are strictly comparable in spite of possible error introduced by the cell constant.

In determining the electrophoretic mobility of any sample, all measurements may be taken and averaged at the level $r_0/\sqrt{2}$ from the axis, or a plot of $r^2/r_0^2$ against velocity may be made, and the observed velocity where $r^2/r_0^2 = 0.50$ noted. (In the quartz standardization both methods were used.)

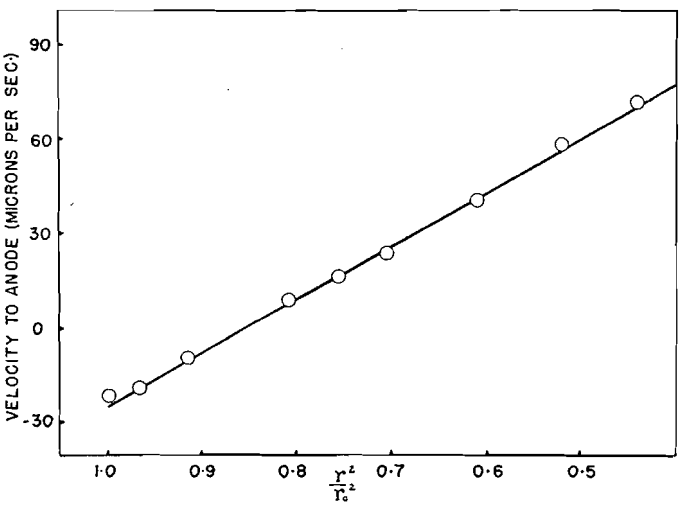



FIG. 5. Electrophoretic velocities of standard latex for different values of $r^2/r_0^2$.

Fig. 5 shows the straight line resulting when $r^2/r_0^2$ was plotted against velocity for a typical polyvinyl acetate emulsion. The depth of zero electrosmosis for single level measurements $r = 0.707\ r_0$ and $r = r_0 - n_w d$, where $r$ = radius of capillary = 1.087 mm. The velocities of electrophoresis of a typical run when $r^2/r_0^2 = 0.50$ and from a determination at constant depth on the same resin dispersion give mobilities which agreed to 2%. The respective values are 3.40 and 3.33 microns per sec. per volt per cm. It was found most practical to conduct all routine measurements at the fixed level of focus only.

All samples for electrophoresis were brought to 20 ± 0.3° C. The cell was rinsed with the diluted latex sample several times before electrophoresis, and periodically between readings to maintain constant temperature and electrolyte concentration in the cell.

Less significance may be attached to temperature control than to other variables. It has been shown that the mobility of a colloidal granule increases with the temperature of the suspension at about the same rate as the conductance of

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the aqueous electrolyte increases or the viscosity of water decreases—about two per cent per degree centigrade near room temperature (13). The errors are mutually compensating.

Heating inside the cell due to electrode processes was nonexistent owing to the extremely low amperage used. However, it was found that noticeable convection currents were brought about by the heat of the light source. These were minimized by shutting off the lamp except when actual timed observations were being made. By reversing the double pole throw switch (Fig. 3) on alternate readings any convection error still present was completely eliminated. In practice it was found that the average of 20 readings, 10 in each direction of current flow, was sufficient to give reproducible results for different samples of the same emulsion. Powney and Wood (9) used a similar technique with a microscope cell for determining the mobility of oil drops in detergents and soap solutions. The necessity of taking as many as 20 readings is not due to intrinsic inefficiency of the apparatus, but rather to slight variation in charge from one droplet to another in the same sample.

Figs. 4*B* and 4*C* show the range of particle sizes for latices which were subsequently studied. As well as being illustrative of the diameter extremities which were encountered, they also exemplify different particle size distributions.

## EFFECT OF DILUTION

Dilution of the samples to 0.01–0.25% total solids was made using double distilled water. For emulsions with large particle size the higher concentration was used whereas for fine emulsions concentrations were kept at less than 0.10% to avoid opacity in the central observation chamber.

In order to investigate the resultant effect on mobility, one anionic and one cationic emulsion were measured electrophoretically at varying percentage of solids. Each determination was carried out at constant specific conductance. That the differences in concentrations used have no effect on the mobility is shown in Figs. 6 and 7.

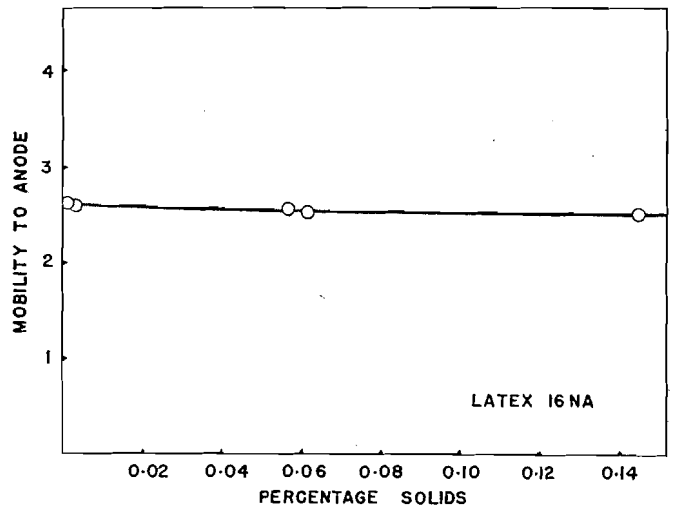



FIG. 6. The effect of dilution on mobility of a typical negative latex.

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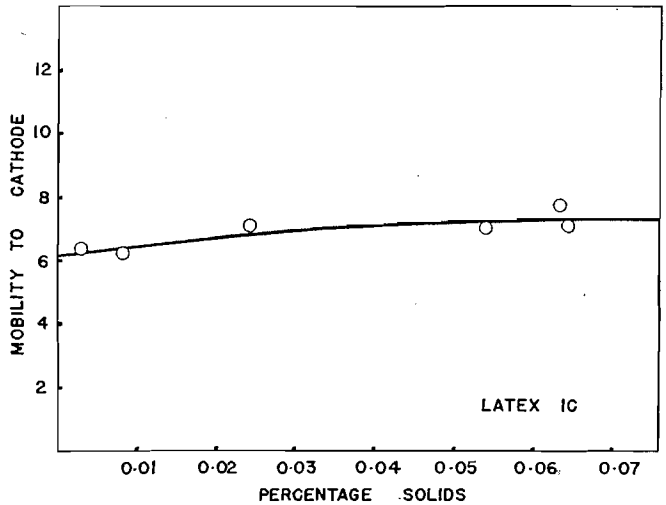



FIG. 7. The effect of dilution on mobility of a typical positive latex.

## HYDROGEN ION CONCENTRATION

The pH of the diluted latices varied from 4–6. In order to evaluate this effect samples of representative diluted emulsions of the same percentage solids were adjusted with hydrochloric acid, sodium chloride, or sodium hydroxide to different pH values, the specific conductance being made equal to that of $2.57 \times 10^{-4} M$

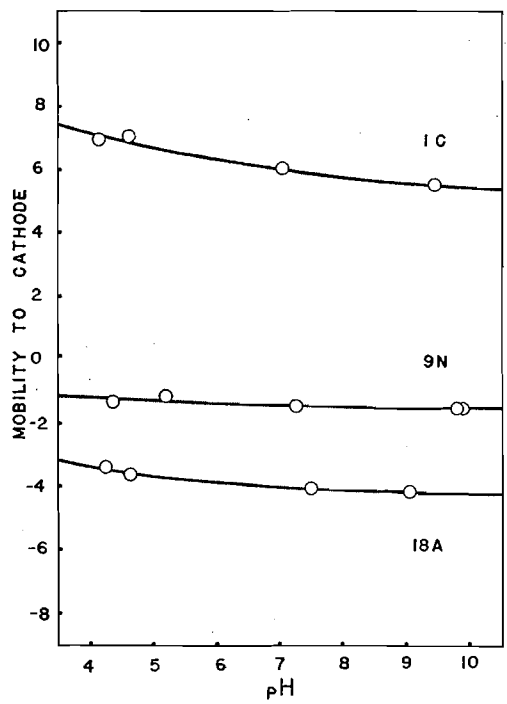



FIG. 8. The effect of pH on the mobility of latex particles.

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sodium chloride in each case. The results indicate that the change in mobility over the pH range studied is very slight (Fig. 8).

## STANDARD MOBILITIES

Table I lists the standard mobilities of a series of emulsions. The standard values are for latices containing 0.01–0.10% solids, electrolyte concentration $= 5.00 \times 10^{-5}M$ sodium chloride, and pH as obtained on dilution with addition of dilute sodium chloride to reach standard conductance. The designation (A) indicates an emulsifier of the anionic type, (C) a cationic type, (N) a nonionic agent.

TABLE I

| Latex | Emulsifying agents or protective colloids | Absolute mobility, $\mu$/sec./v./cm. | pH | Average particle diameter, microns | Particle size variation* | Particle charge variation |
|---|---|---|---|---|---|---|
| 1C | Octadecyl-, hexadecyl-, dodecyldimethyl ammonium chloride and $C_{18}H_{37}NH-P(=O)(OR)(ONH_3C_{18}H_{37})$ | 5.28 | 4.4 | 1–5 | 3 | 2 |
| 2C | Cetyldimethylbenzyl ammonium chloride | 4.29 | 5 | 1–5 | 3 | 1 |
| 3C | Paradiisobutylphenoxyethoxyethyl-dimethylbenzyl ammonium chloride | 3.83 | 5 | 1–5 | 3 | 1 |
| 4CN | Cetyldimethylbenzyl ammonium chloride and polyvinyl alcohol | 2.38 | 5 | 1–5 | 2 | 1 |
| 5CN | Cationic and nonionic | 1.54 | 5.5 | 5–10 | 3 | 2 |
| 6CN | Hydroxyethyl cellulose and paradiisobutylphenoxyethoxyethyldimethylbenzyl ammonium chloride | 0.49 | 5 | 0–2 | 3 | 1 |
| 7N | Nonionic | − 0.49 | 6.3 | 1–5 | 2 | 3 |
| 8N | Polyvinyl alcohol | − 1.27 | 5.5 | 1–5 | 1 | 2 |
| 9N | Polyvinyl alcohol | − 1.35 | 5.5 | 1–5 | 3 | 2 |
| 10NA | Anionic and nonionic | − 1.52 | 6.1 | 0–2 | 1 | 1 |
| 11N | Gelatin | − 1.58 | 4.8 | 0–2 | 1 | 2 |
| 12N | Nonionic | − 1.89 | 5.7 | 5–10 | 1 | 1 |
| 13N | Hydroxyethyl cellulose | − 2.30 | 5.3 | 0–1 | 0 | 1 |
| 14NA | Polyvinyl alcohol and gum tragacanth | − 2.80 | 5.2 | 5–10 | 2 | 1 |
| 15NA | Polyvinyl alcohol and gum tragacanth | − 2.90 | 4.9 | 1–5 | 2 | 1 |
| 16NA | Polyvinyl alcohol and gum tragacanth | − 2.96 | 5.2 | 1–5 | 3 | 1 |
| 17A | Anionic | − 3.10 | 5–6.5 | 0–2 | 1 | 1 |
| 18A | Gum arabic | − 3.30 | 5.3 | 0–2 | 1 | 1 |
| 19A | Gum arabic | − 3.32 | 6.0 | 0–2 | 1 | 1 |
| 20NA | Gum tragacanth and polyvinyl alcohol | − 3.32 | 5.4 | 5–10 | 2 | 1 |

* *0—Uniform. 1—Slight variation. 2—Moderate. 3—Considerable variation (ratio 1-10).*

## DISCUSSION

The results indicate the effect of chemical structure of the emulsifying agent on resin particle charges. At the high latex dilution and low fixed electrolyte

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concentration (or more exactly low fixed conductance), the recorded mobilities are considered to be comparable. Although the particles in each latex varied in size the mobility was relatively uniform for all sizes. This was true for each latex whatever the size distribution.

Furthermore as has been shown the variations in percentage solids and pH from sample to sample have little effect. The adsorbed layer of wetting agent or protective colloid would probably be minimal at this dilution. The ionic strength of the solubilized wetting agents or ionizing hydrophilics would resemble that of the uni-univalent electrolyte.

The anionic or cationic nature of the emulsifying agents found in the various dispersions studied governs their electrophoretic mobility. Positive mobilities are of greater magnitude than negative absolute mobilities. This is largely due to quaternary ammonium halides being strongly ionizing whereas long chain organic acids dissociate weakly. This difference in ionic character for soaps and invert soaps is exhibited in media of low pH such as were encountered with all the polyvinyl acetate emulsions included in the studies. Latex 1C exhibits a steeper curve in Fig. 8 than the anionic and nonionic-stabilized emulsions.

Nonionic agents confer low negative mobility. Where mixtures of wetting agents or protective colloids are used in latex formulation, the mobility may be predicted approximately, provided there is no preferential adsorption of one agent to the exclusion of others from the particle interface. If the latter occurs it is probable that the mobility should approach that of an emulsion made using the single, preferentially adsorbed agent.

The existence of any stable polyvinyl acetate latex possessing a particle charge of zero is most doubtful. Commercial emulsions reported as such have been found to be definitely negative. The so-called nonionic materials with anionic character which were studied are assumed to have become negatively charged by hydrogen-bonding or polarization processes or by actual chemical change.

It will be noted that such agents contain, besides the paraffinic chain, a number of hydrophilic points such as ether or hydroxyl groups. Solution in water takes place through the formation of hydrogen bonds or dipole forces between the oxygen atoms and water. Any ions existing in the aqueous media may attach themselves to the polar groups. Those ions which are generally adsorbed are, according to Abramson (3), not too highly hydrated. With sodium chloride, the chloride ion is adsorbed in preference to the sodium ion. This accounts possibly for the occurrence of negative particles when nonionic emulsifiers are used. The most important nonionic protective colloids studied were hydroxyethyl cellulose and polyvinyl alcohol. The latter was polyvinyl acetate hydrolyzed to an extent of about 80%.

Similar explanations for the predominance of negative charge have been postulated by Price and Lewis (10). They concluded that the charge on the particle was composed of two independent parts, both of which were of comparable magnitude. The total charge was assumed due to:

(*a*) adsorption of hydroxyl ions on the surface of the fatty portions of the particle, and

(*b*) ionization of the amphoteric groups.

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It is of considerable significance that most emulsion polymerizations of vinyl acetate are promoted by peroxide type catalysts. It is possible that rupture of hydrocarbon chains or oxidation of alcohol and other groups by the strongly oxidizing catalysts is responsible in part for observed negative mobilities. Any carboxyl groups thus interjected into emulsifying agent structure would be capable of ionizing as true anionic components.

The absolute mobility of emulsion 11N (gelatin stabilized) was negative at pH of 4.8. Reference to Abramson's data on the isoelectric point of gelatin (3) indicated that the protective colloid probably used in this latex was deaminized grade. Ordinary gelatin would result in positively charged particles if the emulsion was made at pH less than 4.5, and deaminized gelatin confers positive mobility at pH values not exceeding 4.0.

The only strongly positive emulsions are those based on formulations with quaternary ammonium halides or other nitrogenous surfactants such as amines and amides. All of these materials are synthetic.

Gum arabic and gum tragacanth, examples of naturally occurring emulsifiers, are anionic. Tragacanth is a mixture of several gum acids. The chief constituent of gum arabic is arabic acid to which is attached a member of residues of various hexoses, pentoses, and bioses by means of ethereal oxygen linkages. All such acids occur chiefly as calcium, magnesium, and potassium salts.

Natural materials finding predominant use as stabilizing agents but which were not investigated include alginates, caseinates, pectinates, and lecithin. With little reservation it can be said that these are all either anionic or nonionic with anionic character, and will confer corresponding negative mobility.

Although this investigation has been restricted to polyvinyl acetate latices, it is reasonable to believe that the general picture as set forth should apply to any synthetic resin dispersion. Particle sizes and methods of formulation for all such latices are quite comparable.

ACKNOWLEDGMENT

The authors are indebted to the research divisions of Shawinigan Chemicals Ltd. and The American Polymer Corporation for provision of emulsion samples and for permission to use electron micrographs, and to Prof. H. S. Pollock of the Electrical Engineering Department, Queen's University, for the use of electrical apparatus.

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## LIQUID PHASE DEHYDROGENATION OF LAURYL ALCOHOL

By Alexandre Halasz

It is well known that lauryl and other paraffinic alcohols can be easily dehydrogenated to the corresponding aldehydes with various yields by heating them with nickel (1, 2). The yields are lowered by the decomposition of the formed aldehyde and if the reaction is not stopped in time a complete deformylation of the aldehydes to a hydrocarbon occurs.

Reewe and Adkins (4) obtained higher yields by using copper chromite with ethylene under pressure. They obtained a yield of 39% aldehyde and recovered 38% of unreacted alcohol. An inconvenience of this method is the use of ethylene under high pressure; also it does not solve the problem of aldehyde decomposition.

I have noticed that much less decomposition of the aldehyde occurs when the reaction is stopped in time.

For the experiment, pure dodecanol without aldehyde or other impurities was used with 5% copper chromite as catalyst (prepared according to Org. Synth. (3)). The reaction temperature was 250°C. The resulting aldehyde was titrated by the hydroxylamine method and the remaining alcohol determined by acetylation in pyridine. The results can be considered exact within 1% ±. A graph is given below showing the % aldehyde, alcohol, and the sum of the two in the reaction mixture as a function of time.

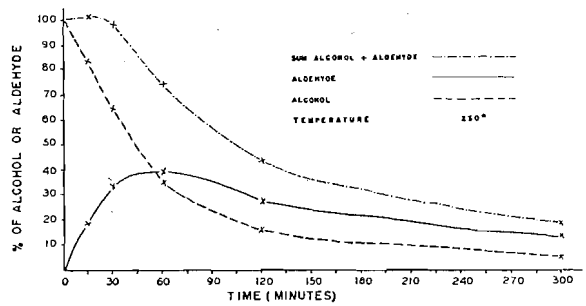



FIG. 1.

As can be seen the maximum yield is attained after 30 min. Up to this time no noticeable decomposition of the aldehyde occurs. The yield of aldehyde at this moment is 34%, but taking in account the unreacted alcohol (65%) the yield is nearly theoretical.

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University of Montreal,
Montreal, Que.

# THE REACTION OF 5-BROMOVANILLIN AND SODIUM METHOXIDE

By R. A. McIvor and J. M. Pepper

Many methods of synthesis of syringaldehyde have been described, the more important of which have been given recently by Pearl (3), while a laboratory procedure has appeared in *Organic Synthesis* (1).

This report concerns preliminary studies of its preparation from vanillin by a two-stage introduction of a methoxyl group. It has recently been reported that universally unsuccessful results were obtained in similar experiments by other workers (4), although they do record a different method for the conversion of vanillin to syringaldehyde. Such a synthesis is of interest because of the ready availability of vanillin as an oxidation product of gymnosperm lignin residues. Of even greater value would be the possibility of thereby converting a mixture of vanillin and syringaldehyde, obtainable from a similar oxidation of hardwood lignin, into the latter chemical.

The reaction studied was the bromination of vanillin to yield 5-bromovanillin which was subsequently treated with methanolic sodium methoxide in the presence of a copper catalyst in an attempt to replace the halogen by the methoxyl grouping. Initial experiments in which the 5-bromovanillin, sodium methoxide, and anhydrous methanol were refluxed, either in the presence or absence of a copper catalyst, resulted only in the recovery of unchanged starting materials. The attempted replacement of the bromine by the fusion of 5-bromovanillin or its triacetate with anhydrous sodium methylate resulted in a very rapid reaction accompanied by a flash and dense white smoke, but a considerable amount of 5-bromovanillin only was recovered from the residue. The nature of this reaction was not further investigated, although qualitative tests showed that ionic bromide and considerable free carbon were formed.

TABLE I

Reaction of 5-bromovanillin and sodium methoxide at high temperatures[a]

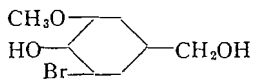
| Run number | Copper turnings, gm. | Average temp., °C. | Maximum temp., °C. | Time, hr. | Remarks |
|---|---|---|---|---|---|
| 2 | 3 | 163 | 183 | 1.8 | *b, c* |
| 5 | 7 | 179 | 205 | 2.0 | *c, d* (3.3 gm.) |
| 6 | 7 | 173 | 186 | 3.0 | *c, d* (2.9 gm.) |
| 7 | 7 | 150 | 175 | 2.0 | *c, b* (0.7 gm.) |
| 8 | 7 | 169 | 189 | 1.0 | *e* |
| 9 | 5 | 158 | 178 | 1.5 | *e* |
| 10 | 5 | 162 | 172 | 4 | *c, f* (5.0 gm.) |
| 11 | 5 | 176 | 180 | 11.5 | *f* (2.5 gm.) |
| 12 | 5 | 186 | 197 | 9.3 | *f* (1.0 gm.) |

[a] *For each run, 5-bromovanillin (15 gm.), methanol (250 ml.), and sodium methoxide (10.0 gm.) were used.*
[b] *Crude 5-bromovanillyl alcohol.*
[c] *Filtrate gave positive test for bromide ion.*
[d] *Crude 5-bromovanillyl methyl ether.*
[e] *5-Bromovanillin all recovered.*
[f] *Crude syringaldehyde.*

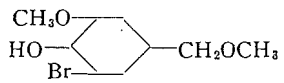
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In order to attempt the replacement at much higher temperatures, a series of runs was made in which the 5-bromovanillin, mixed with anhydrous methanol, sodium methoxide, and copper turnings, was heated in a rocking autoclave. The conditions and results of these experiments are given in Table I. It is believed that the somewhat erratic results obtained under essentially similar conditions were due to the irreproducibility of the copper catalyst. In a forthcoming publication further evidence to support this belief will be presented.

The syringaldehyde was identified by the recrystallization of the crude product from water to yield needles with a melting point of 113° C., undepressed by admixture with an authentic sample (2). The 2,4-dinitrophenylhydrazone melted at 234–235° C., reported m.p. 235.5–236.5 (5). Both the previously unreported compounds, 5-bromovanillyl alcohol (I) (m.p. 129–130° C.) and 5-bromovanillyl methyl ether (II) (m.p. 66° C.), were characterized by an examination of their infrared spectra and the comparison of their




I




II

ultraviolet absorption spectra and their carbon, hydrogen, and methoxyl analyses with those of the synthetic products. Mixed melting point determinations with these authentic samples showed no depressions. No attempt is being made at this time to explain the mechanism of the formation of these derivatives. Fig. 1 includes, for purposes of comparison, the ultraviolet

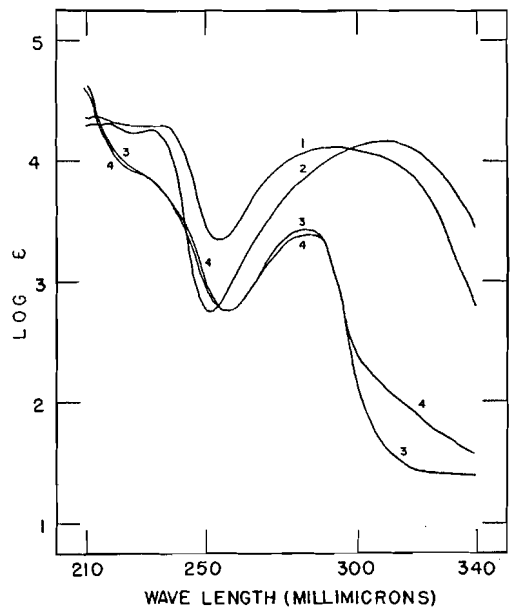



FIG. 1. Ultraviolet absorption spectra (95% ethanol).
1. 5-Bromovanillin.
2. Syringaldehyde.
3. 5-Bromovanillyl alcohol.
4. 5-Bromovanillyl methyl ether.

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absorption spectra of 5-bromovanillin, syringaldehyde, 5-bromovanillyl alcohol, and 5-bromovanillyl methyl ether.

Although the preparation of syringaldehyde from 5-bromovanillin appeared quite promising, similar experiments using 5-iodovanillin gave excellent yields. The results of this later work will be presented in a separate article.

## EXPERIMENTAL

All ultraviolet absorption spectra were observed on a Beckmann Model DU spectrophotometer in purified 95% ethanol solution. The infrared spectra were determined using a Perkin-Elmer single beam Model 12B spectrophotometer.

### *5-Bromovanillin*

Vanillin (150 gm.) and sodium acetate (50 gm.) were dissolved in glacial acetic acid (350 ml.) and a solution of bromine (180 gm.) in acetic acid (300 ml.) was added slowly with shaking. On completion of the addition, sodium hydrosulphite (15 gm.) dissolved in water (75 ml.) was added, and after most of the excess bromine was reduced the mixture was poured into water (2 liters) containing further sodium hydrosulphite (15 gm.). The 5-bromovanillin readily precipitated; yield 221.8 gm. (97.5%). After recrystallization from ethanol the product melted at 164° C., reported by several workers, 164° C.

### *5-Bromovanillin-2,4-dinitrophenylhydrazone*

The previously unreported 2,4-dinitrophenylhydrazone of 5-bromovanillin was prepared in the usual way; melting point, 295.5–296° C., with decomposition. Calc. for $C_{14}H_{11}N_4O_6Br$: C, 40.89; H, 2.70. Found: C, 40.68; H, 3.64.

### *5-Bromovanillin Triacetate*

5-Bromovanillin (25 gm.) was suspended in acetic anhydride (80 ml.) to which a few drops of concentrated sulphuric acid were added. Solution took place immediately and, on cooling, a precipitate separated. This product was recrystallized from dilute ethanol and dilute acetic acid to give white plates melting at 109° C. Calc. for $C_{14}H_{15}O_7Br$: $OCH_3$, 8.3; Ac, 34.4. Found: $OCH_3$, 8.2; Ac, 34.4.

### *Interaction of 5-Bromovanillin and Sodium Methoxide*

The experiments outlined in Table I were carried out in a stainless steel liner, capacity 1080 ml., of an Aminco high pressure hydrogenator, Model No. 406–01 DA. This rocking apparatus served as a high temperature autoclave. The reaction mixture, after cooling and separation of the copper catalyst, was diluted to twice its volume with water and acidified with sulphuric acid. Tarry products often separated at this point, but both the tar and the acidified mixture were exhaustively extracted with ether. This extract, after drying, was concentrated to give an alkali-soluble residue from which the reaction products reported in Table I were isolated. The major part of the syringaldehyde was obtained by re-extraction of the aqueous layers with ethyl acetate.

### *Identification of 5-Bromovanillyl Alcohol*

The crude reaction product was purified to one melting at 129–130° C. by

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two recrystallizations from methanol–water and finally by vacuum distillation. The infrared spectrum was determined in the carbonyl and hydroxyl regions in chloroform solution with a calcium fluoride prism. It showed two sharp bands in the OH stretching region at 3601 cm.$^{-1}$ and 3525 cm.$^{-1}$ with molar extinction coefficients of 63 and 138, respectively, the latter believed due to a phenolic hydroxyl group. The ultraviolet spectrum was identical with that of synthetic 5-bromovanillyl alcohol which is given in Fig. 1. A mixed melting point with an authentic specimen, m.p. 132° C., prepared as given below, was undepressed, m.p. 131° C. Calc. for $C_8H_9O_3Br$: mol. wt. 233.1; $OCH_3$, 13.30; C, 41.22; H, 3.89. Found: mol. wt. (Rast) 235; $OCH_3$, 12.94; C, 40.71; H, 3.70.

*Identification of 5-Bromovanillyl Methyl Ether*

The crude reaction product was purified to one melting at 66° C. by two vacuum sublimations. The infrared spectrum was determined in the 3800 cm.$^{-1}$ to 650 cm.$^{-1}$ region in carbon disulphide solution with a sodium chloride prism. It showed only one peak in the hydroxyl region at 3500 cm.$^{-1}$ with a molar extinction coefficient of 94, doubtless due to the phenolic hydroxyl group. The ultraviolet spectrum was identical with that of synthetic 5-bromovanillyl methyl ether which is given in Fig. 1. A mixed melting point with an authentic specimen, m.p. 64–67° C., prepared as given below was undepressed. Calc. for $C_9H_{11}O_3Br$: C, 43.74; H, 4.49. Found: C, 43.83; H, 4.57.

*Syntheses of Reference Compounds*

*5-Bromovanillyl Alcohol*

5-Bromovanillin (1.884 gm.) was added to an excess of alkali in water (40 ml.). The sodium salt, which formed immediately, did not dissolve. A solution of sodium borohydride (170 mgm.) in water was added. The faint yellow color of the solution gradually disappeared and the precipitated salt dissolved in 10 min. The solution, after standing at room temperature over night, was acidified with concentrated hydrochloric acid. 5-Bromovanillyl alcohol separated as micro needles. Yield, 1.67 gm. (88%), m.p. 132° C. More of the product could be obtained by extraction of the mother liquors.

*5-Bromovanillyl Methyl Ether*

5-Bromovanillyl alcohol (133 mgm.) was dissolved in methanol (5 ml.) and concentrated sulphuric acid (1 ml.) added. After the solution had been allowed to stand at room temperature for 36 hr. it was refluxed for five minutes, made alkaline with sodium hydroxide, and extracted with chloroform. The residual aqueous solution was acidified with hydrochloric acid and again extracted with chloroform. This extract was dried and the excess solvent removed to yield a gum (203 mgm.) which readily crystallized in long needles. Vacuum sublimation gave white crystals (110 mgm., 88%), m.p. 64–67° C. Calc. for $C_9H_{11}O_3Br$: $OCH_3$, 25.12. Found: $OCH_3$, 24.7.

*Absorption Spectra Data*

The following ultraviolet and infrared absorption data were recorded.

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TABLE II

ULTRAVIOLET ABSORPTION DATA FOR 5-BROMOVANILLIN AND DERIVED COMPOUNDS

| Compound | Absorption maxima[a], mμ | Absorption minima[a], mμ |
|---|---|---|
| 5-Bromovanillin | 213.5 (4.36)<br>234 (4.29)<br>291 (4.10) | 226 (4.28)<br>255 (3.34) |
| Syringaldehyde | 215 (4.31)<br>231 (4.25)<br>308.5 (4.16) | 225 (4.23)<br>251 (2.75) |
| 5-Bromovanillyl alcohol | 221 (3.95)<br>286 (3.42) | 257 (2.76) |
| 5-Bromovanillyl methyl ether | 221 (3.93)<br>286 (3.39) | 257 (2.75) |

[a]*Log molar extinction coefficients given in brackets.*

TABLE III

INFRARED ABSORPTION DATA FOR 5-BROMOVANILLYL METHYL ETHER[a]

ABSORPTION BANDS[b], CM.$^{-1}$

| | | |
|---|---|---|
| 3500 (94) | 1237 (139) | 914 (34) |
| 2911 (81) | 1186 (248) | 838 (105) |
| 2824 (70) | 1140 (161) | 827 (158) |
| 1345 (115) | 1100 (185) | 788 (41) |
| 1275 (378) | 1052 (360) | 726 (30) |
| 1250 (112) | 961 (39) | |

[a]*Determination in carbon disulphide with a sodium chloride prism.*
[b]*Molar extinction coefficients given in brackets.*

ACKNOWLEDGMENT

The authors wish to thank The Howard Smith Chemicals Limited for their kind donation of the vanillin used in this investigation. Grateful acknowledgment is given to Dr. R. Norman Jones and Mr. R. Lauzon of the National Research Council Laboratories in Ottawa for their determination of the infrared spectra, to Mr. H. Seguin, also of the National Research Council, for the carbon and hydrogen microanalyses, and to Mr. A. Chisholm and Mr. D. C. Hagerman for methoxyl analyses.

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VOLUME 31 APRIL, 1953 NUMBER 4

# THE CONDUCTANCES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID AT 50° AND 75°[1]

BY A. N. CAMPBELL, E. M. KARTZMARK, D. BISSET, AND M. E. BEDNAS[2]

ABSTRACT

The specific and equivalent conductances of aqueous solutions of sulphuric acid, ranging in concentration from 5 to 95% by weight, have been determined, as well as the densities and viscosities.

The data on the conductance of sulphuric acid available in the literature refer to temperatures of 18° (4) and 25°, 60°, and 95° C. (5). With the exception of 18° these data have only recently appeared and for them an accuracy not greater than 1% is claimed. The author of the work, Roughton, did not determine densities, so that it is impossible to calculate equivalent conductances from his work.

The present work had no theoretical aim and has no connection with our work on strong salt solutions (3). Sulphuric acid has almost zero conductance in the anhydrous state, a behavior characteristic of acids. This means that the mechanism of ionization is fundamentally different from that of salts and therefore cannot be given the same theoretical treatment.

## EXPERIMENTAL

Our technique has already been described (3); it yields an accuracy of 0.1% in the conductance measurements; densities are good to five significant figures; viscosities and fluidities are good to four. Viscosities were determined in Ostwald-Fenske viscometers; they were calibrated with water for solutions of lower viscosity and with sucrose solutions for higher viscosities, as described by Bingham and Jackson (1). The temperature variations of the thermostats were: at 50°, ± 0.01°, at 75° ± 0.02°. The concentrations were determined both volumetrically and gravimetrically as barium sulphate, with an accuracy of 0.1%.

## RESULTS

The results of the measurements are contained in Table I.

[1] *Manuscript received October 23, 1952.*
*Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Man.*

[2] *Holder of National Research Council Bursary.*



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TABLE I

THE SPECIFIC AND EQUIVALENT CONDUCTANCES, DENSITIES, VISCOSITIES, AND FLUIDITIES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID AT 50° AND 75° C.

| Wt. % | Normality | Density, gm./ml. | Specific conductance, mhos | Equivalent conductance, mhos | Viscosity, centipoises | Fluidity, rhes |
|---|---|---|---|---|---|---|
| *A. 50° C.* | | | | | | |
| 5.66 | — | — | 0.3058 | — | — | — |
| 8.95 | 1.870 | 1.0449 | 0.4901 | 262.1 | 0.5802 | 172.4 |
| 10.53 | — | — | 0.5714 | — | — | — |
| 17.11 | 3.76 | 1.1002 | 0.8377 | 222.8 | 0.7828 | 127.7 |
| 21.38 | — | — | 0.9767 | — | — | — |
| 24.15 | 5.56 | 1.1519 | 1.0338 | 185.9 | 0.9355 | 106.9 |
| 30.85 | 7.44 | 1.2049 | 1.1117 | 149.4 | 1.1230 | 89.05 |
| 31.76 | — | — | 1.1234 | — | — | — |
| 36.30 | — | — | 1.1133 | — | — | — |
| 41.12 | — | — | 1.0725 | — | — | — |
| 43.45 | 11.40 | 1.3111 | 1.0258 | 90.0 | 1.6712 | 59.88 |
| 52.15 | — | — | 0.8532 | — | — | — |
| 53.12 | 14.90 | 1.4021 | 0.8169 | 54.82 | 2.3498 | 42.56 |
| 55.74 | 15.92 | 1.4295 | 0.7541 | 47.42 | 2.642 | 37.85 |
| 60.45 | 17.76 | 1.4686 | 0.6616 | 37.25 | 3.076 | 32.51 |
| 61.04 | — | — | 0.6364 | — | — | — |
| 67.65 | 21.86 | 1.5566 | 0.4642 | 22.04 | 4.467 | 28.57 |
| 72.62 | 23.44 | 1.6138 | 0.3620 | 15.44 | 5.891 | 16.98 |
| 75.41 | 24.82 | 1.6461 | 0.3125 | 12.59 | 6.868 | 14.56 |
| 78.70 | — | — | 0.2729 | — | — | — |
| 82.95 | 28.66 | 1.7273 | 0.2403 | 8.385 | 9.543 | 10.48 |
| 87.13 | — | — | 0.2347 | — | — | — |
| 89.99 | — | — | 0.2330 | — | — | — |
| 92.8 | 33.36 | 1.7973 | 0.2285 | 6.850 | 9.696 | 10.31 |
| 96.2 | 34.76 | 1.8065 | 0.1782 | 5.127 | 9.952 | 10.05 |
| *B. 75° C.* | | | | | | |
| 5.66 | — | — | 0.3442 | — | — | — |
| 8.95 | 1.848 | 1.0328 | 0.5608 | 303.5 | 0.3893 | 2.186 |
| 10.53 | — | — | 0.6345 | — | — | — |
| 17.11 | 3.74 | 1.0963 | 0.9791 | 261.8 | 0.4575 | 1.809 |
| 21.38 | — | — | 1.1449 | — | — | — |
| 24.15 | 5.50 | 1.1378 | 1.2351 | 224.6 | 0.5527 | 1.545 |
| 30.85 | 7.34 | 1.1903 | 1.3647 | 185.9 | 0.5529 | 1.282 |
| 31.76 | — | — | 1.3747 | — | — | — |
| 36.30 | — | — | 1.3869 | — | — | — |
| 37.53 | 9.34 | 1.2435 | 1.3827 | 148.0 | 0.7799 | 1.051 |
| 41.12 | — | — | 1.3566 | — | — | — |
| 43.45 | 11.24 | 1.2940 | 1.3127 | 116.8 | 0.9515 | 0.8717 |
| 52.15 | — | — | 1.1349 | — | — | — |
| 53.12 | 14.72 | 1.3859 | 1.1143 | 75.70 | 1.1471 | 0.6190 |
| 55.74 | 15.74 | 1.4126 | 1.0035 | 63.75 | 1.794 | 0.5583 |
| 60.45 | 17.52 | 1.4492 | 0.8915 | 50.88 | 1.791 | 0.4821 |
| 61.04 | — | — | 0.8670 | — | — | — |
| 67.65 | 20.82 | 1.5384 | 0.6594 | 31.67 | 2.074 | 0.4599 |
| 72.62 | 23.14 | 1.5926 | 0.5337 | 23.06 | 2.975 | 0.2693 |
| 75.41 | 24.54 | 1.6266 | 0.4764 | 19.34 | 3.713 | 0.2411 |
| 78.70 | — | — | 0.4290 | — | — | — |
| 82.95 | 28.30 | 1.7061 | 0.3877 | 13.70 | 4.148 | 0.1872 |
| 87.13 | — | — | 0.3699 | — | — | — |
| 89.99 | — | — | 0.3558 | — | — | — |
| 92.80 | 32.98 | 1.7767 | 0.3456 | 10.48 | 5.341 | 0.1765 |
| 96.20 | 34.38 | 1.7872 | 0.2641 | 7.68 | 5.666<br>5.849 | 0.1710 |

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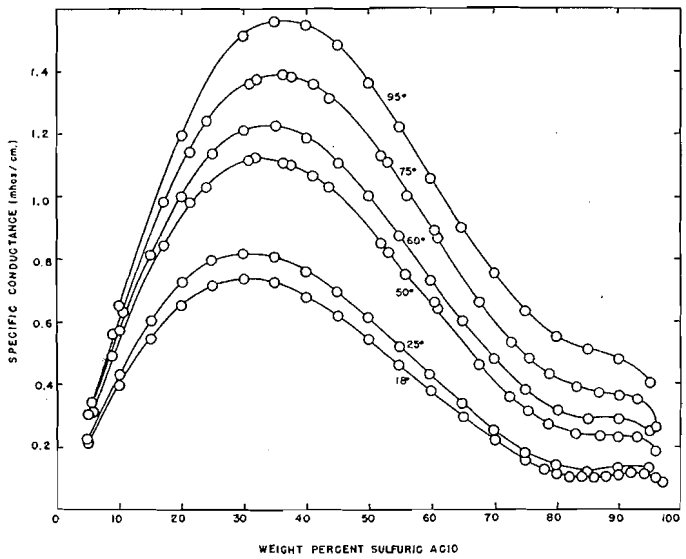



FIG 1. Specific conductance of aqueous sulphuric acid solutions as a function of concentration and temperature.

## DISCUSSION

In the graph (Fig. 1) specific conductance is plotted against weight per cent sulphuric acid, not only for the temperatures of this paper but for 18°, 25°, 60°, and 95°, the latter figures being taken from the literature previously given. All the curves are similar in character in so far as they exhibit a pronounced maximum between 30 and 35% sulphuric acid. A second maximum, much less pronounced, is observed in the lower temperature curves. The graphs show that the first maximum becomes sharper with rising temperature and its composition shifts a little in the direction of higher sulphuric acid content, while the second maximum gets flatter and has disappeared entirely at 75°.

In our work on silver nitrate and ammonium nitrate (2) we have noticed a remarkable degree of constancy in the ratio of the mean temperature coefficient of fluidity to that of conductance, but no such constancy is found here.

## ACKNOWLEDGMENT

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# THE ELECTRODE BEHAVIOR OF MERCURY[1]

By A. K. Wiebe and C. A. Winkler

ABSTRACT

Mercury electrode potentials in *N*/5 sulphuric acid were unaffected when the electrolyte was saturated with hydrogen, nitrogen, or helium but were markedly affected by trace amounts of oxygen or mercury ions. In the absence of oxygen and mercury ions, a constant potential of −0.61 volt (relative to a saturated calomel electrode) was observed. When current was passed for the first time across a fresh electrode face immersed in oxygen-free electrolyte (i.e. from initial potentials of about −0.61 volt), the potential build-up was nonlinear, but subsequent passage of current gave a linear build-up of potential. With traces of oxygen present, differences in the two types of curves were masked by reactions that appeared to involve oxygen or oxide on the electrode surface. The initial build-up curve was ascribed to the deposition of a monatomic hydrogen film (one atom per metal atom in the surface). The potential build-up curves probably result from a number of simultaneous reactions at the electrode.

From recent studies in this laboratory (15) with copper and silver cathodes immersed in sulphuric acid, it was tentatively concluded that measurement of surface areas by the Bowden–Rideal method (8) depends on the rate of charging a condenser at the surface, as distinct from the rate of increase of hydrogen overvoltage, which appeared to be associated with the deposition of a layer of hydrogen on the cathode.

Similar experiments with mercury cathodes have yielded the results recorded in the present paper.

## EXPERIMENTAL AND RESULTS

The cathode ray oscillograph unit and Leeds and Northrup type K potentiometer arrangement were identical with those described in earlier papers (12, 13).

The electrolytic cell, shown in Fig. 1, was provided with a glass cup of 2.20 cm. internal diameter to contain the mercury cathode. The height of the meniscus, measured under experimental conditions with a cathetometer, was 2.23 ± 0.05 mm. Assuming the meniscus to be spherical, and the contact angle of mercury on wet glass to be 140° (1), the area of the mercury surface was estimated to be 4.3 cm.$^2$ Since the cross-sectional area of the cup was 3.8 cm.$^2$, the correction applied for the meniscus was about 12% of the total area. Hence, even assuming a liberal error of 10–20% in the correction, the corrected area should not be in error by more than 1–2%.

All glassware, including the cell, was washed once with chromic acid, three times with alcoholic potassium hydroxide, several times with twice distilled water, and finally steamed out for several hours using twice distilled water in the steam generator.

Hydrogen was purified by the method described in a previous paper (12). Nitrogen and helium were freed from oxygen by passing them through a Pyrex glass tube packed with elemental copper and maintained at a tempera-

[1] *Manuscript received August 15, 1952.*
*Contribution from the physical chemistry laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council.*



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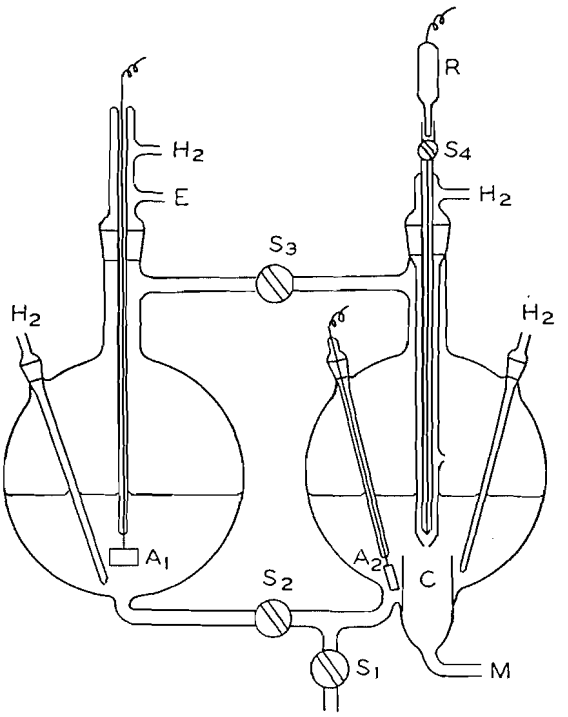



FIG. 1. Diagram of cell.

ture of 400°–450° C. The copper was a porous form obtained by reducing copper oxide wire with electrolytic tank hydrogen. All gases were passed through a potassium hydroxide bubbler before they reached the cell.

The $N/5$ sulphuric acid was made with twice distilled water and distilled reagent grade sulphuric acid. The solution was outgassed under reduced pressure for 24–48 hr., and stored under hydrogen, nitrogen, or helium. It was introduced into the electrolytic cell through "Tygon" (plastic) tubing.

Mercury was purified by first drawing air through the hot (300° C.) liquid for 12 hr., after which it was dropped from a capillary tip three times through each of the following solutions: alcoholic potassium hydroxide (10%), aqueous potassium hydroxide (10%), aqueous nitric acid (10%), and twice distilled water. The mercury was then dried at 110° C., distilled under vacuum, and the distillate subjected to the complete purification treatment a second time. The dry mercury from the second treatment was stored under hydrogen or nitrogen and distilled in batches as required. The second purification produced no observable changes in electrode behavior.

The surface of the mercury cathode was renewed when desired by alternately overflowing mercury from the cup and dropping the level into the narrow tube leading from the cup to the outside of the cell.

All potential measurements were made in reference to a saturated calomel electrode.

The main object of this investigation was to study the potential changes

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observed during the first few minutes of current flow (i.e. potential build-up curves). Some observations of potentials and potential changes on open circuit were also made, since it seemed possible that such information might aid in the interpretation of the potential build-up curves.

The initial potential on a fresh mercury surface became increasingly negative as oxygen was removed from the electrolyte ($N/5$ sulphuric acid) by electrolytic reduction at the mercury cathode (2, 8). Such potentials were not stable, however, and changed rapidly to more positive values unless the initial potential was of the order of $-0.60$ volt. As the initial potential approached this value, the rate of change of potential decreased until a nonvarying and reproducible potential of $-0.617 \pm 0.002$ volt was obtained. (Such a steady-state potential may, for convenience, be termed a zero potential.) The zero potential was now unaffected when nitrogen was used in place of hydrogen to saturate the electrolyte or when the electrolyte was stirred by bubbling hydrogen or nitrogen. In future reference to oxygen-free electrolyte it should be understood that the electrolyte was treated as above until a steady potential of about $-0.61$ volt was obtained.

A reasonably constant potential of $-0.605 \pm 0.008$ volt was generally obtainable after 15 to 20 hr. of pre-electrolysis but much longer periods were required when the system had become thoroughly contaminated with oxygen during a previous experiment. Since hydrogen overvoltage is quite strongly affected by trace quantities of many impurities (cf. 2, 5, 11), it seemed possible that the zero potential might similarly be due, not to the removal of oxygen from the electrolyte, but to some impurity such as sulphide ion, either present in trace amounts under all experimental conditions, or introduced by the prolonged periods of electrolysis.

To examine the possibility that the potential of $-0.61$ volt resulted from introduction of a trace impurity by the prolonged electrolysis, the anode compartment of the cell (Fig. 1) was rinsed and filled with $N/5$ sulphuric acid which had been previously outgassed under reduced pressure. A piece of platinum foil was rendered catalytically active for the hydrogen and oxygen reaction by alternately making it anodic and cathodic in sulphuric acid (6). It was then made anodic in the electrolyte and a small current ($6 \times 10^{-7}$ amp.) was passed for three hours while purified hydrogen was bubbled through the solution and around the activated anode. A renewed mercury surface had a steady zero potential of $-0.599$ volt after the cathode compartment had been rinsed and charged with the anodically treated electrolyte. This value may be compared with the potentials obtained after pre-electrolysis at a mercury cathode (i.e. $-0.61$ volt).

Since a substance (e.g. sulphide ion) cannot be introduced into a system by both cathodic reduction and anodic oxidation, it would seem reasonable to conclude that some potential-determining material, present in the original electrolyte, was capable of being removed either by electrolysis at a mercury cathode or by electrolysis at an activated platinum anode bathed in hydrogen. It is difficult to conceive of any substance other than oxygen that would behave in this manner.

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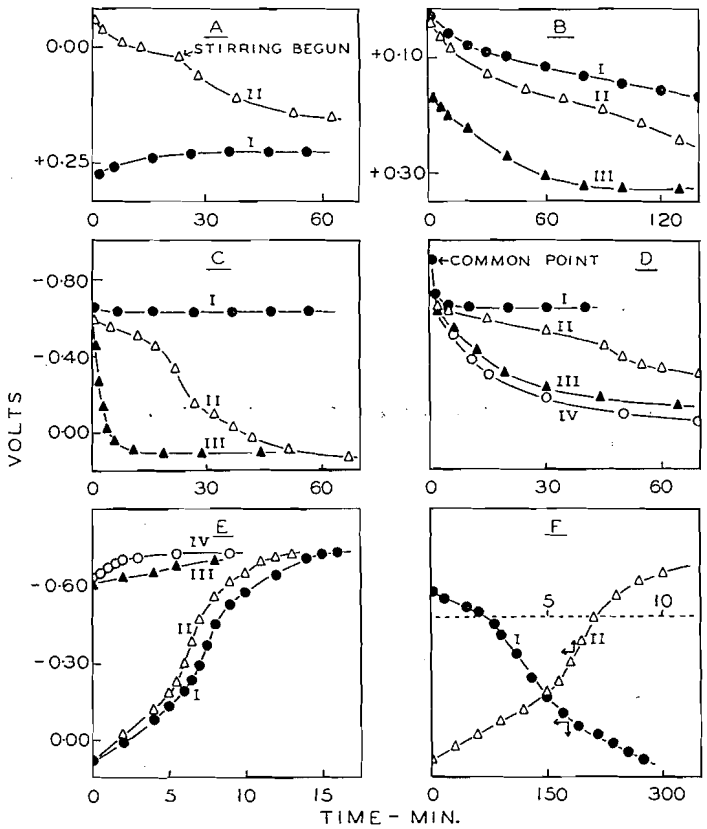



FIG. 2.

| Curve | Number faradays passed | Substance introduced | Condition in electrolyte |
|---|---|---|---|
| *A* I | $2.8 \times 10^{-7}$ | Mercury ion | Oxygen free |
| II | $2.8 \times 10^{-7}$ | " | " |
| | | | (Mercury surface renewed) |
| *B* I | $2.0 \times 10^{-7}$ | Oxygen | $N_2$ saturated—stirred |
| II | $3.0 \times 10^{-6}$ | " | " " |
| III | $1.0 \times 10^{-5}$ | " | " " |
| *C* I | Nil | ..... | $N_2$ saturated—stirred |
| II | $2 \times 10^{-9}$ | Oxygen | " " |
| III | $2 \times 10^{-9}$ | " | Helium " " |
| *D* I | Nil | ..... | $N_2$ saturated—stirred |
| II | $8.0 \times 10^{-9}$ | Oxygen | " " |
| III | $1.9 \times 10^{-8}$ | " | " " |
| IV | $5.6 \times 10^{-8}$ | " | " " |
| *E* I | $10^{-10}$ | Oxygen | (Fresh mercury surface) |
| II | $10^{-10}$ | " | |
| III | Nil | | (Fresh mercury surface) |
| IV | Nil | | |
| *F* I | $10^{-10}$ | Oxygen | Unstirred |
| II | $10^{-10}$ | " | |

The possibility that the potential value of $-0.61$ volt was due to traces of an impurity present in the electrolyte at all times would seem to be ruled out

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by the fact that this potential value was attained almost immediately after the mercury surface was renewed in the deoxygenated electrolyte. With trace amounts of oxygen or mercury ions, potentials changed slowly over periods of one to five hours (Fig. 2, *A* and *B*).

The zero potential was found to be markedly affected by low concentrations of either oxygen or mercury ions. After these substances had been removed by pre-electrolysis until a reasonably constant potential of about −0.61 volt was obtained, small quantities of oxygen were evolved in nitrogen saturated electrolyte at a small auxiliary platinum anode ($A_2$ of Fig. 1), by passing a known small current for definite periods of time. Known quantities of mercury ions were similarly introduced with the mercury electrode now acting as an anode.

The amounts of mercury ion estimated to be introduced into the electrolyte in this way (Table I) represent upper limits. Processes other than solution of

TABLE I

THE EFFECT OF MERCURY IONS AND OXYGEN ON THE ZERO POTENTIAL

| Number faradays passed to introduce mercury ion* | Potential, volt | Number faradays passed to introduce oxygen* | Potential, volt |
|---|---|---|---|
| $7.8 \times 10^{-8}$ | −0.558 | $2 \times 10^{-9}$ | +0.11 } |
| $2.0 \times 10^{-7}$ | +0.120 | $2 \times 10^{-8}$ | +0.16 } Approximate |
| $2.8 \times 10^{-7}$ | +0.200 | $7.6 \times 10^{-8}$ | +0.28 } |
| $4.0 \times 10^{-7}$ | +0.280 | $2.0 \times 10^{-7}$ | +0.326 |
| | | $4.0 \times 10^{-6}$ | +0.326 |
| | | $1.0 \times 10^{-4}$ | +0.334 After 20 hr. |

**Expressed in terms of 1 liter of electrolyte.*

mercury ions during passage of current, or adsorption of mercury ions at the wall, would reduce the amounts present in solution by an unknown amount. Similar considerations apply to the amounts of oxygen in solution. Also, no account is taken here of the amount of oxygen that may be lost to the atmosphere above the solution. For these reasons, the relative amounts of mercury ions or oxygen in the electrolyte are expressed in terms of the number of faradays passed, rather than as actual concentration terms.

When quantities of oxygen calculated as sufficient to react with 2–3% of the cathode surface were introduced into the catholyte, the potential of a mercury surface changed from −0.61 volt to about +0.10 volt while the introduction of corresponding amounts of mercury ions had a negligible effect (Table I). This behavior would seem to eliminate the possibility that mercuric oxide formed on the cathode surface immediately dissolves and that the resulting mercury ions are the sole potential determining factor. When the current was switched off after evolving mercury ions at the mercury electrode, the final value of the potential was approached from the positive side (curve I, Fig. 2*A*). On now renewing the surface the same ultimate potential was approached from the negative side (curve II). This behavior would seem to indicate that mercury ions affect the potential by being adsorbed directly

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onto the electrode surface and that an equilibrium exists between adsorbed ions and the concentrations of ions in solution.

The zero potential in oxygen-free electrolyte remained the same (within experimental error) in solutions saturated with hydrogen, nitrogen, or helium. Similarly, the ultimate value of the potential in the presence of small amounts of oxygen (up to the maximum amount in Table I) was the same in electrolyte saturated with either nitrogen or helium. However, the time required for the potential to reach its final value in electrolyte saturated with nitrogen, although varying with the amount of oxygen introduced (Fig. 2*B*), was always many times that required in electrolyte saturated with helium (Fig. 2*C*). The marked retarding effect of nitrogen on the rate of attainment of a stable potential in solutions containing oxygen indicates that nitrogen is strongly adsorbed on the mercury surface but that the forces of attraction between molecular nitrogen and surface mercury atoms are insufficient to affect the final value of the potential appreciably. It does not seem likely, therefore, that the large effect of trace quantities of oxygen on the mercury electrode potential can be explained on the basis of physical adsorption. The results appear to be more reasonably explained on the assumption that the potential of $+0.330 \pm 0.004$ volt, observed with larger amounts of oxygen, is to be associated with a monatomic layer of chemisorbed oxygen on the surface.

The electrode potential in $N/5$ sulphuric acid saturated with oxygen changed from an initial value of $+0.330$ volt to $+0.393$ volt in three hours. The potential then changed slowly at about 1 mv. per hr. to $+0.413$ volt when the experiment was discontinued. A value of $+0.40$ volt is generally accepted for the zero potential of a mercury cathode in oxygen saturated electrolyte (9). Potentials more positive than $+0.330$ volt may be due to the slow solution of mercuric oxide to form $Hg^{++}$ ions. Much more study is required to clarify the relation between systems containing small traces of oxygen and those saturated with oxygen. However, the fact that the potential of $+0.41$ volt observed in oxygen-saturated electrolyte is the same as that for the mercury–mercurous sulphate electrode may be significant.

The presence of oxygen influences not only the zero potential at a mercury surface, but also alters the behavior of potential decay curves (Fig. 2*D*). These were obtained by allowing the potential to decay on open circuit after current had been passed until the maximum value of the overvoltage (about $-0.90$ volt) had been reached. In oxygen-free electrolyte, the potential decayed to $-0.636$ volt (curve I) which differed by about 20 mv. from the zero potential ($-0.617 \pm 0.002$ volt) previously recorded under the same conditions. Small quantities of oxygen caused the potential to decay to more positive values and over longer periods of time (curves II, III, and IV).

Potential build-up curves, of which those in Fig. 2*E* are typical, also proved to be sensitive to the presence of oxygen. Curves I and III represented the initial potential build-up determined potentiometrically when current was made to flow for the first time across the face of a renewed mercury surface, while curves II and IV were obtained on the same surfaces as I and III and with identical current after allowing the potentials to decay, with the circuit

open, to their initial values. Curves III and IV represent the potential build-up behavior in oxygen-free electrolyte, while curves I and II show the effect of trace quantities of oxygen.

Initial potential build-up curves on a new surface could be reproduced only after the elapse of not less than 30 min. between the renewal of a mercury surface and the commencement of such a curve, since renewing the cathode surface unavoidably brought the mercury into a state of violent agitation. In all subsequent experiments, a minimum period of one hour was allowed for the mercury to come to rest after the surface was renewed before the current was switched on.

Potential build-up curves established from initial potentials in the neighborhood of +0.10 volt fell into three distinct sections (curves I and II, Fig. 2*E*). The initial build-up curve, as well as subsequent curves on the same surface, had linear sections of identical slope between −0.20 volt and −0.45 volt. This range of potential values is attained only in the presence of oxygen or mercury ions, in contrast with stable more negative values (*ca.* −0.61 volt) obtained in electrolyte free of oxygen and mercury ions. Hence, potential changes in the range −0.20 to −0.45 volt would seem to be the result of some reaction involving these substances. The rate of potential change for the linear section in this region measured over a current range ($1.18 \times 10^{-7}$ amp.–$2.45 \times 10^{-5}$ amp.) corresponded to a capacitance of 21 ± 2 microfarads per cm.$^2$ in agreement with values found by other investigators (cf. 3, 7).

Like the potential build-up curve, the zero potential curve (curve I, Fig. 2*F*) exhibited three distinct sections with the breaks between the linear sections occurring at almost identical potentials in both curves. The potential build-up curve of Fig. 2*F* is a reproduction of a portion of curve II, Fig. 2*E*. The zero potential curve was obtained by introducing about $10^{-10}$ mole ($10^{-9}$ mole per liter) of oxygen into an oxygen-free system after which the change of potential on a renewed mercury surface was observed potentiometrically. The solution was unstirred so that the process was diffusion controlled. If it may be assumed that the rate of diffusion of oxygen was approximately constant for the part of the reaction represented by the zero potential curve, then approximately equal quantities of oxygen would react with the cathode surface in equal increments of time. Hence, the fact that both curves have similar shapes would seem to indicate that, during current flow, chemisorbed oxygen is removed from the cathode surface at an approximately constant rate. The potential range −0.20 to −0.45 volt appears to correspond to some critical condition of the electrode surface when the potential is most sensitive to changes in the quantity of chemisorbed oxygen.

When initial potential build-up curves were established under oxygen-free conditions and in electrolyte containing trace amounts of oxygen, equal quantities of current were required to establish the maximum potential (Table III). However, with trace amounts of oxygen present, approximately half the total current was required to change the potential from +0.10 volt to the initial potential (−0.61 volt) of the build-up curve established in an oxygen-free system. An amount of chemisorbed oxygen involving not more

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than a few per cent of the cathode surface has been shown to result in a potential of +0.10 volt. It would appear, then, that at low current densities, this oxygen is reduced with a very low current efficiency.

Potential build-up curves established on a mercury cathode from initial potentials of about −0.61 volt were of two distinct types. The initial build-up curves were nonlinear throughout as shown in curve III of Fig. 2*E*. In contrast, the subsequent build-up curves on the same surface were always linear but the slope varied with the time allowed for the potential to decay after current had been passed. After a period of decay of one minute the rate of build-up corresponded to an apparent capacitance of about 30 microcoulombs per volt cm.$^2$ but as the time allowed for the potential to decay was increased, the subsequent rate of potential build-up on closing the circuit decreased to a limiting value corresponding to an apparent capacitance of 200 microcoulombs per volt cm.$^2$ The limiting value of the rate of potential build-up was obtained when the circuit was closed after allowing the potential decay process to reach completion (curve I, Fig. 2*D*).

Potential build-up curves also yield useful information from the time required for the potential to reach a maximum, in particular as it applies to the initial potential build-up curves. For convenience, the time required to reach the maximum potential when current is made to flow for the first time across the face of a fresh mercury surface (i.e. the initial potential build-up curve) will be designated $t_{max}$. To determine $t_{max}$, a smooth curve was drawn through an open scale plot of the points representing the final 10 to 20 mv. of the potential change. The logarithms of the times for attainment of equal increments of potential in this region were plotted against the corresponding potential and the resultant approximately linear relation was extrapolated to the ordinate corresponding to the potential maximum. Some typical potential build-up curves, and a typical linear extrapolation to $t_{max}$, are shown in Fig. 3.

Determinations of $t_{max}$ were made for a variety of experimental conditions

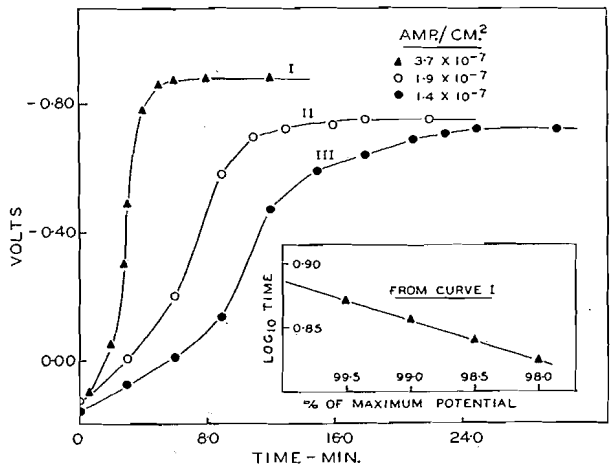



FIG. 3. Typical potential build-up curves, and typical extrapolation to obtain $t_{max}$.

such as varying the current in oxygen-free electrolyte (Table II), varying the initial potential at a given current (Table III), and varying the current in electrolyte which had not been pre-electrolyzed (Table IV). For the latter

TABLE II

TYPICAL VALUES OF $It_{max}$ MEASURED AT VARIOUS CURRENTS IN $O_2$ FREE $N/5$ SULPHURIC ACID

| Time of pre-electrolysis, hr. | Initial potential, volt | Current, amp. | $It_{max}$, microamp-min. | Dev'n. from $It_{max}$ calculated, % |
|---|---|---|---|---|
| 16 | −0.605 | $5.40 \times 10^{-7}$ | 13.0 | + 5 |
| 17 | −0.610 | $5.80 \times 10^{-7}$ | 11.6 | − 6 |
| 19 | −0.597 | $5.89 \times 10^{-7}$ | 13.1 | + 5 |
| 16 | −0.600 | $8.22 \times 10^{-7}$ | 11.2 | −10 |
| 40 | −0.593 | $1.11 \times 10^{-6}$ | 12.6 | + 2 |
| 17 | −0.601 | $2.08 \times 10^{-6}$ | 12.5 | + 1 |
| 15 | −0.592 | $4.10 \times 10^{-6}$ | 11.9 | − 4 |
| 17 | −0.605 | $6.15 \times 10^{-6}$ | 12.3 | − 1 |
| Average | | | 12.3 | − 1 |

TABLE III

TYPICAL VALUES OF $It_{max}$ WITH VARIATION OF THE INITIAL POTENTIAL

| Initial potential, volt | Current, amp. | $It_{max}$, microamp-min. | Dev'n. from $It_{max}$ calculated, % |
|---|---|---|---|
| −0.610 | $5.80 \times 10^{-7}$ | 13.1 | + 5 |
| −0.557 | $5.48 \times 10^{-7}$ | 13.0 | + 5 |
| −0.536 | $5.56 \times 10^{-7}$ | 12.8 | + 3 |
| −0.401 | $5.92 \times 10^{-7}$ | 14.0 | +13 |
| −0.215 | $6.30 \times 10^{-7}$ | 13.6 | +10 |
| −0.008 | $6.46 \times 10^{-7}$ | 12.9 | + 4 |
| +0.088 | $6.71 \times 10^{-7}$ | 14.1 | +14 |

TABLE IV

TYPICAL VALUES OF $It_{max}$ IN NON-PRE-ELECTROLYZED $N/5$ SULPHURIC ACID

| Current, amp. | Initial potential, volt | $It_{max}$, microamp-min. | Dev'n. from $It_{max}$ calculated, % |
|---|---|---|---|
| $6.08 \times 10^{-7}$ | 0.16 | 14.2 | +15 |
| $7.95 \times 10^{-7}$ | 0.12 | 14.0 | +13 |
| $1.26 \times 10^{-6}$ | 0.11 | 13.2 | + 6 |
| $2.03 \times 10^{-6}$ | 0.15 | 12.0 | − 4 |
| $3.81 \times 10^{-6}$ | 0.12 | 14.5 | +17 |
| $6.07 \times 10^{-6}$ | 0.08 | 12.2 | − 2 |

experiments the $N/5$ sulphuric acid was outgassed over a period of several days by alternately evacuating and saturating it with purified hydrogen. A piece of platinum foil, made catalytically active as described previously, reduced further the oxygen concentration. A series of experiments was also conducted in which no special precautions were observed, other than to pre-electrolyze for periods of one to three hours, but the current was varied over

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a much wider range (Table V). Experiments were made in electrolyte saturated with hydrogen and with nitrogen.

TABLE V

TYPICAL VALUES OF $It_{max}$ WITH VARIATION OF CURRENT

| Current, amp. $\times 10^6$ | $t_{max}$, min. | $It_{max}$, microamp-min. | Dev'n. from $It_{max}$ calculated, % |
|---|---|---|---|
| 10.8 | 1.02 | 11.0 | −11 |
| 6.03 | 2.04 | 12.3 | − 1 |
| 2.57 | 4.74 | 12.2 | − 2 |
| 1.59 | 7.25 | 11.5 | − 7 |
| 1.11 | 10.7 | 11.9 | − 4 |
| 0.777 | 16.7 | 13.0 | + 5 |
| 0.540 | 24.1 | 13.1 | + 6 |
| 0.443 | 27.2 | 12.1 | − 3 |
| 0.214 | 59 | 12.6 | + 2 |

For a range of currents ($0.21 \times 10^{-6}$ to $10.8 \times 10^{-6}$ amp.) $t_{max}$ was observed to vary inversely with the current, $I$, such that the product $It_{max}$ was constant (Table V).

Assuming the atoms in liquid mercury to be close-packed and the surface to be uniplanar, a value of 9.24Å$^2$ can be calculated from bulk density for the area occupied by a mercury atom at the liquid surface (14). From a knowledge of the effective area of a surface mercury atom and the true area of the cathode (4.3 cm.$^2$), and assuming the transference of one electron per surface mercury atom, a calculated value of 12.4 microamp-min. was obtained for the product $It_{max}$. The observed values of $It_{max}$ were compared with the calculated value as shown in Tables II, III, IV, and V.

Of a total of 60 separate determinations of $It_{max}$, 46 were within 10% of the calculated value while the greatest deviation of a single experiment was 20%.

When small quantities of oxygen were introduced into pre-electrolyzed solutions, by the method previously described, $It_{max}$ was markedly affected as shown by the solid line in Fig. 4. The dotted line represents the behavior

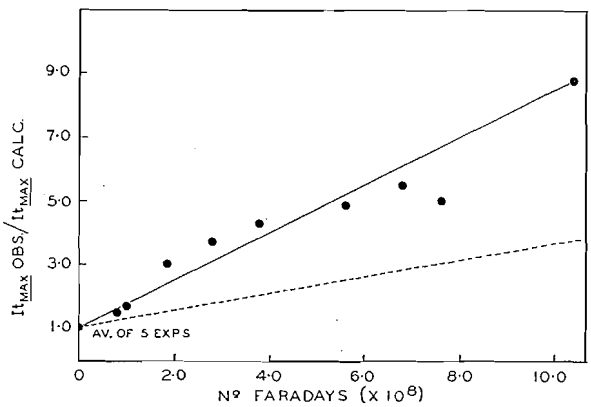



FIG. 4. Effect of oxygen on $It_{max}$ (expressed as number of faradays passed to liberate oxygen in 1 liter of electrolyte).

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that might be expected if all the oxygen in the system reacted with or was adsorbed on the electrode surface and was reduced with 100% current efficiency before any other process occurred. This would seem to support the view, previously stated, that chemisorbed oxygen is reduced with a very low current efficiency.

Mercury ion concentrations up to $2.0 \times 10^{-7}$ mole per liter had no measurable effect on $It_{max}$.

After introducing mercury ions into the electrolyte by making the electrode anodic, the potential was allowed to reach a steady state on open circuit (curve I, Fig. 2*A*). The mercury surface was then renewed by overflowing the mercury cup, the potential was again allowed to reach a steady state (curve II, Fig. 2*A*), and the potential build-up curve was measured for the determination of $t_{max}$. Since the solubility product of mercury sulphide is about $10^{-53}$, any sulphide ion (if present) would have been removed from the system when the cathode surface was renewed preceding the determination of curve II, Fig. 2*A*. It would seem unlikely, therefore, that some reaction involving sulphide or sulphide ion could account for the agreement between the calculated and measured values of $It_{max}$.

From the foregoing, it may be concluded that $It_{max}$ corresponds to the amount of current necessary to transfer one electron across the electrode–solution interface for each mercury atom in the cathode surface. This one to one correspondence conceivably might be due to one of the following:

1. Oxygen present in the solution is adsorbed on, or in some manner reacts with, the mercury atoms of the cathode surface and is reduced when current is made to flow.
2. Some reducible impurity other than oxygen is adsorbed on the cathode surface and is reduced during the first few minutes of current flow.
3. A nonreducible impurity is adsorbed onto the mercury surface and the change of potential with current flow is the result of its desorption.
4. Hydrogen ions are discharged at the cathode where the resulting atoms are adsorbed by the surface mercury atoms in a one to one ratio. The point of maximum potential then corresponds to a complete monatomic film of hydrogen atoms on the mercury surface.

Quantitative studies on the influence of oxygen, reported in the literature, have been conducted through its effect on the Tafel line (cf. 4), a method that appears to be insensitive to oxygen concentrations lower than $10^{-5}$ molar (2). In the present work, the action of oxygen has been studied through its effect on the potential (Table I), potential decay curves (Fig. 2*D*), and the product $It_{max}$ (Fig. 4). Of these three methods, potentials are the most sensitive to small amounts of oxygen at low concentrations. Introducing a quantity of oxygen into the system sufficient to react with only 2–3% of the cathode surface altered the electrode potential from $-0.61$ volt to about $+0.10$ volt. Such a marked effect would seem to indicate that when the potential remained at $-0.61$ volt for periods of one to two hours with or without stirring, the cathode surface could not have been contaminated with oxygen or oxide to a significant extent. Since the observed and calculated values of $It_{max}$ were in

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excellent agreement in the absence of significant quantities of oxygen (Table II), it would appear that the observed one to one correspondence cannot be explained on the basis of any reaction involving oxygen.

A reducible impurity other than oxygen, if it had been present in appreciable amount, presumably would also have markedly affected the value of $It_{max}$. The observed and calculated values of $It_{max}$ were in good agreement (Table IV) for solutions that had not been pre-electrolyzed. Conversely, small quantities of such an impurity would surely have been reduced during the long periods of pre-electrolysis employed in many of the experiments (Table II). The one to one relation between the number of surface mercury atoms and the number of electrons equivalent to $It_{max}$ cannot, therefore, be explained on the basis of any surface active reducible impurity that might possibly be present in the system.

The possibility that some nonreducible impurity might be responsible for the observed behavior seems rather remote. In this case, the change of potential with current flow would presumably correspond to the rate of desorption of the impurity, which in turn would be some function of an interfacial potential resulting from current flow. It does not seem possible to interpret the observed inverse relation between current and $t_{max}$ (Table V) in terms of a current–potential relation. Moreover, if the change of potential from $-0.61$ volt to about $-0.8$ volt with current flow were due to the desorption of some material present in only "trace" amount, then a similar potential change in the opposite direction might be expected to take place when adsorption occurred after renewing the mercury surface. No such potential change was observed at any time.

Since the nature of this investigation makes it extremely difficult, if not impossible, to account for the observed results on the basis of impurities, it becomes necessary to consider the chemical components placed in the electrolyte by design. These are $H^+$, $HSO_4^-$, $SO_4^{--}$, water, and one of the gases hydrogen or nitrogen. For current to flow through an electrolytic cell, some chemical entity must be reduced at the cathode and another oxidized at the anode. The $H^+$ ion is the only substance likely to be reduced under the experimental conditions employed in this study. A reasonable explanation for the observed results would appear to be that when current is made to flow for the first time across a mercury surface, the $H^+$ ions reduced at the cathode are adsorbed as atomic hydrogen. This process is accompanied by a change of potential which is complete when each mercury atom at the surface accommodates one hydrogen atom. Secondary reactions involving current and responsible for potential changes probably occur as well, but if so, they do not appear to have a measurable effect on the value of $It_{max}$ provided the initial potential build-up curves are established from zero potentials more negative than about $+0.15$ volt.

Potential change and rates of potential change attending that property of electrodes referred to as overvoltage have often been considered as resulting from the equivalent of a parallel mesh of resistance and capacitance at or near the electrode surface (cf. 10). Earlier work conducted in this labora-

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tory (15), with copper and silver electrodes appeared to support this view. Two distinct types of potential build-up curves were observed, one of which (the initial curve) was believed to result from the deposition of a close-packed monatomic film of hydrogen on the electrode surface while the other was believed to result from the charging of a condenser.

The earlier view that, at $t_{max}$, the cathode accommodates a monatomic film of hydrogen would seem to receive support from the present study. However, since the film on mercury appears to be distributed in the ratio of one atom of hydrogen per surface atom of mercury, it now seems doubtful that similar film on a copper or silver electrode would be close-packed.

The electrode behavior of copper has been re-investigated since some of the conclusions drawn from the earlier work (15) appeared to be in doubt after the mercury cathode was investigated. Similar studies have been conducted with platinum electrodes. The results of these studies, which seem to support the conclusions drawn here, will be presented for publication in the near future.

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# SILVER - SILVER ION EXCHANGE REACTIONS[1]

By A. Baerg and C. A. Winkler

ABSTRACT

The extent of the exchange between silver foils and silver ions in nitrate solution was compared with surface area measurements made by the Bowden-Rideal method. No quantitative correspondence between the two measurements was observed. During one hour the exchange with mechanically abraded surfaces affected about 30 apparent atomic layers of the metal, but this was reduced to about one-half this value when the surfaces were equilibrated for several days in inactive silver nitrate. Etched foils exchanged during one hour to a depth of only about 2 apparent atomic layers and this was not affected by equilibration. Bowden-Rideal area measurements gave values of roughly 7 and 15 times the planar area for etched and abraded specimens respectively. These values were not altered by equilibration of the surfaces. Only about 50% of the acquired radioactivity was subsequently removable in inactive silver nitrate solution. Part of the measured radioactivity was present on the surface in adsorbed ionic form and was not removable by a simple water wash. The magnitude of this adsorbed activity was found to be measurable electrometrically.

## INTRODUCTION

It has been observed that the exchange between a metal and its ions in solution generally results in multiatomic layer exchange when based on the superficial area of the metal surface (8, 14, 4, 16, 13, 7). Since the effect of diffusion within solid metals is probably negligible, the deep exchange has usually been attributed to local cell action or other surface structural changes. While the effect of surface roughness has seldom been taken into account, some investigators have used exchange data for metals (5) or insoluble salts (11) as a direct measure of the true surface area. In the present study of silver surfaces prepared in several ways, the results of exchange experiments are compared with independent area measurements made by a modified Bowden-Rideal method (cf. (10)).

## EXPERIMENTAL

Since this study was largely concerned with the effects of surface structure, the exchange reactions were restricted to silver solutions of one concentration: $3 \times 10^{-4}N$ in silver nitrate. The silver isotope, $Ag^{110}$, used as tracer was obtained from the National Research Council, Atomic Energy Project, Chalk River. This isotope is a beta and gamma ray emitter with a half-life of 270 days and was prepared by neutron irradiation of Nichols reagent grade silver nitrate in the nuclear reactor. The salt was dissolved in water to give a stock solution of active silver nitrate, the concentration of which was determined by titration of an aliquot against standard potassium iodide using eosin as indicator. Suitable quantities of active and inactive silver nitrate solutions were used to obtain the desired concentration and specific activity of the exchange solution.

Metallic silver disks, 2.5 cm.$^2$ in apparent area and 0.004 in. in thickness,

[1] *Manuscript received December 8, 1952.*
*Contribution from the physical chemistry laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.*

were used in all the experiments. These were attached to holders so that both exchange and area measurements could be made with each specimen. A 24–40 standard taper re-entrant joint was fitted at each end with a lucite plug. The silver disk was cemented to the face of the plug at the re-entrant end by wetting the lucite with a drop of chloroform. A silver spring pressed against the back of the disk, through a hole in the center of the plug, to establish electrical contact with a brass rod through the middle of the joint.

The exchange cell was a 500 ml. round bottom flask with 24–40 standard taper inlets to accommodate the electrodes. A close-fitting constant speed stirrer was used to agitate the exchange solution which was maintained oxygen-free by a stream of nitrogen purified over hot copper. The 400 ml. of solution in this cell contained about 0.3 mc. of radioactive silver and sufficient total silver ion to preclude significant alteration of the ratio of active to inactive silver during any one experiment.

The radioactivity acquired by the silver during exchange was determined with standard counting equipment using an end-window Geiger tube. The lead castle was suitably fitted with a tapered holder to position the electrode about 5 cm. from the tube window. All electrodes used gave the same counting rate, within statistical fluctuations, for equal amounts of radioactive silver. Corrections for background and a small amount of activity adsorbed on the glass were made by counting after the active silver foil was removed from the electrode assembly. These corrections were both less than 100 counts per minute while the activity on the silver was usually greater than 1000 counts per minute. Corrections for decay of the radioactive silver were automatically made by use of an active electrode as a counting standard. It was calibrated by electrodeposition of a known amount of active silver from a silver nitrate electrolyte. For calculation of the apparent depth of exchange, the amount of silver exposed on 2.5 cm.$^2$ true surface was taken as $6.2 \times 10^{-9}$ gm-atom.

The apparatus and experimental procedures for the Bowden-Rideal area measurements were similar in all essential respects to those used previously in this laboratory (10, 15, 19).

## RESULTS

Preliminary experiments were made with silver foils prepared by abrasion with a water slurry of emery on glass. These surfaces gave Bowden-Rideal areas which depended strongly on the pressure applied during abrasion. The exchange affected hundreds of apparent atomic layers of the metal and continued indefinitely, though slowly. Thus, a specimen which measured 52 times the planar area exchanged to a depth of 330 atomic layers during 13 days. However, only a small fraction of the acquired activity was subsequently removable in inactive silver nitrate solution. This appeared to indicate that local cell action played a predominant role in the exchange process.

In an attempt to separate the influence of local cell processes from a reversible exchange the effect of preliminary equilibration in inactive solution was examined. The cell used for equilibrating the specimens was similar to the exchange cell and both solutions were $3 \times 10^{-4}N$ in silver nitrate. Speci-

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mens prepared by abrasion with emery and surfaces etched with 7*N* nitric acid were studied. For comparison, a one hour period of exchange was selected while the time of equilibration was varied. Following the exchange, the electrodes were thoroughly rinsed with water and Bowden-Rideal areas determined. The surfaces were then dried and the acquired radioactivity measured. The results of these experiments are summarized in Table I.

TABLE I

DEPENDENCE OF EXCHANGE ON SURFACE PREPARATION. EXCHANGE TIME—ONE HOUR

| Electrode | Equilibration time, hr. | Apparent atomic layers exchanged | Bowden-Rideal area (times planar) |
|---|---|---|---|
| *Emery surfaced foils* | | | |
| 1 | 0 | 36.8 | 15.2 |
| 2 | 0 | 24.5 | 14.5 |
| 3 | 10 | 13.2 | 14 |
| 4 | 35 | 20.5 | 17.6 |
| 5 | 75 | 21.2 | 18 |
| 6 | 80 | 19.2 | 19 |
| 7 | 288 | 12.6 | 21.5 |
| 8 | 360 | 14.5 | 14.7 |
| 9 | 360 | 13.5 | 13.5 |
| 10 | 408 | 13.7 | 14.8 |
| 11 | 408 | 15.5 | 16.0 |
| *Etched foils* | | | |
| 1 | 0.3 | 2.0 | 6.4 |
| 2 | 3.5 | 3.4 | 10.0 |
| 3 | 6.5 | 3.0 | 9.5 |
| 4 | 14 | 2.0 | 8.0 |
| 5 | 22 | 2.6 | 7.3 |
| 6 | 25 | 1.9 | 7.4 |
| 7 | 25 | 2.2 | 7.2 |
| 8 | 36 | 2.7 | 7.5 |
| 9 | 40 | 2.7 | 7.9 |
| 10 | 48 | 2.5 | 9.7 |
| 11 | 53 | 2.5 | 11.0 |

Although the metal surfaces were poorly reproducible in respect of both exchange and area, some general trends became apparent. Equilibration of abraded surfaces for several days reduced the exchange from about 30 to 15 atomic layers but had no apparent influence on the Bowden-Rideal areas, which were roughly 15 times planar. Similarly, the areas of etched surfaces were not affected and their magnitude was only about one-half that for abraded specimens. On the other hand, the exchange with these surfaces showed a maximum value, during one hour, of only 3.4 atomic layers and this also appeared to be unaffected by equilibration. These results indicate that for abraded foils the local cell action is diminished and the reproducibility of the surfaces in respect of exchange appears much improved by equilibration (cf. emery surfaced electrodes 1 and 2, Table I). However, the local action was evidently not eliminated for either the etched or abraded

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specimens since only 50% to 60% of the acquired activity was subsequently removable by exchange with inactive solution.

The observed exchange appeared from the above experiments to be due in large measure to local surface reactions. Some additional experiments with etched foils, however, suggested that about 25% of the measured activity was present on the surface in ionic form and was not removed by the water wash following the exchange. When an already radioactive etched electrode was again rendered cathodic in the overvoltage cell of the Bowden-Rideal apparatus and then immediately rinsed with water and reimmersed in active solution, it acquired additional radioactivity equivalent to 0.5 to 1 atomic layer of the metal. By repetition of the operations addition of activity could be continued indefinitely. Presumably, adsorbed active silver ions not removed by the water wash were subsequently electrodeposited when the metal was rendered cathodic in the overvoltage cell.

To examine this view further, experiments were made to observe the possible influence of adsorbed silver ions on the overvoltage–time curves obtained with the Bowden-Rideal apparatus. In Fig. 1 is shown the manner in which the

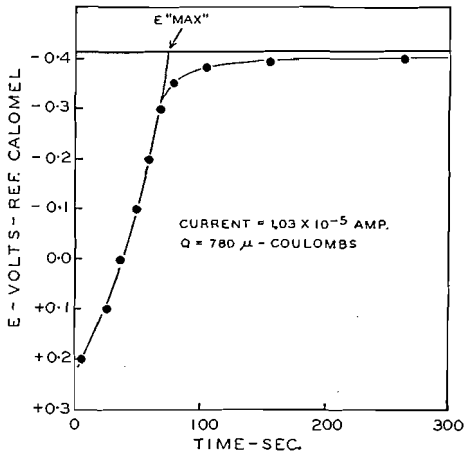



FIG. 1. Change of potential with time at a silver cathode during electrolysis in $N/5$ sulphuric acid.

silver cathode potential varies with time (at constant current) during electrolysis, just after immersion in the $N/5$ sulphuric acid electrolyte. It seemed reasonable that in the initial presence of adsorbed silver ions their quantity should be related to the amount of electricity, $Q$, consumed in the attainment of the hydrogen overvoltage ($E_{max}$). Campbell and Thomas (3) have made use of such curves to determine the thickness of oxide films on metals. In the present experiments the value of $Q$ was obtained by extrapolation of the steep part of the curve to "$E_{max}$" as indicated. The value of the time, $t$, at the point of intersection, multiplied by the constant current was taken to give $Q$.

In a series of experiments made with an etched electrode, the activity gained from the radioactive solution, following cathodic treatment in the overvoltage cell, was compared with the $Q$ values determined immediately

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after removal from the active solution. The freshly etched specimen was first rendered cathodic in the overvoltage cell, then rinsed with water and transferred to the active exchange solution for one minute. Following this it was again rinsed and $Q$ determined as described above. After the acquired radioactivity was measured, the electrode was again rendered cathodic in preparation for the second experiment. The whole process was repeated five times with this electrode; the results are recorded in Table II. The total activity

TABLE II

EFFECT OF CATHODIC TREATMENT. ETCHED SILVER ELECTRODE

| Electrode | Exchange time, min. | Total activity | $Q$ | Activity gain |
|---|---|---|---|---|
| | | Microcoulombs | | |
| 1 | 1 | 1960 | 580 | 1960 |
| 2 | 1.5 | 2580 | 530 | 620 |
| 3 | 1 | 3080 | 530 | 500 |
| 4 | 1 | 3540 | 535 | 460 |
| 5 | 1 | 4140 | 560 | 600 |
| 6 | 1 | 4830 | 590 | 690 |

Mean activity for 2, 3, 4, 5, and 6 = 570 microcoulombs
Mean value of $Q$ for 2, 3, 4, 5, and 6 = 550 microcoulombs

and the increase in activity in each experiment are expressed as coulombic equivalents for comparison with $Q$. These data reveal that the activity gained in each experiment following the first is in good agreement with the corresponding value of $Q$. Similar results were obtained in another series for which the immersion time in active solution was increased to 5 to 10 minutes. Presumably the activity acquired by the metal in the first experiment was due largely to an exchange process while in subsequent experiments the activity gain was due to an adsorption effect.

In addition to these results the value of $Q$ was found to be linearly related to the logarithm of the silver ion concentration in the solution from which adsorption had taken place. The data represented in Fig. 2 were obtained using inactive silver sulphate solutions to avoid the possibility of side effects in the overvoltage cell (containing $N/5$ sulphuric acid) due to the nitrate ion. Concentrations of $10^{-2}$, $10^{-4}$, $10^{-6}$, and $10^{-8}$ equivalents per liter in silver ion were used and the solutions were maintained oxygen free by bubbling pure nitrogen through them.

From the slope of the semilogarithmic plot of the data it is possible to calculate an adsorption capacity, $C$, as

$$C = \Delta Q \Big/ \frac{2.3\ RT}{nF} \Delta \log [Ag^+].$$

The values thus obtained, in $\mu$f. per cm.$^2$ (apparent area of electrode = 2.5 cm.$^2$), for three different electrodes, together with the capacities obtained

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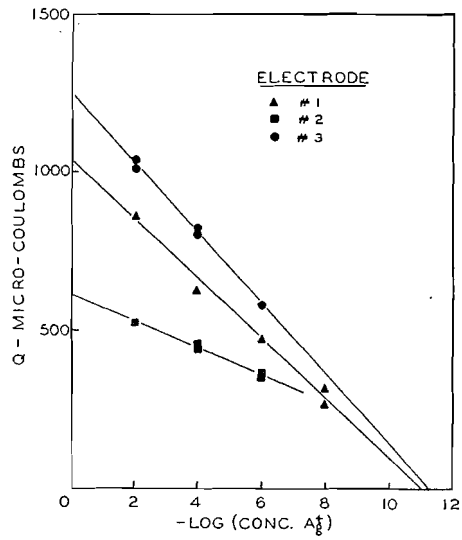



FIG. 2. Relation between $Q$ and logarithm of silver ion concentration.

by the Bowden-Rideal measurements after adequate electrolysis (19), were as follows:

| Electrode | 1 | 2 | 3 |
|---|---|---|---|
| Bowden-Rideal capacity ($\mu$f.) | 150 | 145 | 165 |
| Adsorption capacity ($\mu$f.) | 610 | 250 | 745 |

While the Bowden-Rideal values were all about 150 $\mu$f. per cm.$^2$, the adsorption capacities were two to five times greater. It is at present difficult to account for this discrepancy. These experiments however showed that the $Q$ values gave a reasonable measure of the adsorbed activity.

Hevesy and Blitz (9) have suggested that the presence of an adsorbed ionic double layer reduced the rate of exchange between lead ions and radioactive lead sol. Several series of experiments with etched silver electrodes appeared to indicate a similar behavior. The electrodes of one group were equilibrated for 15 hr. in inactive silver nitrate solution and therefore retained an adsorbed layer of inactive ions before commencement of the exchange reaction. Several electrodes in a second group were rendered cathodic in the overvoltage cell just prior to exchange, and were therefore free of adsorbed ionic silver. The time of exchange was varied among the different specimens to obtain a picture of the kinetic behavior for the two groups of electrodes. Though the surfaces were poorly reproducible, it was evident that several hours were required for the equilibrated electrodes to gain roughly the same total activity (about 3 apparent atomic layers) as that acquired by nonequilibrated surfaces in a rapid initial exchange of only several minutes duration. The adsorbed activity was roughly the same for all electrodes so that the more rapid gain of activity by the fresh specimens must have been due to a more rapid atom–ion exchange.

## DISCUSSION

Although the extent of exchange during one hour with well-equilibrated

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surfaces of abraded silver was in reasonable agreement with the Bowden-Rideal area, wide deviations occurred with all other specimens. This seems to imply that either the exchange or the Bowden-Rideal capacity or both are not directly dependent on the actual area of the metal surface. The method which has been found suitable for determination of the adsorbed silver ions implies that the potential change in the initial attainment of the hydrogen overvoltage is due to metal ion polarization. There remains the question of whether the linear potential buildup of the Bowden-Rideal capacity measurement, following adequate electrolysis and discharge of potential, involves a similar electrode process. If it does, it would seem doubtful that such a capacity measurement is dependent on the true surface area.

Variations in exchange behavior may reasonably be attributed to differences in the submicroscopic structure of the crystalline metal surfaces. The theories of crystal growth, as laid down by Volmer (18) and by Kossel and Stranski (17) predict marked differences in the binding energy of atoms on a crystal surface, depending on the number of atoms surrounding the one in question. An average crystal surface in equilibrium with its solution is visualized as consisting of a series of steps or incompleted atomic layers. The edges of these steps will be straight at the absolute zero of temperature but at higher temperatures they will present a kinked appearance. In addition there will be a number of atoms *on* the terraces between steps with a corresponding number of lattice vacancies in the surfaces. The out-of-lattice atoms are probably highly mobile (1) and may be regarded as a "2-dimensional gas phase" in equilibrium with the atoms at step positions. On the basis of nearest neighbor interactions, these are readily seen to be more strongly bound than those on the surface. Accordingly exchange between ions in solution and crystal surface atoms may be considered to occur most easily by a two way process: (1) exchange of ions with relatively few out-of-lattice atoms on the terraces and (2) interchange of position of the latter with atoms at step positions. This interchange will be facilitated by the existence of kinks in the steps and statistical fluctuations of these will result in incorporation of radioactive atoms into the surface layers. Consideration of the energy required to remove an atom from within a flat surface essentially excludes the possibility of significant exchange by such a direct process. Paneth (12) and Zimens (20) have made use of these concepts to explain the differences in exchange behavior of well-formed natural crystals in contrast to that of precipitated crystals of insoluble salts.

Burton and Cabrera (2) have made an investigation of the concentration of steps or "Frenkel terraces" on a crystal surface in equilibrium. Surfaces are divided into classes, close-packed and stepped. A close-packed crystal face is defined as one in which all the surface atoms are at the same distance from a plane parallel to the face. In all other cases the surface will present a stepped appearance. By way of illustration, in the simple cubic system, (100) and (110) faces are close-packed and all others stepped. In a stepped surface, the terraces are pieces of close-packed surface. For faces of high index the terraces will be (100) surfaces. Calculations also show that the concentration of lattice

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vacancies in a close-packed surface in equilibrium is very small, while the concentration of kinks in a step in equilibrium is high.

It is now easy to understand the different results obtained in the present exchange experiments. Mechanical abrasion may be expected to cleave the silver crystallites on the surface in a variety of directions, to expose a virtually infinite number of crystal faces with completely random orientations (of both low and high indices). Aside from increasing the over-all exposed area this is precisely the condition which should lead to the extensive exchange observed, by way of steps on faces of high index.

On the other hand, with etched foils which showed relatively little exchange, the etching process should, according to the theories, occur largely at the edges of incompleted atomic layers. The steps, largely responsible for exchange, will then tend to disappear leaving the crystallites surrounded by a relative preponderance of low index (nonexchanging) surfaces.

Superimposed on the exchange with surface atoms on crystal faces is the deep seated exchange that presumably results from local cell action. It is well known that different crystal faces exhibit dissimilar chemical reactivities. These differences may be attributed to differential bonding along the few principle directions within the crystal lattice (17). Fricke (6) has calculated the work of formation of crystal surfaces for various metals. For silver he has found 1934 and 1643 erg per cm.$^2$ per atom for the (001) and (111) crystal faces respectively. For crystals in contact with solution these energy differences may be expected to produce slow "anodic" dissolution of incomplete atomic layers on those faces consisting of terraces of low binding energy with corresponding growth of the terraces of higher binding energy (cathodic regions). As the process continues the steps on the surfaces will tend to disappear, hence the number of exchangeable atoms (at step positions) decrease. This would seem to account for the reduced exchange observed with equilibrated specimens of abraded silver foils.

Although the above interpretation of the exchange results seem reasonable, it is probably oversimplified. Adsorbed solvent or ionic material probably would alter the exchange processes quite markedly. A detailed kinetic study of the reaction on individual surfaces would be desirable.

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# THE USE OF INFRARED SPECTROPHOTOMETRY FOR THE ESTIMATION OF SMALL QUANTITIES OF SOME HALOGENATED HYDROCARBONS[1]

By L. Breitman[2] and E. W. R. Steacie

ABSTRACT

The infrared spectra of chloral, carbon tetrachloride, and chloroform have been determined between 1500 and 650 cm.$^{-1}$ over a range of pressures in the gas phase. Absorption bands suitable for the quantitative analysis of binary and ternary mixtures of the components have been selected and their peak intensities shown to obey Beer's Law over the range of pressures studied. Ternary mixtures have been analyzed from the spectra with an accuracy of about 20%.

The spectra of dichloromethane and methyl chloride have also been measured under comparable conditions.

## INTRODUCTION

Kinetic studies of the decomposition of many organic compounds have been made possible by the perfection of techniques used in estimating the small quantities of hydrocarbons that are produced when the decomposition is studied at low conversions. Investigations of the degradation of chlorine-containing compounds have been somewhat handicapped by the difficulties encountered in the analysis of halogenated hydrocarbons in a large excess of the parent substance.

The present problem arose in connection with the photolysis of chloral. This reaction, if analogous to that of acetaldehyde, proceeds by: (1) an intermolecular rearrangement and/or (2) rupture of the C–C bond:

$$CCl_3CHO + h\nu \rightarrow CHCl_3 + CO \qquad (1)$$

$$CCl_3CHO + h\nu \rightarrow CCl_3 + CHO \qquad (2)$$

followed by the abstraction reactions

$$CCl_3 + CCl_3CHO \rightarrow CHCl_3 + CCl_3CO$$

$$CCl_3 + CCl_3CHO \rightarrow CCl_4 + CCl_2CHO$$

Carbon monoxide was found to be the only 'noncondensable' product in a preliminary photolysis of chloral, but presumably because of insufficient differences in the vapor pressures of the condensable products, no other pure components could be isolated by distillation from a Ward still. It seemed reasonable to assume that the mixture resulting from the photolysis of chloral contained chloroform and carbon tetrachloride in a large excess of the aldehyde.

This paper describes a method of detecting and estimating the components of a mixture of chloral, carbon tetrachloride, and chloroform with the infrared spectrophotometer.

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## EXPERIMENTAL

### *Apparatus*

The optical cell was of pyrex, 10 cm. long, to which plane polished sodium chloride windows were affixed with Benolite cement. The cylindrical cell, of total volume 139.3 cc., was provided with a stopcock and ground glass joint to permit filling and evacuation, and a cold finger for condensation of gas samples.

The gas samples to be analyzed were prepared in a suitable high vacuum line containing liquid air traps, calibrated volumes, and a high speed, two-stage mercury diffusion pump. Dow Corning high vacuum silicone grease was used on all joints and stopcocks to minimize absorption of the samples. The optical densities of the gases were measured with a Perkin-Elmer Model 21 double beam recording infrared spectrophotometer (1, 4, 5) using a sodium chloride prism.

### *Materials*

Chloral was a Fisher Scientific Company product of unspecified purity. It was distilled in air at a 5:1 reflux ratio. The portion boiling constantly at 97.8° C. was distilled *in vacuo* through a U-tube containing anhydrous phosphorus pentoxide and stored in a dark brown bottle. This product had a vapor pressure of 49.5 mm. at 24.4° C. and melted at −59° C.

Carbon tetrachloride, reagent grade, was obtained from Merck and dichloromethane, research grade, from Anachemia. Both compounds were distilled *in vacuo* and stored in the dark.

Chloroform was a Mallinckrodt analytical reagent grade product. It was passed through a column of silica gel before use to remove traces of alcohol and water.

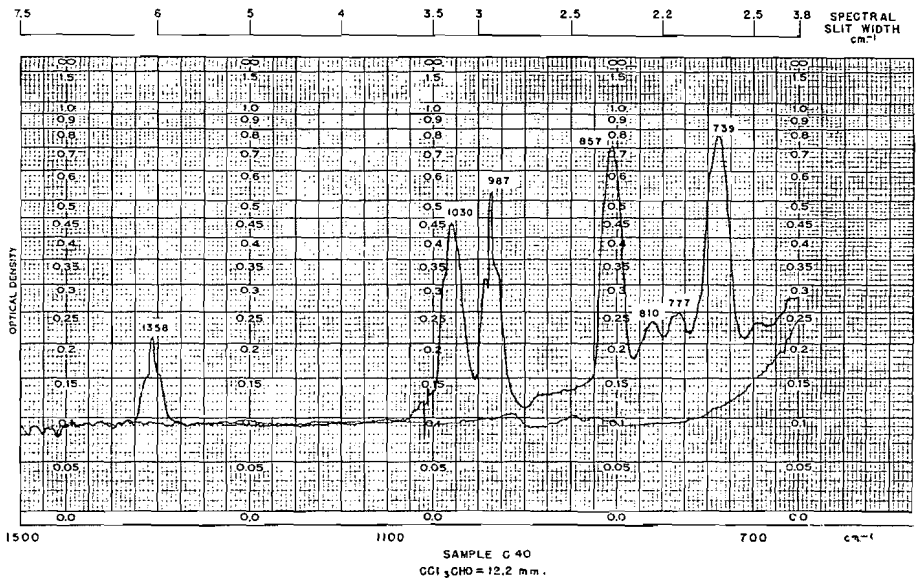



FIG. 1. Infrared spectrum of chloral (12.2 mm.).

Methyl chloride of unspecified purity was obtained from the Matheson Company and was purified by repeated bulb-to-bulb distillations *in vacuo*.

## RESULTS AND DISCUSSION

### *Spectra of the Individual Components*

Typical infrared spectra of chloral, carbon tetrachloride, and chloroform

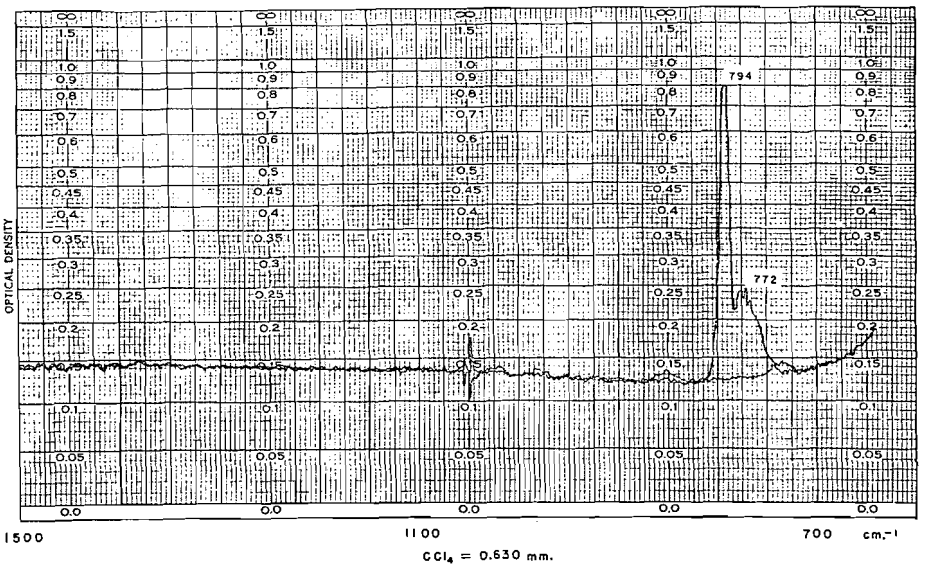



FIG. 2. Infrared spectrum of carbon tetrachloride (0.630 mm.).

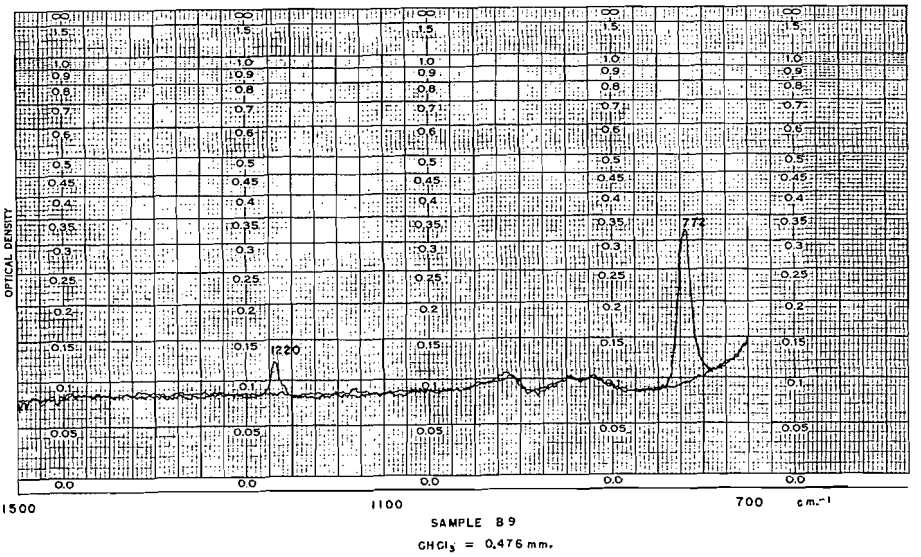



FIG. 3. Infrared spectrum of chloroform (0.476 mm.).

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are reproduced in Figs. 1–3 respectively. All measurements were made at comparable spectral slit widths without a matching optical cell in the control beam of the spectrophotometer. The lower lines in Figs. 1–3 were obtained with the optical cell evacuated and all optical densities were measured from these reference lines. Inspection of these spectra suggested that the strong band of carbon tetrachloride at 794 cm.$^{-1}$ and the weaker, but distinctive band of chloroform at 1220 cm.$^{-1}$ might serve most conveniently for the analysis of these two components. The stronger chloroform band at 772 cm.$^{-1}$ is less suitable because of overlap with both carbon tetrachloride and chloral absorp-

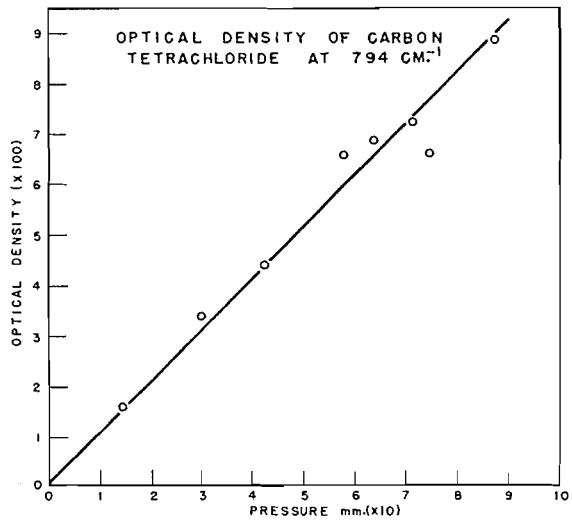



FIG. 4. Optical density of carbon tetrachloride at 794 cm.$^{-1}$

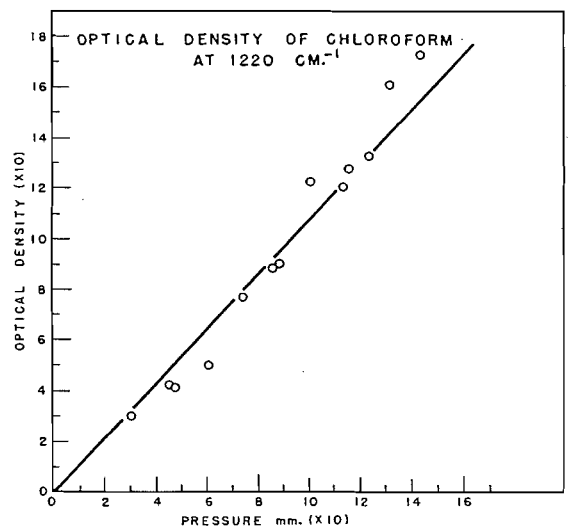



FIG. 5. Optical density of chloroform at 1220 cm.$^{-1}$ as a function of pressure.

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tion. The conformity of these bands with Beer's Law is shown by the linear plots of peak optical density against partial pressure in Figs. 4 and 5. The numerical data are given in Tables I and II.

TABLE I

OPTICAL DENSITY OF CARBON TETRACHLORIDE

| Sample | Pressure, mm. | Optical density | |
|---|---|---|---|
| | | 794 cm.$^{-1}$ | 772 cm.$^{-1}$ |
| A8 | 0.421 | 0.440 | 0.076 |
| A9 | 0.292 | 0.338 | 0.056 |
| A10 | 0.120 | 0.156 | 0.026 |
| A11 | 0.633 | 0.686 | 0.120 |
| A12 | 0.742 | 0.685 | 0.133 |
| A13 | 0.710 | 0.720 | 0.133 |
| A14 | 0.869 | 0.885 | 0.180 |
| A16 | 0.568 | 0.656 | 0.116 |

TABLE II

OPTICAL DENSITY OF CHLOROFORM

| Sample | Pressure, mm. | Optical density | |
|---|---|---|---|
| | | 769 cm.$^{-1}$ | 1220 cm.$^{-1}$ |
| B1 | 0.574 | 0.266 | ..... |
| B2 | 1.41 | 0.695 | ..... |
| B3 | 1.16 | 0.660 | 0.127 |
| B4 | 0.859 | 0.450 | 0.088 |
| B5 | 1.32 | 0.726 | 0.160 |
| B6 | 1.44 | 0.800 | 0.172 |
| B7 | 0.888 | 0.467 | 0.090 |
| B8 | 1.01 | 0.601 | 0.122 |
| B9 | 0.476 | 0.225 | 0.041 |
| B10 | 0.746 | 0.392 | 0.077 |
| B11 | 1.14 | 0.582 | 0.120 |
| B12 | 0.457 | 0.213 | 0.042 |
| B13 | 1.24 | 0.610 | 0.132 |
| B14 | 0.304 | 0.142 | 0.030 |
| B15 | 0.610 | 0.285 | 0.050 |

Chloral in the liquid phase exists in equilibrium with its trimer. The latter can be removed by simple distillation, but the equilibrium concentration of the trimer, about 10% (3), is attained on standing. The presence of the trimer in the gas phase, however, was not detected: there were no significant differences between the infrared spectrum of stored chloral and that of the freshly distilled material. The aldehyde absorbs moisture to precipitate the hydrate and decomposes readily on exposure to light or oxygen in the atmosphere (2). To obtain reproducible spectra it was necessary to dry the chloral quite frequently by passage over phosphorus pentoxide and to store it in the dark after distillation.

The infrared spectrum of chloral has major peaks at 1358, 1030, 987, 857, and 739 cm., and two small maxima at 777 and 810 cm.$^{-1}$. The relative magnitudes of absorption at 857, 739, 777, and 810 cm.$^{-1}$ were useful criteria for

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purity of the aldehyde. Pure chloral is practically transparent at 1250–1200 cm.$^{-1}$. The appearance of appreciable structure in this region probably denotes decomposition of the compound. This phenomenon is of importance because of overlap with the peak at 1220 cm.$^{-1}$ in the spectrum of chloroform. The optical densities of chloral at 794 cm.$^{-1}$ and 772 cm.$^{-1}$ were also measured because the spectrum of carbon tetrachloride shows maxima at these positions and there are no peaks in the carbon tetrachloride spectrum where chloral is transparent. The data for the optical densities of chloral at the important

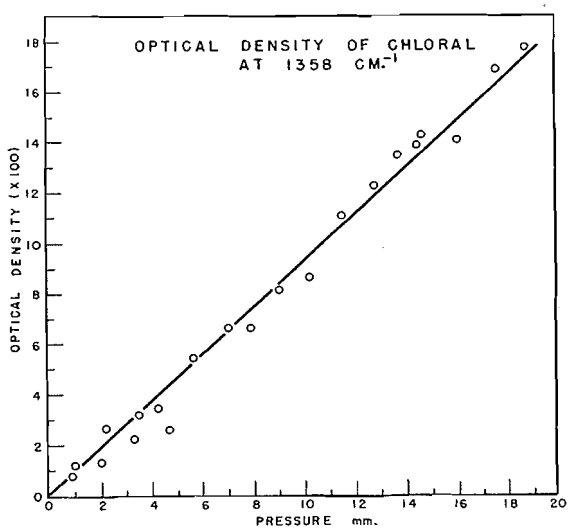



FIG. 6. Optical density of chloral at 1358 cm.$^{-1}$ as a function of pressure.

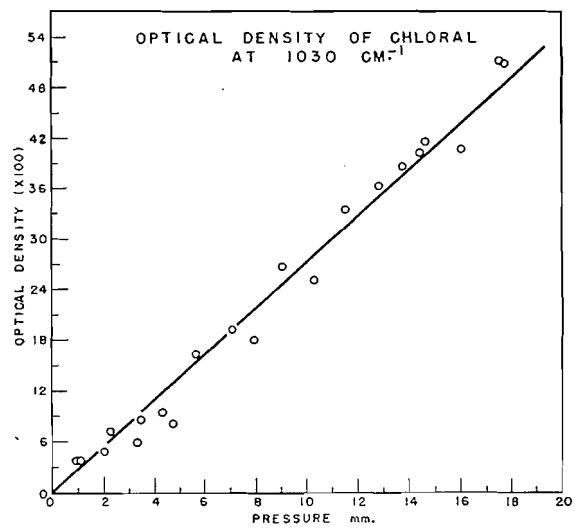



FIG. 7. Optical density of chloral at 1030 cm.$^{-1}$ as a function of pressure.

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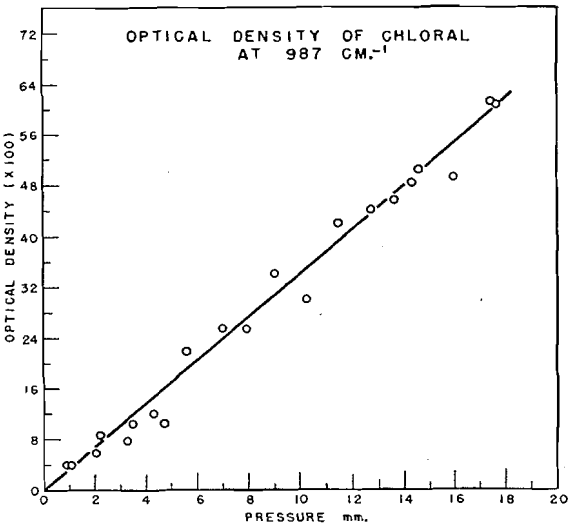



FIG. 8. Optical density of chloral at 987 cm.$^{-1}$ as a function of pressure.

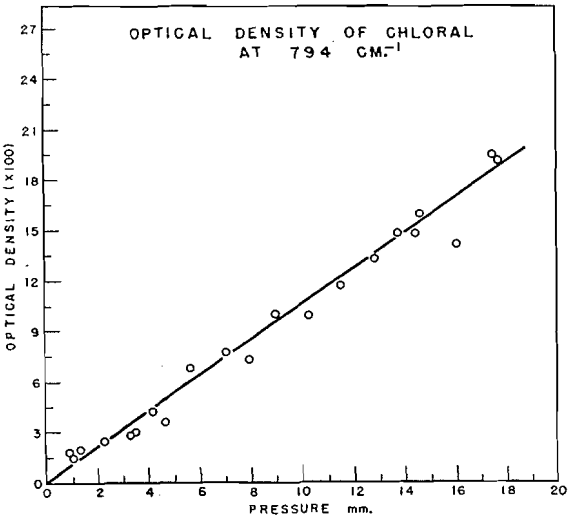



FIG. 9. Optical density of chloral at 794 cm.$^{-1}$ as a function of pressure.

wave numbers are collected in Table III, and the conformity with Beer's Law established by the linear plots in Figs. 6–9.

*Spectra of Mixtures*

Table IV lists the analytical results obtained for a series of mixtures of chloral, carbon tetrachloride, and chloroform. The infrared spectrum of a typical mixture is reproduced in Fig. 10.

Chloroform and carbon tetrachloride are transparent at 1358, 1030, 987, and 857 cm.$^{-1}$ where chloral has spectral peaks. The optical densities at these

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TABLE III

OPTICAL DENSITY OF CHLORAL

| Sample | Pressure, mm. | Optical density, cm.$^{-1}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1358 | 1030 | 987 | 857 | 794 | 772 | 739 |
| 1C | 10.24 | 0.086 | 0.251 | 0.300 | 0.523 | 0.097 | 0.106 | 0.512 |
| 3C | 13.70 | 0.134 | 0.383 | 0.455 | 0.650 | 0.147 | 0.153 | 0.652 |
| 4C | 14.60 | 0.142 | 0.412 | 0.505 | 0.714 | 0.158 | 0.160 | 0.713 |
| 5C | 17.50 | 0.168 | 0.508 | 0.610 | 0.816 | 0.194 | 0.212 | 0.810 |
| 13C | 5.59 | 0.054 | 0.162 | 0.216 | 0.342 | 0.067 | 0.094 | 0.338 |
| 14C | 7.91 | 0.066 | 0.176 | 0.252 | 0.382 | 0.073 | 0.105 | 0.386 |
| 15C | 4.68 | 0.026 | 0.080 | 0.104 | 0.162 | 0.035 | 0.047 | 0.162 |
| 16C | 3.47 | 0.032 | 0.083 | 0.104 | 0.166 | 0.030 | 0.036 | 0.166 |
| 17C | 3.29 | 0.022 | 0.060 | 0.078 | 0.126 | 0.028 | 0.035 | 0.133 |
| 18C | 2.00 | 0.013 | 0.048 | 0.058 | 0.085 | 0.020 | 0.023 | 0.096 |
| 19C | 0.911 | 0.008 | 0.038 | 0.043 | 0.061 | 0.018 | 0.022 | 0.070 |
| 30C | 7.00 | 0.066 | 0.192 | 0.254 | 0.364 | 0.076 | 0.074 | 0.394 |
| 31C | 16.00 | 0.140 | 0.404 | 0.490 | 0.718 | 0.140 | 0.143 | 0.702 |
| 32C | 14.40 | 0.138 | 0.398 | 0.482 | 0.712 | 0.146 | 0.140 | 0.702 |
| 33C | 11.45 | 0.110 | 0.332 | 0.418 | 0.614 | 0.116 | 0.116 | 0.623 |
| 34C | 12.80 | 0.122 | 0.360 | 0.440 | 0.676 | 0.132 | 0.128 | 0.668 |
| 35C | 17.70 | 0.170 | 0.508 | 0.605 | 0.858 | 0.190 | 0.198 | 0.860 |
| 36C | 1.02 | 0.012 | 0.036 | 0.043 | 0.060 | 0.015 | 0.014 | 0.074 |
| 37C | 9.00 | 0.081 | 0.266 | 0.340 | 0.510 | 0.099 | 0.094 | 0.522 |
| 38C | 4.28 | 0.034 | 0.094 | 0.120 | 0.194 | 0.039 | 0.035 | 0.196 |
| 39C | 2.20 | 0.026 | 0.074 | 0.087 | 0.143 | 0.025 | 0.025 | 0.145 |

TABLE IV

ANALYSIS OF SYNTHETIC MIXTURES

| Sample | Composition of mixture, mm. | | Infrared analysis,* mm. | |
|---|---|---|---|---|
| M1 | $CCl_3CHO$: | 8.52 | $CCl_3CHO$: | 9.9 |
| | $CCl_4$: | 0.312 | $CCl_4$: | 0.27 |
| M2 | $CCl_3CHO$: | 18.9 | $CCl_3CHO$: | 19.9 |
| | $CCl_4$: | 0.328 | $CCl_4$: | 0.30 |
| M3 | $CCl_3CHO$: | 10.1 | $CCl_3CHO$: | 10.8 |
| | $CHCl_3$: | 0.610 | $CHCl_3$: | 0.55 |
| M4 | $CCl_3CHO$: | 4.61 | $CCl_3CHO$: | 4.3 |
| | $CHCl_3$: | 0.821 | $CHCl_3$: | 0.65 |
| M6 | $CHCl_3$: | 0.719 | $CHCl_3$: | 0.78 |
| | $CCl_4$: | 0.802 | $CCl_4$: | 0.70 |
| M7 | $CHCl_3$: | 0.558 | $CHCl_3$: | 0.50 |
| | $CCl_4$: | 0.630 | $CCl_4$: | 0.44 |
| M8 | $CCl_3CHO$: | 5.56 | $CCl_3CHO$: | 5.0 |
| | $CCl_4$: | 0.480 | $CCl_4$: | 0.57 |
| | $CHCl_3$: | 0.462 | $CHCl_3$: | 0.49 |
| M9 | $CCl_3CHO$: | 5.13 | $CCl_3CHO$: | 4.8 |
| | $CCl_4$: | 0.470 | $CCl_4$: | 0.40 |
| | $CHCl_3$: | 0.330 | $CHCl_3$: | 0.31 |

* *The data for chloral in this column are average values from optical density measurements at appropriate wave numbers.*

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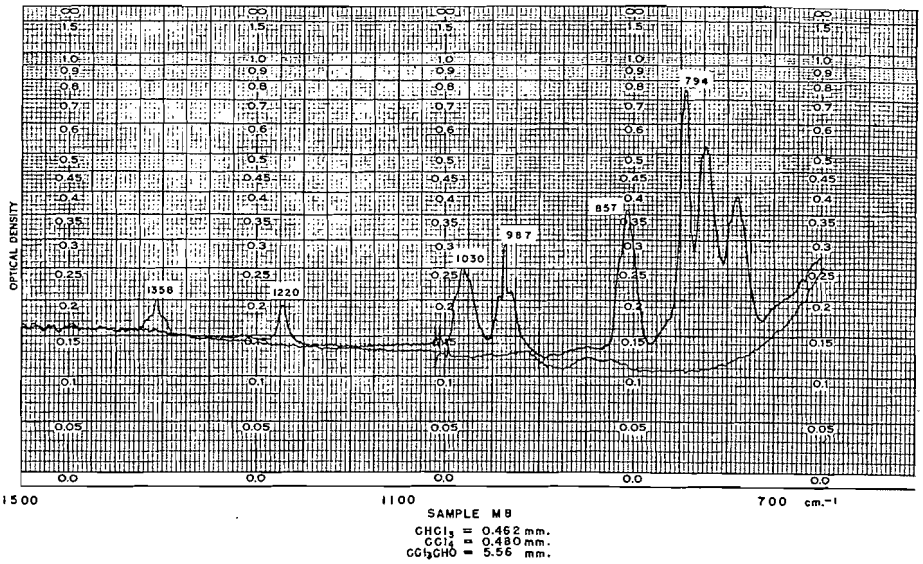



FIG. 10. Infrared spectrum of a typical mixture of chloroform, carbon tetrachloride, and chloral.

wave numbers, obtained from the infrared spectrum of a mixture of chloral, carbon tetrachloride, and chloroform, then give directly the concentration of chloral in the mixture. The chloroform content is measured similarly from the optical density at 1220 cm.$^{-1}$ since the spectra of both carbon tetrachloride and chloral show no structure at this wave number.

Since chloroform is practically transparent at 794 cm.$^{-1}$, the optical density of the mixture at this wave number, less the contribution of the previously determined quantity of chloral, is used to estimate the concentration of carbon tetrachloride.

A sample calculation is given for the analysis of sample M8:

Optical density at 1358 cm.$^{-1}$ = 0.054, equivalent to 5.5 mm. chloral
" " " 1030 cm.$^{-1}$ = 0.128, " " 4.7 mm. "
" " " 987 cm.$^{-1}$ = 0.166, " " 5.0 mm. "
" " " 857 cm.$^{-1}$ = 0.247, " " 4.9 mm. "

Mean value of concentration of chloral = 5.0 mm.

Optical density at 1220 cm.$^{-1}$ = 0.054, equivalent to 0.49 mm. chloroform
Optical density at 794 cm.$^{-1}$ = 0.650
Optical density at 794 cm.$^{-1}$ due to 5.0 mm. of chloral = 0.054
" " " " " " 0.49 mm. " chloroform = 0.000
" " " " " " carbon tetrachloride
= 0.650 − 0.054
= 0.596, equivalent to 0.57 mm. of carbon tetrachloride.

The deviations between the data for the synthetic mixtures and those obtained spectrophotometrically in Table IV are due mainly to the difficulty

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in preparing mixtures whose composition in the gas phase is accurately known. The chlorinated compounds dissolve to some extent in the Silicone grease used in the vacuum line and the Benolite cementing the sodium chloride windows to the pyrex optical cell. The extent of absorption is a function of the time of exposure of the compounds to grease, the surface area of the grease, and the pressure at which the gaseous sample is prepared. Under these circumstances, it is not feasible to make empirical corrections for the absorption effects.

A standard procedure in preparing and analyzing the samples was adhered to as closely as possible. While reproducible data were obtained in this way, it is felt that the elimination of stopcocks wherever possible would considerably increase the accuracy of analysis of these chlorinated compounds by infrared spectrophotometry.

*Spectra of Other Chlorinated Hydrocarbons*

With a view to extending these studies to more complex mixtures of chlorinated hydrocarbons, the infrared spectra of dichloromethane and methyl chloride have also been measured at 1 mm. and 10 mm. respectively under comparable experimental conditions.

The absorption bands in these compounds are relatively weak; dichloromethane showed maxima at 1277, 1262, 762, and 747 $cm.^{-1}$ and methyl chloride at 1370, 1340, 745, 726, and 710 $cm.^{-1}$

ACKNOWLEDGMENTS

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# PHYSICOCHEMICAL EFFECTS OF RADIO-FREQUENCY FIELDS[1]

By H. H. Yates[2] and C. A. Winkler

ABSTRACT

The outgassing of liquids has been studied under a variety of conditions including the application of a radio-frequency electric field. A large acceleration of the outgassing rate in the electric field was shown to result from convection currents established by the temperature gradient set up by the field. The significance of such a temperature gradient in a comparison of the chemical behavior in such a field with that under normal thermal conditions has been considered. When account was taken of the thermal gradients induced by the field, a field of approximately 2000 volts per cm. and 1.5 megacycles had no measurable effect on the rate of polymerization of styrene in bulk at 80°C.

## INTRODUCTION

In a previous paper from this laboratory (2) it was reported that the bulk polymerization of styrene was inhibited by as much as 80% in the presence of a radio-frequency electric field. In these experiments, as in commercial practice, temperature was measured with an alcohol thermometer, and it was believed that the observed inhibition could not be attributed to thermal effects. It was later found (9) that both alcohol and mercury thermometers, suspended in the vapors of a boiling liquid, have higher than normal readings in the electric fields used. A method was therefore devised by which a thermocouple–potentiometer arrangement was used to compare the temperature of a field reaction with that of a control reaction. Under conditions similar to those used in the polymerization study, the decomposition of benzoyl peroxide in toluene solution was apparently inhibited, although analytical difficulties at the low concentrations used seemed to be a source of considerable error. A red color appeared about an hour earlier in the field reaction than in the control reaction. When nitrogen was bubbled through the system, neither the control nor the field reaction suffered this color change.

These results were sufficiently interesting to encourage further study of a similar reaction, and the decomposition of benzene diazoacetate, described in detail by Waters and others (1, 3, 7, 12), was finally chosen for the purpose. The kinetics of this reaction may be studied over a wide range of concentrations by measuring the evolution of nitrogen. This eliminates the necessity for sampling the reaction mixture, with attendant readjustments to the electrical system.

## EXPERIMENTAL AND RESULTS

In preliminary experiments, both a control cell and a field cell were used, and the reactions were followed by measuring the increase in nitrogen pressure at constant volume in a partially evacuated system. At high concentrations, where the pressure increase was derived mainly from the decomposition of benzene diazoacetate, the effect of the field was negligible. However, at very low concen-

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*Contribution from the physical chemistry laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.*
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trations, where the pressure increase was due largely to the release of dissolved gas into the partial vacuum, the field caused a marked acceleration. Subsequent experiments established that the field caused a large increase in the rate of the outgassing process, which increased with the dielectric constant of the liquid, but was not significantly different for different gases. Improved reproducibility was necessary for a detailed study of the effect. In the method finally adopted a single cell was used, and the field was applied for only a part of each experiment. Nitrogen dissolved in methyl benzoate was the only system studied in detail by this more precise method.

The equipment for applying the radio-frequency field has been described by Bryce *et al.* (2). There was also a cell to hold the gas–liquid solution and a pressure measuring system. The cell was a pyrex cylindrical annulus about 10 cm. high, 6 cm. in outside diameter, and 1 cm. thick. It incorporated two outlets and a well. One outlet, fitted with a ground glass ball joint, was connected through a flexible spiral of 3 mm. tubing to the pressure measuring system. The other outlet, with a 10/30 standard taper joint, was used for a variety of purposes, including flushing, filling, saturating, and stirring. The well served to hold the thermocouple used for temperature determinations. Copper electrodes, fixed externally to the cell walls with liquid solder, formed a capacitor in which the dielectric was composed of the pyrex cell walls and the solution.

Pressures were measured on a mercury manometer connected directly to the cell. The mercury level in the pressure arm was maintained constant with a levelling bulb during an experiment. Partial evacuation of the system was accomplished by connecting it momentarily to an evacuated bulb of suitable size.

The cell was immersed in a constant temperature bath to within half an inch of the top of the outlets. Adequate flow of oil around the electrodes was ensured by a propeller attached to the end of a glass shaft extending down through the "core" of the cell. The temperature was determined by the thermocouple method (9). A potentiometer was maintained in balance with a thermocouple placed in an auxiliary thermostat at the desired temperature. A thermocouple was held near the same temperature by storing it in a well in the thermostat containing the cell. To determine the temperature of the solution, the second thermocouple was transferred to the cell just as the field was turned off. The potentiometer was immediately switched to record the temperature of this thermocouple, which was found to rise to the cell temperature in about three seconds, remain steady for about five to eight seconds, and then begin to fall as the heat supplied by the field was dissipated.

The cell was carefully cleaned and dried before each experiment. The quantity of solution used was just sufficient to cover the electrodes (about 90 ml.). The pressure attained after 24 hr. was adopted as the final value; subsequent increase of pressure was found to be negligible in an extended experiment.

It was assumed, following Schweitzer and Szebehely (11), that the rate of gas evolution would be proportional to the degree of supersaturation, which in this case was represented

$$\frac{d(\Delta p)}{dt} = k\,(\Delta p_\infty - \Delta p)$$

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where $\Delta p$ is the pressure increase at time $t$, $\Delta p_\infty$ is the final pressure increase, and $k$ is the rate constant. The integrated equation was written

$$\log \frac{\Delta p_\infty}{\Delta p_\infty - \Delta p} = k't$$

where $2.303\ k' = k$. The rate constants $k'$ were obtained by plotting $\log [\Delta p_\infty/(\Delta p_\infty - \Delta p)]$ against $t$.

In one set of experiments, the outgassing was allowed to proceed under normal conditions at 30.0°C. for 50 to 60 min. During the next five minutes the bath temperature was lowered to, and maintained at, 27.5°C. (this bath temperature gave a solution temperature of 30.0°C. in the field). At this time the field was turned on and left on until the outgassing was almost complete. The results of a typical experiment are shown in Fig. 1, A; the rate constants $k'$ obtained under a

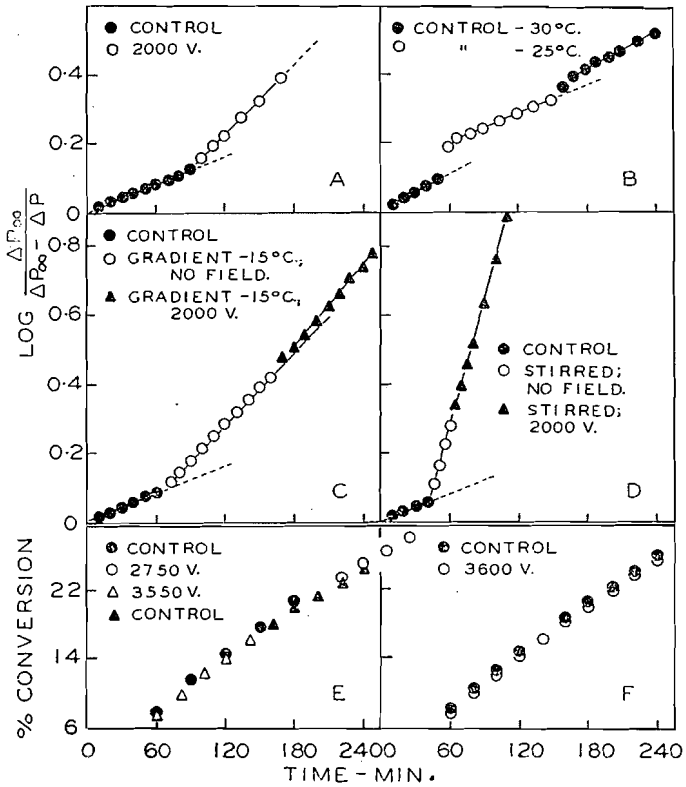



FIG. 1. The outgassing of a solution of nitrogen in methyl benzoate* at 30°C. (A-D), and the polymerization of styrene in bulk at 80°C. (E-F) for the conditions shown. "Control" indicates an unstirred system of uniform temperature in the absence of the field.

variety of conditions are compared in Table I. Exposure of the cell to the laboratory atmosphere prior to filling resulted in a value of 7 for the ratio of the rate constant in the field to the normal rate constant ($k'_f/k'_c$). Where such exposure

*The results shown in B were obtained when the solution was prepared externally and transferred to the cell under laboratory atmosphere. All other results were obtained when the solutions were prepared in the cell.

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TABLE I

A COMPARISON OF $k'_c$† (NORMAL) AND $k'_f$† (2000 V.) UNDER VARIOUS CONDITIONS AS NOTED IN COLUMN 1

| Condition | $k'_c$, min.$^{-1}$ | Deviation from mean | $k'_f$, min.$^{-1}$ | Deviation from mean | Ratio, $k'_f/k'_c$ |
|---|---|---|---|---|---|
| Saturated solution transferred to cell under atmospheric conditions | 0.00205 | 0.00035 | 0.0143 | 0.0016 | 6.98 |
| Saturated solution transferred to evacuated cell under vacuum | 0.00145 | 0.00003 | 0.00400 | 0.00033 | 2.76 |
| Solution in cell at end of 24 hr. experimental period resaturated with $N_2$ in cell | 0.00153 | 0.00017 | 0.00336 | 0.00012 | 2.20 |

†*All values of k' are the average of two determinations.*

was prevented the normal outgassing rate was decreased only slightly, but the ratio $k'_f/k'_c$ dropped from 7 to about 2.5.

In a second set of experiments the effects of temperature and stirring were studied. Temperature gradients were produced by sealing the "core" of the cell for the circulation of a second oil at a temperature different from that of the surrounding bath oil. Stirring was accomplished by the introduction of a ring type stirrer of 3 mm. pyrex rod with its shaft extending through the 10/30 standard taper joint. The stirrer was moved up and down by a small electromagnet surrounding a sealed tube fitted to the 10/30 joint.

The results of these experiments are illustrated in Fig. 1, B to D. A decrease in temperature from 30 to 25°C. caused a normal decrease in the outgassing rate, but the rate obtained during a cooling or a heating period was considerably greater than that when the temperature was held constant at either value.This effect was also noticed during the short cooling periods in the earlier experiments. A temperature difference of 15°C. between the cell walls caused an increase in the rate of outgassing roughly equivalent to that of the 2000 volt field, and application of the field under these conditions caused only a very slight further increase (Fig. 1, C). A temperature difference of 25°C. eliminated the effect of the field entirely. Stirring with an oscillation period of 13 sec. increased the rate ninefold and also eliminated the effect of the field (Fig. 1, D). An oscillation period of one second increased the rate 60-fold.

The effect of the field on the bulk polymerization of styrene was reinvestigated with the thermocouple–potentiometer method of temperature measurement. A field of 3600 volts and 1.5 megacycles was used, and the control temperature was set at 80°C. The benzoyl peroxide catalyst concentration used was that corresponding to the maximum effect reported by Bryce *et al.* (1 gm. per liter). A field of about 3600 volts was applied during the later part of one experiment, and during the earlier part of an otherwise similar experiment. As indicated in Fig. 1, E, the field had negligible effect on the polymerization. During the third experiment, the field was applied throughout the course of the polymerization except during the induction period. Fig. 1, F compares the results from this

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experiment with those from an otherwise similar one in which no field was used. Again, no field effect is indicated.

## DISCUSSION

### *The Outgassing Process*

The results of this investigation are best discussed in terms of a mechanism based on the premise that gas evolution from liquids is dependent on the presence of certain types of nuclei. Foreign particles, microbubbles, and even certain conditions existing in the container walls have been cited as active centers for the process (4, 5, 6, 8).

The mechanism of gas release at a nucleus remains vague, but existing evidence suggests that a nucleus acts as a discontinuity into which dissolved gas can evaporate. The movement of dissolved gas to a nucleus will occur by diffusion in a stagnant system or by a combination of diffusion and mass motion in an agitated system. For a given gas–liquid system at a given temperature, the rate of gas release at a nucleus will be constant, and the rate of the over-all process will depend jointly on the activity of the container wall and the degree of agitation.

In the present study, mechanical stirring increased the rate of gas evolution several-fold, as did also the stirring that resulted from convection currents established by temperature gradients. It is suggested that the increase in rate caused by the electric field was also due to convection currents arising from a temperature gradient. In this case the temperature gradient would result from the absorption of energy from the field, and its subsequent dissipation through the container walls to the bath oil.

This mechanism will explain the results obtained, as follows. For normal outgassing, diffusion would be the main rate controlling process, and differences in wall activity should cause only small differences in the rate of the process. In the field, however, convection would replace diffusion, and the wall activity would become rate controlling. Under these conditions, differences in wall activity should cause much larger differences in the outgassing rate. Hence the small changes in $k'_c$ produced by different methods of filling the cell, and the much larger changes in $k'_f$ (Table I).

There is also the possibility that the field affects the wall activity as a rate controlling factor, either by increasing the activity of the nuclei present, or by creating additional nuclei. If this were the case, however, some field effect should remain even in the presence of mechanical stirring. On the other hand, if the field acts only through the convection currents set up, its effect should become negligible in a sufficiently agitated system. The results of the second set of experiments show that the field had no effect on a well stirred system, nor when a 25°C. temperature difference was maintained across the cell. A slight residual effect remained when the temperature difference was only 15°C.

A comparison of the accelerations caused by field temperature gradients and thermally produced temperature gradients suggests that a field of 2000 volts is roughly equivalent to a temperature difference of 15°C. across the cell, or about 7°C. from the center of the cell to the walls. A temperature difference of this

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magnitude may be of great importance in investigations of a kinetic nature.

*Kinetic Studies in Alternating Electric Fields*

The absorption of energy from an alternating electric field by a liquid in a container, the walls of which are maintained at constant temperature, must result in temperature gradients in the liquid. In the absence of stirring, both conduction and natural convection contribute to transfer of energy from the system.

The kinetics of chemical reactions are normally studied under conditions of a constant uniform temperature throughout the reacting medium. Under these conditions the rate of a reaction of the simple type

$$n\,B \longrightarrow \text{products}$$

is described in terms of the concentration of reactant $B$ by the equation

$$[1] \qquad -\frac{dc}{dt} = kc^n$$

where $c$ is the concentration of reactant $B$ at time $t$, and $k$ and $n$ are the rate constants and order of the reaction respectively. This integrates to give

$$[2] \qquad c = g(c_0, n, k, t)$$

where $g$ denotes a functional relationship, and $c_0$ is the concentration of $B$ at zero time. For a liquid system the volume $V$ is essentially constant, and the total quantity of reactant is given by

$$[3] \qquad q = \int_V c\,dV = c.V,$$

whence from [1] and [3]

$$[4] \qquad -\frac{dq}{dt} = -V\frac{dc}{dt} = Vkc^n.$$

In an alternating electric field the temperature is not uniform, but is a function of position. Under these conditions $k$, which increases with temperature according to the Arrhenius equation

$$k = A\,e^{-E/RT},$$

and $c$, which is a function of $k$ (equation 2), both vary with position. Equations 1 and 2, therefore, describe the reaction only at some given point in the system, and the over-all reaction must be described by

$$[5] \qquad -\frac{dq}{dt} = -\frac{d}{dt}\int_V c^*\,dV = -\int_V \frac{dc^*}{dt}\,dV = \int_V k^*\,c^{*n}\,dV$$

in which the asterisks denote quantities which vary with position. This expression will be equivalent to equation 4 for the reaction at uniform temperature only if

$$[6] \qquad Vkc^n = \int_V k^*\,c^{*n}\,dV,$$

i.e. only if the uniform temperature $T$ is chosen so that $kc^n$ is equal to $\frac{1}{V}\int_V k^*c^{*n}dV$, the volume average of this expression for the nonuniform temperature.

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For a zero order reaction $n = 0$, and the required condition is

$$k = \frac{1}{V}\int_V k^* dV, \qquad 7]$$

or substituting for $k$ using the Arrhenius equation,

$$e^{-E/RT} = \frac{1}{V}\int_V e^{-E/RT^*} dV.$$

Equivalent expressions for the higher order reactions involve $t$ in such a way that the uniform temperature $T$ can be chosen to make the two reactions equivalent only at some instant of time, i.e. it is impossible to choose a constant uniform temperature to ensure thermal equivalence of control and field reactions.

When the temperature range in the field cell is not too great, the task of determining the uniform temperature for the control cell may be simplified by substituting for the Arrhenius equation the linear function

$$k = k_1 + a(T - T_1)$$

where $a$ is a constant, and $k_1$ and $T_1$ are corresponding values of the rate constant and temperature at some point within the given range. Substitution for this expression into equation 7 gives

$$T = \frac{1}{V}\int_V T^* dV.$$

Thus control and field reactions will approximate to thermal equivalence provided:

1. The reaction is zero order.
2. The control temperature is the volume average of the temperature in the field.

The effects of stirring and oxygen on the reaction must also be considered if a true field effect is to be isolated. Reactions affected by mixing must be stirred mechanically at a sufficient rate to ensure negligible effect due to convection. In a system capable of reaction with oxygen, the oxygen concentration will depend upon the rate at which it is used up and the rate at which it is absorbed. Schlapfer *et al.* (10) have reported that, even in a practically stagnant column of water, the absorption of air depends mainly upon convection. Such a system will be sensitive to mixing unless an inert atmosphere is used.

It is interesting to recall here the color effect observed in the studies with benzoyl peroxide mentioned previously (9). Although some inhibition of the decomposition of benzoyl peroxide in toluene solution was apparently caused by the field used, an orange color appeared much earlier in the "inhibited" system. The color did not arise when nitrogen was bubbled through the system and it now seems probable that the phenomenon was caused by a more rapid absorption of oxygen under the influence of the field.

The foregoing discussion indicates that the bulk polymerization of styrene should be suitable for investigation in alternating electric fields. It is zero order, and with the fields employed in this study use of the linear expression for $k$ should not lead to serious error. The major problem is the determination of the volume

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average temperature in the field. The method used by Bryce *et al.* (2) does not seem adequate because the thermometer bulb was located at the hottest point in the liquid (the top central part). Thus the control reaction took place at a temperature slightly higher than the volume average temperature in the field, and an apparent inhibition resulted. The thermocouple–potentiometer method, however, appears to be more satisfactory. Interaction of the field and thermocouple is prevented by momentarily turning off the field, while the temperature gradient is temporarily eliminated through stirring set up by introduction of the thermocouple, which is immersed to the mid-point. The absence of any field effect under these conditions suggests that the inhibition reported earlier (2) was probably a result of the method used for temperature determinations.

Indeed, neglect of temperature, or the use of improper methods for its determination, might well be responsible for many so-called field effects reported in the literature. Certainly in the absence of a precise description of the methods used for the determination of temperatures, the validity of reports claiming athermal effects produced by alternating electric fields is open to question.

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# THE REACTIONS OF ACTIVE NITROGEN WITH BUTENES[1]

By H. Gesser,[2] C. Luner,[3] and C. A. Winkler

ABSTRACT

The reactions of nitrogen atoms with butene-1, *cis*-butene-2, and isobutene at 88°C. and 240°C. were found to produce hydrogen cyanide, propylene, and ethylene as the main products, together with smaller amounts of butane, propane, ethane, methane, and hydrogen. Trace quantities were also obtained of acetylene, a $C_5$ hydrocarbon, and a mixture, probably of $C_6$ and $C_7$ hydrocarbons. The order of reactivities with nitrogen atoms was butene-1> *cis*-butene-2> isobutene. Increased temperature favored the reactions of butene-1 and *cis*-butene-2, but no noticeable increase in reactivity was observed with isobutene.

The reactions of active nitrogen with the lower saturated and unsaturated hydrocarbons have been discussed in previous papers from this laboratory and its marked reactivity attributed to nitrogen atoms (2-5). The reactions of active nitrogen with the butenes appeared to be of particular interest because of the opportunity for studying the effect that the position of the double bond might have on the reactivity of the hydrocarbon molecule in these reactions.

## EXPERIMENTAL

The apparatus was essentially similar to that described in the earlier papers. Preliminary experiments showed that hydrogen cyanide was absorbed quantitatively by ascarite (sodium hydroxide on asbestos) with the liberation of water of neutralization. The products of the reaction, after they had been trapped at the temperature of liquid nitrogen, were therefore cycled several times through a previously weighed and evacuated absorption tube containing ascarite, with anhydrous magnesium perchlorate on either side of the ascarite to absorb the liberated water. Hydrocarbon products were estimated by the low temperature distillation and combustion methods used in a previous study (4).

Butene-1, *cis*-butene-2, and isobutene, all of 99% purity, were obtained from the Ohio Chemical Company, Phillips Petroleum, and Polymer Corporation, respectively, and were used after a single bulb to bulb fractionation.

## RESULTS AND DISCUSSION

In all experiments, the flow rate of nitrogen was $1.17 \times 10^{-4}$ mole per sec., and the pressure in the system was 1.7 mm. of mercury.

The results are plotted in Fig. 1. The yields of methane and hydrogen were small and erratic, and varied from $0.1 \times 10^{-6}$ to $0.5 \times 10^{-6}$ mole per sec. and from $1 \times 10^{-6}$ to $3 \times 10^{-6}$ mole per sec. respectively. Acetylene, a $C_5$ hydrocarbon fraction, and a higher boiling fraction (surmised to be a mixture of $C_6$ and $C_7$ hydrocarbons) were obtained in trace quantities. The carbon balance showed an extreme variation from 96% to 104%, with an average value of 99.7%. The average hydrogen balance was 95%.

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[2] *Holder of a National Research Council Studentship.*
[3] *Holder of Quebec Provincial Scholarships, 1948-51.*



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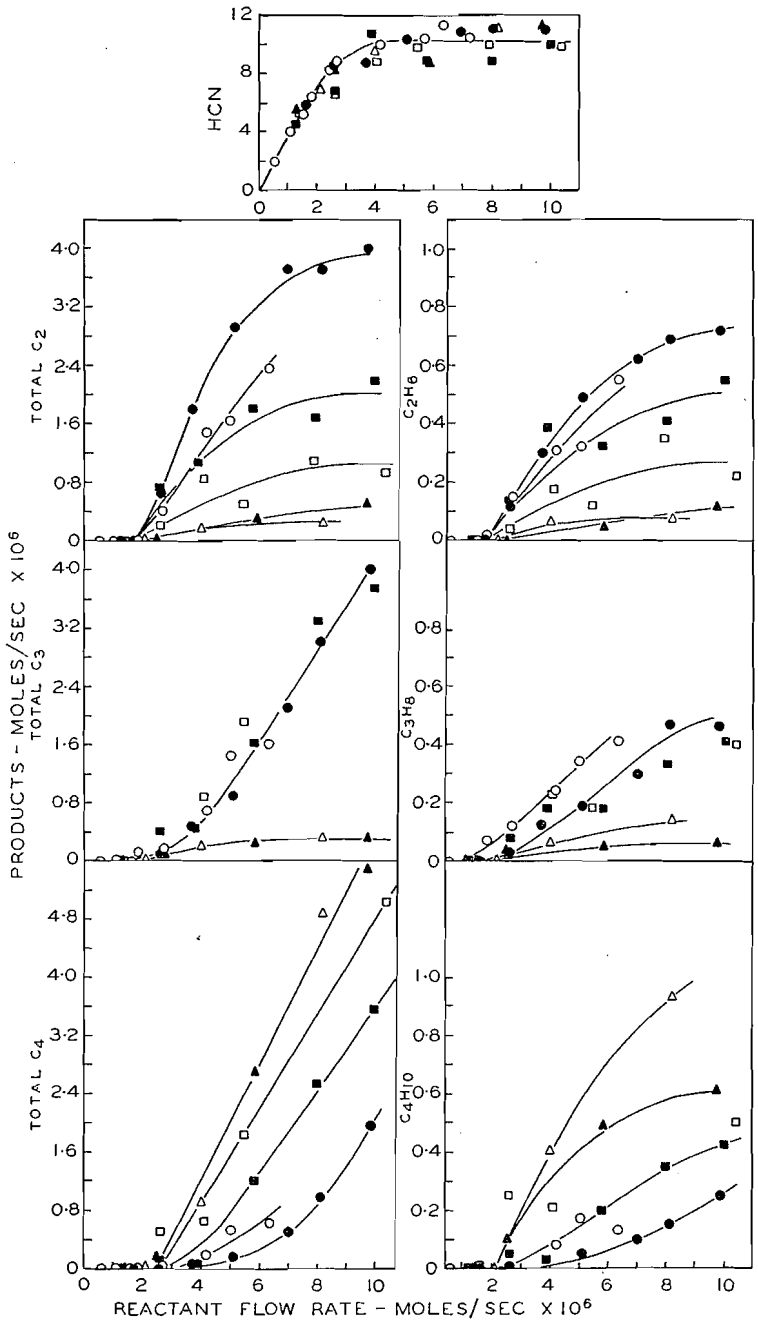



FIG. 1. Rate of formation of various products in the nitrogen atom – butene reactions.

| Reactant | Temp. = 88°C. | Temp. = 240°C. |
|---|---|---|
| Butene-1 | ○ | ● |
| *cis*-Butene-2 | □ | ■ |
| Isobutene | △ | ▲ |

The yields of hydrogen cyanide (Fig. 1) show that, at hydrocarbon flow rates above about $4 \times 10^{-6}$ mole per sec., the butenes reacted to consume completely the available nitrogen atoms. At lower hydrocarbon flow rates the mole ratio of hydrogen cyanide produced to hydrocarbon consumed was about 4 : 1. The maximal yield of hydrogen cyanide was $10 \pm 1 \times 10^{-6}$ mole per sec.; this value may be compared with an average atom flow rate of $15 \pm 3 \times 10^{-6}$ mole per sec. as determined by measurements with the Wrede gauge.

Previous studies of the reaction of nitrogen atoms with hydrocarbons have shown that unsaturated hydrocarbons are much more reactive with nitrogen atoms than saturated hydrocarbons. It has previously been suggested, and the suggestion supported by rather convincing argument, that the point of attack of the nitrogen atom is the double bond, with the formation of a collision complex. It would therefore be expected that the butenes would behave in a similar manner.

The absence of significant yields of higher hydrocarbons in the ethylene–nitrogen atom reaction (3, 5) and in the propylene – nitrogen atom reaction (4), and the formation of only trace quantities of $C_5$ and higher hydrocarbons in the present reactions, makes it reasonable to assume that the propylene formed is a primary hydrocarbon product in the reaction of nitrogen atoms with the butenes.

For butene-1, the primary reaction step may be represented as follows:

$$CH_3CH_2CH = CH_2 + N \rightarrow \left[ CH_3CH_2\underset{\diagdown\,\diagup}{CH}\!-\!CH_2 \right] \rightarrow CH_3CH_2\dot{C}H: + H + HCN \qquad [1]$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad N$$

The propylidene radical, by analogy with the ethylidene radical, might be expected to rearrange immediately to propylene.

$$CH_3CH_2\dot{C}H: \rightarrow CH_3CH = CH_2 \qquad [2]$$

For isobutene the primary reaction step may be represented as:

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C = CH_2 + N \rightarrow \left[ \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C - CH_2 \right] \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\dot{C}: + HCN + H \qquad [3]$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad N$$

$$CH_3\ddot{C}CH_3 \rightarrow CH_3CH = CH_2 \qquad [4]$$

Reaction [4] is reasonable since Bawn and Dunning (1) found that sodium atoms react with 2,2-dibromopropane with weak chemiluminescence which was associated with a hydrogen shift, probably due to the following reactions:

$$CH_3CBrCH_3 + Na \rightarrow CH_3\ddot{C}CH_3 + NaBr$$

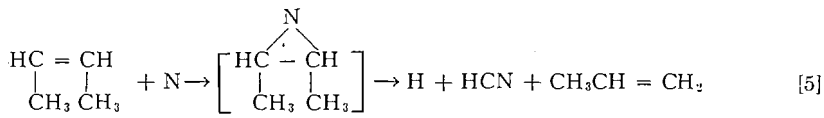
$$CH_3\ddot{C}CH_3 \longrightarrow CH_3CH = CH_2 + h\nu$$

Hence the isopropyl diradical apparently does not have an appreciable life and rearranges to propylene immediately upon formation.

The primary reaction step for *cis*-butene-2 with nitrogen atoms to yield propylene cannot consist of a simple rupture at the double bond since this would result in the formation of ethylene as one of the primary products. It is therefore suggested that the nitrogen atom reacts with *cis*-butene-2 at the double bond to form a collision complex of the same type as that formed with other olefins, but

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that a rearrangement within the complex occurs simultaneously with ejection of a secondary hydrogen atom and dissociation of the complex into hydrogen cyanide and propylene.



$$\begin{matrix} HC = CH \\ | \quad | \\ CH_3 \; CH_3 \end{matrix} + N \rightarrow \left[ \begin{matrix} HC - CH \\ | \quad | \\ CH_3 \; CH_3 \end{matrix} \right] \rightarrow H + HCN + CH_3CH = CH_2 \qquad [5]$$

The propylene formed in all three butene reactions might be considered to undergo further reactions with nitrogen atoms in the manner suggested by Trick and Winkler (4) to form ethylene, which in turn may further react with nitrogen atoms to form methylene radicals.

Reactions [1], [3], and [5] indicate that hydrogen atoms are a primary product of the reactions of nitrogen atoms with the butenes. The parallel trends in total and in saturated hydrocarbon products seem to indicate that the most important reaction leading to the formation of the saturated compounds is hydrogenation of the corresponding unsaturated hydrocarbon.

Acetylene, in the trace amounts observed, is probably formed from the dehydrogenation of ethylene by hydrogen atoms, while the methane formed may be adequately accounted for by hydrogenation of methylene radicals.

It is inherent in the proposed mechanisms that for every molecule of hydrogen cyanide formed, one atom of hydrogen is produced. Since the rate of production of hydrogen cyanide is constant, beyond the butene flow rate corresponding to complete nitrogen atom consumption, the rate of formation of hydrogen atoms in this region is also constant. Hence at high flow rates of butene, it would be expected that the yields of the saturated products should be constant if they are formed as postulated. This conforms, in general, to the observed behavior. However, only about one-quarter of the atomic hydrogen produced is used to form saturated products and methane. This is probably due to the competitive recombination reaction of hydrogen atoms, by a three-body collision with a nitrogen molecule;

$$H + H + N_2 \quad \rightarrow \quad H_2 + N_2.$$

This reaction appears to be almost independent of flow rate of butene, probably because of the large excess of nitrogen molecules in the reaction mixture.

The tendency for the curves of total $C_2$ hydrocarbon to level off is probably due to the fact that consecutive steps are involved in the reaction. Thus if the nitrogen atoms are in excess, the propylene formed in the primary reaction can further react to form ethylene. However if the butenes were in sufficiently great excess, essentially all the nitrogen atoms may be expected to be consumed by the primary reaction step to form only propylene and no ethylene. Hence the $C_2$ curves should show a maximum, and decrease to zero at sufficiently large carbon–nitrogen atom ratios. In practice it was impossible to work at the high butene flow rates necessary to realize such a maximum experimentally.

Most of the $C_4$ hydrocarbon is unreacted butene in both reactions. With iso butene there is practically no change in amount of $C_4$ hydrocarbon recovered as the temperature is increased (i.e. amount of isobutene reacted remains essentially

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constant), while with butene-1 and *cis*-butene-2 the amount of $C_4$ hydrocarbon decreased significantly with increase of temperature (i.e. the amounts of butene-1 and *cis*-butene-2 reacted increased significantly). This would indicate that the activation energy for the reaction of isobutene with nitrogen atoms is somewhat less than for the analogous reactions of butene-1 and *cis*-butene-2. It would seem necessary, then, to attribute the lower rate of the isobutene reaction to a smaller steric factor.

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# SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

## PART VI. FORMALDEHYDE-$d_2$ AND FORMALDEHYDE-$d$[1]

By R. A. B. Bannard[2], A. T. Morse[3], and L. C. Leitch[3]

ABSTRACT

Formaldehyde-$d_2$ was prepared in 62.5% over-all yield from 1,2-dibromoethane-$d_4$ via the corresponding glycol diacetate and glycol. Formaldehyde-$d$ was prepared by the same method from *sym*-1,2-dibromoethane-$d_2$. From the high isotopic purity of the deuterated formaldehydes obtained, it has been definitely established that it is a pair of hydrogen atoms from the hydroxylic groups of the glycols that generates acetic acid during dialdehyde fission with lead tetra-acetate. The densities and refractive indices of the deuterated ethylene glycol diacetates and ethylene glycols used as intermediates in the synthesis of the deuterated formaldehydes have been determined.

## INTRODUCTION

This investigation was undertaken to obtain a quantity of formaldehyde-$d_2$ which was required by Steacie and co-workers (25) for use in the study of hydrogen abstraction reactions. A synthetic method was required which would provide formaldehyde-$d_2$ of maximum deuterium content in a physical state from which the monomer could be readily generated for use in photochemical reactions. Further, it was desirable that the over-all yield be high, that the starting material be readily available in a high state of isotopic purity, and that intermediates should not be prone to loss of deuterium by exchange reactions during manipulation.

In 1938 Ebers and Nielsen (7) prepared formaldehyde-$d_2$ by irradiating a mixture of carbon monoxide and deuterium in a quartz mercury arc, but gave no experimental details. The formaldehyde-$d_2$ thus obtained was contaminated with glyoxal and required considerable purification before it could be used in spectroscopic studies (7). It was therefore considered that this method of preparation would not be suitable for the present investigation.

It was reported by Klar (17) that both hydrogen atoms in formaldehyde are readily exchangeable by the reaction shown in Equation 1.

$$CH_2O + D_2O \rightleftarrows CD_2O + H_2O \qquad [1]$$

Subsequently, Wirtz and Bonhoeffer (31) found that this exchange process does not occur even in the presence of acidic or alkaline catalysts after several months' equilibration. The latter results were confirmed by Waters (30) who obtained $\alpha$-polyoxymethylene containing no deuterium by polymerization of formaldehyde in deuterium oxide under either acidic or alkaline conditions.

The availability of paraformaldehyde by the catalytic oxidation of methanol (27, pp. 1–17) has made unnecessary, heretofore, the development of laboratory methods for the direct synthesis of anhydrous formaldehyde. Application of the catalytic method to the preparation of formaldehyde-$d_2$ was excluded because the necessary deuteromethanol is not readily available.

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*Contribution from the Division of Chemistry (Applied), National Research Laboratories. Issued as N.R.C. No. 2936.*
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The thermal decomposition of metallic formates to either methanol or formaldehyde was extensively studied before the successful application of the high pressure methanol synthesis (21). The best yield of formaldehyde was obtained from stannous formate which decomposed at 180° C. according to Equation 2 (9).

$$3(H\text{–}\overset{\overset{O}{\|}}{C}\text{–}O)_2Sn \xrightarrow{\Delta} CH_2O + HCOOCH_3 + 3SnO + 3CO_2 \qquad [2]$$

Some formaldehyde-$d_2$ was obtained by this method in the present work. However, yields were not sufficiently high to warrant a detailed study because, according to Equation 2, at least two-thirds of the deuterium initially employed would be converted to methyl-$d_3$ formate-$d$.

Some interest has recently arisen in the synthesis of formaldehyde-$C^{14}$. Jones and Skraba (15) subjected methanol-$C^{14}$ to acetylation with acetyl chloride to form methyl-$C^{14}$ acetate. Chlorination and hydrolysis of the latter substance followed by dilution with carrier formalin gave, on distillation, paraformaldehyde containing paraformaldehyde-$C^{14}$. Cox and Warne (3) have more recently prepared formaldehyde-$C^{14}$ in aqueous solution by oxidative fission of ethylene-$C^{14}$ glycol with sodium bismuthate.

A serious objection to the application of the two foregoing methods is that the formaldehyde-$C^{14}$ is obtained as a dilute aqueous solution. According to Walker (27, pp. 58–63), the isolation of monomeric formaldehyde from aqueous solutions by distillation is not realizable in practice, although it is theoretically possible. Under the best conditions of formaldehyde recovery, the end product is paraformaldehyde containing 7% combined water (13). Isolation via derivatives might be helpful in effecting concentration without substantial loss but regeneration of the formaldehyde by hydrolysis would still necessitate isolation as paraformaldehyde. To obtain good yields of anhydrous formaldehyde it would first be necessary to prepare alkali-precipitated $\alpha$-polyoxymethylene from the paraformaldehyde (28). The yield in this step is, at best, only 58% of theoretical (24). The conversion of alkali-precipitated $\alpha$-polyoxymethylene to anhydrous monomeric or polymeric formaldehyde has been elaborated by Walker (28). These considerations made any synthetic method in which formaldehyde-$d_2$ is generated in aqueous solution appear most unattractive and expensive. It was, therefore, considered essential to develop a method which would produce directly formaldehyde in an anhydrous condition.

The cleavage of ethylene glycol to two moles of formaldehyde can be carried out nearly quantitatively. Reagents which must be used in aqueous solution, such as periodic acid (14, 19), sodium bismuthate (10, 22, 3), the unstable trivalent silver ion (10), and chromyl chloride (23), were ignored because of the difficulty of obtaining a good yield of anhydrous formaldehyde from the resulting solution (see above). Hence attention was centered on the use of lead tetraacetate in organic solvents (4, 5).

In a recent patent, Drewitt (6) claims to have obtained almost quantitative yields of formaldehyde by mixing red lead, glacial acetic acid, and ethylene glycol

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at room temperature, followed by heating at 60–70° C. with vigorous stirring until the red lead dissolved. Experiments were performed according to Drewitt's directions but in no case was monomeric formaldehyde isolated by heating the resultant solution under reflux with adequate facilities for condensing volatile effluent gases. It was possible to isolate small amounts of formaldehyde polymer on fractionation of the solution, but the yields were too low (15%) to warrant further study of the method. Drewitt's claim (6) must refer to the yield of formaldehyde in solution, available for reaction, but not isolable as anhydrous formaldehyde.

Hockett and co-workers (12) obtained formaldehyde from the carbohydrate "arlitan" by a technique in which the carbohydrate, dissolved in a small quantity of glacial acetic acid, was added to dry lead tetraacetate. The formaldehyde was swept out of the reaction system by heating the mixture under reflux in a slow current of dry air. The effluent gases were adsorbed in an acidic 2,4-dinitrophenylhydrazine solution, and the quantity of formaldehyde evolved estimated as the 2,4-dinitrophenylhydrazone. By this method 62% of the theoretical yield of formaldehyde was obtained. Control experiments were also performed using ethylene glycol as substrate. The yield of formaldehyde was not reported in this instance but the authors state that the procedure and apparatus are not wholly satisfactory (12). Acetic acid is known to form loose addition compounds with formaldehyde which are probably monoesters of methylene and polyoxymethylene glycols (27, p. 191). Furthermore, solutions of formaldehyde in hydroxylic solvents do not evolve formaldehyde quantitatively on heating (28). However, solutions of formaldehyde in nonhydroxylic solvents evolve monomeric formaldehyde gas almost quantitatively on warming to room temperature (27, p. 28). Evidently, maximum yields of formaldehyde from ethylene glycol by oxidative cleavage with lead tetraacetate would most probably be realized in a nonhydroxylic solvent. Benzene was selected as solvent because it can be readily dried and dissolves lead tetraacetate more readily than most other nonhydroxylic solvents (5).

Glycol cleavage with lead tetraacetate proceeds only if the hydroxyl groups of the glycol are unsubstituted (5). It was logical to conclude from this observation that the two hydrogen atoms lost from the glycol during dialdehyde cleavage, which appear ultimately as acetic acid, are hydrogen atoms originally bound to oxygen rather than to carbon. This view is in agreement with that of Waters (29), who considers that primary attack by the lead tetraacetate is at a hydroxylic and not a carbon-bound hydrogen atom. It was therefore not considered necessary to prepare ethylene-$d_4$ glycol-$d_2$ as starting material for the synthesis of formaldehyde-$d_2$, because two deuterium atoms would merely be lost as acetic acid-$d$ during dialdehyde cleavage. Attention was therefore turned to the synthesis of ethylene-$d_4$ glycol.

1,2-Dibromoethane-$d_4$ (I) was chosen as starting material for the preparation of ethylene-$d_4$ glycol, since it was readily available in a high state of isotopic purity by the method of Leitch and Morse (18). The synthetic scheme is shown in Equations 3, 4, and 5.

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$$\begin{array}{l} CD_2Br \\ | \\ CD_2Br \end{array} + 2CH_3COOK \rightarrow \begin{array}{l} CD_2OCOCH_3 \\ | \\ CD_2OCOCH_3 \end{array} + 2KBr \qquad [3]$$

I II

$$\begin{array}{l} CD_2OCOCH_3 \\ | \\ CD_2OCOCH_3 \end{array} + 2C_2H_5OH \xrightarrow{Na} \begin{array}{l} CD_2OH \\ | \\ CD_2OH \end{array} + 2CH_3COOC_2H_5 \qquad [4]$$

III

$$\begin{array}{l} CD_2OH \\ | \\ CD_2OH \end{array} + Pb(OCOCH_3)_4 \rightarrow \underset{IV}{2CD_2O} + Pb(OCOCH_3)_2 + 2CH_3COOH \qquad [5]$$

Pilot experiments were first performed with undeuterated substances to establish the range of yields to be expected for the syntheses with deuterated compounds to be undertaken later.

Ethylene glycol diacetate was prepared in 88.5% yield by the action of fused potassium acetate on 1,2-dibromoethane, using a modification of the method of Henry and Henry (11). The use of silver acetate in this reaction gave greatly reduced yields (32). Ethylene glycol diacetate was converted to ethylene glycol in 93.0% yield by a modification of the transesterification procedure of Bainbridge (1). An attempt to obtain ethylene glycol from 1,2-dibromoethane by oxidation with silver oxide was unsuccessful. This result agrees with the previous observations of Beilstein and Wiegand (2). Formaldehyde was prepared in 80% yield by cleavage of the ethylene glycol with lead tetraacetate in benzene suspension heated under reflux. The product was obtained first as anhydrous gas which was condensed, distilled *in vacuo*, and redistilled *in vacuo* into anhydrous ether. The formaldehyde dissolved in the ether polymerized slowly to eu-polyoxymethylene on standing at 0° C. in a sealed tube for three days. The over-all yield of formaldehyde, based on 1,2-dibromoethane, was 66%.

Difficulty was at first experienced with the polymerization step and several explosions resulted by allowing the trap containing formaldehyde solution in ether to warm too rapidly (16). This hazard was at first overcome by conducting the polymerization in ether at −80° C. with addition of *n*-butylamine as polymerization catalyst (28). It was found, however, that the polymer thus obtained could not be depolymerized by heating *in vacuo*. Consequently, addition of the polymerization catalyst was omitted in subsequent preparations in favor of polymerization at 0° C.

In a similar manner *sym*-1,2-dibromoethane-$d_2$ was converted to *sym*-ethylene-$d_2$ glycol diacetate in 90.0% yield. Transesterification of the latter substance gave 81.5% of *sym*-ethylene-$d_2$ glycol, oxidative cleavage of which produced formaldehyde-*d* as anhydrous polymer in 76% yield.

1,2-Dibromoethane-$d_4$ (I) was converted to ethylene-$d_4$ glycol diacetate (II) in 94.0% yield, transesterification of which produced an 88.5% yield of ethyl-

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ene-$d_4$ glycol (III). Oxidative cleavage of the latter substance produced a 75% yield of formaldehyde-$d_2$ (IV) as anhydrous polymer.

The fact that the yield of formaldehyde is not quantitative by the method elaborated in this paper may be readily explained by the assumption that some formaldehyde is retained in solution by the acetic acid which is generated in accordance with Equation 5. The lower yields which Hockett and co-workers obtained (12) seem to substantiate this view. It was noted that the residual benzene solution possessed a definite odor of formaldehyde even after prolonged boiling to the point where no further liquid formaldehyde was being condensed by the cooling system. The same phenomenon was observed in the unsuccessful attempts to evolve monomeric formaldehyde by oxidative fission in acetic acid media. A quantitative yield of monomer could only be realized by neutralizing the acetic acid as it is generated. The basic substance used for this purpose must not promote the irreversible polymerization of the monomer.

The isotopic purity of the deuterated 1,2-dibromoethanes used as starting materials was determined by mass spectrometer analysis, whereas the isotopic purity of the deuterated formaldehydes was established by conversion to deuterated methylene chlorides, followed by mass spectrometer analysis. Since the isotopic purity of the formaldehyde-$d_2$ exceeded 98%, it is evident that it is the hydroxylic hydrogen atoms of the glycol which are eliminated as acetic acid during oxidative fission with lead tetraacetate.

The deuterium content of the deuterated ethylene glycol diacetates and ethylene glycols could not be determined by their mass spectra. However, the densities and refractive indices of the deuterated substances in relation to the same physical constants for the undeuterated compounds should serve as an indication of isotopic purity. McLean and Adams (20) developed an equation by means of which the densities of deuterated organic compounds can be calculated if the extent of deuterium substitution and density of the ordinary compound are known. Table I shows the observed densities for the deuterated

TABLE I

DENSITIES AND REFRACTIVE INDICES OF ETHYLENE GLYCOL DIACETATES AND ETHYLENE GLYCOLS

| Compound | Refractive index, $n_D^{20}$ | Density, $d_4^{20}$ | |
|---|---|---|---|
| | | Calculated | Found |
| Ethylene glycol diacetate | 1.4154 | | 1.1051; 1.1052 |
| *sym*-Ethylene-$d_2$ glycol diacetate | 1.4150 | 1.1204 | 1.1210; 1.1211 |
| Ethylene-$d_4$ glycol diacetate | 1.4147 | 1.1356 | 1.1372; 1.1371 |
| Ethylene glycol | 1.4313 | | 1.1137; 1.1135 |
| *sym*-Ethylene-$d_2$ glycol | 1.4302 | 1.1496 | 1.1507; 1.1505 |
| Ethylene-$d_4$ glycol | 1.4293 | 1.1858 | 1.1895; 1.1894 |

ethylene glycol diacetates and ethylene glycols in relation to those calculated by McLean and Adams' equation. The refractive indices of the compounds are also given in this table.

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In Table I it is noted, as would be expected, that the densities increase progressively as the degree of substitution of deuterium for hydrogen increases. The effect of deuterium substitution on the densities of the glycols is much greater per deuterium atom introduced than in the case of the glycol diacetates because of the much higher molecular weights of the latter substances.

The densities found agree well with the calculated values in the case of the $d_2$ compounds but not for the $d_4$ compounds. In all cases the observed densities exceed the calculated values. These results differ from those of McLean and Adams (20) who found that where the observed and calculated values were in poor agreement, the calculated always exceeded the observed. The discrepancies were attributed to one of two causes (20). Either the deuterated compounds were not of sufficiently high isotopic purity, or the fundamental assumption that the molecular volumes of hydrogen and deuterium in organic compounds are identical—made by McLean and Adams in developing their equation—was invalid, and that the molecular volumes of deuterated compounds must exceed those of nondeuterated compounds. In the light of the results of the present investigation both of these explanations appear inadequate since the error is in the wrong direction. It is certain, however, that such calculations cannot be relied upon as an absolute measure of isotopic purity, and further studies along this line are necessary to determine the cause of the discrepancies.

## EXPERIMENTAL

### *Ethylene Glycol Diacetate*

Sixty gm. (0.612 mole) of fused potassium acetate, 63.0 gm. (0.335 mole) of 1,2-dibromoethane, and 19 cc. of glacial acetic acid were mixed in a 500 cc. round-bottomed flask fitted with a reflux condenser protected by a calcium chloride drying-tube. The mixture was heated under reflux for three hours, after which the liquid portion was removed by distillation, first at atmospheric pressure (60 cc.) and finally at 20 mm. pressure (2 cc.). The distillate was transferred to a 500 cc. round-bottomed flask containing 80.0 gm. (0.816 mole) of fused potassium acetate and 60.0 gm. (0.309 mole) of 1,2-dibromoethane. The mixture was heated under reflux for three hours, following which the liquid portion was distilled as described above, yielding 100 cc. of distillate at atmospheric pressure and a further 3.7 cc. at 20 mm. pressure. The combined distillates were fractionated at atmospheric pressure and the fraction of b.p. 182–188° C. (mostly at 186–188° C.) was retained. The column and pot residue were extracted with anhydrous ether, and the extract combined with the above-mentioned fraction. The resultant solution was fractionated *in vacuo* yielding 84.5 gm. (88.5%) of colorless liquid, b.p. 91–93° C. at 23 mm.; $n_D^{20}$ 1.4154; $d_4^{20}$ 1.1051, 1.1052. Taylor and Rinkenbach (26) report the refractive index of ethylene glycol diacetate as $n_D^{20}$ 1.4150.

### *sym-Ethylene-$d_2$ Glycol Diacetate*

The procedure was the same as for the preparation of ethylene glycol diacetate except that 50.0 gm. (0.263 mole) of *sym*-1,2-dibromoethane-$d_2$, 59.0 gm. (0.602 mole) of fused potassium acetate, and 8 cc. of glacial acetic

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acid were used. Ethylene-$d_2$ glycol diacetate was obtained as a colorless liquid (35.0 gm.; 90.0%) b.p. 185–188° C.; $n_D^{20}$ 1.4150; $d_4^{20}$ 1.1210, 1.1211. The *sym*-1,2-dibromoethane-$d_2$ used in this preparation was found to contain 95.5 mole % $C_2D_2H_2Br_2$ by mass spectrometer analysis.

*Ethylene-$d_4$ Glycol Diacetate*

The procedure was the same as for the preparation of ethylene glycol diacetate except that 51.0 gm. (0.265 mole) of 1,2-dibromoethane-$d_4$, 59.0 gm. (0.602 mole) of fused potassium acetate, and 8 cc. of glacial acetic acid were used. Ethylene-$d_4$ glycol diacetate was obtained as a colorless liquid (37.4 gm.; 94.0%), b.p. 186–188° C.; $n_D^{20}$ 1.4147; $d_4^{20}$ 1.1372, 1.1371. The 1,2-dibromoethane-$d_4$ used in this preparation was found to contain 97.9 mole % $C_2D_4Br_2$ by mass spectrometer analysis.

*Ethylene Glycol*

A sodium ethoxide solution was prepared—from 0.5 gm. of sodium and 200 cc. of absolute ethanol—in a 500 cc. round-bottomed flask equipped with a reflux condenser protected by a calcium chloride drying tube. A solution of 43.8 gm. (0.300 mole) of ethylene glycol diacetate in 100 cc. of absolute ethanol was added at room temperature to the sodium ethoxide solution, and the resultant solution heated under reflux for six hours. The ethyl acetate and most of the ethanol were removed by distillation at atmospheric pressure. The residue was transferred to a 50 cc. modified Claisen flask and fractionated *in vacuo* when 17.3 gm. (93.0%) of ethylene glycol was obtained as a colorless liquid; b.p. 99–104° C. at 22–23 mm.; $n_D^{20}$ 1.4313; $d_4^{20}$ 1.1137, 1.1135. Gallaugher

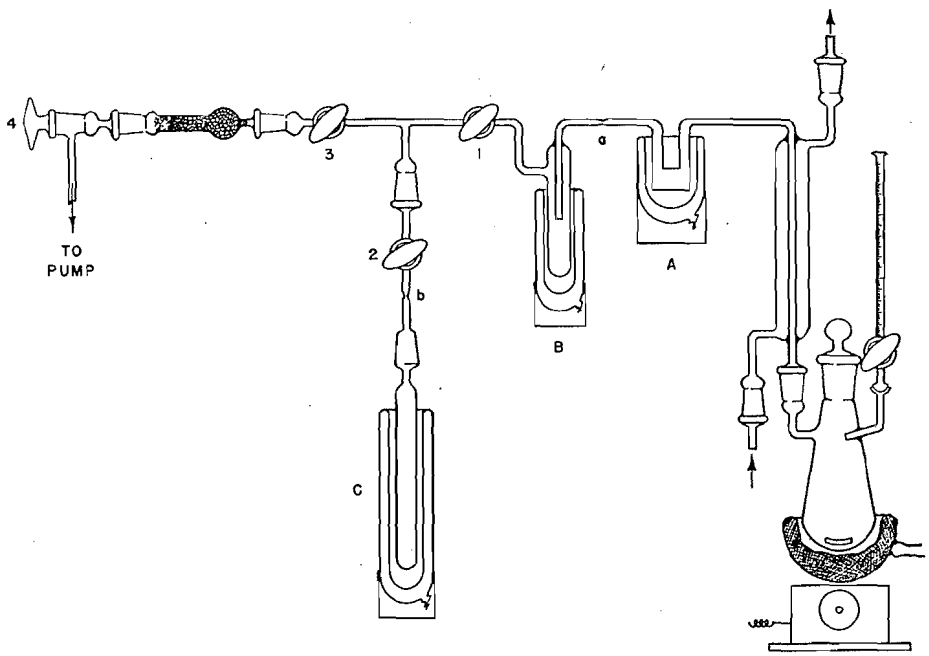



FIG. 1. Apparatus for preparation of formaldehyde-*d* and formaldehyde-$d_2$.

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and Hibbert (8) report the refractive index of ethylene glycol as $n_D^{20}$ 1.4314.

*sym-Ethylene-$d_2$ Glycol*

The procedure was the same as for the preparation of ethylene glycol except that 29.0 gm. (0.196 mole) of *sym*-ethylene-$d_2$ glycol diacetate, 240 cc. of absolute ethanol, and 0.6 gm. of sodium were used. *sym*-Ethylene-$d_2$ glycol was obtained as a colorless liquid (10.2 gm.; 81.6%); b.p. 86–87° C. at 8 mm.; $n_D^{20}$ 1.4302; $d_4^{20}$ 1.1507; 1.1505.

*Ethylene-$d_4$ Glycol*

The procedure was the same as for ethylene glycol except that 35.5 gm. (0.236 mole) of ethylene-$d_4$ glycol diacetate, 250 cc. of absolute ethanol, and 0.5 gm. of sodium were used. Ethylene-$d_4$ glycol was obtained as a colorless liquid (13.8 gm.; 88.5%) b.p. 86–87° C. at 8 mm.; $n_D^{20}$ 1.4293; $d_4^{20}$ 1.1895, 1.1894.

*Formaldehyde*

The apparatus was assembled as shown in Fig. 1. Lead tetraacetate, 56 gm. (0.12 mole) was placed in the reaction flask and the system evacuated to 0.05 mm. pressure for 30 min. while the apparatus was heated gently with a bare flame to remove moisture. Dry air was introduced through stopcock No. 4 and 200 cc. of anhydrous reagent benzene was added via the burette. Stirring was begun, water at 0° C. was circulated through the condenser, traps 1 and 2 were immersed in dry ice and acetone, and the mixture was heated under gentle reflux. Ethylene glycol, 6.2 gm. (0.10 mole), was added dropwise over a 15 min. period by means of the burette. During this period, the originally dark brown mixture became pale yellow and a white precipitate of lead diacetate separated. Simultaneously, liquid formaldehyde collected in trap A, and formaldehyde polymer appeared on the upper walls of the condenser and delivery tube leading to trap A. The burette was rinsed with 10 cc. of anhydrous reagent benzene, and the mixture was heated under reflux with stirring for a further hour. The reaction vessel was cooled in an ice bath, and the formaldehyde polymer which had formed on the upper walls of the flask depolymerized by gentle heating with a bare flame. The reaction flask was disconnected, the lower end of the condenser closed by means of a cap, trap B immersed in liquid nitrogen, and stopcock No. 1 shut. The system was evacuated to 0.1 mm. pressure, and stopcock No. 1 opened very slowly to minimize loss of formaldehyde during evacuation of the remainder of the system to 0.1 mm. pressure. Stopcock No. 1 was shut and the liquid formaldehyde distilled into trap B by allowing trap A to warm slowly after removal of the dry ice and acetone from the latter. The rate of distillation was controlled by occasional immersion of trap A in dry ice and acetone. After the liquid formaldehyde had distilled, the condenser jacket was heated with nitrobenzene under reflux to depolymerize the formaldehyde polymer which had collected on the walls. At the same time, trap A and the delivery tube leading to trap B was heated gently with a bare flame for the same purpose. Trap B was sealed off at constriction *a*. Trap C, containing 20 cc. of anhydrous reagent ether, was connected to the system, evacuated to 0.1 mm. pressure. Stopcock No. 3 was shut, the ether allowed to melt, then

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trap C was cooled in dry ice and acetone. The formaldehyde was distilled into trap C after opening stopcock No. 1. Trap C was sealed off at constriction *b*. The trap was kept overnight in dry ice and acetone at −78° C., throughout the following day at −25 to −10° C., then for three days at 0° C. during which time the polymer separated as a white flocculent solid. The trap was cooled once more in dry ice and acetone, opened, inserted on a vacuum line and evacuated. The ether was distilled slowly from the polymer into another trap immersed in liquid nitrogen. Distillation of ether was continued until the trap containing the formaldehyde polymer was at 35° C. Formaldehyde, 4.8 gm. (80%), was thus obtained as a colorless polymeric powder. Found % $CH_2O$; 100.1; 99.8%.

*Formaldehyde-d*

*sym*-Ethylene-$d_2$ glycol (6.2 gm.; 0.10 mole) was oxidized in exactly the same manner. Formaldehyde-*d*, 4.65 gm. (75%), was obtained as colorless polymer, which on treatment with phosphorus pentachloride gave methylene-*d* chloride of the following composition, as determined by mass spectrometer analysis:

$$93.3 \pm 0.2 \text{ mole \% } CHDCl_2.$$

These figures establish that the formaldehyde-*d* also contains 93.3 ± 0.2 mole % CHDO.

*Formaldehyde-$d_2$*

Formaldehyde-$d_2$ was prepared in 76% yield (4.8 gm.) from 6.5 gm. (0.098 mole) of ethylene-$d_4$ glycol by the same method as described for formaldehyde. The colorless polymer was converted into methylene-$d_2$ chloride. Mass spectrometer analysis of the chloro-compound gave the following composition: 97.0 mole % $CD_2Cl_2$; 2.7 mole % $CHDCl_2$. The formaldehyde-$d_2$ therefore contains 97.0 mole % $CD_2O$ (98.3 atom % D).

## ATTEMPTED ISOLATION OF FORMALDEHYDE MONOMER BY GLYCOL CLEAVAGE IN GLACIAL ACETIC ACID

Seventy-five gm. (0.11 mole) of red lead, 250 gm. of glacial acetic acid, and 6.2 gm. (0.10 mole) of ethylene glycol were mixed in the reaction flask of the formaldehyde generator shown in Fig. 1 and heated with mechanical stirring at 60–70° C. for 30 min. until the red lead had dissolved. The solution was heated under reflux for a further 30 min. but no liquid formaldehyde collected in the traps, and only an insignificant amount of polymeric formaldehyde collected at the lower end of the condenser. The solution possessed a strong odor of acetic acid, but the pungent odor of formaldehyde was also perceptible. The solution was fractionated at atmospheric pressure, but although the formaldehyde concentrated in the heads fraction of b.p. 101–115° C., as shown by the strong odor of formaldehyde which this fraction possessed, no separation of polymer occurred.

A second experiment was performed as described for the preceding experiment, except that 56.5 gm. (0.125 mole) of lead tetraacetate was used instead of the red lead, and the ethylene glycol was added dropwise. No liquid for-

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maldehyde was obtained on heating the solution under reflux, but on fractionation of the solution, polymeric formaldehyde separated from the fraction of b.p. 100–114° C. on standing. The polymer was collected by filtration and washed with 25 cc. of anhydrous ether. Weight, 0.9 gm. (15.0%).

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# A KINETIC STUDY OF THE HYDROLYSIS OF BENZALANILINE[1]

By A. V. Willi[2] and R. E. Robertson

ABSTRACT

The rates of the acid catalyzed hydrolysis of a series of para substituted benzalanilines have been studied in 50/50 methanol–water in the presence of acetate buffers. Special and general acid catalysis were observed. The effect of para substituents on the rate is different for the charged and uncharged catalyst, and Hammett's relation cannot be applied. Similarly the effect of substituents on the Arrhenius constants for the two cases is different. The para dimethylamino derivative provides an interesting special case. For low buffer concentrations and in unbuffered solutions certain deviations were observed which show that the dependence of the rate on the catalyst concentration is more complicated than the equation

$$k = k_{H^+} \times [H^+] + k_{HAc} \times [HAc]$$

## INTRODUCTION

In a study of the hydrolysis of benzalanilines reported by Porai-Koshits and co-workers (4) the effects of certain para substituents seemed so unusual as to warrant reinvestigation. That work was done in water, in the presence of strong acids, the reaction being followed by titration methods. A more convenient method was available to us since the ultraviolet absorption of benzalaniline, in the region of 320–350 mμ, is much larger than for a mixture of benzaldehyde and aniline (Fig. 1). By this means, a kinetic study of the acid catalyzed hydrolysis of benzalaniline and some para substituted derivatives with Me, MeO, Cl, $NO_2$, and $(CH_3)_2N$ was carried out. Because it was found that the solubility of these substances was too low in pure water, a

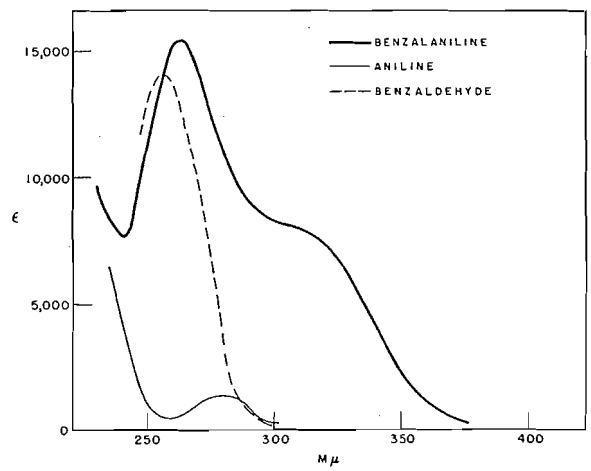



FIG. 1. Absorption spectra of benzalaniline, aniline, and benzaldehyde.

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[2] *National Research Laboratories Postdoctorate Fellow, 1950-52, Division of Pure Chemistry.*

50/50 w/w methanol–water mixture was used as a solvent. In contrast to the findings of Porai-Koshits and co-workers, we found that benzalaniline hydrolyzed far too rapidly for measurement in strong acids at room temperature. It is probable that these workers were following the rate of solution rather than the rate of hydrolysis. Convenient rates were obtained, however, at lower hydrogen ion concentrations. This paper gives a preliminary report on our findings in acetate buffers at constant ionic strength and in unbuffered solutions. It will be apparent, however, that further measurements will be necessary to establish the detailed mechanism.

## EXPERIMENTAL

The kinetic cell of 380 ml. contained a circulating stirrer which both mixed the solution and forced circulation through a quartz cell (1 cm.$^2$ cross section, with plane faces) which was held in the normal position in a Model DU Beckman Spectrophotometer (Fig. 2). The cell was thermostated to within $\pm 0.03°$ C. A quartz reference cell was attached to the kinetic cell; the whole was fixed on a frame mounted on an optical bench in such a fashion that the absorption of either the kinetic or reference cell could be measured conveniently.

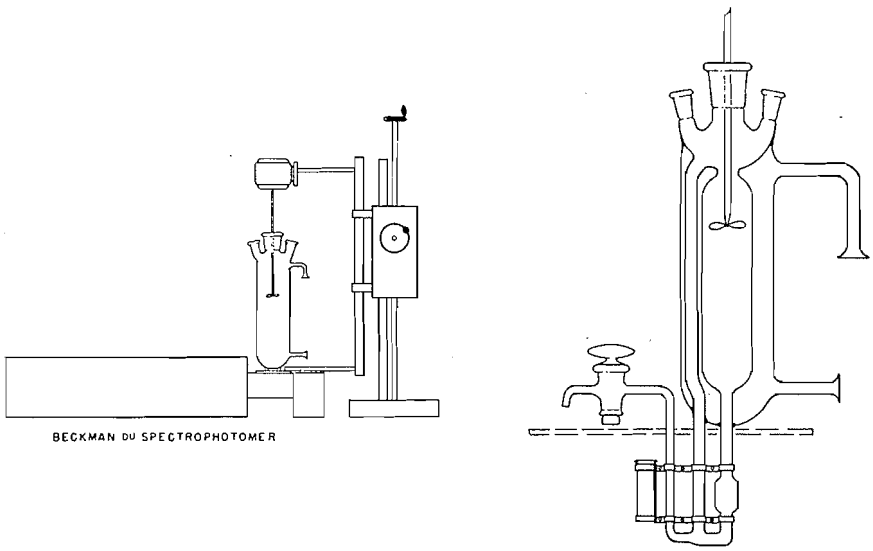



FIG. 2. Kinetic apparatus and reaction cell.

In measuring a reaction, the cell was filled with the requisite buffer solution and permitted to reach temperature equilibrium. After one-half hour the required amount of the benzalaniline was quickly added in a methanol solution with a 2 ml. hypodermic syringe. After 90 sec. absorption measurements were begun with either the normal Beckman DU Photometer or, in the case of fast runs, by substituting an IP28 Photomultiplier and an Esterline Angus recorder.

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Rates were determined from the equation

$$k = \frac{\log \frac{E_1 - E_\infty}{E_2 - E_\infty}}{t_2 - t_1}$$

where $E_1$, $E_2$ . . . . $E_\infty$ are the measured extinctions and $t_1$, $t_2$ the corresponding time in minutes.

pH *Control*

As usual, variations due to primary and secondary salt effects were avoided by using a constant ionic strength, $\mu = 0.110$, in all comparable experiments. In the general case the solvent contained 0.100 molar potassium chloride, 0.0100 $M$ buffer salt, and the corresponding uncharged form of the buffer $2 \times 10^{-3} - 1 \times 10^{-2}$ molar.

In those cases where it was necessary to increase the buffer salt, the potassium chloride was decreased correspondingly to maintain $\mu = 0.110$. The contribution of potassium chloride to the total ionic strength was always greater than 75%. Thus the possibility of specific salt effects was reduced, though probably not eliminated.

For the solvent mixture 50/50 w/w methanol–water the activity coefficients of the hydrogen ion and the acidity constants of acids are not well known. However, since $\mu$ was held constant, the activity coefficient of the hydrogen ion was constant and the activity was therefore proportional to the concentration. In this way all kinetic constants for $[H^+]$ catalysis have been referred to hydrogen-ion concentrations. The pH measurements were done with a Beckman (1190–80) glass electrode in a cell, with negligible liquid junction potential, of the type

| | | | |
|---|---|---|---|
| Glass electrode | KCl 0.100 $M$<br>Buffer salt 0.0100 $M$<br>Uncharged buffer $3 \times 10^{-3}$ $M$ | 0.100 KCl | AgCl<br>Ag |

As a reference point a known solution of perchloric acid (say 0.00600 $N$ perchloric acid, corresponding to a pH = 2.222) was made up to $\mu = 0.110$ with potassium chloride in the given solvent. By relating the measured potential of a buffer solution to the potential of the reference solution, $\mu$, solvent, and temperature being identical, the hydrogen-ion concentration was obtained.

From the hydrogen-ion concentration and the ratio $[Ac^-]/[HAc]$ it was possible to derive the value of the acidity constant of acetic acid valid for the given solvent and $\mu = 0.110$ by the usual equation

$$K_c = \frac{[H^+]\,[Ac^-]}{[HAc]}.$$

Table I gives the value of $K_c$ for three temperatures.

## RESULTS

In all experiments the rates of hydrolysis of the compounds investigated have been found to be first-order with respect to benzalaniline concentrations. No trends in the first-order constants were observed within the runs (as is

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TABLE I

ACIDITY CONSTANTS OF ACETIC ACID IN 50/50 (w/w) METHANOL–WATER. $\mu = 0.110$

| $t°$ | $K_c \times 10^6$ |
|---|---|
| 0° C. | 4.28 |
| 10° C. | 4.59 |
| 20° C. | 4.68 |

TABLE I*a*

HYDROLYSIS OF BENZALANILINE IN 50/50 METHANOL–WATER—UNBUFFERED
$\mu = 0.110$; KCl = 0.0110; a trace of $HClO_4$ added; pH = 6.40; temperature +10.0° C.; $\lambda = 320$ m$\mu$; 13 mgm. benzalaniline added to 230 cc. cell.

| $t$, min. | $E$ | $E-E_\infty$ | $\log(E-E_\infty)$ | ${}_4\Delta$ | $-{}_4\Delta t$ | $k$ | $\Delta$ | $-\Delta t$ | $k$ |
|---|---|---|---|---|---|---|---|---|---|
| 3.95 | 1.063 | 1.015 | 0.006 | | | | .. | .... | .... |
| 5.42 | 0.815 | 0.767 | $\bar{1}$.885 | | | | 0.000 | 0.00 | .... |
| 6.07 | 0.731 | 0.683 | $\bar{1}$.834 | 0.341 | 4.30 | 0.0793 | .... | .... | .... |
| 7.60 | 0.569 | 0.521 | $\bar{1}$.717 | 0.310 | 3.96 | 0.0783 | 0.168 | 2.18 | (0.0771) |
| 8.25 | 0.510 | 0.462 | $\bar{1}$.665 | 0.320 | 4.06 | 0.0788 | 0.220 | 2.83 | 0.0777 |
| 9.38 | 0.424 | 0.376 | $\bar{1}$.575 | 0.331 | 4.18 | 0.0792 | 0.310 | 3.96 | 0.0783 |
| 10.13 | 0.375 | 0.327 | $\bar{1}$.514 | 0.373 | 4.77 | 0.0782 | 0.371 | 4.71 | 0.0788 |
| 11.78 | 0.291 | 0.243 | $\bar{1}$.386 | 0.323 | 4.12 | 0.0784 | 0.499 | 6.36 | 0.0785 |
| 13.02 | 0.244 | 0.196 | $\bar{1}$.292 | 0.353 | 4.55 | 0.0776 | 0.593 | 7.60 | 0.0780 |
| 13.50 | 0.227 | 0.179 | $\bar{1}$.252 | 0.259 | 3.32 | 0.0780 | 0.633 | 8.08 | 0.0783 |
| 14.68 | 0.193 | 0.145 | $\bar{1}$.161 | 0.224 | 2.90 | 0.0772 | 0.724 | 9.26 | 0.0782 |
| 15.10 | 0.182 | 0.134 | $\bar{1}$.127 | 0.222 | 2.92 | (0.0760) | 0.758 | 9.68 | 0.0783 |
| 15.92 | 0.165 | 0.117 | $\bar{1}$.068 | | | | 0.817 | 10.50 | 0.0778 |
| 16.42 | 0.155 | 0.107 | $\bar{1}$.030 | | | | 0.855 | 11.00 | 0.0777 |
| 60′ | 0.048 | | | | | 0.0783 | | | 0.0782 |

$H^+ = 3.55 \times 10^{-7}$
$k_{H^+} = 1.97 \times 10^{+5}$ (±5%)

TABLE I*b*

HYDROLYSIS OF BENZALANILINE IN 50/50 w/w METHANOL–WATER WITH PHOSPHATE BUFFER
Temperature +10.0° C.; $\mu = 0.110$; KCl = 0.105; $KHPO_4 = 0.00125M$; $KH_2PO_4 = 0.00125M$; $\lambda = 350$ m$\mu$; pH = 7.63

| $t$, min. | $E-E_\infty$ | $\log(E-E_\infty)$ | $\Delta$ | $-\Delta t$ | $\Delta x/\Delta t \times 10^3$ | $\Delta$ | $-\Delta t$ | $k \times 10^3$ |
|---|---|---|---|---|---|---|---|---|
| 1.52 | 1.354 | 0.132 | | | | | | |
| 3.68 | 1.313 | 0.118 | | | | 0.000 | 0.00 | — |
| 7.03 | 1.245 | 0.096 | 0.120 | 16.41 | 7.32 | — | — | — |
| 11.90 | 1.139 | 0.057 | 0.153 | 20.12 | 7.61 | 0.061 | 8.22 | 7.42 |
| 17.93 | 1.029 | 0.012 | 0.161 | 20.87 | 7.71 | 0.106 | 14.25 | 7.45 |
| 23.80 | 0.922 | $\bar{1}$.965 | 0.164 | 21.37 | 7.68 | — | — | — |
| 27.90 | 0.861 | $\bar{1}$.935 | 0.157 | 20.10 | 7.81 | 0.183 | 24.22 | 7.56 |
| 33.27 | 0.781 | $\bar{1}$.893 | 0.171 | 22.47 | 7.60 | 0.225 | 29.59 | 7.60 |
| 38.03 | 0.716 | $\bar{1}$.855 | 0.179 | 23.25 | 7.70 | 0.263 | 34.35 | 7.66 |
| 46.27 | 0.622 | $\bar{1}$.794 | 0.173 | 22.86 | 7.57 | 0.324 | 42.59 | 7.60 |
| 51.15 | 0.570 | $\bar{1}$.756 | 0.175 | 23.40 | 7.48 | 0.362 | 47.47 | 7.62 |
| 56.73 | 0.524 | $\bar{1}$.720 | 0.168 | 21.88 | 7.68 | 0.398 | 52.45 | 7.60 |
| 61.43 | 0.479 | $\bar{1}$.680 | 0.174 | 22.77 | 7.65 | 0.438 | 57.75 | 7.58 |
| 68.15 | 0.423 | $\bar{1}$.626 | — | — | — | 0.492 | 64.47 | 7.64 |
| 73.92 | 0.382 | $\bar{1}$.582 | — | — | | 0.536 | 70.24 | 7.64 |
| | | | | | $k_{av} = 7.62 \times 10^{-3}$ | | | $k_{av} = 7.61 \times 10^{-3}$ |

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TABLE Ic

HYDROLYSIS OF BENZALANILINE IN 50/50 w/w METHANOL–WATER AT 10.0° C.
$\mu$ = 0.110; KCl = 0.1000 $M$; NaAc = 0.0100 $M$; HAc = 0.002297;
$\lambda$ = 320 m$\mu$; $I_0$ = 50$\mu$Å; 13 mgm. of benzalaniline used.

| $t = t' - 4''$ | $I$ | $E$ | $E-E_\infty$ | log $E-E_\infty$ | $\Delta$ | $-\Delta t$ | $k$ | $\Delta$ | $-\Delta t$ | $k$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1′ 45″ | 42 | 1.076 | 0.961 | $\bar{1}$.983 | | | | | | |
| 2′ 00″ | 57 | 0.943 | 0.828 | $\bar{1}$.918 | | | | | | |
| 2′ 15″ | 74 | 0.830 | 0.715 | $\bar{1}$.854 | | | | 0.00 | 0.00 | |
| 2′ 30″ | 90 | 0.745 | 0.630 | $\bar{1}$.799 | | | | — | — | |
| 2′ 45″ | 106 | 0.674 | 0.559 | $\bar{1}$.747 | $\bar{1}$.236 | 1.00 | 0.236 | 0.197 | 0.50 | (0.214) |
| 3′ 45″ | 185 | 0.432 | 0.317 | $\bar{1}$.501 | 0.482 | 2.00 | (0.241) | 0.353 | 1.50 | 0.235 |
| 4′ 00″ | 200 | 0.398 | 0.283 | $\bar{1}$.452 | 0.466 | 2.00 | 0.233 | 0.402 | 1.75 | 0.230 |
| 4′ 15″ | 217 | 0.362 | 0.247 | $\bar{1}$.393 | 0.461 | 2.00 | 0.231 | 0.561 | 2.00 | 0.231 |
| 4′ 30″ | 233 | 0.332 | 0.217 | $\bar{1}$.337 | 0.462 | 2.00 | 0.231 | 0.517 | 2.25 | 0.230 |
| 5′ 45″ | 300 | 0.222 | 0.107 | $\bar{1}$.030 | 0.471 | 2.00 | 0.236 | 0.824 | 3.50 | 0.235 |
| 6′ 00″ | 308 | 0.210 | 0.095 | $\bar{2}$.978 | 0.474 | 2.00 | 0.237 | 0.876 | 3.75 | 0.234 |
| 6′ 15″ | 315 | 0.200 | 0.085 | $\bar{2}$.930 | 0.463 | 2.00 | 0.231 | 0.924 | 4.00 | 0.231 |
| 6′ 30″ | 321 | 0.192 | 0.077 | $\bar{2}$.886 | 0.451 | 2.00 | (0.225) | 0.968 | 4.25 | (0.228) |
| | | | | | | | $k_{av}$ = 0.234 | | | $k_{av}$ = 0.232 |

*Note: Av. % deviation from the mean = about 1%.*

evident from the data of three typical runs given in Table I*a*, I*b*, and I*c*) and these were normally followed to 85% completion. The hydrolysis proceeds to at least 98% based on the disappearance of the benzalaniline. The average values of the over-all rate constants were reproducible to 1%. Deviations of points within any one run were random and seldom exceeded 3%. Under our experimental conditions, the pH readings could be made to 0.01 pH unit and this error was consequently added to those in the over-all rate when calculating $k_{H^+}$.

It is clear that the rate is strongly dependent on the hydrogen ion concentration although these data do not show complete linearity. The addition of sodium hydroxide, $10^{-3}$ molar, gave a value of $k < 10^{-4}$ at room temperature, indicating that base catalysis and water catalysis are negligible.

Further investigation in acetate buffers showed that, where the pH was kept constant the rate varied with the amount of buffer ($\mu$ remaining constant). These data have been summarized in Fig. 3. It can be seen that the slopes of the curves are determined by the increase of [HAc] and not that of [Ac$^-$]. This leads to the general rate equation

$$k = a[\mathrm{HAc}] + b([\mathrm{H}^+] = \text{const.}) \qquad [1]$$

TABLE II

RATE CONSTANTS FOR THE HYDROLYSIS OF BENZALANILINE IN DIFFERENT BUFFERS AT +10.0° C., $\mu$ = 0.110.
SOLVENT METHANOL–WATER 50/50 w/w

| Buffer | pH | $k$, min.$^{-1}$ | $k/[\mathrm{H}^+]$ min.$^{-1}$ |
|---|---|---|---|
| Acetate | 5.68 | $4.49 \cdot 10^{-1}$ | $2.16 \cdot 10^{+5}$ |
| Phosphate | 7.6 | $7.28 \cdot 10^{-3}$ | $2.9 \cdot 10^{+5}$ |
| Veronal | 8.7 | $6.36 \cdot 10^{-4}$ | $3.2 \cdot 10^{+5}$ |

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where $b$ is proportional to the $[H^+]$ as can be seen from Table III. Thus it is evident that the rate equation has the form of special and general acid catalysis

$$k = k_{H^+}[H^+] + k_{HAc}[HAc]. \quad [2]$$

However, at buffer concentrations lower than $10^{-2}$ $M$ in NaAc, deviations from linearity are found in the plot of $k$ versus [HAc] at constant pH(Fig.4). This indicates that Equation 2 is no longer valid.

TABLE III

PARAMETERS FOR EQUATION [1] FOR DIFFERENT ACETATE BUFFERS

| Curve | $[H^+]$ | $a$ | $b$ | $b/[H^+]$ |
|---|---|---|---|---|
| 1 | $2.072 \cdot 10^{-6}$ | 20.0 | 0.357 | $1.72 \cdot 10^{+5}$ |
| 2 | $1.20 \cdot 10^{-6}$ | 21.6 | 0.200 | $1.67 \cdot 10^{+5}$ |
| 3 | $1.055 \cdot 10^{-6}$ | 19.3 | 0.187 | $1.77 \cdot 10^{+5}$ |

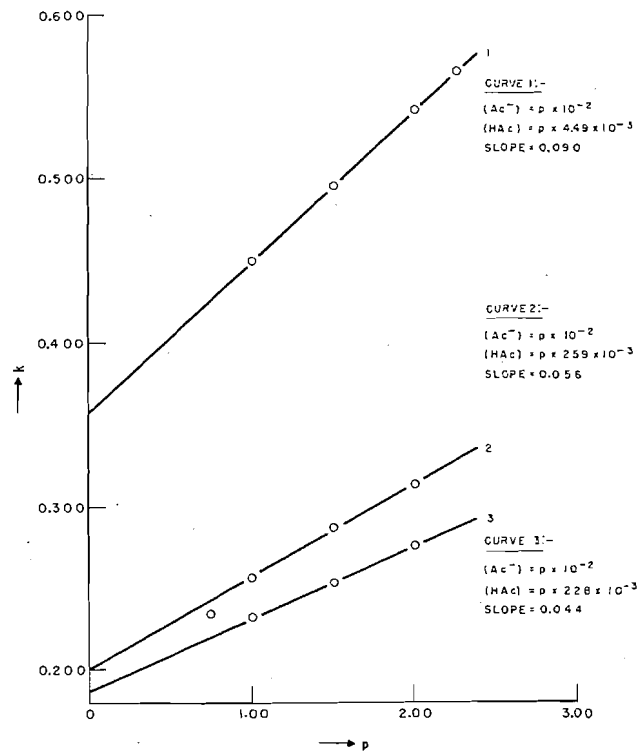



FIG. 3. Variation of the rate constant of benzalaniline with the buffer concentration at +10.0° C.

At −0.1° C. the dependence of $k$ on [HAc] departs from linearity up to $2.50 \times 10^{-2}$ $M$ NaAc, but the curvature is very small as can be seen from the graph (Fig. 4).

For the data at 20° C. the linear region lies between $7.5 \times 10^{-3}$ and $1.5 \times 10^{-2}$ $M$ NaAc.

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The experimental data for the rate of hydrolysis in various acetate buffers for the substituted benzalanilines are given in Table IV.

An explanation for the deviations from Equation 2 has not yet been found. However, since there is always a region of linearity at sufficiently high buffer concentrations (except for the small deviations already noted at −0.1° C.), values of $k'_{H+}$ and $k'_{HAc}$ could be calculated in every case by omitting the points obtained at low buffer concentrations. At the lowest temperature (−0.1° C.) the values of $k$ at $[Ac^-] = 1.50 \times 10^{-2}$; $2.00 \times 10^{-2}$; and $2.50 \times 10^{-2}$ $M$ had been used to obtain approximate values for $k'_{H+}$ and $k'_{HAc}$. The analysis of the experimental data in terms of $k'_{H+}$ and $k'_{HAc}$ obviously involves an approximation and although $k'_{H+}$ and $k'_{HAc}$ may not be equivalent

TABLE IV

FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF BENZALANILINES IN ACETATE BUFFERS FOR THE IONIC STRENGTH $\mu = 0.110$

| Substance | $C_{KCl}$ | $C_{NaAc}$ | $C_{HAc}$ | $k$ |
|---|---|---|---|---|
| *−0.1° C.* | | | | |
| Benzalaniline | 0.1025 | 0.00750 | $1.90 \times 10^{-3}$ | 0.136 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.147 |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | 0.164 |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | 0.177 |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | 0.189 |
| Benzal-*p*-toluidine | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.1190 |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | 0.1276 |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | 0.1378 |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | 0.1465 |
| *p*-Methoxybenzalaniline | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | $8.78 \times 10^{-2}$ |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | $9.83 \times 10^{-2}$ |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | $10.49 \times 10^{-2}$ |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | $11.06 \times 10^{-2}$ |
| Benzal-*p*-anisidine | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | $8.91 \times 10^{-2}$ |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | $9.53 \times 10^{-2}$ |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | $10.11 \times 10^{-2}$ |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | $10.5 \times 10^{-2}$ |
| *p*-Chlorobenzalaniline | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.144 |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | 0.150 |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | 0.155 |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | 0.159 |
| Benzal-*p*-chloroaniline | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.1518 |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | 0.169 |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | 0.180 |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | 0.188 |
| *p*-Nitrobenzalaniline | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | $8.04 \times 10^{-2}$ |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | $8.40 \times 10^{-2}$ |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | $8.63 \times 10^{-2}$ |
| | 0.0850 | 0.0250 | $6.32 \times 10^{-3}$ | $8.82 \times 10^{-2}$ |
| Benzal-*p*-dimethylaminoaniline | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | $5.10 \times 10^{-2}$ |
| | 0.0950 | 0.0150 | $3.80 \times 10^{-3}$ | $5.28 \times 10^{-2}$ |
| | 0.0900 | 0.0200 | $5.06 \times 10^{-3}$ | $5.52 \times 10^{-2}$ |

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TABLE IV (continued)

| Substance | $C_{KCl}$ | $C_{NaAc}$ | $C_{HAc}$ | $k$ |
|---|---|---|---|---|
| *10.0° C.* | | | | |
| Benzalaniline | 0.1075 | 0.00250 | $1.12 \times 10^{-3}$ | 0.254 |
| | 0.1050 | 0.00500 | $2.24 \times 10^{-3}$ | 0.321 |
| | 0.1025 | 0.00750 | $3.37 \times 10^{-3}$ | 0.391 |
| | 0.1000 | 0.01000 | $4.49 \times 10^{-3}$ | 0.443 |
| | 0.0950 | 0.01500 | $6.74 \times 10^{-3}$ | 0.496 |
| | 0.0900 | 0.02000 | $8.98 \times 10^{-3}$ | 0.540 |
| | 0.0875 | 0.02250 | $10.10 \times 10^{-3}$ | 0.565 |
| | 0.1025 | 0.00750 | $1.94 \times 10^{-3}$ | 0.234 |
| | 0.1000 | 0.01000 | $2.59 \times 10^{-3}$ | 0.255 |
| | 0.0950 | 0.01500 | $3.89 \times 10^{-3}$ | 0.287 |
| | 0.0900 | 0.02000 | $5.19 \times 10^{-3}$ | 0.312 |
| | 0.1000 | 0.0100 | $2.28 \times 10^{-3}$ | 0.232 |
| | 0.0950 | 0.0150 | $3.42 \times 10^{-3}$ | 0.252 |
| | 0.0900 | 0.0200 | $4.56 \times 10^{-3}$ | 0.276 |
| Benzal-*p*-toluidine | 0.1000 | 0.0100 | $2.59 \times 10^{-3}$ | 0.212 |
| | 0.0950 | 0.0150 | $3.89 \times 10^{-3}$ | 0.229 |
| | 0.0900 | 0.0200 | $5.19 \times 10^{-3}$ | 0.246 |
| | 0.0875 | 0.0225 | $5.84 \times 10^{-3}$ | 0.255 |
| | 0.1000 | 0.0100 | $4.51 \times 10^{-3}$ | 0.358 |
| | 0.0950 | 0.0150 | $6.77 \times 10^{-3}$ | 0.397 |
| | 0.0900 | 0.0200 | $9.02 \times 10^{-3}$ | 0.413 |
| *p*-Methoxybenzalaniline | 0.1000 | 0.0100 | $5.99 \times 10^{-3}$ | 0.377 |
| | 0.0950 | 0.0150 | $8.99 \times 10^{-3}$ | 0.404 |
| | 0.0900 | 0.0200 | $11.98 \times 10^{-3}$ | 0.428 |
| | 0.1000 | 0.0100 | $4.51 \times 10^{-3}$ | 0.280 |
| | 0.0900 | 0.0200 | $9.02 \times 10^{-3}$ | 0.325 |
| Benzal-*p*-anisidine | 0.1000 | 0.0100 | $4.51 \times 10^{-3}$ | 0.201 |
| | 0.0950 | 0.0150 | $6.77 \times 10^{-3}$ | 0.217 |
| | 0.0900 | 0.0200 | $9.02 \times 10^{-3}$ | 0.229 |
| | 0.1000 | 0.0100 | $5.99 \times 10^{-3}$ | 0.268 |
| | 0.0950 | 0.0150 | $8.99 \times 10^{-3}$ | 0.289 |
| | 0.0900 | 0.0200 | $11.98 \times 10^{-3}$ | 0.303 |
| *p*-Chlorobenzalaniline | 0.1000 | 0.0100 | $4.51 \times 10^{-3}$ | 0.303 |
| | 0.0950 | 0.0150 | $6.77 \times 10^{-3}$ | 0.318 |
| | 0.0900 | 0.0200 | $9.02 \times 10^{-3}$ | 0.338 |
| | 0.1000 | 0.0100 | $5.99 \times 10^{-3}$ | 0.403 |
| | 0.0900 | 0.0200 | $11.98 \times 10^{-3}$ | 0.449 |
| Benzal-*p*-chloroaniline | 0.1000 | 0.0100 | $2.59 \times 10^{-3}$ | 0.188 |
| | 0.0950 | 0.0150 | $3.89 \times 10^{-3}$ | 0.205 |
| | 0.0900 | 0.0200 | $5.19 \times 10^{-3}$ | 0.219 |
| | 0.1000 | 0.0100 | $5.99 \times 10^{-3}$ | 0.431 |
| | 0.0900 | 0.0200 | $11.98 \times 10^{-3}$ | 0.504 |
| *p*-Nitrobenzalaniline | 0.1000 | 0.0100 | $4.51 \times 10^{-3}$ | 0.177 |
| | 0.0900 | 0.0200 | $9.02 \times 10^{-3}$ | 0.186 |
| | 0.1000 | 0.0100 | $5.99 \times 10^{-3}$ | 0.239 |
| | 0.0950 | 0.0150 | $8.99 \times 10^{-3}$ | 0.247 |
| | 0.0900 | 0.0200 | $11.98 \times 10^{-3}$ | 0.251 |

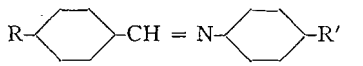
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TABLE IV (concluded)

| Substance | $C_{KCl}$ | $C_{NaAc}$ | $C_{HAc}$ | $k$ |
|---|---|---|---|---|
| *20.0° C.* | | | | |
| Benzalaniline | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.358 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.388 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.416 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.448 |
| Benzal-*p*-toluidine | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.313 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.328 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.339 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.359 |
| *p*-Methoxybenzalaniline | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.243 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.254 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.265 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.272 |
| Benzal-*p*-anisidine | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.171 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.177 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.188 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.196 |
| *p*-Chlorobenzalaniline | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.255 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.266 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.282 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.297 |
| Benzal-*p*-chloroaniline | 0.1050 | 0.0050 | $1.26_5 \times 10^{-3}$ | 0.243 |
| | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.268 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.291 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.311 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.327 |
| *p*-Nitrobenzalaniline | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.155 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.158 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.161 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.167 |
| Benzal-*p*-dimethylaminoaniline | 0.1025 | 0.0075 | $1.82 \times 10^{-3}$ | 0.133 |
| | 0.1000 | 0.0100 | $2.53 \times 10^{-3}$ | 0.138 |
| | 0.0975 | 0.0125 | $3.64 \times 10^{-3}$ | 0.139 |
| | 0.0950 | 0.0150 | $5.06 \times 10^{-3}$ | 0.145 |

TABLE V

RATE CONSTANTS FOR HYDROGEN-ION CATALYSIS AND ACETIC ACID CATALYSIS OF THE HYDROLYSIS OF SUBSTITUTED BENZALANILINES CALCULATED FROM MEASUREMENTS IN ACETATE BUFFERS




| R | R′ | −0.1° C. | | +10.0° C. | | +20.0° C. | |
|---|---|---|---|---|---|---|---|
| | | $k'_{H+}$ | $k'_{HAc}$ | $k'_{H+}$ | $k'_{HAc}$ | $k'_{H+}$ | $k'_{HAc}$ |
| H– | –H | $1.17 \cdot 10^{+5}$ | 9.9 | $1.70 \cdot 10^{+5}$ | 20.0 | $2.29 \cdot 10^{+5}$ | 45.9 |
| H– | $-CH_3$ | $9.28 \cdot 10^{+4}$ | 7.2 | $1.49 \cdot 10^{+5}$ | 12.8 | $2.25 \cdot 10^{+5}$ | 24.1 |
| $CH_3O$– | –H | $7.37 \cdot 10^{+4}$ | 4.9 | $1.19 \cdot 10^{+5}$ | 8.57 | $1.81 \cdot 10^{+5}$ | 15.8 |
| H– | $-OCH_3$ | $5.20 \cdot 10^{+4}$ | 3.0 | $8.45 \cdot 10^{+4}$ | 6.1 | $1.23 \cdot 10^{+5}$ | 13.2 |
| Cl– | –H | $8.87 \cdot 10^{+4}$ | 2.8 | $1.25 \cdot 10^{+5}$ | 7.78 | $1.80 \cdot 10^{+5}$ | 21.7 |
| H– | –Cl | $9.30 \cdot 10^{+4}$ | 5.4 | $1.30 \cdot 10^{+5}$ | 12.1 | $1.81 \cdot 10^{+5}$ | 29.6 |
| $NO_2$– | –H | $5.12 \cdot 10^{+4}$ | 1.2 | $8.20 \cdot 10^{+4}$ | 2.0 | $1.21 \cdot 10^{+5}$ | 6.3 |
| H– | $-N(CH_3)_2$ | $4.32 \cdot 10^{+4}$ | 1.7 | | | $1.02 \cdot 10^{+5}$ | 6.3 |
| $^{+}H(CH_3)_2N$– | –H | 3.71 | — | | | 15.7 | — |

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to the true catalytic constants for special and general acid catalysis, nevertheless they do provide a basis for comparing the effect of substituents.

The data for $k'_{H+}$ and $k'_{HAc}$ for three temperatures are given in Table V. It must be emphasized that it may not be permissible to apply these $k'_{H+}$ values to buffer solutions other than acetate or to unbuffered solutions before the anomalous behavior at low buffer concentrations has been explained.

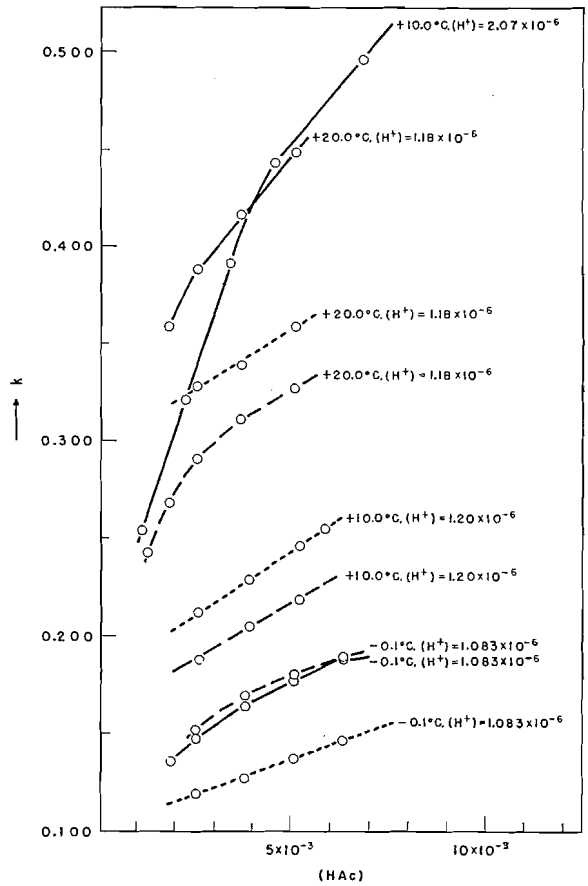



FIG. 4. Deviations from linearity for the general acid catalysis of substituted benzalanilines. Benzalaniline————, Benzal-*p*-toluidine- - - - - - -, Benzal-*p*-chloroaniline– – – – – – –.

Para-dimethylaminobenzalaniline provides a special case. Whereas the rate constants in acetate buffers are of the same magnitude as the other compounds, the rate in strong acid ($[H^+] = 10^{-3} - 10^{-2}$), in contrast, is still measurable. Fig. 5 shows the dependence of rate on the $[H^+]$ in the region mentioned. This figure leads to the empirical equation

$$-dX/dt = 2.303\, kX = 2.303\, X\, \{k_1[H^+] + k_2\} \qquad [3]$$

in which $k_1 = 15.7$ and $k_2 = 0.337$ for 20° C. There are two possibilities: either

$$X = [B]$$

or

$$X = [BH^+]$$

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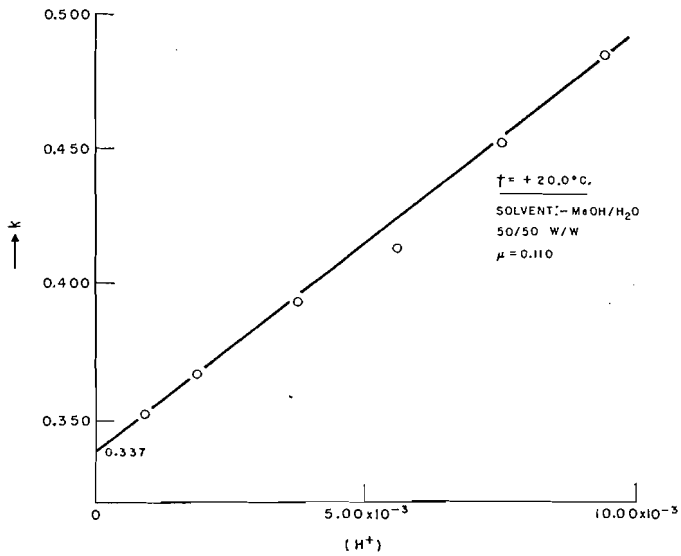



FIG. 5. Dependence of the rate of hydrolysis of *p*-dimethylaminobenzalaniline in strong acids on the hydrogen ion concentration.

where $B$ is the *p*-dimethylaminobenzalaniline and $B\text{H}^+$ the corresponding ammonium ion.

If $X = [B]$, then it is not clear why an uncatalyzed reaction is observed, when at the same time the hydrogen catalyzed reaction is four powers of 10 lower than for the unsubstituted benzalaniline and this in spite of the fact that the *p*-dimethylamino compound in acetate buffer hydrolyzes with a rate comparable to the other benzalanilines. However, if $X = [B\text{H}^+]$, where a proton is on the substituted nitrogen, we have to expect that the acid catalyzed hydrolysis of this ion will be slower by a few powers of 10. This follows from the general experience of the influence of this substituent on acidity constants and rate constants (5, 7). Furthermore it is reasonable that dimethylaminobenzalaniline should possess the same order of basicity as the corresponding azobenzene (6) or stilbene (1) compounds which are transformed into cations in the region of pH 4.5.

Equation 3 can now be written

$$-dX/dt = 2.303\, k_1\, [B\text{H}^+]\, [\text{H}^+] + 2.303\, k_2\, [B\text{H}^+]\,. \qquad [4]$$

The second term of [4] does not refer to an uncatalyzed reaction, but rather to the hydrogen ion catalyzed hydrolysis of the free base, which is present in very low concentration. If a substitution is made in terms of the acidity equilibrium for $[B\text{H}^+]$

$$[B\text{H}^+] = \frac{[B]\,[\text{H}^+]}{K}$$

in equation [4], then

$$-\frac{dX}{dt} = 2.303\, k_1\, [B\text{H}^+]\, [\text{H}^+] + 2.303\, \frac{k_2}{K}\, [B][\text{H}^+] \qquad [5]$$

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where $k_1 = k_{H^+}^{BH^+}$ and $\frac{k_2}{K} = k_{H^+}^{B}$.

The measured value, $k_2$, is the product of the rate constant, $k_{H^+}^{B}$, for the hydrogen ion catalyzed reaction of $B$ and the acidity constant, $K$, of the cation $BH^+$.

In the case of the compound with the dimethylamino group on the aniline side, the hydrolysis in acid solution, $[H^+] = 10^{-3}$ molar, is too fast to be measured. If some of the substance is added to such a solution there is the development of a red color probably caused by the formation of $BH^+$ which disappears after a few seconds. The rate in acetate buffer (Table V) is, however, quite normal.

*Effect of Substituents*

From a comparison of rate data (Table V) it is evident that the effects of para substituents differ from those that normally lead to the Hammett relation. Here the general effect of a substituent is to reduce the rate, whether

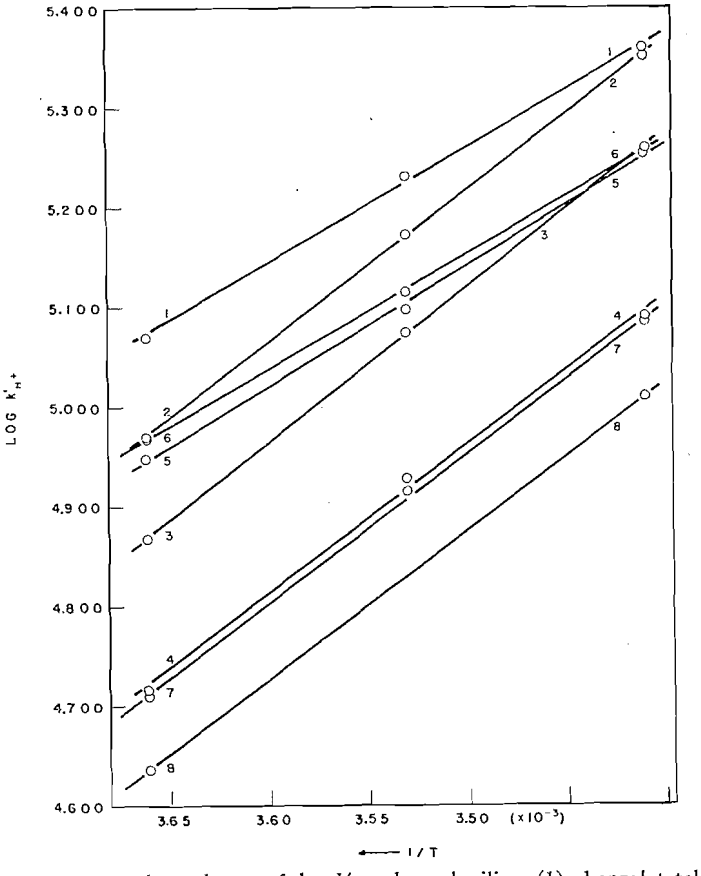



FIG. 6. Temperature dependence of log $k'_{H^+}$, benzalaniline (1), benzal-*p*-toluidine (2), *p*-methoxybenzalaniline (3), benzal-*p*-anisidine (4), *p*-chlorobenzalaniline (5), benzal-*p*-chloroaniline (6), *p*-nitrobenzalaniline (7), benzal-*p*-dimethylaminoaniline (8).

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that substituent would normally be considered to render the nitrogen more or less basic. Even in the case of the Cl and $NO_2$ substituents where the shift in rate is in the predicted direction, the magnitude of the change is not related to Hammett's $\sigma$ values. It will be noted that the effect of substituents is larger for the uncharged catalyst, HAc. Further, the relative order of the rate constants is not the same at each temperature.

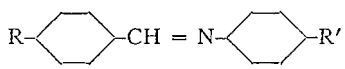
The rate for the charged *p*-dimethylammoniumbenzalaniline is reduced by a factor of $10^4$. This very large change is attributed to the electrostatic repulsion of the proton attacking the N of the azomethine bond.

*Arrhenius Constants*

The temperature dependence of $k'_{H+}$ for the hydrolysis of the series of para substituted benzalanilines is given by the plot of log $k'_{H+}$ versus $1/T$ in Fig. 6. The approximation to linearity is good and may be taken as support for our method of treating the experimental data. In conformity with normal practice, we have calculated the coefficients for the temperature dependence in terms of the two-constant Arrhenius equation, although we are well aware that such a treatment is but approximate and the terminology implies certain unsupported assumptions. These constants with their average error are given in Table VI.

TABLE VI

ACTIVATION ENERGIES AND LOG *PZ*-VALUES FOR THE ACID CATALYZED HYDROLYSIS OF BENZALANILINES




| R | R′ | *E*, kcal. | log *PZ* |
|---|---|---|---|
| *a. Hydrogen ion catalysis* | | | |
| H | H | 5.3 ± 0.25 | 9.32 [min.$^{-1}$] |
| H | $CH_3$ | 7.0 ± 0.15 | 10.57 " |
| $CH_3O$ | H | 7.1 ± 0.15 | 10.58 " |
| H | $OCH_3$ | 6.8 ± 0.50 | 10.17 " |
| Cl | H | 5.6 ± 0.40 | 9.44 " |
| H | Cl | 5.3 ± 0.18 | 9.20 " |
| $NO_2$ | H | 6.8 ± 0.34 | 10.17 " |
| H | $N(CH_3)_2$ | 6.8 ± .30 | 10.08 " |
| $^+H(CH_3)_2N$ | H | 11.4 ± .25 | 9.70 " |
| *b. Acetic acid catalysis* | | | |
| H | H | 13.0 ± .75 | 11.36 [min.$^{-1}$] |
| H | $CH_3$ | 9.9 ± 0.35 | 8.76 " |
| $CH_3O$ | H | 9.8 ± 0.5 | 8.51 " |
| H | $OCH_3$ | 12.3 ± 0.6 | 10.26 " |
| Cl | H | 16.6 ± 0.6 | 13.72 " |
| H | Cl | 14.2 ± 0.6 | 12.05 " |
| $NO_2$ | H | (13.3 ± 0.8) | (10.71) " |
| H | $N(CH_3)_2$ | (12.0 ± 0.8) | (9.88) " |

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It is evident that the effect of a substituent is to change both $E_A$ and $PZ$. For the hydrogen-ion catalyzed reaction the unsubstituted compound has the lowest value of $E_A$ but the variations resulting from substitution are less than 2 kcal. For the protonated dimethylaminobenzalaniline the activation energy is 6.1 kcal. higher, but the $PZ$ term changes very little. This result is just the one we would expect on the basis of the electrostatic explanation already proposed.

For the acetic acid catalyzed reaction it is noted that the activation energy for the unsubstituted compound is among the highest, in contrast to the previous series, and the two chlorine substituted compounds are even higher.

As has been found for many other series there is a roughly linear relation between log $PZ$ and $E_A$ for both the proton catalyzed and acetic acid catalyzed reaction, Fig. 7. The slope of these curves is approximately 1.3.

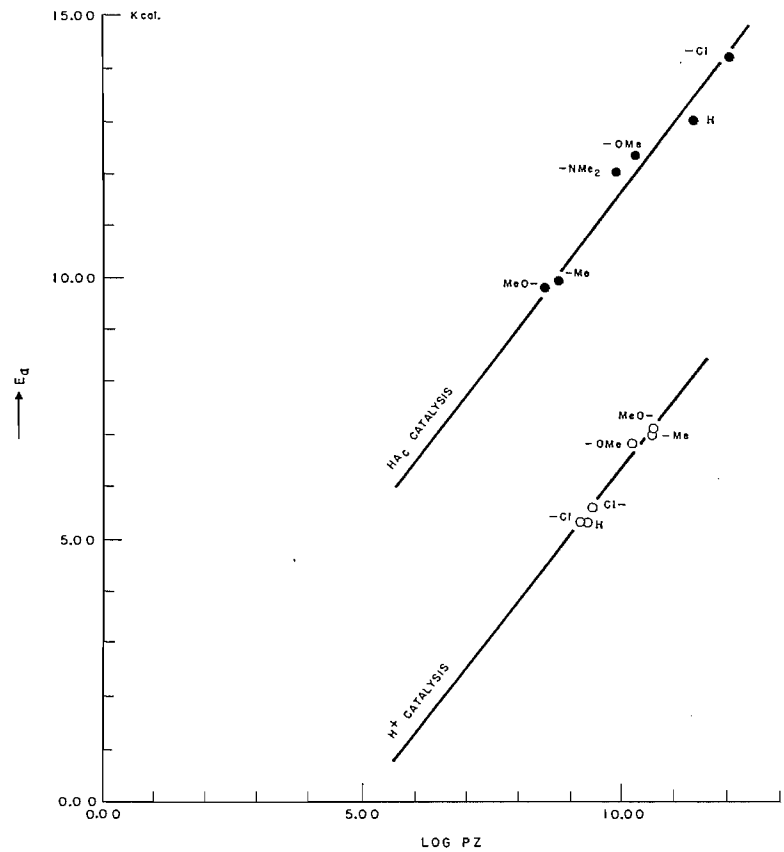



FIG. 7. Relation between $E_a$ and log $PZ$.

*Rate Constants in Unbuffered Solutions*

The constancy of $k'_{H+}$ for benzalaniline at +10.0° C. already shown by the data in Table III could be tested in the buffer region of acetic acid between $[H^+] = 2 \times 10^{-6}$ and $[H^+] = 1 \times 10^{-6}$. However, in order to extend the

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measurements beyond this pH region and to avoid the uncertainties connected with the deviations from Equation 2 in acetate buffers, it was preferable to carry out rate measurements in very dilute "strong" acids or "strong" bases.

The pH values of these unbuffered solutions have been measured by the aid of a glass electrode and a silver chloride half-cell, with a negligible liquid junction potential, introduced directly into the kinetic cell. Before each kinetic run the glass electrode and the AgCl half-cell were calibrated in a separate thermostated cell containing perchloric acid or acetate buffer of a known pH value.

The results for rate constants of benzalaniline, benzal-*p*-chloroaniline, and *p*-dimethylaminobenzalaniline in unbuffered solutions are given in Table VII

TABLE VII

HYDROLYSIS OF BENZALANILINES IN UNBUFFERED SOLUTIONS OF 50/50 W/W METHANOL–WATER WITH 0.110 *N* KCl AT 10.0° C.

| pH | $k$ | log $k$ | $k/[H^+]$ |
|---|---|---|---|
| *Benzalaniline* | | | |
| $5.65_5$ | 0.135 | $\bar{1}.130$ | $6.08 \times 10^{+4}$ |
| 6.00 | 0.101 | $\bar{1}.004$ | $1.01 \times 10^{+5}$ |
| 6.78 | 0.0362 | $\bar{2}.559$ | $2.18 \times 10^{+5}$ |
| (8.06) | (0.0025) | $\bar{3}.398$ | $2.88 \times 10^{+5}$ |
| (8.24) | (0.0016) | $\bar{3}.204$ | $2.78 \times 10^{+5}$ |
| 9.28 | 0.00030 | $\bar{4}.477$ | $5.72 \times 10^{+5}$ |
| 10.23 | 0.000116 | $\bar{4}.064$ | $1.97 \times 10^{+6}$ |
| (The data in brackets are taken from measurements in which the pH was changing during the course of the run.) | | | |
| *Benzal-p-chloroaniline* | | | |
| 5.57 | 0.0875 | $\bar{2}.942$ | $3.25 \times 10^{+4}$ |
| 5.98 | 0.0537 | $\bar{2}.730$ | $5.11 \times 10^{+4}$ |
| 7.89 | 0.0025 | $\bar{3}.398$ | $1.94 \times 10^{+5}$ |
| 9.96 | $7.70 \times 10^{-5}$ | $\bar{5}.886$ | $7.00 \times 10^{+5}$ |
| *p-Dimethylaminobenzalaniline* | | | |
| 6.39 | 0.44 | $\bar{1}.644$ | $1.08 \times 10^{+6}$ |
| 6.49 | 0.38 | $\bar{1}.580$ | $1.17 \times 10^{+6}$ |
| 10.52 | $3.93 \times 10^{-4}$ | $\bar{4}.594$ | $1.30 \times 10^{+7}$ |

and Fig. 8. For each substance it is evident that the rate constant divided by the hydrogen-ion concentration does not give a constant and the equation

$$k = k_{H^+}[H^+]$$

cannot be valid. The plots of log $k$ versus pH in Fig. 8 indicate that the dependence of the rate of the hydrogen-ion concentration is more complicated and further measurements will be necessary before an empirical equation for $k$ as a function of $[H^+]$ can be given.

In this investigation there are two effects which cannot be completely

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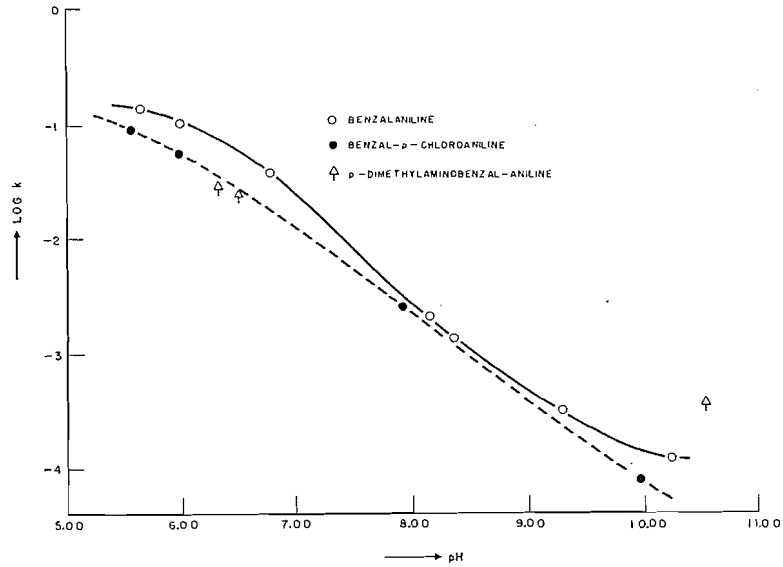



FIG. 8. Benzalaniline-hydrolysis in unbuffered solutions.

understood from the point of view of Brönsted's theory of special and general acid catalysis alone:

(*a*) In buffer mixtures of low buffer concentrations the experimental rates are lower than the values computed from Equation 2.

(*b*) In unbuffered solutions the equation $k = k_{H^+}[H^+]$ is not valid. Both effects have also been found by C. V. King and E. D. Bolinger (3) for the acid catalyzed hydrolysis of diazoacetate ion in aqueous solution and an effect similar to (*a*) was observed by Brönsted, Nicholson, and Delbanco (2) for the decomposition of nitramide in *m*-cresol catalyzed by negatively charged bases.

Before it is possible to reach a fuller understanding of acid catalysis in the hydrolysis of the benzalanilines and to give a more satisfactory treatment of the experimental work reported in this paper, it will be necessary to find the cause of these deviations.

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# THE PHOTOLYSIS OF AZOISOPROPANE[1]

By R. W. Durham[2] and E. W. R. Steacie

ABSTRACT

Azoisopropane has been photolyzed by 3660 Å radiation over the temperature range 30–120° C. The effect of pressure indicates an excited molecule mechanism. Excited molecules which decompose give nitrogen and isopropyl radicals; the latter either combine, disproportionate, or react with azoisopropane. The activation energy difference between the two reactions

$$C_3H_7\cdot + C_3H_7.N{:}N.C_3H_7 \rightarrow C_3H_8 + C_3H_6.N{:}N.C_3H_7$$
$$2C_3H_7\cdot \rightarrow C_6H_{14}$$

has been found to be $6.5 \pm 0.5$ kcal. per mole.

The difference in activation energy between the disproportionation and combination reactions is rendered ambiguous by the possibility of $C_3H_7.N{:}N$ existing at the lower temperatures; but this is certainly small. The ratio of the rates of the two reactions is 0.5 at room temperature.

## INTRODUCTION

The photolysis of azoisopropane has not been previously reported in the literature although the thermal decomposition has been studied by Ramsperger (10). This author did not analyze the gaseous reaction products and did not propose any free radical mechanism for the decomposition. It seems reasonable to suppose that the initial reaction in decomposition is to form nitrogen and isopropyl radicals, these radicals then would react with themselves and the remaining azoisopropane.

Weininger and Rice (12) have shown that a molecule of azoethane on absorbing a quantum of radiation is raised to an excited state having a lifetime reasonably long compared to the time between collisions with a normal molecule and hence a proportion of the radiation absorbed by the azoethane is dissipated without reaction. The quantum yield of nitrogen formation is therefore pressure dependent, and although recent work on the photolysis of azomethane (3) has shown that this effect does not occur with the lower homologue it should appear in the photolysis of azoisopropane which has a greater number of internal degrees of freedom.

The object of this research has been therefore to investigate the disproportionation and combination reactions of isopropyl radicals, the rate of reaction of isopropyl with azoisopropane, and to determine whether an excited molecule is produced in the photolysis of azoisopropane.

## EXPERIMENTAL

The azoisopropane was prepared after the method of Lochte, Noyes, and Bailey (6). It was purified by vacuum fractionation and stored in a darkened trap attached to the apparatus by means of a mercury cutoff. About 0.2 per cent of $C_6H_{14}$ was always present in the stored azoisopropane which, if allowed to remain, would cause an appreciable error in the $C_6H_{14}$ analysis of runs of low conversion. The procedure used in filling the reaction cell therefore entailed con-

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densing a sample of azoisopropane into the analysis section, removing the residual $C_6H_{14}$, and then expanding into the filling section of the apparatus. The pressure was measured with a mercury manometer, and the cell then closed off for irradiation. The reaction cell was 10 cm. in length, with a volume of 196 cc., and was almost completely filled by the light beam.

The analysis section consisted of a modified Ward still as described by LeRoy (5), a Toepler pump, and McLeod gauge. A trap ahead of the Ward still maintained at − 75°C. removed the bulk of the unchanged azoisopropane.

The mercury vapor lamp used was the Hanovia 100 watt Alpine burner, its beam collimated with two lenses and two stops. The absorption maximum for azoisopropane is at 3600 Å so that the 3660 Å mercury line was used for the photolysis and was isolated by using two Corning 5860 filters. A selenium photocell connected directly to a sensitive microammeter was placed at the back of the reaction cell to measure the transmitted intensity.

The aluminum block furnace had quartz windows at each end to cut down cooling by convection and the temperature varied only by about 1°C. during a 12 hr. run. The voltage at the furnace and lamp was maintained constant by using a Sorenson voltage stabilizer.

*Results*

The absorption coefficient of azoisopropane for 3660 Å radiation was found to increase appreciably with temperature. Curves of pressure against log transmission were therefore determined for the temperature at which arbitrary quantum yields were measured. In this way the absorption occurring during a run was known by measuring the pressure of azoisopropane in the cell.

The analytical procedure following a run was as follows.

Most of the unreacted azoisopropane and condensable products was condensed in a side tube with liquid nitrogen before the cell was opened to the analytical section. The remaining condensables were removed by leaving the cell open to the Ward still, cooled with liquid nitrogen for two to three hours, and then the residual nitrogen was pumped into the gas burette. Mass spectrometer analysis of a sample of this gas confirmed that it was pure nitrogen.

On warming the Ward still to − 135°C. the propane and propylene were brought off together and, after the volume and pressure had been measured, a sample of the mixture was analyzed by absorption of the propylene onto a bead of fused mercuric acetate (9).

By plotting a vapor pressure curve at low temperatures for carefully purified azoisopropane and comparing it with that for 2,3-dimethyl butane, the expected $C_6$ hydrocarbon produced from the combination of two isopropyl radicals, it appeared that a separation of the two compounds could be obtained at a maximum vapor pressure of about $5 \times 10^{-2}$ mm. By holding the Ward still at − 85°C. and using the preliminary trap described above, it was possible to separate the $C_6H_{14}$ hydrocarbon and measure its volume and pressure; the spread of the points in Figs. 1 and 2 probably represent the analytical error in the $C_6H_{14}$ estimation. The cracking pattern of this hydrocarbon in the mass spectrometer was used to identify it with an authentic specimen of 2,3-dimethyl butane.

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A material balance of $N_2 = \frac{1}{2}(C_3H_8 + C_3H_6) + C_6H_{14}$ was obtained with a standard deviation of $\pm 5\%$ about 100% balance, except for one run where the low pressure made analysis difficult. In three runs it was found that all the $C_6H_{14}$ had not been removed before the runs were started so that the correct amount was calculated by difference from the nitrogen and propane plus propylene analyses. The rate of nitrogen production was found to be directly proportional to the incident intensity of the radiation for a constant azoisopropane concentration.

*Discussion*

The following reaction scheme is proposed to account for the variation in products with varying radiation intensity, absorption, and concentration of azoisopropane. AP refers to the normal molecule of azoisopropane whilst $AP^x$ is the excited state.

$$C_3H_7.N{:}N.C_3H_7 \xrightarrow{h\nu} AP^x$$

$$AP^x \rightarrow N_2 + 2\ \text{iso-}C_3H_7 \quad [1]$$

$$AP + AP^x \rightarrow 2\ AP \quad [2]$$

$$2\ \text{iso-}C_3H_7 \rightarrow C_3H_6 + C_3H_8 \quad [3]$$

$$\rightarrow C_6H_{14} \quad [4]$$

$$\text{iso-}C_3H_7 + AP \rightarrow C_3H_8 + C_3H_6.N{:}N.C_3H_7 \quad [5]$$

It is seen by inspection of the above scheme that

$$\frac{R_{C_3H_6}}{R_{C_6H_{14}}} = \frac{k_3}{k_4}$$

so that the rate of combination of isopropyl radicals compared with the disproportionation rate can be obtained from the propylene to $C_6H_{14}$ ratio. By assuming a constant steady state concentration of isopropyl the following two equations, analogous to those obtained in the photolysis of diethyl ketone (4), can be applied

$$\frac{R_{C_3}}{R_{C_6H_{14}}} = \frac{2k_3}{k_4} + \frac{k_5}{k_4^{\frac{1}{2}}} \cdot \frac{[AP]}{R_{C_6H_{14}}^{\frac{1}{2}}} \quad [7]$$

$$\frac{\Delta R_{C_3}}{R_{C_6H_{14}}} = \frac{k_5}{k_4^{\frac{1}{2}}} \cdot \frac{[AP]}{R_{C_6H_{14}}^{\frac{1}{2}}} \quad [8]$$

$R_{C_3}$ represents the rate of formation of $C_3H_6 + C_3H_8$ and $\Delta R_{C_3}$ is $(C_3H_8 - C_3H_6)$. $R_{C_6H_{14}}$ is expressed in molecules/sec./cc. of cell volume and the concentration of azoisopropane in molecules/cc.

The large radical appearing in reaction [5] appears to be relatively stable and probably disappears by dimerization. It does not seem to remove isopropyl radicals to form $C_6H_{13}.N{:}N.C_3H_7$ because a good material balance is obtained. Also it does not appear to react with an isopropyl radical to give $C_6H_{14}$ and $C_3H_6$. Such a reaction as this would cause $R_{C_6H_{14}}$ to increase with temperature through the $C_3H_6.N{:}N.C_3H_7$ concentration increasing with temperature whereas $R_{C_6H_{14}}$ actually decreases with temperature. Similarly the reaction

$$C_3H_6.N{:}N.C_3H_7 \rightarrow C_3H_6 + N_2 + C_3H_7$$

is not important as $C_3H_6$ does not increase with temperature.

Table I shows the results obtained by varying concentration of azoisopropane, radiation intensity, and temperature, and they have been used in Figs. 1 and 2

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TABLE I

PHOTOLYSIS OF AZOISOPROPANE

| [AP] molecules, cc.$^{-1}$ $\times 10^{-18}$ | $R_{C_3H_6}/R_{C_6H_{14}}$ | $\Delta R_{C_3}/R_{C_6H_{14}}$ | $R_{C_3}/R_{C_6H_{14}}$ | $R_{C_6H_{14}}$ molecules, cc.$^{-1}$ sec.$^{-1}$ $\times 10^{-12}$ | $R_{C_6H_{14}}{}^{\frac{1}{2}}$ $\times 10^{-6}$ | $[AP]/R_{C_6H_{14}}{}^{\frac{1}{2}}$ molecules$^{\frac{1}{2}}$ cc.$^{-\frac{1}{2}}$ sec.$^{\frac{1}{2}}$ $\times 10^{-12}$ | $T$, °K. | $R_{N_2}$ molecules per sec. per cc. of reaction volume | Incident intensity, arbitrary units |
|---|---|---|---|---|---|---|---|---|---|
| 0.55 | 0.58 | 0.042 | 1.20 | 1.99 | 1.41 | 0.390 | 303 | 3.26 | 1.00 |
| 0.90 | 0.55 | 0.096 | 1.19 | 2.82 | 1.68 | 0.536 | | 4.87 | 1.00 |
| 1.32 | 0.51 | 0.082 | 1.10 | 3.56 | 1.89 | 0.698 | | 5.02 | 1.00 |
| 0.27 | 0.53 | 0.050 | 1.12 | 1.23 | 1.11 | 0.243 | | 1.86 | 1.00 |
| 0.69 | 0.57 | 0.070 | 1.21 | 2.20 | 1.49 | 0.463 | | 3.49 | 0.954 |
| 0.18 | 0.53 | 0.050 | 1.12 | 0.86 | 0.93 | 0.194 | | 1.254 | 0.952 |
| 1.29 | 0.53 | 0.120 | 1.18 | 1.03 | 1.02 | 1.264 | | 1.57 | 0.312 |
| 0.53 | 0.57 | 0.088 | 1.24 | 1.42 | 1.19 | 0.445 | | 2.38 | 0.767 |
| 1.00 | 0.54 | 0.096 | 1.17 | 1.97 | 1.41 | 0.709 | | 3.13 | 0.797 |
| 0.80 | 0.56 | 0.075 | 1.20 | 1.67 | 1.29 | 0.620 | | 2.65 | 0.797 |
| 0.93 | 0.55 | 0.100 | 1.19 | 1.88 | 1.37 | 0.679 | | 2.93 | 0.775 |
| 1.017 | 0.48 | 0.119 | 1.07 | 0.753 | 0.869 | 1.170 | | 1.21 | 0.347 |
| 0.670 | 0.56 | 0.116 | 1.23 | 0.521 | 0.720 | 0.931 | | 1.02 | 0.338 |
| 1.18 | 0.29 | 0.57 | 1.14 | 1.92 | 1.39 | 0.849 | 394 | 2.76 | 0.513 |
| 0.70 | 0.35 | 0.51 | 1.22 | 1.15 | 1.07 | 0.654 | | 1.84 | 0.496 |
| 1.14 | 0.36 | 0.86 | 1.59 | 1.46 | 1.21 | 0.942 | | 2.59 | 0.500 |
| 0.57 | 0.37 | 0.53 | 1.26 | 1.02 | 1.01 | 0.564 | | 1.57 | 0.516 |
| 0.38 | 0.40 | 0.47 | 1.25 | 0.66 | 0.81 | 0.469 | | 1.07 | 0.485 |
| 0.18 | 0.41 | 0.17 | 1.20 | 0.38 | 0.62 | 0.290 | | 0.61 | 0.490 |
| 1.11 | 0.44 | 0.38 | 1.25 | 1.23 | 1.11 | 1.000 | 354 | 2.00 | 0.487 |
| 0.79 | 0.40 | 0.254 | 1.05 | 1.13 | 1.06 | 0.745 | | 1.55 | 0.487 |
| 0.44 | 0.43 | 0.25 | 1.10 | 0.657 | 0.81 | 0.544 | | 1.01 | 0.472 |
| 0.22 | 0.46 | 0.10 | 1.03 | 0.402 | 0.63 | 0.350 | | 0.56 | 0.460 |
| 1.53 | 0.40 | 0.64 | 1.42 | 0.966 | 0.98 | 1.560 | | 0.85 | 0.190 |
| 0.88 | 0.40 | 0.45 | 1.25 | 0.425 | 0.65 | 1.350 | | 0.68 | 0.180 |
| 0.11 | 0.46 | 0.125 | 1.06 | 0.134 | 0.37 | 0.300 | | 0.30 | 0.434 |
| 1.24 | 0.50 | 0.270 | 1.27 | 1.03 | 1.02 | 1.220 | 335 | 1.75 | 0.434 |
| 0.72 | 0.50 | 0.200 | 1.20 | 0.834 | 0.914 | 0.788 | | 1.34 | 0.425 |
| 1.62 | 0.47 | 0.298 | 1.24 | 1.16 | 1.08 | 1.500 | | 1.90 | 0.428 |
| 1.59 | 0.48 | 0.382 | 1.35 | 0.684 | 0.828 | 1.920 | | 1.20 | 0.253 |
| 0.926 | 0.49 | 0.302 | 1.28 | 0.527 | 0.725 | 1.280 | 335 | 0.90 | 0.246 |
| 0.841 | 0.50 | 0.222 | 1.23 | 0.723 | 0.850 | 0.989 | | 1.21 | 0.372 |
| 0.571 | 0.49 | 0.206 | 1.17 | 0.579 | 0.760 | 0.751 | | 0.92 | 0.363 |
| 0.231 | 0.44 | 0.170 | 1.04 | 0.295 | 0.544 | 0.425 | | 0.47 | 0.350 |
| 0.428 | 0.46 | 0.227 | 1.14 | 0.452 | 0.673 | 0.636 | | 0.80 | 0.310 |
| 0.115 | 0.50 | 0.129 | 1.13 | 0.138 | 0.372 | 0.310 | | 0.32 | 0.338 |

to obtain $k_6/k_4^{\frac{1}{2}}$ by plotting $\Delta R_{C_3}/R_{C_6H_{14}}$ against $[AP]/R_{C_6H_{14}}$. The logarithms of the least squares values of $k_5/k_4^{\frac{1}{2}}$ have been plotted against the reciprocal temperatures in order to evaluate $E_5 - \frac{1}{2}E_4$; from Fig. 3 this activation energy difference is calculated by the method of least squares to be 6.5 ± 0.5 kcal. per mole and the ratio of the steric factors $P_5/P_4^{\frac{1}{2}}$ is $5 \times 10^{-4}$; 6.5 kcal. would be a minimum value for the activation energy involved in the abstraction of a tertiary hydrogen atom from azoisopropane as it is possible that $E_4$ is not zero. Trotman-Dickenson, Birchard, and Steacie (11) obtained values of 7.6 and 7.8 kcal. for the abstraction of tertiary hydrogen atoms from isobutane and 2,3-dimethyl butane by methyl radicals which are similar reactions to the above. The reaction involving an isopropyl radical would be expected to be slightly higher in energy due to the formation in this reaction of the weaker secondary C–H bond of propane. The ratio of the steric factors in the methyl radical work was also

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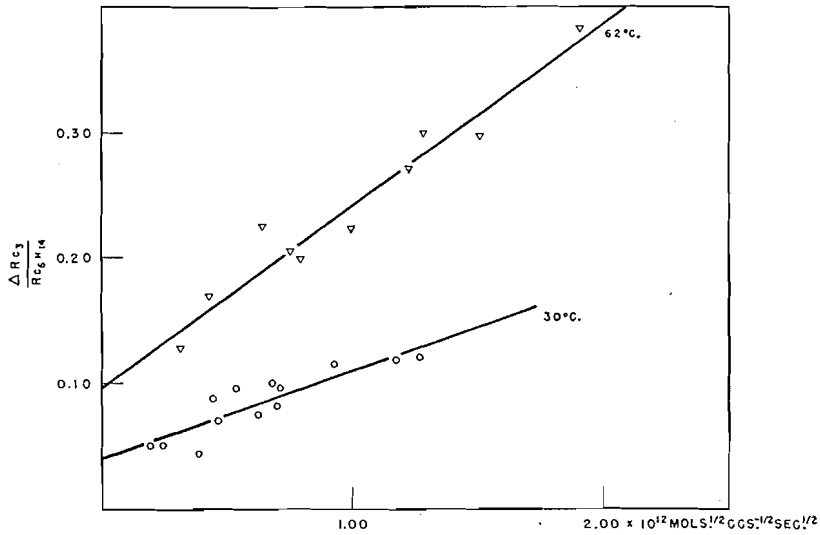



FIG. 1. $\Delta R_{C_3}/R_{C_6H_{14}}$ plotted against $[AP]/R_{C_6H_{14}}^{1/2}$ at 30° and 62°C.

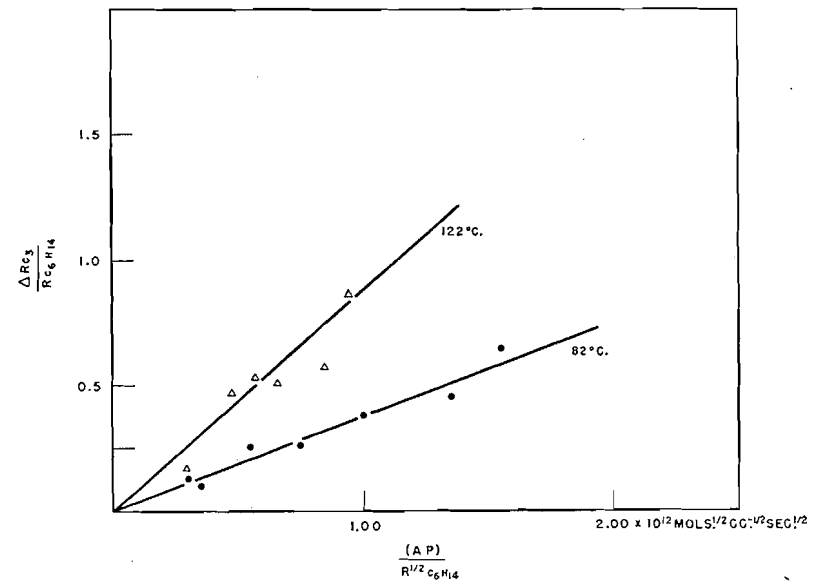



FIG. 2. $\Delta R_{C_3}/R_{C_6H_{14}}$ plotted against $[AP]/R_{C_6H_{14}}^{1/2}$ at 82° and 122°C.

of the order of $10^{-3}$. Kutschke, Wijnen, and Steacie (4) obtained an activation energy of 7.5 kcal. for the reaction of an ethyl radical with diethyl ketone, while Ivin and Steacie (2) found 6.2 kcal. for the similar reaction between an ethyl radical and mercury dimethyl. The difference between these reactions and reaction [5] is that a secondary C–H bond is broken compared with a tertiary in azoisopropane, whilst a primary is formed in ethane and a secondary in propane. As the activation energies are in reasonable agreement the primary

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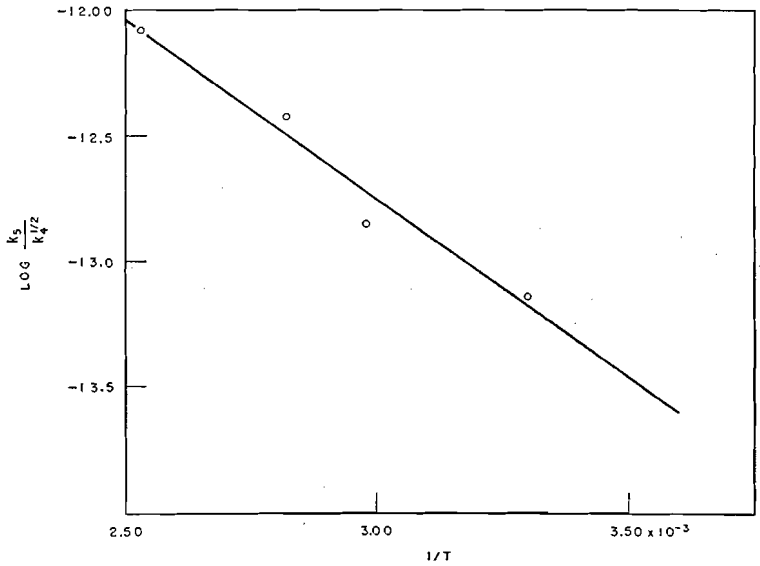



FIG. 3. Arrhenius plot of $k_5/k_4^{\frac{1}{2}}$.

and secondary C–H bond dissociation energy difference must be practically equal to the secondary and tertiary difference in ethane and propane. From a study of the photolysis of di-*n*-propyl ketone, Masson (7) has found the activation energy needed for removal of a secondary hydrogen atom from di-*n*-propyl ketone by the *n*-propyl radical to be 6.5 kcal.; in this case a primary C–H bond is formed in the reaction.

Equation [8] should give a straight line passing through the origin but positive intercepts are obtained on extrapolating the 30°C. and 62°C. graphs to zero value of $[AP]/R_{C_6H_{14}}^{\frac{1}{2}}$. This might be due to the presence of the radical $C_3H_7N{:}N.$ at lower temperatures which would give $C_3H_8 + C_3H_6$ probably more readily than $C_6H_{14}$ by the following reaction.

$$C_3H_7 + C_3H_7.N{:}N. \rightarrow N_2 + C_3H_8 + C_3H_6 \qquad [9]$$

It is also possible that at low pressures the diffusion of radicals to the walls becomes important. Table II shows the variation of $k_3/k_4$ with increasing temperature. The values in the first column have been obtained by averaging those for a series of runs at each temperature and those in the second column have been calculated from graphs of equation [7] correcting for the intercepts

TABLE II

VARIATION OF RATE CONSTANTS WITH TEMPERATURE

| Temperature, °C. | $k_3/k_4$ average | $k_3/k_4$ from intercepts |
|---|---|---|
| 30 | 0.54 | 0.51 |
| 62 | 0.48 | 0.48 |
| 81 | 0.43 | 0.47 |
| 121 | 0.36 | 0.38 |

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appearing in Figs. 1 and 2, after the manner of Kutschke, Wijnen, and Steacie (4). It is interesting to note that the value of $k_3/k_4$ obtained at 30°C. agrees with that of 0.5 obtained by Blacet and Calvert (1) during an investigation of the photolysis of isobutyraldehyde at room temperature. A similar result, namely 0.4 was estimated by Moore and Taylor (8) from the ratio of propane to hexane formation during the mercury photosensitized hydrogenation of propylene at room temperature. The somewhat lower ratio of 0.15 has been obtained in the photolysis of di-*n*-propyl ketone by Masson (7) and is probably related to the different configurations of the normal and isopropyl radicals.

The value of $k_3/k_4$ appears to fall off with increasing temperature but the effect is relatively small and in view of uncertainty of explanation of intercepts is perhaps not worth discussing in detail. It is, however, possible that the presence of $C_3H_7.N:N.$ may be a complication. The activation energy difference between disproportionation and recombination is almost certainly zero and the value of 0.5 for $k_3/k_4$ a steric effect.

The production of an excited molecule of azoisopropane in the primary step is indicated by the way the rate of nitrogen formation drops off with increasing azoisopropane concentration as is required by reaction [2]. An arbitrary primary process quantum yield $\phi_a$ has been calculated by dividing the rate of nitrogen production, corrected for variations in incident intensity, by the percentage absorption and making $\phi_a$ equal to 1 at the extrapolated value of zero azoisopropane concentration. In Fig. 4, $\phi_a$ has been plotted against concentration for

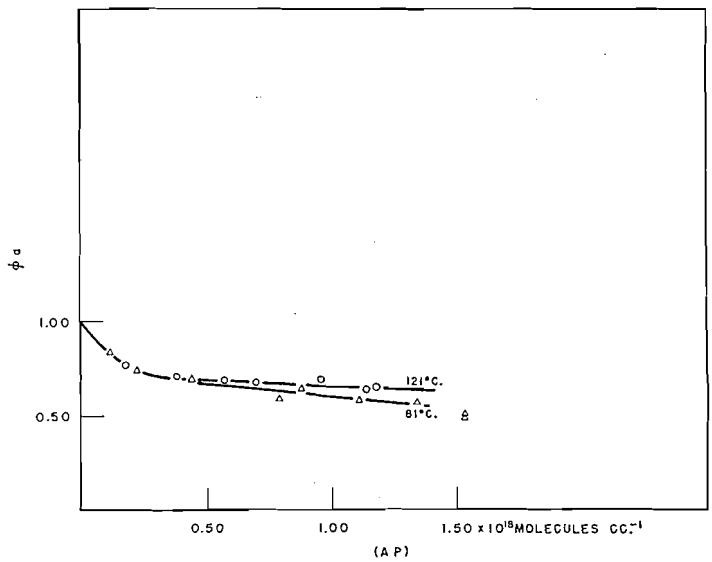



FIG. 4. Plot of $\phi_a$ against azoisopropane concentration.

two temperatures showing a small increase in quantum yield with temperature at higher azoisopropane concentrations.

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# ORGANIC DEUTERIUM COMPOUNDS

## V. THE CHLORINATION OF PROPYNE AND PROPYNE-$d_4$[1]

By L. C. Leitch[2]

ABSTRACT

Chlorination of propyne at 70° C. gave 60 to 65% yields of 1,1,2,2-tetrachloropropane and 15 to 20% yields of *trans*-1,2-dichloro-1-propene. 1,1,2,2-Tetrachloropropane-$d_4$ was similarly prepared from propyne-$d_4$. Nearly theoretical yields of *cis*- and *trans*-1,2-dichloro-1-propene were obtained by partial dechlorination of tetrachloropropane. Deuterated *cis*- and *trans*-1,2-dichloro-1-propene were obtained in the same manner from 1,1,2,2-tetrachloropropane-$d_4$.

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### INTRODUCTION

Some time ago normal and deuterated *cis*- and *trans*-1,2-dichloro-1-propene were required to establish the configuration of this pair of geometrical isomers. The spectroscopic results of this investigation have already been reported by Bernstein and Powling (1). Since these compounds were prepared from propyne and propyne-$d_4$ by a novel method, it was felt that the synthetic part of the work should be reported in a separate paper.

*cis*- and *trans*-1,2-Dichloro-1-propene have been previously prepared from sodium 2,3,3-trichlorobutyrate (7) and 1,2,2-trichloropropane (4) respectively. Neither of these methods is suitable for the preparation of the deuterated dichloropropenes. These compounds might be obtainable, however, from propyne-$d_4$ (5) by chlorination to 1,1,2,2-tetrachloropropane-$d_4$ followed by partial dechlorination with zinc dust in ethanol.

Although the literature on the chlorination of acetylene is voluminous (3) the reaction of other acetylenic hydrocarbons with chlorine has not been extensively investigated. Hexyne-1 was reported by Hennion and Welsh (2) to give a 30.6% yield of 1,1,2,2-tetrachlorohexane and a 19.6% yield of *trans*-1,2-dichloro-1-hexene when chlorinated at 40° C. in carbon tetrachloride in the presence of antimony pentachloride. Rengert and Schumacher (6) obtained a mixture of compounds which were not all characterized from the vapor phase chlorination of vinylacetylene at 150° C.

In the present work, the chlorination of propyne was first investigated in carbon tetrachloride at −20, −40, and −60° C. in the presence of antimony pentachloride. The reaction products boiled over a wide range and only low yields of 1,1,2,2-tetrachloropropane were obtained. Chlorination by substitution as well as by addition appeared to have taken place. In the vapor phase, however, propyne reacted smoothly at 65 to 70° C. to give, in 60 to 65% yields, 1,1,2,2-tetrachloropropane. In addition, *trans*-1,2-dichloro-1-propene was obtained in 15 to 20% yields. The *cis*- isomer was prepared by fractional distillation of the mixture resulting from the dechlorination of 1,1,2,2-tetrachloropropane. The corresponding deuterated compounds were prepared from propyne-$d_4$.

[1] *Manuscript received December 8, 1952.*
*Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2948.*
[2] *Present address—Division of Pure Chemistry, National Research Council, Ottawa, Canada.*

## EXPERIMENTAL

### *1,1,2,2-Tetrachloropropane*

The apparatus used in these experiments was similar to that described by Taylor and Morey (8). The reactor (2 liters) was heated by means of an infrared lamp at a distance of six inches from the flask. Dry chlorine and propyne were introduced into the reactor through flowmeters in the ratio 2:1. After a short induction period, during which the temperature of the gases in the reactor rose to 60 to 70° C., the reaction started and liquid product began to form. When 17.0 liters of propyne had been introduced at the rate of 2.0 liters per hour, the liquid product was withdrawn, washed with aqueous potassium carbonate, and dried over anhydrous potassium carbonate. The yield was 107 gm.

On distillation at atmospheric pressure in a Stedman column (12 in. × $\frac{3}{4}$ in.) a fraction, b.p. 62 to 98° C., largely at 75° C., was collected. This product was redistilled in a smaller Stedman column (12 in. × $\frac{3}{8}$ in.); it was mainly *trans*-1,2-dichloro-1-propene, b.p. 75° C., $n_D^{20}$ 1.4498. Yield: 15.0 gm. (20%).

The 1,1,2,2-tetrachloropropane was fractionated under reduced pressure. After collecting a forerun (5.5 ml.) up to 79° C. at 64 mm., the main product distilled at 81° C. at 64 mm. The yield of 1,1,2,2-tetrachloropropane, $n_D^{20}$ 1.4866, was 82.5 gm. (63% of the theoretical amount).

Propyne-$d_4$ prepared as described in a previous paper (5) gave similar yields of 1,1,2,2-tetrachloropropane-$d_4$, $n_D^{20}$ 1.4848.

### *cis- and trans-1,2-Dichloro-1-propene*

1,1,2,2-Tetrachloropropane (37.5 gm.) was added gradually to a boiling suspension of zinc dust (20.0 gm.) in 200 ml. of ethanol in a 1 liter three-necked round-bottomed flask equipped with a stirrer and reflux condenser. Any allene which was formed owing to the presence of isomeric 1,2,2,3-tetrachloropropane was condensed in a trap cooled to −78° C. by dry ice and acetone. The reaction mixture was heated under reflux for one hour after the chlorocompound had been added. The mixed dichloropropenes formed were then distilled off through a Stedman column as azeotropes with ethanol and water. The yield was nearly quantitative. The product was separated into the *cis*- and *trans*-isomers boiling at 92° and 75° C. respectively by means of a Stedman column. For *trans*-1,2-dichloro-1-propene, $n_D^{20}$ 1.4498; for the *cis* form, $n_D^{20}$ 1.4549.

The corresponding deuterated compounds were prepared in exactly the same way. For *trans*-1,2-dichloro-1-propene, $n_D^{20}$ 1.4479 and for the *cis* form, $n_D^{20}$ 1.4528.

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# THE PAPILIONACEOUS ALKALOIDS

## XX. *LUPINUS WYETHII* S. WATS. AND *BAPTISIA VERSICOLOR* LODD.[1]

By François Turcotte, Raymond Leduc[2], and Léo Marion

ABSTRACT

An investigation of the basic components of *Lupinus wyethii* S. Wats. has revealed the presence of at least four alkaloids, three of which, i.e., *l*-sparteine, *d*-lupanine, and hydroxylupanine, are known. The fourth has not been found in sufficient quantity to permit proper characterization. A similar investigation of *Baptisia versicolor* Lodd. has yielded three alkaloids, i.e., *d*-sparteine, *l*-lupanine, and *l*-anagyrine.

The first plant under investigation was collected in 1948 through the courtesy of Messrs. S. B. Penick Co., in Paddock No. 1, U.S. Sheep Experiment Station, Dubois, Idaho. It has been identified as *Lupinus wyethii* S. Wats., and voucher specimens are kept under No. 539 (Lichtenfelder) in the Herbarium of the State College of Washington, Pullman, Wash. The plant has been found to contain three well known alkaloids together with a small quantity of a base which could not be identified and was obtained in too scanty a quantity to make its proper characterization possible. The most abundant alkaloid present was *l*-sparteine, while the next in importance was *d*-lupanine. The third, hydroxylupanine, was present in small quantity only. This is the fourth reported occurrence of hydroxylupanine which was first found in *L. polyphyllus* L. (2) and later in *L. angustifolius* L. (1). Octalupine isolated from *L. sericeus* var. *flexuosus* C. P. Smith (4) has been shown to be identical with hydroxylupanine (6). The hydroxylupanine now isolated was characterized by direct comparison with an authentic sample kindly supplied by Dr. F. Galinovsky. The infrared absorption spectra of both bases were superimposable.

The second plant investigated, *Baptisia versicolor* Lodd., was grown at the Dominion Experimental Farm, Ottawa. It was found to contain at least three alkaloids, i.e., *d*-sparteine, *l*-lupanine, and *l*-anagyrine. It has been stated that *B. versicolor* is identical with *B. australis* (5). However, the main alkaloids contained in the latter were *d*-sparteine, cytisine, and N-methylcytisine (7) and therefore the earlier distinction of *B. versicolor* as an individual species was probably justified.

### EXPERIMENTAL[3]

#### A. *Lupinus wyethii*

The dried and ground plant material (whole plant) weighed 8560 gm. It was extracted with methanol in Soxhlet extractors, and the combined methanolic liquor concentrated on the steam bath until most of the solvent had been

[1] *Manuscript received January 7, 1953.*
*Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada, and the Department of Chemistry, University of Montreal, Montreal, Que. Issued as N.R.C. No. 2949.*
[2] *At the time holder of Canadian Industries Limited Fellowship at the University of Montreal.*
[3] *All melting points are corrected.*



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removed. The residue was worked up as previously described (7).

The basic product thus obtained consisted of a heavy oil which separated into two layers on standing. It was distilled *in vacuo* and yielded the following fractions: (I) b.p. 90–110° at 0.1 mm., colorless mobile oil, wt. 34.7 gm.; (II) b.p. 120–135° at 0.1 mm., viscous oil, wt. 18.9 gm.; (III) b.p. 150–165° at 0.1 mm., pale yellow resin, wt. 3.7 gm.; (IV) undistilled residue.

*l-Sparteine*

Fraction I was redistilled and the oil boiling at 95–100° at 0.2 mm. collected while the residue was combined with fraction II. A quantity (1.0 gm.) of the distillate in methanol was converted to the picrate which after recrystallization from boiling methanol consisted of yellow needles, m.p. 208° either alone or in admixture with *l*-sparteine dipicrate. Calcd. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.80; H, 4.62. Found: C, 46.87, 47.03; H, 4.58, 4.76%.

The bulk of the distillate was dissolved in methanol and to the solution 70% perchloric acid was added dropwise to a phenolphthalein end point. The perchlorate which crystallized was filtered and recrystallized from methanol–ether from which it separated as colorless prismatic needles, m.p. 173° either alone or in admixture with an authentic sample of *l*-sparteine monoperchlorate. Calcd. for $C_{15}H_{26}N_2.HClO_4$: C, 53.83; H, 8.07; N, 8.30. Found: C, 53.60, 53.79; H, 7.99, 7.93; N, 8.09, 8.28%.

*d-Lupanine*

Fraction II was dissolved in methanol and the solution made acid to Congo red by the dropwise addition of 70% perchloric acid. A crystalline perchlorate separated which after repeated recrystallization from methanol melted at 211° either alone or in admixture with an authentic sample of *d*-lupanine perchlorate. A small quantity of the perchlorate was decomposed and the liberated base redistilled, b.p. 110–115° at 0.1 mm. The free base consisted of a colorless oil, $[\alpha]_D^{23} + 61.1°$ (*c*, 1.145 in acetone). The literature gives $[\alpha]_D + 61.4°$ in acetone for *d*-lupanine (3).

*Hydroxylupanine*

Fraction III was dissolved in methanol and the solution made acid to Congo red by the cautious addition of 70% perchloric acid. The solution was combined with the mother liquors of the crystallization of *d*-lupanine perchlorate, concentrated, and allowed to stand. It yielded a further small quantity of *d*-lupanine perchlorate which was filtered. The filtrate was concentrated, diluted with water, and alkalized with ammonium hydroxide. The regenerated bases were extracted with chloroform, the extract evaporated to dryness, and the residue dissolved in anhydrous benzene. The solution was chromatographed on activated alumina and the adsorbed base eluted with benzene–ether (90–10), with ether–methanol (99–1), and finally with ether–methanol (95–5). The benzene–ether eluate yielded *d*-lupanine while the two ether–methanol eluates yielded a crystalline base which after recrystallization from acetone consisted of colorless prisms, m.p. 169–170°, either alone or in admixture with an authentic specimen of hydroxylupanine. Calcd. for $C_{15}H_{24}O_2N_2$: C, 68.14;

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H, 9.15; N, 10.60. Found: C, 68.46, 68.65; H, 9.27, 9.14; N, 10.73%. The identity of this base with hydroxylupanine was confirmed by comparison of the infrared absorption spectra of both bases which were exactly superimposable.

The undistilled residue (fraction IV) was dissolved in dilute (1:1) hydrochloric acid, the solution filtered through charcoal to remove some insoluble material, alkalized with ammonium hydroxide, and extracted with chloroform. The base recovered from the extract was treated as the original crude base. It yielded further quantities of the same alkaloids.

The final mother liquors which yielded hydroxylupanine were concentrated and made just acid to Congo red with 70% perchloric acid. On concentration and dilution with ether, a very small quantity of a perchlorate crystallized out in long silky needles, m.p. 250–251° (dec.). Found: C, 54.03, 53.99; H, 7.00, 7.17%. Owing to paucity of material it was not possible to purify this salt further nor to characterize it properly.

B. *Baptisia versicolor*

The ground plant (both aerial part and root) (1282 gm.) was extracted with methanol and the extract worked up as described above. The crude base thus obtained (0.995 gm.) was distilled *in vacuo*. It yielded the following fractions: (I) b.p. 65–130° at 0.2 mm., colorless oil, wt. 25 mgm.; (II) b.p. 130–180° at 0.2 mm., yellow oil, wt. 120.5 mgm.; (III) b.p. 180–230° at 0.15 mm., yellow resin, wt. 312 mgm., and an undistilled residue, wt. 538 mgm. Fraction I proved to be untractable. Both fractions II and III were combined and redistilled into the following fractions: (*a*) colorless oil, b.p. 90–120° at 0.15 mm., wt. 39.3 mgm.; (*b*) viscous oil, b.p. 120–140° at 0.15 mm., wt. 96.3 mgm.; (*c*) yellow resin, b.p. 140–180° at 0.15 mm., wt. 95.6 mgm.; (*d*) reddish resin, b.p. 180–230° at 0.15 mm., wt. 26.2 mgm.; (*e*) residue undistilled at 230°, wt. 14.5 mgm.

*d-Sparteine*

Fraction *a* (39.3 mgm.) was dissolved in methanol and added to a methanolic solution of twice its weight of picric acid. A picrate crystallized as lemon yellow needles, m.p. 207°, and after recrystallization from methanol, m.p. 208°. Calcd. for $C_{15}H_{26}N_2.2C_6H_3O_7N_3$: C, 46.82; H, 4.65; N, 16.18. Found: C, 46.46, 46.67; H, 4.43, 4.38; N, 16.79, 16.59%. Admixture with authentic *d*-sparteine dipicrate failed to alter the melting point whereas admixture with *l*-sparteine dipicrate lowered the melting point to 203°.

The picrate was decomposed by shaking with hydrochloric acid and the recovered base redistilled. It was immediately dissolved in a little methanol and the solution titrated with perchloric acid to a phenolphthalein end point. Addition of ether caused the precipitation of a perchlorate as long colorless needles, m.p. 173°, either alone or in admixture with *d*-sparteine monoperchlorate.

*l-Lupanine*

Fraction *b* (96.3 mgm.) was dissolved in methanol and the solution made just acid to Congo red by the dropwise addition of 70% perchloric acid. A

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perchlorate separated which after recrystallization from methanol–ether melted at 213° and admixture with *l*-lupanine perchlorate failed to depress the melting point. The X-ray powder pattern of this salt and that of *l*-lupanine perchlorate were identical.

*l-Anagyrine*

Fraction *c* (95.6 mgm.) was converted to perchlorate in methanol in the usual way. The crystalline perchlorate was recrystallized from methanol–ether from which it separated as fine colorless needles, m.p. 310–315° (immersed at 300°) either alone or in admixture with *l*-anagyrine perchlorate. The X-ray powder pattern of the perchlorate and that of anagyrine perchlorate were superimposable.

Fraction *d* and the undistilled residue failed to yield anything tractable.

ACKNOWLEDGMENT

The authors are indebted to Dr. W. H. Barnes and Mrs. H. Sheppard for the X-ray powder patterns and to Dr. R. N. Jones and Mr. R. Lauzon for taking the infrared spectra. One of us (R.L.) expresses his gratitude to Prof. L. Lemay for his help and interest in this problem.

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# DETERMINATION OF THE NEUTRON CAPTURE CROSS SECTION FOR THE $Co^{59}(n,\gamma)Co^{60m}$ REACTION[1]

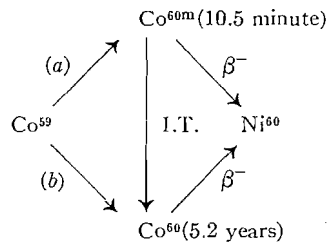
By N. Moss and L. Yaffe[2]

ABSTRACT

A determination of the neutron capture cross section of $Co^{59}$ leading to the excited state of $Co^{60}$ has been made by the activation method. Samples of cobalt were irradiated in the center of the Chalk River nuclear reactor in a pure iron capsule using a pneumatic delivery device. The cobalt activity was counted in a windowless counter and compared with the activity of a strip of pure gold irradiated under identical conditions in the same container. The cobalt and gold were counted with and without cadmium wrapping and the contribution due to epicadmium neutrons allowed for in the calculation. The mean value obtained was $18.3 \pm 1.7$ barns relative to $\sigma_{Au^{197}} = 93$ barns.

## METHOD

Cobalt is monoisotopic of mass 59. On bombardment with slow neutrons the following reactions occur:




The cross section for the reaction leading to the ground state which included the contribution from the $Co^{60m}$ by isomeric transition has been measured by Yaffe, Hawkings, Merritt, and Craven (8) using the activation method. They obtained a value of 34.2 barns which was confirmed soon after by Pomerance (5) using the pile oscillation technique.

It was considered of some interest to determine the cross section for reaction (*a*) leading directly to the excited state. A value of 0.66 barns had previously been obtained by Seren, Friedlander, and Turkel (6). They measured the ratio of $\beta$-rays formed by direct transition to $Ni^{60}$ to the soft electrons produced from the $\gamma$-rays of the isomeric transition to the $Co^{60}$ ground state. The cross section they obtained was based on this $\beta,\gamma$ branching ratio of 10.8/89.2 assuming that each particle, hard or soft, represented a disintegration.

More recently, a much lower value for this ratio has been obtained by Deutsch and Scharf-Goldhaber (2). Using an anthracene scintillation spectrometer to study the decay scheme of $Co^{60m}$, they found, as in Fig. 1, that only a small fraction ($0.28 \pm 0.06\%$) of the disintegrations went directly to $Ni^{60}$. The greater proportion (i.e., 99%) decays by isomeric transition to the ground state. An almost insignificant amount ($<10^{-4}\%$) decays by $\beta$ emission directly to the stable

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*Contribution from Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 23.*
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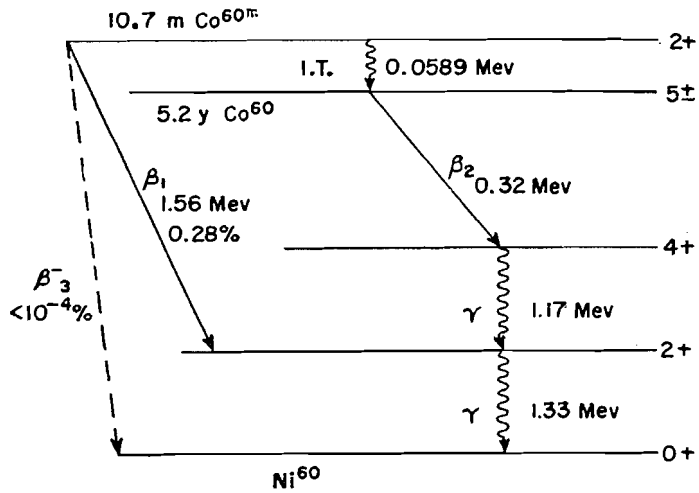



FIG. 1. Decay scheme of $Co^{60}$.

$Ni^{60}$. From the observed intensities of the hard $\gamma$ radiation of the ground state and metastable state activities of $Co^{60}$ they were able to compute the ratio of the neutron capture cross sections for the production of these two states. They found

$$\frac{b}{a} = 1.4 \pm 0.6$$

where $a$ and $b$ represent reactions leading to the excited state and ground state respectively. The value found by Yaffe *et al.* (8) of 34.2 barns includes the contribution for the formation of the $Co^{60m}$ activity, and hence we can write

$$\sigma_b + 99.72\%\ \sigma_a = 34.2 \text{ barns.}$$

Therefore it follows that a value of

$$\sigma_a = 14.2\ {}^{+\ 4.8}_{-\ 2.8} \text{ barns}$$

should be expected rather than the much lower value of 0.66 barns reported by Seren *et al.* (6).

After a given nuclide is bombarded with neutrons for a time $T$, the disintegration rate at any time $t$ can be shown to be

$$\frac{dN}{dt} = N(\rho v)\sigma(1 - e^{-\lambda T})e^{-\lambda t}$$

where $N$ = number of atoms of nuclide present
$\lambda$ = disintegration constant of active product
$\sigma$ = cross section of nuclide under bombardment
$T$ = time of irradiation
$t$ = time elapsed after irradiation
$\rho v$ = neutron flux

If two nuclides $A$ and $B$ are irradiated at the same time under identical conditions, we get

$$\frac{dN_A}{dt} = N_A(\rho v)\sigma_A(1 - e^{-\lambda_A T})e^{-\lambda_A t}$$

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and $$\frac{dN_B}{dt} = N_B(\rho v)\sigma_B(1 - e^{-\lambda_B T})e^{-\lambda_B t}.$$

Hence, $$\sigma_A = \frac{dN_A/dt}{dN_B/dt} \cdot \frac{N_B}{N_A} \cdot \frac{1 - e^{-\lambda_B T}}{1 - e^{-\lambda_A T}} \cdot \frac{e^{-\lambda_B t}}{e^{-\lambda_A t}} \cdot \sigma_B .$$

If the cross section of $B$ is known, it is then possible to determine the cross section of $A$ using the above equation.

## EXPERIMENTAL

Small samples (ranging from 0.1 to 10 mgm.) of spectroscopically pure cobalt were irradiated in the center of the Chalk River nuclear reactor (flux $\sim 5 \times 10^{13}$ n./cm.$^2$/sec.) for known periods of time ranging from 10 sec. to 10 min.

Accurately measured aliquots (50 $\mu$liters each) were taken from a large volume of known cobalt concentration. The samples were evaporated on a small piece of polythene film, which was carefully folded and encased in a very pure iron capsule in which it was despatched to and from the reactor (some 1200 ft.) by a pneumatic tube. The transit time was of the order of 20 seconds. Electric stop watches activated by magnetic relays accurately recorded times of the beginning and end of irradiation.

Spectroscopically pure gold was used as a monitor and accurately weighed samples of this element were irradiated simultaneously with the cobalt. The cross section for the reaction $Au^{197}(n,\gamma)Au^{198}$ was taken to be 93 barns (4).

Immediately after irradiation the cobalt was dissolved off the polythene with nitric acid, made up to a known volume, and a suitable aliquot placed on an aluminum counting tray. The gold foil was dissolved in aqua regia, boiled to prevent aggregate formation, and made up to 2 ml. in a graduated tube. A known aliquot was taken and further diluted in concentrated nitric acid in order to obtain a suitably sized sample for counting.

The activity of the samples was measured in a windowless methane flow chamber (3) which was connected to an amplifier and scaling unit of 1000. The dead time of the chamber was found to be 11 microseconds and counting rates were corrected for this, the greatest correction being of the order of 3%. The background ($\sim 0.5$ counts per sec.) was subtracted where the correction was relevant.

In order that any residual air from the chamber might be swept out, methane gas was passed above and below the absorber for a full minute before counting. The cobalt activity was measured through a 12.85 mgm. per cm.$^2$ aluminum absorber to cut out conversion electrons from the 60 kev. internal transition to the 5.3 year ground state. Corrections were made for this branching ratio (0.28%). Decay curves were obtained with various aluminum absorbers and corrections made for the absorption of the 1.56 Mev. $\beta$-ray in the aluminum absorber (12.85 mgm. per cm.$^2$) which was used in the experiment.

The back-scattering contribution was found by removing all backing from the counter and depositing sources on thin plastic film ($\sim 50$ $\mu$gm. per cm.$^2$ of Zapon). The sources on the films, mounted on aluminum rings, were then counted with and without "saturation" back-scattering (9). The $Au^{198}$ (max. energy 0.96 Mev.) contribution was measured directly. That for the $Co^{60m}$ (max. energy

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1.56 Mev.) was found by using $P^{32}$ (max. energy 1.71 Mev.) and interpolating a value for the $Co^{60m}$ contribution assuming a linear variation over the small energy range considered. The difference in the contribution due to back-scattering from the $Au^{198}$ (6.3%) and $P^{32}$ (8.0%) was quite small and the cobalt contribution was estimated as 7.6% with very little error. Self-absorption corrections were not made since the sources were essentially "weightless".

The $Au^{198}$ decay curve gave a half-life of 2.69 days and a graphical extrapolation to the end of the irradiation was made to obtain the counting rate at zero time. A typical curve obtained for the $Co^{60m}$ decay is shown in Fig. 2. It can be seen that about one per cent of the disintegrations at zero time were due to relatively long-lived components presumably due to sodium impurities and the 5.3 year ground state. When these components were subtracted by the standard "peeling-off" technique, a small amount (1%) of a substance of half-life of about one hour was found. When this constituent had been subtracted, the $Co^{60m}$ activity at zero time could be obtained. The half-life found was 10.5 ± 0.2 min. which is in good agreement with recent unpublished data on the half-life of $Co^{60m}$ obtained using a continuous recording electroscope (7). The "zero time" value was obtained by graphical extrapolation.

Two of the samples were irradiated for short periods only (10 sec. and 1 min.) to decrease the abundance of the longer-lived components. The cross-section values obtained were substantially the same showing that no large errors were involved in the graphical interpretation.

To allow for the activity due to epicadmium neutrons, successive irradiations of cobalt and gold were made with and without cadmium wrapping. The contribution due to these epicadmium neutrons was 4.0% in the case of cobalt and 10.6% in the case of gold.

## RESULTS

The final results are shown in Table I.

TABLE I

| Experiment | Co irradiated as | Irradiation time | $\sigma_a \times 10^{24}$ cm.$^2$ |
|---|---|---|---|
| 1 | Nitrate (0.1 mgm.) | 10 min. | 17.4 |
| 2 | Nitrate (0.1 mgm.) | 10 min. | 19.1 |
| 3 | Nitrate (0.1 mgm.) | 10 min. | 19.7 |
| 4 | Nitrate (0.1 mgm.) | 10 min. | 20.8 |
| 5 | Wire (10 mgm.) | 10 sec. | 15.8 |
| 6 | Wire (0.2 mgm.) | 1 min. | 17.2 |
| | Mean $\sigma_a = 18.3 \pm 1.7$ | | |

The mean value obtained for the cross section for neutrons of 2200 meters per sec. velocity was 18.3 ± 1.7 barns. This is in good agreement with the value calculated from the data of Deutsch and Scharf-Goldhaber (2). The error quoted is the standard deviation. No attempt has been made to assess systematic errors inherent in the method, since these are assumed to be quite small.

The cross sections leading to the formation of the two cobalt isomers are approximately equal. This confirms a recent observation by Coryell (1) that where an isomeric pair is formed by neutron capture in a target nucleus of spin value

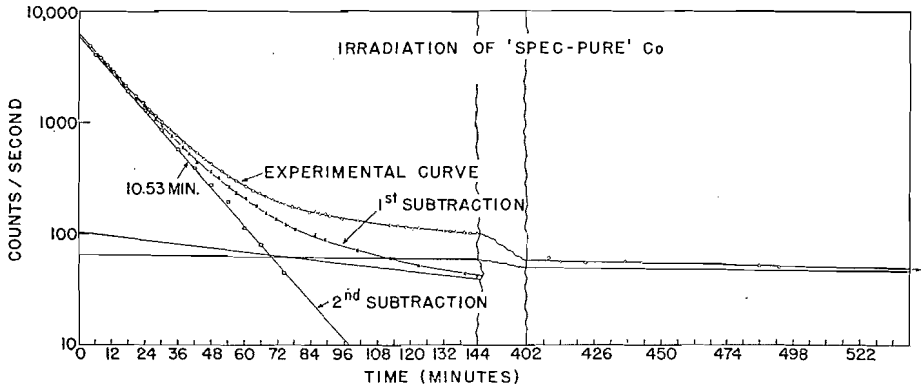



FIG. 2. Decay curve of neutron-irradiated 'spec-pure' cobalt metal.

about midway between the spin values of the two product isomers, then both isomers are formed in about equal amounts. The spin of $Co^{59}$ is 7/2, the two isomers are 2 and 5.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance afforded by H. Taniguchi in the counting of the last two experiments.

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# BIOCHEMISTRY OF THE USTILAGINALES

## VIII. THE STRUCTURES AND CONFIGURATIONS OF THE USTILIC ACIDS[1]

By R. U. Lemieux

ABSTRACT

Methanolysis of ustilagic acid and hydrolysis of the methyl esters formed yielded a crystalline acidic fraction which was essentially a mixture of two substances termed the ustilic acids A and B. The acids were separated as their isopropylidene derivatives. The ustilic acids cocrystallize to mixtures with melting points intermediate between those of the pure compounds. Conversion of ustilic acid A, m.p. 112–113° C., $[\alpha]_D$ −8° in methanol, which made up about 70% of the mixture, by hydrogenolysis to palmitic acid, by oxidation with chromic oxide to pentadecanedioic acid, and by lead tetraacetate oxidation followed by hydrogenation to 15-hydroxypentadecanoic acid showed the substance to be an optically active form of 15,16-dihydroxyhexadecanoic acid. Conversion of ustilic acid B, m.p. 140–141° C., $[\alpha]_D$ −10° in methanol, by sodium bismuthate oxidation followed by hydrogenation to 1,14-dihydroxytetradecane, by chromic acid oxidation of its methyl ester followed by hydrolysis of the product, and peroxide oxidation of the α-keto acid thus formed to tetradecanedioic acid, and by hydrogenolysis of the C2-carbon atom through a series of reactions to ustilic acid A, showed the substance to be an optically active form of 2,15,16-trihydroxyhexadecanoic acid. Optically active forms of 2,15-dihydroxypentadecanoic and 2-hydroxypentadecanoic acids were prepared from ustilic acid B. Application of certain empirical rules of rotation to derivatives of these 2-hydroxyacids showed them to possess the D-configuration. Reduction of ustilic acid B with lithium aluminum hydride gave *meso*-1,2,15,16-tetrahydroxyhexadecane. Thus, ustilic acid B was the 2D,15D,16-trihydroxyhexadecanoic acid and the ustilic acid A was the 15D,16-dihydroxyhexadecanoic acid. Several derivatives of the above described acids were prepared.

## INTRODUCTION

The new antibiotic (8) termed ustilagic acid was shown (15) to be a mixture of closely related, partially acylated D-glucolipides. Alkaline hydrolysis of ustilagic acid yielded an amorphous substance designated glucoustilic acid and removal of the glucose residues in the latter material yielded a crystalline substance termed ustilic acid (15).

Repeated crystallizations of crude methyl ustilate from methanol yielded a substance with the composition expected for the methyl ester of a dihydroxyhexadecanoic acid and hydrolysis of this ester gave a ustilic acid, m.p. 114–115° C. (15). It was later found, however, that if the crude methyl ustilate, obtained on the methanolysis of glucoustilic acid, was not subjected to purification prior to hydrolysis a ustilic acid preparation was obtained which melted at a higher temperature, in the range 120–126° C., than the above dihydroxyhexadecanoic acid. Furthermore, repeated recrystallizations of the crude ustilic acid did not yield the latter substance but instead gave higher melting materials of indeterminate composition. The infrared spectrum of recrystallized ustilic acid mixture (see Fig. 1) was much different to that of the acid with melting point 114–115° C. and it was therefore apparent that crude ustilic acid was a mixture.

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Methanolysis of 17.2 me. of ustilagic acid, neutral equivalent 801 and saponification equivalent 396, which contained 1.01 acetyl, 0.67 3L-hydroxyhexanoyl, 0.27 3L-hydroxyoctanoyl, 0.05 hexanoyl groups, and 1.96 glucose residues per neutral equivalent, and hydrolysis of the methyl ustilate fraction yielded 17.4 me. of crude ustilic acid, m.p. 122–126° C., with neutral equivalent 296. Periodate oxidation of the crude ustilic acid liberated one mole of formaldehyde per neutral equivalent (see Table II) and it was thus apparent that the components of the ustilic acid mixture contained, on the average, one terminal $\alpha$-glycol group. Only a trace of steam-volatile acidity was formed in terminal methyl group assays and the ustilic acids therefore appeared free of $CH_3$–C groups.

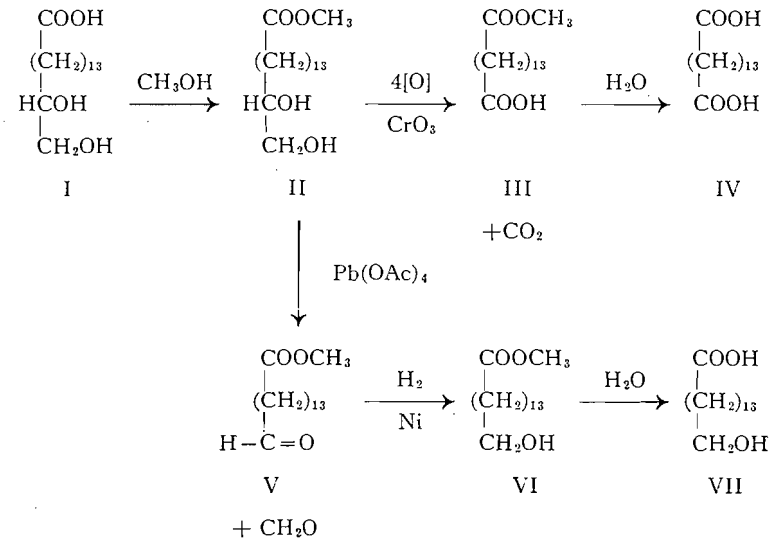
Treatment of the crude ustilic acid mixture with dry acetone containing sulphuric acid yielded a mixture of isopropylidene derivatives. On converting the acid isopropylidene derivatives to methyl ester using diazomethane, it was noticed that considerably less than the calculated amount of diazomethane was required. The esters thus formed were found to possess an isopropylidene group content, 15.3%, which was higher than that which would be expected if the ustilic acids had formed monoisopropylidene derivatives. Furthermore, treatment of the mixture with alkali liberated acetone and it was therefore apparent that the material contained carboxyl groups which were esterified through isopropylidene group linkages. Fractional distillation at about 0.05 mm. pressure separated the mixture of esters, 4.20 gm., into two main fractions; 2.52 gm., b.p. 133–136° C. and 1.16 gm., b.p. 154–156° C. It was thus established that the lower boiling material was a derivative of the major component of the ustilic acid mixture.

Purification of the above described lower boiling fraction by recrystallization from methanol gave a material, m.p. 46–47° C., $[\alpha]_D$ +12° in chloroform, with the composition expected for a methyl isopropylidenedihydroxyhexadecanoate. Methanolysis gave a compound, m.p. 85.5–86° C., $[\alpha]_D$ −7° in methanol, with the composition expected for a methyl dihydroxyhexadecanoate, and hydrolysis of this ester yielded a dihydroxyhexadecanoic acid, m.p. 112–113° C., $[\alpha]_D$ −8° in methanol. This acid is a purer sample of the previously described (15) ustilic acid, m.p. 114–115° C. and is designated ustilic acid A (17). The substance is further characterized by its infrared spectrum (see Fig. 1) and its hydrazide derivative, m.p. 140.5–141.5° C.

Purification of the above described higher boiling fraction by recrystallization from methanol gave a material, m.p. 42.5–43° C., $[\alpha]_D$ +18° in chloroform, with the composition expected for a diisopropylidenetrihydroxyhexadecanoate. Methanolysis of this compound yielded a substance, m.p. 74–75° C., $[\alpha]_D$ −8.5° in methanol, with the composition expected for a methyl trihydroxyhexadecanoate, and hydrolysis of this ester yielded a new trihydroxyhexadecanoic acid, m.p. 140–141° C., $[\alpha]_D$ −10° in methanol, termed ustilic acid B. The substance is further characterized by its infrared spectrum (see Fig. 1) and its hydrazide derivative, m.p. 164–165° C.

Treatment of ustilic acid A with hydrogen iodide and hydrogenation of the product in alkaline solution in the presence of Raney nickel gave an acid with

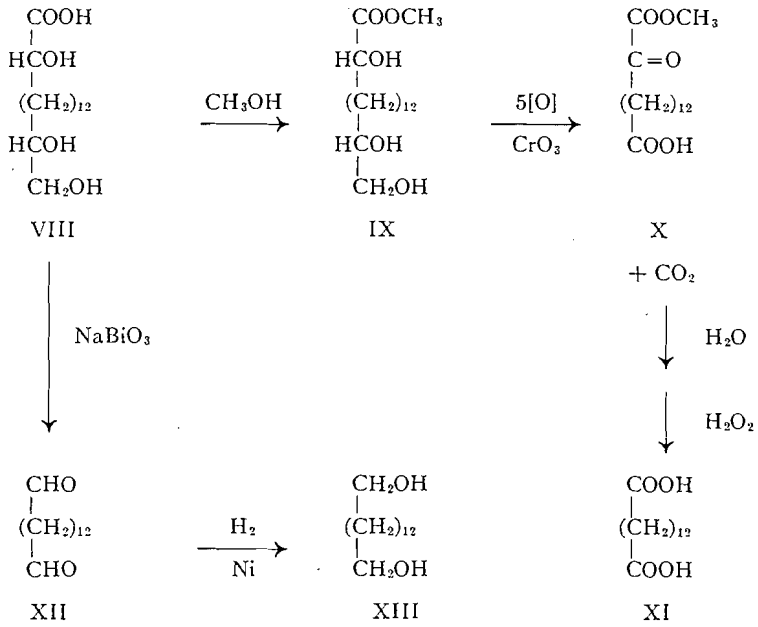
a melting point, 59–61° C., which was not depressed by admixture of palmitic acid, m.p. 61.5–62° C. Periodate oxidation of ustilic acid A liberated one mole of formaldehyde, characterized through its methone derivative and determined colorimetrically using chromotropic acid (14). It was thus apparent that ustilic acid A was an optical isomer of 15,16-dihydroxyhexadecanoic acid (I). This conclusion was confirmed by the following observations. Oxidant equivalent to four atoms of oxygen was rapidly consumed on oxidation of methyl ustilate A (II) with chromium trioxide in acetic acid solution. Hydrolysis of the product (III) gave the known pentadecanedioic acid (IV) (4). Oxidation of methyl ustilate A (II) with lead tetraacetate yielded an aldehyde (V) which on hydrogenation gave the methyl ester (VI) (5) of the known 15-hydroxypentadecanoic acid (VII) (3). 15-Hydroxypentadecanohydrazide melted at 142.5–143.5° C.




Oxidant equivalent to five atoms of oxygen was rapidly consumed on oxidation of methyl ustilate B (IX) with chromium trioxide in glacial acetic acid. Hydrolysis of the product (X), m.p. 87–87.5° C., and oxidation with hydrogen peroxide yielded a substance with the composition and melting point of the known tetradecanedioic acid (XI) (4). It was thus apparent that ustilic acid B was an optically active form of 2,15,16-trihydroxyhexadecanoic acid (VIII). This conclusion was confirmed by oxidation of ustilic acid B with sodium bismuthate in glacial acetic acid (28) to the dialdehyde XII which was converted by hydrogenation to a compound with the melting point and composition expected for the known 1,14-dihydroxytetradecane (XIII) (4).

A convenient method for the separation of the ustilic acids was based on the fact that, while ustilic acid A yielded an acidic monoisopropylidene derivative, ustilic acid B yielded a neutral diisopropylidene derivative. The extraction procedure was based on the method used for the determination of the quantity of neutral oil in acidic crude oils described by Jamieson (12).

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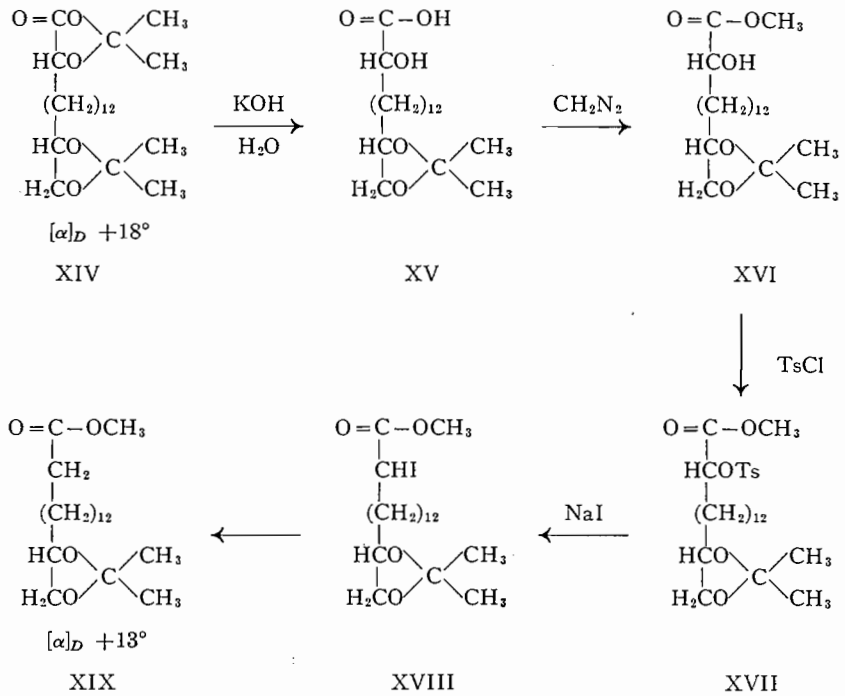



A mixed melting point curve was determined for the ustilic acids A and B by mixing weighed amounts of the materials and, after grinding the mixture in a mortar, determining its melting point. There was a continual rise in melting point with increasing amount of ustilic acid B such that the melting point curve appeared to be roughly a straight line joining the melting points of the two substances.

Alkaline hydrolysis of diisopropylideneustilate B (XIV) and methylation of the product (XV) with diazomethane yielded methyl 15,16-isopropylideneustilate B (XVI), m.p. 42.5–43° C., $[\alpha]_D$ +6° in chloroform. Tosylation of XVI and treatment of the product (XVII) with sodium iodide in acetone and hydrogenolysis of the iodocompound formed (XVIII) gave a material from which methyl isopropylideneustilate A (XIX) was prepared. It was thus established that the C15-carbon atoms of the ustilic acids A and B possess identical relative configurations. It is noteworthy that this conclusion is in accord with that expected on the basis of a comparison of the rotations, measured in chloroform, of methyl isopropylideneustilate A (XIX), $[\alpha]_D$ +12°, diisopropylideneustilate B (XIV), $[\alpha]_D$ +18°, and 1,2-isopropylidene-2,15-dihydroxypentadecanoate (XXVIII, see below), $[\alpha]_D$ +5°.

Reduction of diisopropylideneustilate B (XIV) with lithium aluminum hydride and hydrolysis of the product yielded *meso*-1,2,15,16-tetrahydroxyhexadecane (XX), m.p. 133–134° C. The structure of this substance was confirmed by the observation that it rapidly consumed two moles of lead tetraacetate and its optical inactivity was substantiated by the preparation of optically inactive diisopropylidene and tetraacetyl derivatives, XXI and XXII, respectively. Under the conditions of measurement used, XX appeared to be very slightly levorotatory. This observation indicates that the substance

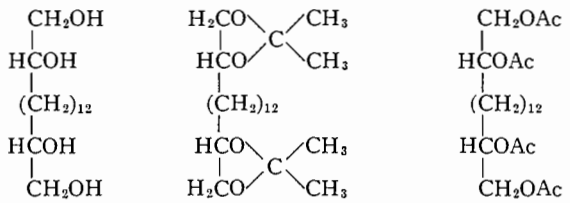
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XIV XV XVI

XIX XVIII XVII

contained an optically active impurity. It is well known that α-hydroxyacids can undergo epimerization relatively easily and it seems likely that the saponification of methyl ustilate B in the preparation of ustilic acid B would be accompanied by the formation of a diastereoisomer which would be extremely difficult to completely separate from ustilic acid B. Therefore, the C2- and C15-hydroxyl groups of ustilic acid B were configurationally *cis* and a Fischer projection formula for ustilic acid B would possess these two hydroxyl groups on the same side of the carbon skeleton.

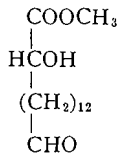


XX XXI XXII

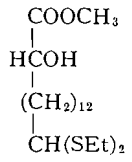
Oxidation of methyl ustilate B (IX) with lead tetraacetate yielded methyl 2-hydroxyaldehydopentadecanoate (XXIII) which was converted to the diethyldithioacetal (XXIV). Reductive desulphurization of the latter compound and hydrolysis of the product gave levorotatory 2-hydroxypentadecanoic acid (XXV), m.p. 89.5–90° C., $[\alpha]_D$ −0.8° in ethanol, which possessed a dextrorotatory sodium salt (see Table I). Hydrogenation of the aldehyde (XXIII) yielded the methyl ester (XXVI), m.p. 74.3–75.3° C., of weakly

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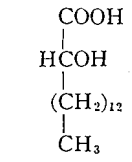
levorotatory 2,15-dihydroxypentadecanoic acid (XXVII), m.p. 102–103° C. Treatment of the latter compound with acetone and sulphuric acid afforded the dextrorotatory isopropylidene derivative XXVIII, m.p. 49–50° C., $[\alpha]_D$ +5° in chloroform.



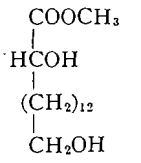
XXIII



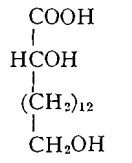
XXIV



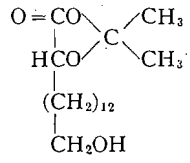
XXV



XXVI

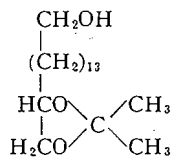


XXVII

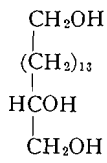


XXVIII

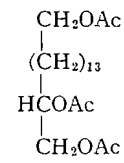
Reduction of methyl isopropylideneustilate A (XIX) with lithium aluminum hydride yielded the dextrorotatory isopropylidene derivative (XXIX), m.p. 60–61° C., $[\alpha]_D$ +12° in chloroform, of levorotatory 1,15,16-trihydroxyhexadecane (XXX), m.p. 108.5–109° C., $[\alpha]_D$ −7° in methanol. The triacetyl derivative (XXXI) of the triol melted at 24–25° C. with $[\alpha]_D$ −0.8° in chloroform.



XXIX

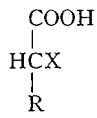


XXX



XXXI

Table I lists the rotations of certain derivatives of the ustilic acids and of related compounds of known configuration. A comparison of these values allows a decision as to the configurations of the ustilic acids. The configurations are assigned on the basis of the conventions for nomenclature which were discussed in an earlier paper in this series (18). Levene and Kuna (21) have pointed out that the molar rotation of a given acid of the general type XXXII, in which X is a functional group and R is an alkyl group, will vary not only with variations in X but also with variations in R. Levene and Marker (22) have shown that the molar rotations of successive members of a configuration-



XXXII

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TABLE I

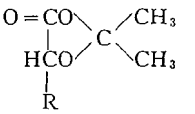
OPTICAL ROTATIONS OF USTILIC ACID DERIVATIVES AND RELATED COMPOUNDS

| Compound | Mol. wt. | $[M]_D$ | ° C. | $c$ | Solvent | Reference |
|---|---|---|---|---|---|---|
| A. Free acids | | | | | | |
| 1. 2L-Hydroxypropanoic | 90 | +340 | 25 | .. | $H_2O$ | 21 |
| 2. 2L-Hydroxybutanoic | 104 | +370 | 25 | .. | " | 21 |
| 3. 2L-Hydroxyhexanoic | 118 | +500 | 25 | .. | " | 21 |
| 4. 2D-Hydroxypentadecanoic | 258 | −206 | .. | 5 | $C_2H_5OH$ | .. |
| 5. 2D-Hydroxyhexadecanoic | 272 | −272 | .. | 5.2 | " | 13 |
| B. Sodium salts | | | | | | |
| 1. 2L-Hydroxypropanoate | 112 | −1400 | .. | 0.84 | $H_2O$ | 27 |
| 2. 2L-Hydroxypentanoate | 140 | −2040 | .. | 1 | " | .. |
| | | −2310 | .. | 1 | 25% $C_2H_5OH$ | .. |
| | | −2900 | .. | 1 | 50% " | .. |
| | | −3380 | .. | 1 | 75% " | .. |
| | | −3700 | .. | 1 | $C_2H_5OH$ | .. |
| 3. 2L-Hydroxyhexanoate | 154 | −2300 | 25 | .. | $H_2O$ | 21 |
| 4. 2D-Hydroxypentadecanoate | 280 | +4200 | .. | 1 | 50% $C_2H_5OH$ | .. |
| C. Hydrazide | | | | | | |
| 2D,15-Dihydroxypentadecanohydrazide | 288 | +6930 | .. | 0.2 | 50% $C_2H_5OH$ | .. |
| D. Isopropylidene lactones | | | | | | |
| 1. 1,2D,3L,4-Diisopropylidenetetrarate | 230 | +14,500 | 17 | 2.1 | $(CHCl_2)_2$ | 7 |
| 2. 1,2-Isopropylidene-2D,15-dihydroxypentadecanoate | 314 | +1570 | .. | 0.8 | $CHCl_3$ | .. |
| E. Isopropylidene ketals | | | | | | |
| 1. 2,3-Isopropylidene-1,2D,3-trihydroxypropane | 132 | +1430 | 20 | 15.2 | $C_6H_6$ | 1 |
| 2. 1,2-Isopropylidene-1,2L,16-trihydroxyhexadecane | 314 | +2350 | .. | 1 | $C_6H_6$ | .. |

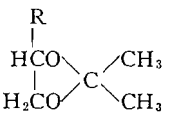
ally related homologous series progressively move in the same direction. Thus, as shown by the first three acids listed in Table I, the molar rotations of the normal $\alpha$-hydroxyacids increase with increasing molecular weight. It is not possible to state with certainty that the same relationship will hold for the rotations of these acids measured in ethanol. Nevertheless, it seems highly probable that the levorotatory 2-hydroxypentadecanoic acid prepared from ustilic acid B and the levorotatory 2-hydroxyhexadecanoic acid, rotations measured in ethanol, isolated from the wool wax of Merino sheep by Kuwata (13), possessed configurations opposite to the homologous dextrorotatory 2L-hydroxyacids, rotations measured in water. Levene (19) has pointed out that the sodium salts of aldonic acids are more dextrorotatory than the free acids when the 2-carbon atom has the D-configuration and this relationship is well established for the simple 2-hydroxyacids (20,24). As shown in Table I, the molar rotations measured in water of the sodium salts of normal 2-hydroxyacids increase with increasing molecular weight. Also, the molar rotations of sodium 2L-hydroxypentanoate in 0, 25, 50, 75, and 100% aqueous ethanol increased with increase in ethanol concentration. Thus, a comparison of the molar rotation, +4150, of the sodium 2-hydroxypentadecanoate and that, −2900, of sodium 2L-hydroxypentanoate (both measured in 50% ethanol), as well as the fact that the former substance is more dextrorotatory in 50%

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ethanol than its free acid in ethanol, indicates that the C2-carbon atoms of the 2-hydroxypentadecanoic acid and its parent substance, ustilic acid B, possessed the D-configuration. Hudson (10) and Levene and Meyer (23) have shown that the phenylhydrazides of aldonic acids with D-C2-carbon atoms are dextrorotatory and Van Marle (29) has shown that this relationship applies to unsubstituted hydrazides when measured in water. Therefore, the dextrorotation, $[M]_D$ +6930°, found for the 2,15-dihydroxypentadecanohydrazide derived from ustilic acid B confirms the above allocation of configuration. The established success of Hudson's Rules of Isorotation (11, p. 17; 16) in the correlation of rotation with configuration for lactol carbon atoms situated in ring structures leaves no doubt that configurationally related homologous compounds such as XXXIII and XXXIV would possess the same sign of rotation. Therefore, the fact, as seen in Table I, that

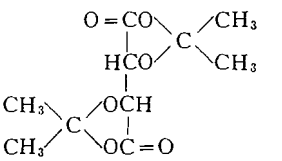


XXXIII



XXXIV

1,2D,3L,4-diisopropylidenetetrarate (XXXV) (7) is dextrorotatory supports the contention that the dextrorotatory 1,2-isopropylidene-2,15-dihydroxy-

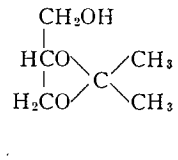


XXXV

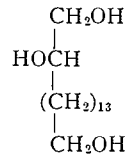
pentadecanoate (XXVIII) possessed the D-configuration. These arguments leave no doubt that ustilic acid B was the 2D,15D,16-trihydroxyhexadecanoic acid shown in VIII and that the configurationally related ustilic acid A was the 15D,16-dihydroxyhexadecanoic acid (I). Finally, the fact, as seen in Table I, that 2,3-isopropylidene-1-2D,3-trihydroxypropane (XXXVI) (1) is dextrorotatory indicates that the dextrorotatory 15,16-isopropylidene-1,15,16-trihydroxyhexadecane (XXIX) prepared from ustilic acid A possessed the same relative configuration, a conclusion which is in agreement with the above allocated configurational relationships. It is to be noted, however, that the presently widely accepted rules of nomenclature (6,18) infer that the substance XXX be oriented as shown in XXXVII for purposes of nomenclature. Thus, the asymmetric centers in the substances XXIX, XXX, and XXI, which were derived from 15D,16-dihydroxyhexadecanoic acid, possess the L-configuration. It is noteworthy that the system for nomenclature recently proposed by Cahn and Ingold (2) is free of such aberrations.

The above described separation of the ustilic acids, by distillation of the esterified isopropylidene derivatives, indicated that the mixture contained

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XXXVI



XXXVII

approximately twice as much ustilic acid A as ustilic acid B. Treatment of crude ustilic acid, neutral equivalent 296, obtained in quantitative yield from ustilagic acid, with acetone gave a purified ustilic acid mixture with neutral equivalent 293 in 96% yield. The calculated neutral equivalent for a mixture consisting of 70% ustilic acid A and 30% ustilic acid B is 293.2. This indication as to the composition of the ustilic acid mixture was confirmed by the yields of formaldehyde obtained on periodate oxidation of the crude and purified ustilic acid mixtures listed in Table II and by quantitative studies of the rates

TABLE II

FORMATION OF FORMALDEHYDE ON PERIODATE OXIDATION OF USTILIC ACIDS

| Time, hr. | Moles of formaldehyde formed per neutral equivalent of ustilic acid | | | |
|---|---|---|---|---|
| | Ustilic acid | | Ustilic acid mixture | |
| | A | B | Crude | Purified |
| 1 | 1.01 | 1.04 | 0.98 | 1.01 |
| 2 | 1.00 | 1.04 | 0.99 | 1.00 |
| 4 | 1.00 | 1.01 | 0.99 | 1.01 |

of oxidation by chromic oxide in acetic acid of methyl ustilate A, methyl ustilate B, and the mixture of methyl ustilates obtained on treatment of the purified ustilic acid mixture with diazomethane. The results of the latter studies are presented in Fig. 2. It is seen that the initial rapid uptake of oxidant by the methyl ustilates A and B, determined by extrapolation to zero time of the portions of the rate curves corresponding to the slow oxidation by the excess oxidant of the initial products, corresponded to 75.5 gm. (0.25 mole) and 63.6 gm. (0.20 mole) per atom of oxygen consumed, respectively. A similar extrapolation of the rate curve obtained on the oxidation of the methyl ustilate mixture gave a reduction equivalent per atom of oxygen of about 71 gm., the value to be expected if the methyl ustilate mixture were composed of 70% methyl ustilate A and 30% methyl ustilate B.

In a previous publication in this series (17) evidence was provided which indicated that in all probability the ustilagic acid mixture consists almost entirely of monoacetyl-mono-3L-hydroxyhexanoyl (65–70%) and monoacetyl-mono-3L-hydroxyoctanoyl (25–30%) substituted glucoustilic acids. Since the ustilic acid mixture was composed of about 70% ustilic acid A and 30% ustilic acid B, it seems highly probable that the mixture of ustilagic acids is composed essentially of two substances, ustilagic acid A (a monoacetyl-mono-

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3L-hydroxyhexanoyl substituted di-β-D-glucosyl-15D,16-dihydroxyhexadecanoic acid) and ustilagic acid B (a monoacetyl-mono-3L-hydroxyoctanoyl substituted di-β-D-glucosyl-2D,15D,16-trihydroxyhexadecanoic acid). It is noteworthy that on the basis of these structures, ustilagic acid A possesses the molecular formula $(C_{2\cdot12}H_{3\cdot65}O)_{17}$ while the molecular formula for ustilagic acid B is $(C_{2\cdot11}H_{3\cdot67}O)_{18}$. This similarity in composition accounts, to a certain degree, for the difficulties encountered in the separation of these substances. The origin of the *n*-caproic acid found in the hydrolyzates of all ustilagic acid preparations (15, 17) remains obscure. Presumably this acid was derived from a third component which made up about 5% of the ustilagic acid mixture.

## EXPERIMENTAL

### *Instrumentation*

The infrared spectra and specific rotations were determined as previously described (15). The melting points are corrected.

### *Crude Ustilic Acid Mixture*

Analysis (17) of the ustilagic acid sample used in this work showed it to contain 1.01 acetyl, 0.67 L-3-hydroxyhexanoyl, 0.27 L-3-hydroxyoctanoyl, and 0.05 hexanoyl groups and 1.96 glucose residues per neutral equivalent, 801. The saponification equivalent was 396.

A solution of the ustilagic acid, 13.8 gm. (17.2 me.), in 280 ml. of 4.3% methanolic hydrogen chloride was refluxed for 19 hr. The solution was poured into 600 ml. of water and the aqueous mixture was extracted with chloroform. The chloroform extract was dried and evaporated to a crystalline solid which was dissolved in 100 ml. of ethanol and 40 ml. of 2*N* potassium hydroxide. After the solution was refluxed for two hours, it was poured into 500 ml. of 0.2 *N* hydrochloric acid. The precipitate which formed was gathered by filtration and washed free of chloride with water. After it was dried *in vacuo* at 60° C., the tan-colored material, 5.16 gm. (17.4 me.), neutral equiv. 296, melted at 122–126° C. On the basis that one equivalent of ustilic acids should be obtained per equivalent of ustilagic acid, the yield of crude ustilic acid mixture was 101%.

### *Purification of the Ustilic Acid Mixture*

The above described crude ustilic acid mixture, 590 mgm., was ground to a fine powder and refluxed with 5 ml. of dry acetone. After the mixture was cooled to −10° C., the ustilic acid precipitate was collected by filtration and washed with 5 ml. of cold dry acetone. Evaporation of the acetone filtrates yielded 24 mgm. of a darkly colored residue. Thus, the acetone extraction removed 4% of the ustilic acid mixture. After it was dried *in vacuo* at 60° C., the white ustilic acid mixture, neutral equivalent 293, melted at 123–128° C., with sintering at 120–123° C.

### *Methyl Ustilate Mixture*

The above described purified ustilic acid mixture, 300 mgm., was dissolved in 20 ml. of methanol and the solution was treated with an excess of a freshly distilled ethereal solution of diazomethane. The excess diazomethane was re-

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moved by distillation and the solution was evaporated *in vacuo* to a white crystalline solid, m.p. 76–80° C., with sintering at 72–76° C.

*Separation of Ustilic Acid Derivatives by Distillation*

The above described crude ustilic acid mixture, 4.00 gm., was ground to a fine powder and shaken at room temperature for five hours with 100 ml. of dry acetone and eight drops of concentrated sulphuric acid (26). The ustilic acids, which are only sparingly soluble in acetone, soon dissolved. The yellow-colored solution was poured into a separatory funnel which contained 500 ml. of water and 100 ml. of chloroform. After the mixture was shaken for about 20 seconds, the chloroform layer was separated and washed with 200 ml. of water. The chloroform solution was dried by percolation through a column of dry Celite and evaporated *in vacuo* to a yellow oil which was treated with an excess of an ethereal solution of diazomethane. The ether was removed by distillation and the residue was dried at 0.1 mm. and 100° C. The yellow-colored product which crystallized at room temperature weighed 4.24 gm. and contained 15.3% isopropylidene groups. Fractional distillation of the material, 4.20 gm., at about 0.05 mm. pressure, yielded three fractions. The first fraction, b.p. 133–136° C., weighed 2.52 gm. and contained 12.8% isopropylidene groups. The second fraction was an intermediate fraction, b.p. 136–154° C. which contained 15.4% isopropylidene groups and weighed 0.27 gm. The third fraction distilled at 154–156° C., weighed 1.16 gm., and contained 20.5% isopropylidene groups.

*Methyl Isopropylideneustilate A*

The first fraction from the above distillation was recrystallized twice from methanol to yield a material, m.p. 46–47° C., $[\alpha]_D$ +12° (*c*, 1.1 in chloroform). Calc. for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18; $(CH_3)_2C$, 12.29%. Found: C, 69.85; H, 11.28; $(CH_3)_2C$, 12.3%.

*Diisopropylideneustilate B*

After two recrystallizations from methanol, the isopropylidene derivative from the third fraction of the above distillation melted at 42.5–43° C. with $[\alpha]_D$ +18° (*c*, 1.0 in chloroform). Calc. for $C_{22}H_{40}O_5$: C, 68.71; H, 10.49%. Found: C, 68.27; H, 10.48%. Acid hydrolysis liberated acetone equivalent to an isopropylidene group content of 22.0%. Calc. for a diisopropylidene derivative 21.9%. Alkaline hydrolysis liberated acetone equivalent to an isopropylidene group content of 12.3%. Calc. for one alkali-labile isopropylidene group, 10.94%. Absorption characteristic of hydroxyl groups was not present in its infrared spectrum. The substance possessed a strong absorption band at 5.54$\mu$, a considerably shorter wave length than is found for the carbonyl group of acyclic esters of carboxylic acids. For example, methyl isopropylideneustilate A possessed a carbonyl absorption band at 5.88$\mu$.

*Methyl Ustilate A*

The methyl isopropylideneustilate A, 600 mgm., was treated with 15 ml. of boiling 2% methanolic hydrogen chloride for two hours. The colorless solution was poured into water and the precipitate was extracted with chloro-

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form. The dried chloroform extract was evaporated *in vacuo* to a crystalline solid which, after two recrystallizations from methanol, melted at 85.5–86° C. with $[\alpha]_D$ −7° (*c*, 1 in methanol). Calc. for $C_{17}H_{34}O_4$: C, 67.53; H, 11.33%. Found: C, 67.94; H, 11.38%.

*Ustilic Acid A*

Alkaline hydrolysis of the above described methyl ustilate A yielded a substance, m.p. 112–113° C., $[\alpha]_D$ −8° (*c*, 1 in methanol). Calc. for $C_{16}H_{32}O_4$: C, 66.64; H, 11.19%; neutral equiv. 288.4. Found: C, 66.92; H, 11.22%; neutral equiv. 288. Its infrared absorption spectrum is shown in Fig. 1.

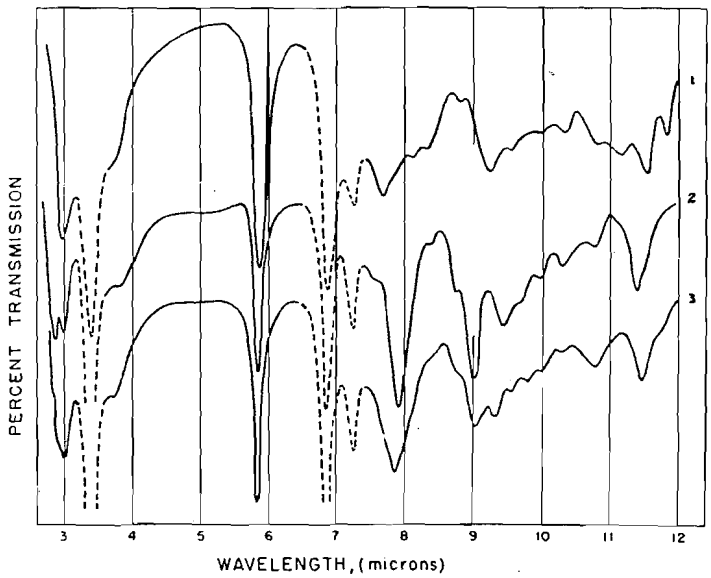



FIG. 1. Infrared spectra. Curve 1, ustilic acid A; Curve 2, ustilic acid B; Curve 3, ustilic acid mixture. – – – – Nujol absorption bands.

*Methyl Ustilate B*

The diisopropylideneustilate B, 2 gm., was treated with 25 ml. of boiling 2% methanolic hydrogen chloride for two hours. The resulting yellow-colored solution was poured into water, the mixture was extracted with chloroform, and the chloroform extract was washed with water and dried by filtration. The chloroform was removed *in vacuo* to yield a crystalline material which, after three recrystallizations from methanol, melted at 74–75° C. with $[\alpha]_D$ −8.5° (*c*, 1.0 in methanol). Calc. for $C_{17}H_{34}O_5$: C, 64.13; H, 10.76%. Found: C, 64.55; H, 10.91%.

*Ustilic Acid B*

Alkaline hydrolysis of the above described methyl ustilate B yielded a material, m.p. 140–141° C., $[\alpha]_D$ −10° (*c*, 1.0 in methanol). Calc. for $C_{16}H_{32}O_5$: C, 63.14; H, 10.60%; neutral equiv. 304.4. Found: C, 63.09, 63.27; H, 10.62, 10.27%; neutral equiv. 305. Its infrared absorption spectrum is shown in Fig. 1.

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*Separation of Ustilic Acid Derivatives by Extraction*

A ustilic acid mixture, m.p. 123–128° C., 47.3 gm., was dissolved by being shaken in 500 ml. of dry acetone which contained 5 ml. of concentrated sulphuric acid. The solution was allowed to stand at room temperature for five hours. After this time, the solution was diluted with 800 ml. of Skellysolve C and 800 ml. of ice-cold water was added. The mixture was shaken vigorously for 30 sec., the layers were allowed to separate, and the bottom aqueous layer was withdrawn and discarded. The hydrocarbon layer was washed three times with 200 ml. amounts of water to remove the sulphuric acid and most of the acetone. A cold solution of 20 gm. of potassium hydroxide in 130 ml. of water was then added and the mixture was shaken vigorously for one minute. On the addition of 150 ml. of 50% aqueous ethanol, the emulsion broke and the bottom aqueous layer was separated. The Skellysolve C solution was washed twice with 100 ml. amounts of the 50% ethanol and these extracts were combined with the main aqueous extract. The combined aqueous extracts were extracted with 200 ml. of Skellysolve C and this extract was combined with the main Skellysolve C solution. Chloroform, 150 ml., was added to the combined aqueous layers and this mixture was acidified by the addition of 200 ml. of 2 *N* sulphuric acid. The chloroform layer was washed three times with 100 ml. volumes of water, dried over sodium sulphate and evaporated to a yellow oil which soon crystallized. The yield was 34.8 gm. of crude monoisopropylideneustilic acid A which on hydrolysis gave essentially pure ustilic acid A. The Skellysolve C solution was washed with 50 ml. amounts of water until neutral and dried over sodium sulphate. Evaporation gave 15.1 gm. of a crystalline material which after recrystallization from 25 ml. of methanol melted at 42–42.5° C. Pure diisopropylideneustilate B melted at 42.5–43° C. Hydrolysis yielded essentially pure ustilic acid B.

*Palmitic Acid*

Methyl ustilate A, 500 mgm., was treated with 10 ml. of boiling 47% hydriodic acid and 2 gm. of red phosphorus for four hours. The reaction mixture was poured into water and the aqueous mixture was extracted with chloroform. The chloroform extract was evaporated to a partially crystalline oil which was dissolved in a mixture of 25 ml. of ethanol, 4 ml. of 10% sodium hydroxide, and 2 ml. of settled Raney nickel catalyst. The mixture was stirred in a hydrogen atmosphere at slightly positive pressure for one hour. The catalyst was removed by filtration and washed several times with boiling water. The combined alcoholic and aqueous filtrates were evaporated to about 75 ml. and the solution was made strongly acid with sulphuric acid. The colorless precipitate was collected by filtration and washed with water. After three recrystallizations from ethanol, the material melted at 59–61° C. and this melting point was not depressed on admixture with an authentic sample of palmitic acid, m.p. 61.5–62° C.

*Periodate Oxidation of the Ustilic Acids and Determination of the Formaldehyde Formed*

The ustilic acid, 100 mgm., was dissolved in 5 ml. of 0.1 *N* sodium hydroxide

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and the solution was made neutral to phenolphthalein with 0.1 *N* sulphuric acid. After the addition of 25 ml. of 0.1 *N* sodium periodate and 25 ml. of water, the mixture was distilled at atmospheric pressure to about 25 ml. volume. In the case of the ustilic acid B the distillate contained a small amount of a steam-distillable, water-insoluble solid which was removed by filtration. In each case, on adding the clear filtrate to 100 ml. of a buffered dimedon solution (25) a precipitate formed which, after isolation and recrystallization from ethanol, possessed, and did not depress, the melting point of the methone derivative of formaldehyde.

A weighed amount of the ustilic acid, 15 to 20 mgm., was dissolved in 20 ml. of 0.1 *N* sodium hydroxide by heating on the steam bath and the cooled solution was diluted to 100 ml. Three 25 ml. aliquots were transferred to 100 ml. flasks and 5 ml. volumes of 0.1 *M* periodic acid were added to each flask. After one, two and four hours, 10 ml. of *N* sulphuric acid and 5 ml. of *M* sodium arsenite solution were added to a flask and the solution was diluted to 100 ml. One milliliter aliquots were transferred to test tubes for development of the chromotropic acid–formaldehyde color reaction in the manner described by Lambert and Neish (14). A standard curve was established by oxidizing, under the above conditions, 5, 10, and 15 ml. volumes of a standard 0.002 *M* solution of mannitol. A reagent blank was used to set the spectrometer at 100% transmittance. The results obtained with the ustilic acids A and B and the above described crude and purified ustilic acid mixtures are shown in Table II.

*Rates of Oxidation of Methyl Ustilates by Chromic Oxide*

Chromic oxide, 1.00 gm., was dissolved in 2 ml. of water and the solution was diluted to 250 ml. with pure acetic acid. The methyl ustilate, 80–85 mgm., was dissolved in 40 ml. of acetic acid and, at zero time, 50 ml. of the chromic oxide solution was added. The resulting solution was diluted to 100 ml. with acetic acid and, at the various times, 10 ml. aliquots were added to 50 ml. of 0.2 *N* sulphuric acid followed by the addition of about 0.5 gm. of potassium iodide. The liberated iodine was determined by titration with standard sodium thiosulphate solution to the starch end point. The difference in titer between the oxidation mixture and a reagent blank was taken as equivalent to the oxidant consumed by the methyl ustilate. The data plotted in Fig. 2 show that the methyl ustilates A and B rapidly consumed oxidant equivalent to four and five atoms of oxygen, respectively, and that, on this basis, the above described purified methyl ustilate mixture contained about 70% methyl ustilate A and 30% methyl ustilate B.

*Pentadecanedioic Acid*

Methyl ustilate A, 200 mgm. (0.662 mM.), was dissolved in 5 ml. of glacial acetic acid and 5.30 me. of chromic oxide in 6 ml. of acetic acid was added. After 24 hr. at room temperature, the solution was diluted with 100 ml. of water and the precipitate which formed was gathered by filtration and washed with water. The material was dissolved in 10 ml. of 0.5 *N* sodium hydroxide solution and the mixture was heated on the steam bath for 0.5 hr. The solution

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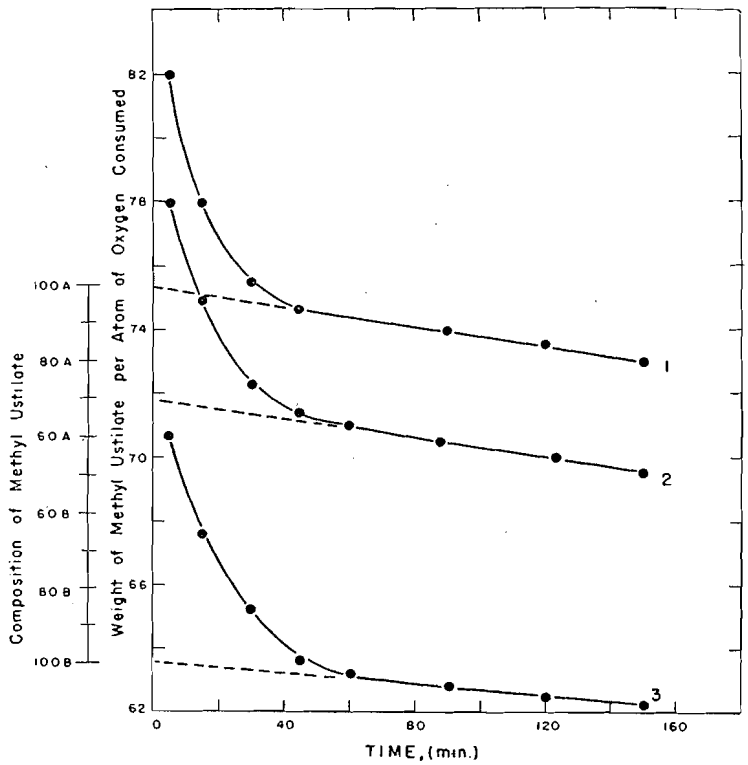



FIG. 2. Oxidation with chromic oxide in acetic acid of methyl ustilate A (Curve 1), methyl ustilate mixture (Curve 2), and methyl ustilate B (Curve 3).

was filtered and acidified with 10 ml. of *N* hydrochloric acid. The precipitate was collected, washed with water, dried, and recrystallized four times from ethyl acetate to yield 71 mgm. of material, m.p. 113–114° C. The melting point recorded for pentadecanedioic acid is 114.6–114.8° C. (4). Calc. for $C_{13}H_{26}(COOH)_2$: C, 66.15; H, 10.36%; neutral equiv., 136.2. Found: C, 66.12; H, 10.36%; neutral equiv., 136.

*Methyl 2-Keto-15-carboxypentadecanoate*

Chromic oxide, 5.00 gm., in 10 ml. of water was added to 50 ml. of acetic acid and the resulting solution was added to a stirred solution of 3.20 gm. of methyl ustilate B in 50 ml. of acetic acid kept at 0° C. The mixture soon became homogeneous and the solution was kept at 4° C. for 25 hr. The precipitate which had formed on the addition of 250 ml. of water and cooling to 4° C. for three hours was collected and washed with water. The yield was 2.61 gm. of a greenish powder which was extracted with 100 ml. of boiling Skellysolve C. On cooling the extract, 1.96 gm. of a white crystalline solid, m.p. 71–74° C., was deposited. Recrystallization from two parts acetone gave 1.74 gm., m.p. 84.5–86°C. Three further recrystallizations from acetone gave a nicely crystalline product, m.p. 87–87.5° C. This ester, like other $\alpha$-keto esters, was highly susceptible to alkaline hydrolysis and it was not possible to determine the

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neutral equivalent by direct titration. Titration of an alcoholic solution with 0.1 *N* aqueous sodium hydroxide to phenolphthalein indicator gave a combined neutral and saponification equivalent of 150.5. Calculated, 150.2. Calc. for $C_{16}H_{28}O_5$: C, 63.98; H, 9.39%. Found: C, 64.13; H, 9.55%.

*Tetradecanedioic Acid*

The monomethyl ester of 2-ketopentadecanedioic acid, 230 mgm., was hydrolyzed to yield 217 mgm. of the 2-ketopentadecanedioic acid as a white powder which was not purified. The material, 200 mgm., was stirred at room temperature with 10 ml. of 30% hydrogen peroxide (13) for 20 hr. The resulting material was washed with water and air-dried. After recrystallization, first from 70% ethanol, then twice from ethyl acetate, and once more from 70% ethanol, the yield was 68 mgm., m.p. 124.5–125° C. Tetradecanedioic acid is reported (4) to melt at 125.8° C. Calc. for $C_{14}H_{26}O_4$: C, 65.06; H, 10.14%; neutral equiv., 129.2. Found: C, 65.20; H, 10.11%; neutral equiv., 129.

*1,14-Dihydroxytetradecane*

Ustilic acid B, 3.18 gm. (10.5 mM.), was suspended in 45 ml. of acetic acid and the stirred mixture was heated to 45° C. Commercial sodium bismuthate (28), about 80% pure, 7.50 gm. (about 21.5 mM.), was added over a period of 20 min. and the reaction mixture, kept in a nitrogen atmosphere, was stirred for a total of 40 min. Benzene, 50 ml., and water, 45 ml., were added and, after vigorous shaking, the aqueous layer was withdrawn and re-extracted with 50 ml. of benzene. The benzene extracts were washed with 20 ml. of 50% aqueous acetic acid, combined, and washed free of acetic acid with water. After it was dried over sodium sulphate the solution was filtered and evaporated *in vacuo* to an oil which hardened at room temperature. The material, which was extremely prone to auto-oxidation, was dissolved in 50 ml. of ethanol and hydrogenated at 1500 p.s.i. for four hours at 100° C. using Raney nickel catalyst. The catalyst was removed by filtration and the filtrate was evaporated *in vacuo* to a crystalline solid which was triturated with low-boiling petroleum ether to yield 2.19 gm. of a faintly greenish-tinted material, m.p. 78–82° C. Distillation at $10^{-2}$ mm. pressure gave 1.81 gm., m.p. 83–85° C., of a substance which melted at 85–86° C. after one recrystallization from benzene. Chuit (4) has reported 1,14-dihydroxytetradecane to melt at 84.8° C. Calc. for $C_{14}H_{30}O_2$: C, 72.96; H, 13.12. Found: C, 72.95; H, 13.08. The crude yield was 91%.

*Lead Tetraacetate Oxidations*

About 0.25 mM. of the compound was dissolved in 5 ml. of acetic acid, 15 ml. of 0.13 *N* lead tetraacetate in glacial acetic acid solution was added, and the solution was diluted to 25 ml. After one and two hours, the excess oxidant in 10 ml. aliquots was determined in the usual manner (9). Both methyl ustilate A and methyl ustilate B consumed one mole of oxidant per mole of ester.

*15-Hydroxypentadecanoic Acid*

Methyl ustilate A, m.p. 84–85° C., 4.19 gm., was dissolved in 80 ml. of

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acetic acid and 8 gm. of lead tetraacetate was added. The reaction mixture was shaken until homogeneous and left at room temperature for one hour. Benzene, 50 ml., was added and the mixture was poured into 200 ml. of water which contained a little glycerol to destroy the excess oxidant. After vigorous shaking, the water layer was withdrawn and re-extracted with 25 ml. of benzene. The combined benzene extracts were washed with water until free of acetic acid and evaporated to an oil which soon crystallized. This substance, methyl aldehydopentadecanoate, could not be obtained in a highly pure condition because of its strong tendency to undergo auto-oxidation and was hydrogenated directly at 1500 p.s.i. for two hours at 100° C. over Raney nickel catalyst in 75 ml. of ethanol. The catalyst was removed by filtration and the ethanol solution was evaporated to yield 3.70 gm., 98% yield, of a crystalline solid, m.p. 48–51° C. Recrystallization from one part methanol gave pure methyl 15-hydroxypentadecanoate, m.p. 51.5–52° C. Calc. for $C_{16}H_{32}O_3$: C, 70.56; H, 11.84%. Found: C, 70.11; H, 11.63%. Chuit and Hausser (5) reported this substance to melt at 52–52.5° C. Alkaline hydrolysis of this ester gave an acid which after three recrystallizations from ether melted at 84.5–85° C. 15-Hydroxypentadecanoic acid is reported (5) to melt at 84° C. Calc. for $C_{15}H_{30}O_3$: C, 69.74; H, 11.70%; neutral equiv., 258.4. Found: C, 69.66; H, 11.97%; neutral equiv., 259.

*Methyl 2D,15-Dihydroxypentadecanoate*

Methyl ustilate B, m.p. 73–74° C., 1.92 gm., was dissolved in 60 ml. of acetic acid and 3.2 gm. of lead tetraacetate was added. The mixture was shaken until homogeneous and left at room temperature for one hour. The methyl 2-hydroxyaldehydopentadecanoic acid which formed was isolated as described above. The crude crystalline product was hydrogenated at 1500 p.s.i. for three hours at 100° C. over Raney nickel catalyst in 25 ml. of ethanol. The catalyst was removed by filtration and the filtrate was evaporated *in vacuo* to a crystalline solid, 1.57 gm., 90% yield, m.p. 68–72° C. Several recrystallizations from two parts methanol gave pure methyl 2D,15-dihydroxypentadecanoate, m.p. 74.3–75.3° C. Calc. for $C_{16}H_{32}O_4$: C, 66.64; H, 11.19%. Found: C, 66.80; H, 10.96%.

*2D,15-Dihydroxypentadecanoic Acid*

Alkaline hydrolysis of the above described ester gave a substance which melted at 102–103° C. after three recrystallizations from methanol and which was very weakly levorotatory in methanol. Calc. for $C_{15}H_{30}O_4$: neutral equiv., 274.4. Found: neutral equiv., 275.

*1,2-Isopropylidene-2D,15-dihydroxypentadecanoate*

The dihydroxyacid, 80 mgm., was treated with 5 ml. of dry acetone and two drops of sulphuric acid for 20 hr. at room temperature. The product, isolated in the usual manner, was recrystallized from ligroin to yield 62 mgm. of material, m.p. 49–50° C., with $[\alpha]_D$ +5° (*c*, 0.8 in chloroform). Calc. for $C_{18}H_{34}O_4$: C, 68.75; H, 10.90%. Found: C, 69.43; H, 11.06%.

*2D-Hydroxypentadecanoic Acid*

Crude methyl 2D-hydroxyaldehydopentadecanoate, prepared as described

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above from 1.90 gm. of methyl ustilate B, was dissolved at 0° C. in 10 gm. of ethyl mercaptan which contained 1.0 gm. of anhydrous zinc chloride (30). The solution was kept at 4° C. for four hours and poured into 100 ml. of aqueous sodium bicarbonate solution. The precipitate, collected by filtration, was extracted three times with boiling chloroform and the combined chloroform extracts were used to extract the aqueous phase. The chloroform solution was dried over sodium sulphate and evaporated *in vacuo* to an oil, which was dried *in vacuo* at 60° C. Calc. for $C_{20}H_{40}O_3S_2$: C, 61.18; H, 10.27%. Found: C, 60.99; H, 10.46%. The substance, $n_D^{25}$ 1.4890, was dissolved in 50 ml. of ethanol containing 40 ml. of settled Raney nickel, and the mixture was refluxed for 2.5 hr. The catalyst was collected by filtration and twice extracted with 50-ml. amounts of ethanol. The combined ethanolic solutions were evaporated *in vacuo* to an oil which crystallized at room temperature. The substance was distilled to yield a 1.21 gm. fraction, b.p. 117–118° C. at about 0.05 mm., which melted at 23–29° C. Alkaline hydrolysis of the material, 1.12 gm., saponification equivalent 260, gave an acidic product which was dissolved in 5 ml. of chloroform and petroleum ether was added to turbidity. On cooling, there crystallized 0.99 gm. of a substance, m.p. 88–89° C. Three recrystallizations from three parts 90% methanol gave a substance, m.p. 89.5–90° C., $[\alpha]_D$ −0.8° (*c*, 5 in ethanol). Calc. for $C_{15}H_{30}O_3$: C, 69.74; H, 11.70%; neutral equiv., 258.4. Found: C, 69.39; H, 11.12%; neutral equiv., 258.

*Sodium 2D-hydroxypentadecanoate*

2D-Hydroxypentadecanoic acid, 130 mgm., was dissolved in 15 ml. of ethanol and the solution was neutralized to phenolphthalein with 0.1 *N* sodium hydroxide solution. Evaporation gave a solid which was recrystallized first from 50% ethanol then from pure ethanol to yield 101 mgm. of a nicely crystalline product, $[\alpha]_D$ +15° (*c*, 1 in 50% aqueous ethanol). Calc. for $C_{15}H_{29}O_3Na$: C, 64.26; H, 10.43%. Found: C, 64.11; H, 10.23%.

*Sodium 2L-Hydroxypentanoate*

The previously described (18) methyl 2L-hydroxypentanoate, $[\alpha]_D$ +16.6° (*c*, 1.2 in chloroform), 446 mgm., was heated on the steam bath for one hour with 35 ml. of 0.1 *N* sodium hydroxide. The neutral solution was evaporated to a crystalline solid which was dissolved in 20 ml. of ethanol. On the addition of 40 ml. of dry acetone and cooling to −8° C., there crystallized 300 mgm. of the salt in a nicely crystalline condition. The substance was not very hygroscopic. Calc. for $C_5H_9O_3Na$: H, 6.47%. Found: H, 6.54%. The rotations for this substance are given in Table I.

*15D,16-Dihydroxyhexadecanohydrazide (Ustilohydrazide A)*

Methyl ustilate A, 0.5 gm., was heated under reflux for 30 min. with 0.5 ml. of hydrazine hydrate and 1 ml. of ethanol. Four milliliters of ethanol was added and the heating was continued for 30 min. On cooling, a near quantitative yield of the hydrazide crystallized. After recrystallization from ethanol the substance melted at 140.5–141.5° C. Calc. for $C_{16}H_{34}O_3N_2$: C, 63.54; H, 11.33%. Found: C, 63.59; H, 10.74%.

*2D,15D,16-Trihydroxyhexadecanohydrazide (Ustilohydrazide B)*

This substance, prepared as described above and purified by recrystallization

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from ethanol, melted at 164–165° C. Calc. for $C_{16}H_{34}O_4N_2$: C, 60.34; H, 10.76%. Found: C, 60.27; H, 10.68%.

*2D,15-Dihydroxypentadecanohydrazide*

This substance, prepared as described above and purified by recrystallization from ethanol, melted at 129–130° C. with $[\alpha]_D$ +24° (*c*, 0.2 in 50% aqueous ethanol) measured in a 4 dm. tube. Calc. for $C_{15}H_{32}O_3N_2$: C, 63.14; H, 11.19%. Found: C, 63.28; H, 11.22%.

*15-Hydroxypentadecanohydrazide*

This substance, prepared as described above and purified by recrystallization from ethanol, melted at 142.5–143.5° C. Calc. for $C_{15}H_{32}O_2N_2$: C, 66.15; H, 11.84%. Found: C, 66.06; H, 12.18%.

*Meso-1,2,15,16-tetrahydroxyhexadecane*

Diisopropylidene ustilate B, m.p. 42.5–43° C., 3.84 gm. (10 mM.), was dissolved in 50 ml. of dry ether and an excess of an ethereal solution of lithium aluminum hydride was added. After the solution had been allowed to stand at room temperature for two hours, it was poured into ice-water and acidified with 10% sulphuric acid. The resulting mixture was extracted twice with chloroform and the filtered extract was evaporated to a crystalline solid. The material was dissolved in 25 ml. of ethanol and 10 ml. of 0.1 *N* hydrochloric acid was added. After the solution had been boiled for 15 min., 20 ml. of water was added and the solution was kept at 4° C. for two hours. The crystalline precipitate, 2.89 gm., 95% yield, melted at 127–130° C. After one recrystallization from methanol, the yield was 2.70 gm., m.p. 132–134° C. Further recrystallizations from methanol or acetic acid did not raise the melting point above 133–134° C. The material was insoluble in ethyl acetate, chloroform, ether, or water and only sparingly soluble in cold pyridine, acetic acid, methanol, or ethanol. The substance appeared to possess a slight optical activity, $[\alpha]_D^{40} < -0.5°$ (*c*, 1 in methanol). Calc. for $C_{16}H_{34}O_4$: C, 66.18; H, 11.80%. Found: C, 66.15; H, 11.46%. Oxidation with an excess of lead tetraacetate in acetic acid resulted in the consumption of 2.0 moles of the oxidant after one- and two-hour reaction times.

*Diisopropylidene-meso-1,2,15,16-tetrahydroxyhexadecane*

The 1,2,15,16-tetrahydroxyhexadecane, m.p. 133–134° C., 500 mgm., was suspended in 20 ml. of dry acetone which contained two drops of sulphuric acid. After the mixture had been shaken for one hour, solution was complete. The mixture was left at room temperature overnight and poured into 100 ml. of aqueous bicarbonate solution. The material, which crystallized immediately, was gathered by filtration and washed with water. The yield was 630 mgm., 99%, m.p. 65–66° C. Recrystallization from methanol gave a pure product, m.p. 66.5–67° C., which was optically inactive (*c*, 1.5 in chloroform). Calc. for $C_{22}H_{42}O_4$: C, 71.29; H, 11.42%. Found: C, 70.98; H, 11.81%.

*Meso-1,2,15,16-tetraacetoxyhexadecane*

*Meso*-1,2,15,16-tetrahydroxyhexadecane, 240 mgm., was heated on the

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steam bath for one hour with 10 ml. of acetic anhydride and 200 mgm. of sodium acetate. The mixture was stirred overnight with 100 ml. of water. The crystalline precipitate which had formed was washed with water and dried. The yield was 380 mgm., 100%, m.p. 79–80° C. Recrystallization from methanol gave coarse crystals, m.p. 79.5–79.7° C., of an optically inactive substance (*c*, 1.5 in chloroform). Calc. for $C_{24}H_{42}O_8$: C, 62.87; H, 9.23%. Found: C, 62.87; H, 9.15%.

*1,2-Monoisopropylidene-1,2L,16-trihydroxyhexadecane*

Methyl isopropylideneustilate A, 1 gm., was dissolved in 25 ml. of ether and the solution was treated with an excess of an ethereal solution of lithium aluminum hydride. After 0.5 hr. at room temperature, the solution was poured into 50 ml. of ice-water which contained 2 ml. of acetic acid and the mixture was extracted several times with ether. The ether extracts were combined, washed with water, dried over sodium sulphate, and evaporated to a crystalline solid. Recrystallization from ligroin gave 590 mgm. of a substance, m.p. 60–61° C., $[\alpha]_D$ +7.5° (*c*, 1 in benzene) and +12° (*c*, 1 in chloroform). Calc. for $C_{19}H_{38}O_3$: C, 72.49; H, 12.18%. Found: C, 72.42; H, 12.05%.

*1,2L,16-Trihydroxyhexadecane*

Acid hydrolysis of the above described isopropylidene derivative, 225 mgm., yielded 190 mgm. of product, m.p. 107.5–108.5° C. After two recrystallizations from methanol, the material melted at 108.5–109° C. with $[\alpha]_D$ −7° (*c*, 1 in methanol). Calc. for $C_{16}H_{34}O_3$: C, 70.04; H, 12.49%. Found: C, 70.52; H, 12.28%.

*1,2L,16-Triacetoxyhexadecane*

Acetylation of the above described 1,2L,16-trihydroxyhexadecane, 80 mgm., with acetic anhydride and sodium acetate and isolation of the product which crystallized on decomposing the reaction mixture with water gave 105 mgm., 90% yield, of a low melting compound. After recrystallization from 30–40 petroleum ether, the material melted at 24–25° C. with $[\alpha]_D$ −0.8° (*c*, 1 in chloroform). Calc. for $C_{22}H_{40}O_6$: C, 65.97; H, 10.07%. Found: C, 66.19; H, 10.20%.

*Conversion of Ustilic Acid B to Ustilic Acid A*

Diisopropylidene ustilate B, 2.56 gm., was dissolved in 20 ml. of ethanol and 5 ml. of 2 *N* potassium hydroxide was added. The solution was refluxed for 30 min., diluted with 40 ml. of water, 35 ml. of chloroform, and 15 ml. of *N* hydrochloric acid. After shaking, the chloroform layer was isolated and washed twice with water, dried over sodium sulphate, and evaporated to a crystalline solid. The material was treated with an excess of diazomethane in ether, the ether was removed by evaporation, and the residue was dissolved in 5 ml. of methanol. The solution was filtered and diluted with water to turbidity. On cooling there crystallized 2.19 gm., 92%, of methyl 15,16-isopropylideneustilate B, m.p. 42–43° C. After recrystallization from ligroin, the material melted at 42.5–43° C. with $[\alpha]_D$ +6° (*c*, 1 in chloroform). Calc. for $C_{20}H_{38}O_5$: C, 67.00; H, 10.68%. Found: C, 67.38; H, 10.50%. This material,

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1.68 gm., was dissolved in 10 ml. of dry pyridine which contained 1.60 gm. of *p*-toluenesulphonyl chloride and the solution was left at room temperature for two days. The mixture was stirred with 50 ml. of 50% aqueous acetone for 30 min. and extracted with chloroform. The chloroform extract was washed several times with water and evaporated to an oil which did not crystallize. The oil was dissolved in 25 ml. of dry acetone which contained 10 gm. of sodium iodide and the mixture was heated at 140° C. for five hours. The reaction mixture was poured into 50 ml. of water and the free iodine was reacted with sodium thiosulphate. Extraction with chloroform gave a brown-colored oily product which gave a strong test for iodine. The substance was dissolved in 25 ml. of ethanol containing 10 ml. of 2 *N* aqueous sodium hydroxide and about 2 ml. of Raney nickel catalyst. The solution was hydrogenated for two hours at 1000 p.s.i. pressure. After removal of the catalyst, the solution was concentrated to about 10 ml., acidified with hydrochloric acid to Congo red indicator, and the solid precipitate was washed with water, dried at 65° C. *in vacuo*, and dissolved in 25 ml. of dry acetone which contained four drops of concentrated sulphuric acid. The solution was left at room temperature for seven hours, diluted with 50 ml. of chloroform, and the mixture poured into 50 ml. of water. After shaking, the chloroform layer was isolated and washed several times with water, dried over sodium sulphate, and evaporated *in vacuo* to yield a brown-colored oil which was treated with an excess of diazomethane in ether. Solvent removal gave an oil which was distilled at about 0.1 mm. to yield a 463 mgm. fraction, b.p. 140–143° C. The substance, $[\alpha]_D$ +13° (*c*, 1 in chloroform), melted at 46–47° C. and a mixed melting point with methyl isopropylideneustilate A, m.p. 47–47.5° C., was 46–47.5° C. The over-all yield from methyl 15,16-isopropylideneustilate B was 29%. Methanolysis to remove the isopropylidene group gave methyl ustilate A, m.p. 85–86° C.

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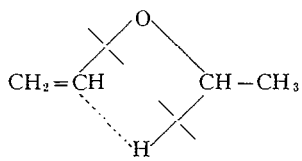
# THE KINETICS OF THE THERMAL DECOMPOSITION OF VINYL ISOPROPYL ETHER[1]

By Arthur T. Blades

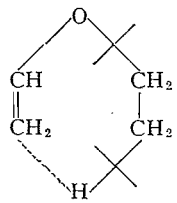
ABSTRACT

The thermal decomposition of vinyl isopropyl ether in the presence of toluene has been studied in a flow system in the temperature range 447-521°C. In this range, the data indicate a purely intramolecular decomposition into propylene and acetaldehyde, the activation energy for the reaction being in close agreement with that found for the decomposition of vinyl ethyl ether. At 570°C. a minor free radical decomposition of the ether becomes apparent. Some qualitative studies of the decomposition of vinyl isobutyl ether are also reported.

Recent studies of the decomposition of vinyl ethyl ether (1, 4) indicate a simple intramolecular split into ethylene and acetaldehyde as the major reaction. Two possible mechanisms have been suggested (4) for this decomposition, both of which involve cyclic transition states.




I




II

The Type I transition state was supported by Wang and Winkler (4) on the basis of energy considerations, while the Type II has gained support from the comparison of the entropy of activation with that for the rearrangement of vinyl allyl ether (3). Since the predicted products from vinyl isopropyl ether depend on the mechanism of the decomposition, further support for one of these transition states may be obtained from its pyrolysis, the assumption being made that a similar transition state applies for both ethers.

## EXPERIMENTAL

Vinyl isopropyl ether (stabilized with 0.01% phenyl α-napthyl amine) was donated by the Ohio Chemical Company and was distilled over calcium oxide on a 10 plate column b.p. 54.7 (741 mm.) $n_D^{25} = 1.3841$.

Vinyl isobutyl ether (stabilized) was purchased from General Aniline and Film Corp. and distilled b.p. 81.4 (740 mm.) $n_D^{25} = 1.3938$.

The toluene was Merck and Company Reagent Grade and was distilled over sodium on the same column.

The apparatus was similar to that described previously. The reacting gas, consisting of toluene and the ether in a molar ratio of about thirty to one, passed through a 1.8 cm. diameter, 20 cm. long, quartz reaction cell maintained

[1] *Manuscript received December 5, 1952.*
*Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wis.*



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to ± 0.2° in an aluminum bronze block furnace. The temperature was continuously monitored on a Brown Recording Potentiometer from a triple junction chromel – P alumel thermocouple. The pressures were measured frequently during a run on an oil–mercury manometer with a magnification factor of 10. The effluent gases were forced to pass through a flow limiting capillary and were then condensed in dry ice – acetone and liquid air traps. Permanent gases were collected by an automatic Toepler pump and analyzed on a modified Haden and Luttropp (2) type apparatus.

*Vinyl Isopropyl Ether*

The main products of this decomposition with and without toluene as the carrier gas were shown by infrared analyses to be propylene and acetaldehyde. The presence of toluene served to prevent the production of permanent gases (carbon monoxide, methane, hydrogen) over the complete temperature range (447-521°C.) of the kinetic study. At 570°C., however, very small quantities of equal proportions of hydrogen, carbon monoxide, and methane, and traces of bibenzyl were also produced when toluene was used as the carrier gas.

Rate measurements were made by aldehyde analyses using a Beckman Spectrophotometer at 302, 305, and 310 mμ where the acetaldehyde absorbs strongly but the ether is transparent.

By varying the contact time from 0.34-1.1 sec. the decomposition into acetaldehyde and propylene was shown to obey a first order rate law (Table I, R. 14, 15, 16, 17, and 18).

TABLE I

RATE STUDIES IN THE PRESENCE OF TOLUENE

| Run No. | Total moles | Pressure, cm. Hg | Contact time, sec. | % Decomposition | $k$, sec.$^{-1}$ | $T$, °K. |
|---|---|---|---|---|---|---|
| 2 | .0570 | 1.88 | 0.523 | 87 | 3.92 | 794.6 |
| *A* (Av. of 9 runs) | | | | — | 2.93 | 785.7 |
| 21 | .0545 | 1.90 | 0.571 | 62 | 1.70 | 770.3 |
| 13 | .0898 | 1.74 | 0.324 | 23 | 0.812 | 751.9 |
| 14 | .0883 | 1.76 | 0.336 | 19 | 0.620 | 746.4 |
| 15 | .0430 | 2.04 | 0.804 | 43 | 0.689 | 745.8 |
| 16 | .0337 | 2.15 | 1.08 | 50 | 0.650 | 746.3 |
| 17 | .0836 | 1.96 | 0.594 | 33 | 0.671 | 746.4 |
| 18 | .0828 | 1.93 | 0.596 | 32 | 0.648 | 745.3 |
| 19 | .0690 | 1.93 | 0.600 | 23 | 0.428 | 734.8 |
| 22 | .0457 | 2.09 | 1.10 | 24 | 0.254 | 722.6 |
| 20 | .0827 | 1.91 | 0.607 | 14 | 0.250 | 720.2 |

The data conform to the Arrhenius equation as may be seen from Fig. 1 and

$$k = 3.8 \times 10^{12} \exp(-43{,}560/RT) \text{ sec.}^{-1}$$

When compared with the Absolute Rate Theory equation

$$k = \kappa \frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H_a/RT}$$

a value of $\Delta S^{\ddagger} = -4.8$ e.u. at 760°K. is obtained if the transmission coefficient $\kappa$ is assumed to be unity.

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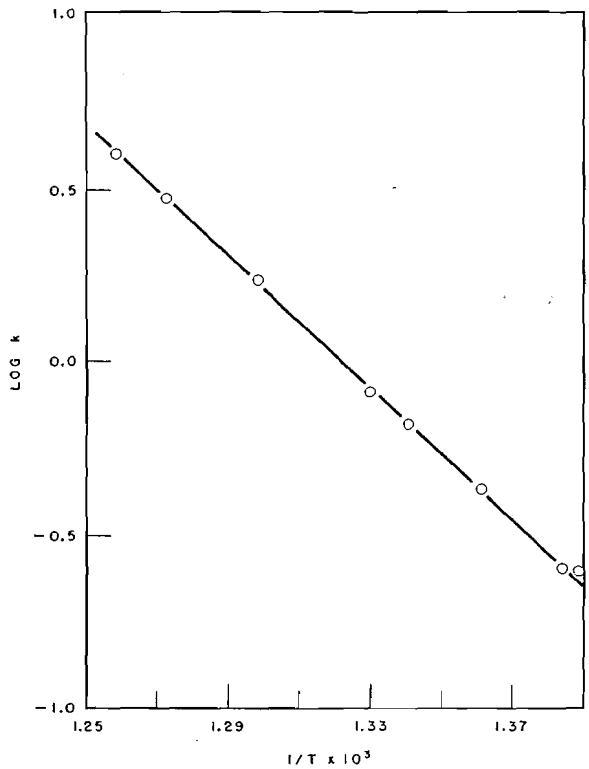



FIG. 1.

The quantities of permanent gases produced proved to be too small to make any measurements on their rate of production.

*Vinyl Isobutyl Ether*

Preliminary studies of the decomposition of vinyl isobutyl ether indicate that the major products are acetaldehyde and isobutene as identified by boiling points and infrared spectra. In addition, however, small quantities of propylene and propionaldehyde were also identified along with fairly large quantities of permanent gases.

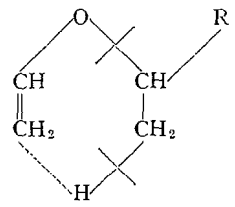
When the decomposition was carried out in the presence of toluene, these permanent gases were found to consist of about 25% carbon monoxide, 2-5% hydrogen, and the remainder methane. No attempt was made to identify the liquid products in the presence of toluene.

## DISCUSSION

The production of acetaldehyde and the corresponding alkene in the pyrolysis of isopropyl and isobutyl vinyl ethers rather than the products predicted by transition state I lends considerable support to the Type II for the decomposition of vinyl ethyl ether. In addition, the similarity of the activation energies (43.8 and 43.56 kcal. per mole) found for the ethyl and isopropyl vinyl ether

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decompositions strongly suggests that both take place via a similar transition state.




The negative entropy of activation found for the vinyl isopropyl ether is also consistent with a cyclic transition state since three internal rotational degrees of freedom are frozen out in the process of activation. The large difference in the entropies of activation of ethyl (− 10.2 e.u. at 530°C.) and isopropyl (− 4.8 e.u. at 490°C.) vinyl ether can presumably be explained on the basis of the restriction of internal rotation due to the presence of an extra methyl group in isopropyl vinyl ether.

The simultaneous occurrence of the permanent gases and the traces of bibenzyl in the decomposition of vinyl isopropyl ether suggests that these gases arise from an initial free radical decomposition of the ether, presumably into the vinyloxy and isopropyl radicals. The meager data available, however, add little to the understanding of this mode of decomposition.

The permanent gases collected in the decomposition of vinyl isobutyl ether in the presence of toluene are not entirely as would be predicted from the above mechanism; no attempt has been made to explain this anomaly.

The author wishes to thank Mr. D. Johnson for the infrared analyses, Dr. G. W. Murphy for many inspiring discussions, and the University Research Committee for support from funds supplied by the Wisconsin Alumni Research Foundation.

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# THE ELECTROLYTIC POLISHING OF AMPHOTERIC METALS[1]

By E. J. Casey and R. E. Bergeron

ABSTRACT

Experimental determinations of conditions necessary for the electrolytic polishing of amphoteric metals in alkali hydroxide solutions are described. The effects of temperature, electrolyte concentration, current density, and time of current flow are presented, as are differences among lithium, sodium, and potassium hydroxide solutions. Interpretation of the results in terms of a theory involving anodic polarizations has indicated the importance of the formation and maintenance of an anodic film whose electrical and mechanical properties determine critically the nature of the surface resulting from anodic treatment. Further applications of such studies toward the elucidation of mechanisms of anodic processes are indicated.

## INTRODUCTION

In the past few years electrolytic methods of finishing metal surfaces have assumed considerable practical importance. Mechanical polishing has its disadvantages: for instance, the friction between metal piece and polishing wheel results often in "flow" of the metal surface, resulting in cold working and deformation of the metallic surface. In some cases certain parts of the metallic piece are impossible to polish because of shape. In the case of very hard metals, the useful life of the polishing wheel is short. About 1935 serious consideration began to be given to an electrolytic method of polishing. The specimen is made the anode in an electrochemical cell, and under certain fairly critical conditions the burrs and rough spots are stripped from the surface. The necessary conditions seem to be (*a*) a high polarization at the anode, whether in the form of true concentration polarization of the anode (2, 8, 9) or as an adsorbed layer on the anode surface (5, 17), (*b*) a fairly high viscosity of the electrolyte, (*c*) high viscosity of anode layer (17), (*d*) ability of the electrolyte to dissolve the reaction products; (*e*) and at the same time the practical considerations of high enough current density to effect the polishing in reasonable time.

Many methods are described in both the patent (3) and nonpatent literature for electrolytic polishing of metals, for example the reviews of Faust (3), Jacquet (10), and Zmeskal (18). Stress has been placed of course on media for polishing steels. Usually the electrolyte used is some combination of glycerol, sulphuric acid, phosphoric acid, acetic acid, acetic anhydride, chromic acid, hydrochloric acid, hydrofluoric acid—in general, strongly acidic solutions. However, other methods involve slightly acid, neutral, and even slightly alkaline media (pH 10)—sodium cyanide, sodium orthophosphate, and sodium pyrophosphate.

Although alkaline solutions would seem to be ideal media for polishing the amphoteric metals—those whose gelatinous hydroxides manifest acidic as well as basic properties—very little work has been done along this line.

[1] *Manuscript received November 6, 1952.*
*Contribution from the Electrochemistry Laboratory, Defence Research Chemical Laboratories, Ottawa, issued as D.R.C.L. Report No. 113.*



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Vernon and Stroud (16) report electropolishing of zinc in 25% of potassium hydroxide at a critical current density. Kerr (11) noticed the formation of brown anodic films on tin in sodium hydroxide solution; analysis of these showed oxides of tin to be present. Shepherd (13) has found that the X-ray diffraction pattern of the dried anodic film formed on zinc in potassium hydroxide is characteristic of zinc oxide. Huber's electron and X-ray diffraction work (6) has indicated that anodization of magnesium, cadmium, and zinc produces as the primary product, magnesium oxide, cadmium oxide, and zinc oxide respectively on the surface. Indications are that the resistance of such tightly bound films may be very high.

It is the purpose of this paper to present, analyze, and discuss some experimental work which provides considerable information on the nature of the electropolishing phenomenon and on the mechanism of anodic reactions in general.

## THEORY

Consider the small volume just on the solution side of the electrode–solution interface, a volume with cross-sectional area equal to the planar, apparent area of the electrode, and having an average depth of a few hundred microns. If the electrode is made the anode, metal ions are liberated into this surface layer compartment of the solution. Chemical reactions or ionic associations may follow, producing an increased concentration of metal ion compounds in the layer, even to the extent, in some cases, of exceeding the solubility of some soluble salt (17). The composition of the layer and the exact nature of the compounds thus formed critically determine such electrical and mechanical properties of the layer as: mechanical strength, or extent and nature of cross-bonding; the viscosity of the layer; the conductivity and diffusion coefficient of charged and uncharged particles in the layer. If the layer is insoluble in the bulk solution, resistance polarization is soon so high that very little current can flow, even with high impressed terminal voltage. If the layer is soluble in the bulk solution, the steady state thickness and composition of the film will be determined by (1) the nature and extent of the solubility of the film in the bulk solution, (2) the rate of solution, (3) the diffusion of various reactants and products through this layer toward or away from the anode under the steady-state concentration gradients. A further factor enters at high current density. If the rate of removal of the soluble film is too slow, the metal ions will pile up at the anode producing a back-e.m.f. of concentration polarization: then in order that the chosen current pass, the terminal voltage must be raised above that necessary for the discharge of water or $OH^-$, and oxygen is released. The vigorous stirring thus provided completely changes again the electrical and mechanical properties of the film. The electrical and mechanical properties of the steady-state surface layer may be expected to change radically with changing experimental conditions. For any particular case the ultimate film-determining process is difficult to evaluate.

Since the surface of the anode is rough, with burrs and pits on the surface, the depth of this layer above one point may be considerably different from the depth above another point. The concentration of the reaction product

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involving the metallic ion would be higher at the anode surface than in the bulk solution, and since the concentration gradient determines the rate of movement, the thickness of the film is critical: the gradient above a burr would be higher than the gradient above a pit. Hence the current through a burr would be greater than the current through a pit: metal would be removed faster from above a burr than from above a pit, and a smoothed surface would result.

That the thickness of the layer is of critical importance can easily be shown. The probability that the surface of a real film is not planar but rather follows the general contour of the surface does not affect the argument. In Fig. 1 two

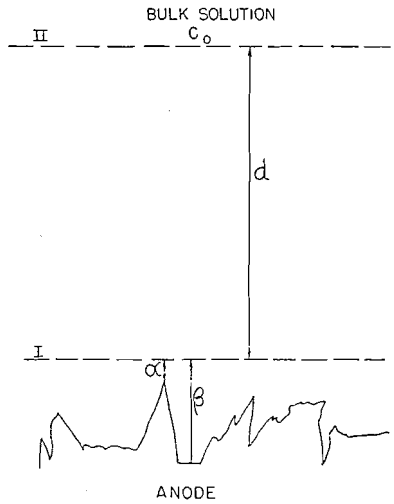



FIG. 1. Imaginary rough anode surface with two imaginary and arbitrary thicknesses of the film.

imaginary thicknesses of layer are indicated. When the steady state in the process has been reached, a uniform concentration of metal ions, $c$, would be expected to exist at the metal-layer interface, no matter what the contour, while the concentration, $c_0$, in the bulk solution would be uniform. In the case of a thin film (I), the concentration gradient above a burr, $(dc/dx)_b$, is given, in approximation, by $(c-c_0)/\alpha$, while the concentration gradient above a pit, $(dc/dx)_p$, is $(c-c_0)\beta$. Because $\beta \gg \alpha$ $(dc/dx)_b \gg (dc/dx)_p$; and, assuming the same small area of anode, $i_b \gg i_p$.

In the case of a thick film (II), however, $d \gg \alpha$ or $\beta$. Then $(dc/dx)_b = (c-c_0)/(\alpha + d)$, and $(dc/dx)_p = (c-c_0)/(\beta + d)$; and since $\alpha$ and $\beta$ are both small with respect to $d$, $(dc/dx)_b \approx (dc/dx)_p$, or $i_b \approx i_p$.

For anodic electrolytic polishing, then, it is necessary that physical, chemical, and electrochemical conditions be such that there is established and maintained during current flow a surface layer (1) whose resistivity to ion or molecular movement approaches some optimum value: a resistivity higher than that of the bulk solution, yet low enough to permit passage of ions and water molecules and to discourage oxygen liberation; (2) whose thickness approaches some optimum value such that $i_b \gg i_p$.

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Strong basic solutions should be ideal for electropolishing those amphoteric metals whose oxides or hydroxides are not too difficultly soluble in strong solutions. Above some minimum apparent current density the concentration of metal ions, $X^{n+}$, liberated into the anode surface layer would become high enough to supersaturate the anode layer with respect to the gelatinous $X(OH)_n$. This $X(OH)_n$ is dissolved by the alkali metal hydroxide, MOH, to give the zincate ion, aluminate ion, etc., $XO_n^{n-}$. Stoichiometrically, the process may be expressed:

$$X^{n+} + n\text{MOH} \rightarrow X(OH)_n + n\text{M}^+$$

$$\text{and } X(OH)_n + n\text{MOH} \rightarrow n\text{M}^+ + XO_n^{n-} + n\text{H}_2\text{O}.$$

However, there is indication that at least in some cases the primary product of the process is the oxide, subsequent conversion to the hydroxide taking place if the hydroxide is more stable (6). In such cases the rate of conversion from a tight oxide film to the more loose gelatinous hydroxide would be expected to be governed by the rates of the diffusion processes through the film, as already discussed.

Those amphoteric metals which form at practical current densities viscous, permeable, gelatinous oxide or hydroxide films when anodized in basic solutions would be expected to be electropolished with ease. Metals whose oxides or hydroxides are difficultly or only slowly soluble and form tight, impermeable, highly resistive layers on the surface would be expected to be impossible to electropolish in basic solution.

## EXPERIMENTAL

Samples of several of the amphoteric metals (14), including zinc, aluminum, tin, bismuth, antimony, and lead, were made the anode under a wide range of conditions of caustic concentration, apparent anode current density, temperature, and time. Preparation of the surfaces was standardized in order that relative times of anodization would have a meaning. The metal specimens were filed, and then mechanically polished to a fine, but rough, surface with emery paper. The specimens, 2.5 cm. × 1.2 cm. × 0.16 cm., were mounted midway between parallel platinum plates, 2.5 cm. × 2.5 cm., connected together externally. The specimens were half submerged, so that the anodes were actually 1.2 cm. × 1.2 cm. Four temperatures, 0°, 25°, 53°, and 90° C., and six concentrations of aqueous potassium hydroxide, 1 *N*, 5.36 *N*, 8 *N*, 12 *N*, and 19 *N*, and 25 *N*, were used to scan for possible electropolishing conditions.

### *Aluminum and Zinc*

These gave brilliantly electropolished surfaces over a wide range of experimental conditions. Since aluminum oxide and hydroxide are easily soluble in potassium hydroxide, 5.36 *N* potassium hydroxide proved to be too concentrated to permit formation of an anodic film at reasonable current densities; the aluminum was simply electrolytically stripped from the surface leaving the macrocrystalline structure of the aluminum visible. However, in 1 *N* potassium hydroxide, treatment at a current density of 0.1 amp. cm.$^{-2}$ for 30 min., for instance, produced a brilliantly electropolished surface. Zinc is treated in detail below.

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*Antimony*

A polished luster could not be obtained on antimony. However, with difficulty, under extended treatment at a current density of 0.02 amp. cm.$^{-2}$ for 30 min. in 5.36 *N* potassium hydroxide, deburring of a rough surface could be obtained. Under these conditions the finish was smooth but rather dull.

*Lead*

Lead behaved similarly to antimony. A brightly electropolished surface could not be obtained, although the dull surface of oxided lead seemed to be deburred. Formation of heavy dark films during the process was noted, but, although these were fairly easily removed in most cases, the underlying surface remained dull grayish.

*Bismuth*

Anodic current under various conditions produced no electropolished bismuth surface. The oxide produced on the surface is apparently electrically highly resistive, yet brittle and not bound tightly enough to the bismuth surface, for the anodization is accompanied by intermittent, explosive liberation of oxygen. During these explosions on the surface, pieces of the yellowish oxide film are broken off and the current surges by a factor of 10. The oxide(s) formed on the surface are soluble in hot concentrated potassium hydroxide, but electropolishing of bismuth could not be obtained in a reasonable length of time even under these conditions. Presumably the rate of dissolution of the oxides is slow.

*Tin*

Kerr (11) has shown that in basic solutions: (1) anodization of tin at 20° C. produces a dark brown film, regardless of conditions; analyses showed the film to contain 81% stannic oxide, 9% stannous oxide, and 10% water, the film, thick and dense; (2) anodization at 50° produces a yellowish film, 68.5% stannic oxide, 12.5% stannous oxide, and 19% water, thin and unstable. Under the first condition tin was found to be electroetched, as in the case of aluminum. That is, after the film has been removed from the surface, the bright, polycrystalline structure (formed by multiple nucleation during solidification from the molten state) of the ingot tin is visible. The dark film is only loosely bound to the surface, and the film falls off in pieces during treatment. This, perhaps, is at least partially responsible for the slight pitting in an otherwise bright and deburred surface. No satisfactory brilliantly electropolished surface could be obtained in 0.1 *N*, 5.36 *N*, or 19 *N* potassium hydroxide from 1 ma. cm.$^{-2}$ to 0.1 amp. cm.$^{-2}$ at 25° C.

*Zinc*

The conditions for electropolishing zinc were determined in detail in potassium hydroxide solutions over a wide range of concentration, current density, and time, at 0°, 25°, and 53° C.; and then less completely in sodium hydroxide solutions and lithium hydroxide solutions for comparison. The zinc used was of purity 99.99%, obtained from Consolidated Mining and Smelting Co., Trail, B.C.

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Three different surface conditions were observed after anodic treatment of zinc in alkaline solution.

(1) At very low current densities there was little or no liberation of gas at either electrode. The surface of the zinc seemed to have undergone little change, and the metal was either unpolished or very slightly polished.

(2) In that range of current densities which proved favorable for good polishing, a thick black deposit was formed on the zinc.* There was little or no oxygen liberated at the anode although hydrogen liberation at the cathode was quite heavy. At the end of an anodic treatment this black layer was removed by either of two methods. The more satisfactory manner consisted of increasing the current through the cell for a fraction of a second, and then cutting it off. After two or three such cycles, the bursts of oxygen gas had caused the layer to lift off the surface, fall to the bottom of the cell, and subsequently to dissolve. This method was satisfactory for both thick and thin films. Alternatively, washing in warm, distilled water or dilute basic solution served to remove the thicker and more loosely bound films, but the washing technique was not very effective for the removal of some very thin and tightly bound films. At fairly high current densities, the rate of removal of metal is very high, and the time necessary for formation of the film and polishing is very short. Some oxygen evolution was noticeable at the higher current densities. Although the thick, black deposit was not maintained under these conditions, mild oxygen evolution apparently did not seriously affect the critical part of the anode layer, for polishing could be obtained under such conditions.

(3) At very high current densities gassing was violent, no film could be maintained, and the surfaces became electroetched. That is, the metal had simply been stripped off, leaving visible the bright polycrystalline surface, as noticed in the case of tin and aluminum. The anodization in this case was accompanied by vigorous stirring due to considerable oxygen evolution.

In Fig. 2 are shown electropolishing templates for zinc in various concentrations of potassium hydroxide at 53° C. It can be seen that with decreasing concentrations of potassium hydroxide the range of time and current density suitable for electropolishing collapses inward and upward. The boundary at high current density represents the current density above which an electroetched surface, instead of an electropolished surface, is obtained. The curved boundary between polished and unpolished zinc is not a critical dividing line, but is a rather diffuse boundary across which the zinc surface must pass as it is being electropolished. At any chosen current density, for example, it has been verified by experiment that as time of anodic treatment increases the zinc surface passes through such qualitatively descriptive phases as "not electropolished", "slightly electropolished", "electropolished", and "brilliantly

* *Recently it was demonstrated by Hoar and Farthing (5) by an amalgamation technique, that even in orthophosphoric acid – water electrolyte a "solid" anodic film is a necessary condition for electropolishing of copper and α-brass: that electroetching or random stripping of the metal from the surface to reveal the underlying structure takes place when conditions are such that no solid film is present. The nature of solid film in this case is not known with certainty, but indications are that it may not be an oxide (1).*

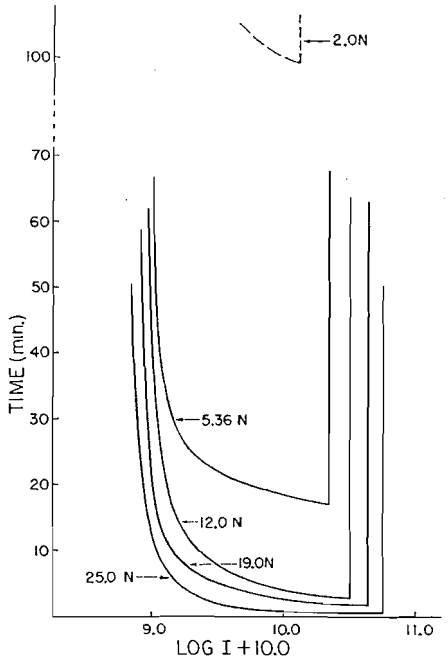



FIG. 2. Templates for the electrolytic polishing of zinc at 53.0° in different concentrations of potassium hydroxide. Each curve outlines the region of time and apparent current density within which zinc can be polished.

electropolished". Although the boundary is diffuse, the curve through the quality "electropolished" is quite definite and is easily reproduced once the standard for the degrees of polish has been set up. The photomicrographs in Fig. 7 serve to indicate the types of surfaces produced. Note that even a fairly well polished specimen, although apparently continuous and smooth to the

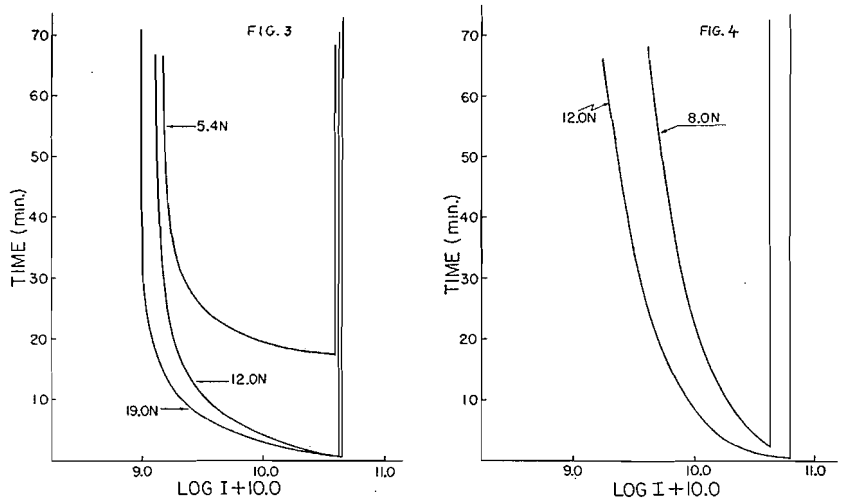
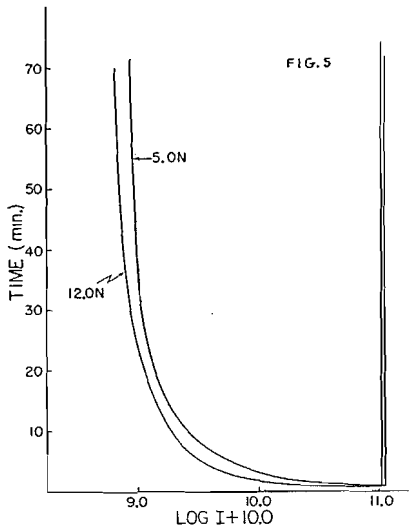



FIG. 3. Templates for the polishing of zinc at 25° C. in potassium hydroxide solutions.
FIG. 4. Templates for the polishing of zinc at 0° C. in potassium hydroxide solutions.

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naked eye, is covered with very small pits and craters on and slightly underneath the surface (Fig. 7(*c*)). Electron reflection patterns of these surfaces were those of zinc oxide, and from these the thickness of the zinc oxide film was estimated to be between 40 and 200Å. These polished surfaces have tarnished only slightly after one year in the corrosive fumes of the laboratory.

Fig. 3 shows the range of conditions for electropolishing at 25° C. in potassium hydroxide solutions, and Fig. 4 shows how the range has been reduced by reducing the temperature to 0° C. Fig. 5 shows the boundaries for electropolishing zinc in sodium hydroxide solutions at 25° C., and Fig. 6 for lithium hydroxide at one concentration for comparison.



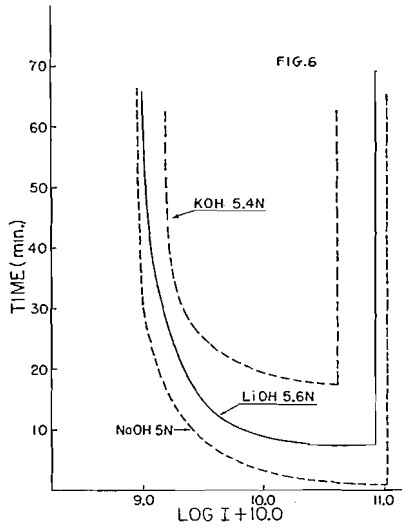




FIG. 5. Templates for the polishing of zinc at 25° C. in sodium hydroxide solutions.
FIG. 6. Template for the polishing of zinc at 25° C. in 5.6 *N* lithium hydroxide solution, with corresponding templates for potassium hydroxide and lithium hydroxide added for comparison.

In each case, that part of the electropolishing range best suited for the production of brilliantly electropolished surfaces is that toward high current density and short time of current flow. The terminal voltage of the electrodes is not presented, as in another case (12), since it is the resistive component of the anodic polarizations which determines the quality of the anodized surface. Hence the terminal voltage may be misleading since it depends critically on certain properties not directly concerned with the electropolishing process, for instance: (1) the thermodynamic, open circuit potential of anode and cathode—these are essentially foreign ion half-cells, capable of considerable variation in e.m.f., (2) true concentration polarizations at both anode and cathode, (3) any hydrogen or oxygen overvoltages, (4) the resistance of the solution between the electrodes.

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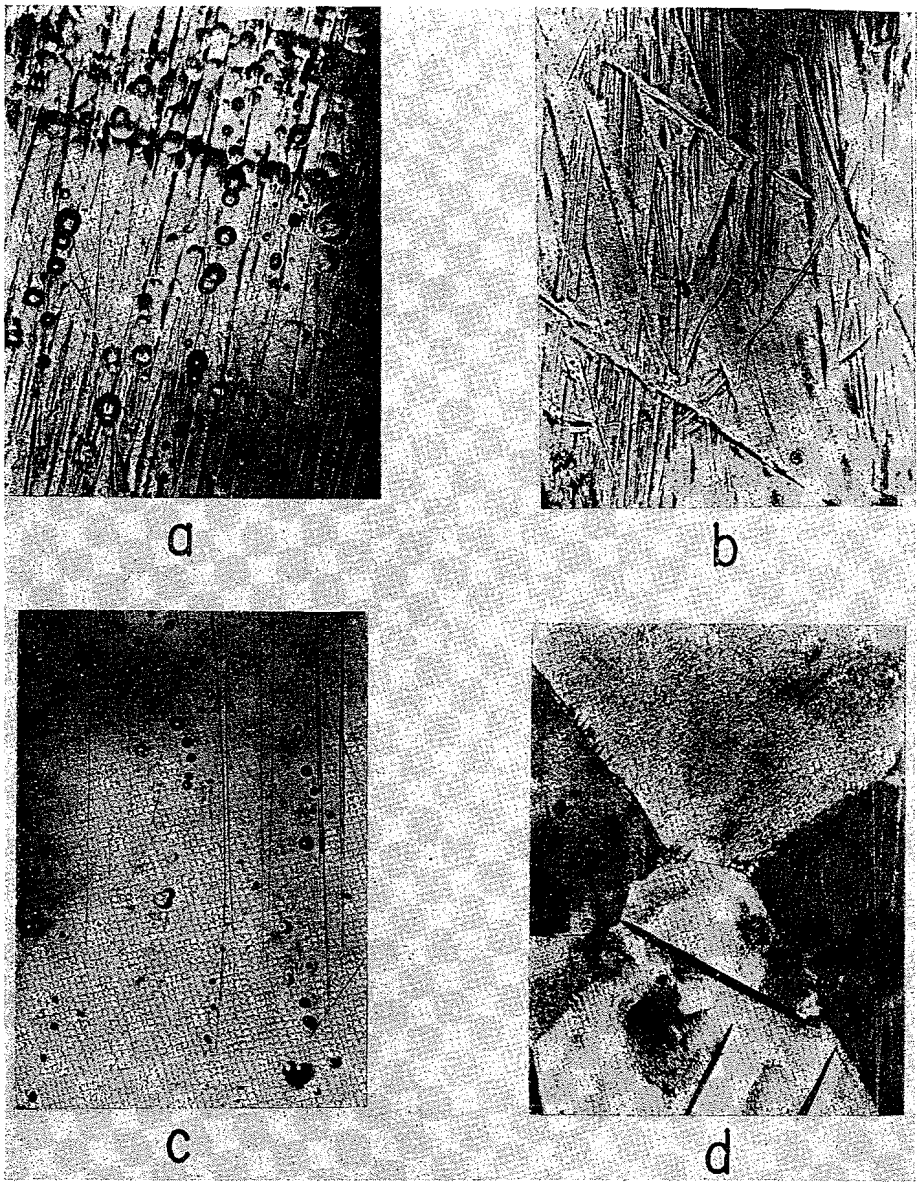



FIG. 7. Photomicrographs (approx. × 250) of surfaces given anodic treatment (*a*) not polished, (*b*) partially deburred and slightly electropolished, (*c*) well polished, (*d*) electroetched.

## ANALYSIS AND DISCUSSION

### *General Trends*

#### *Concentration Effect*

Experimentally it was found that at any chosen current density the polishing is done more efficiently at higher concentrations of $OH^-$. A consideration of the process involved indicates that at low concentrations the rate of solution

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of the film is probably slower than at high concentration, and one might expect that the film could grow thicker. As discussed above, the thicker the film, the less efficient it is for electropolishing. At higher concentrations of potassium hydroxide the film would be expected to be removed faster, and thus at the same current density the film is probably thin and more efficient for electropolishing.

*Current Density Effect*

Below some fairly critical current density in each case, electropolished surfaces could not be obtained, presumably because the rate of solution of the surface film was greater than its rate of production; that is, no film effective for electropolishing was formed. Of course, it is very probable that even at very low current densities, a very tight film, Angstroms thick, exists, following closely the surface contour, but this film would be too thin to be effective for polishing. Above some critical high current density, the anode concentration polarization becomes so high that the potential of decomposition of water of $OH^-$ is exceeded and oxygen is liberated. This causes violent stirring in the vicinity of the electrode, the film is broken mechanically as well as is dissolved, and the result is an electroetch—even removal of metal from each part of the surface.

*Temperature Effect*

Increased temperature was found to widen the electropolishing range of current density and time, as is noticed in Figs. 1, 2, and 3. Higher temperature, as well as increased concentration of $OH^-$, would be expected to increase the rate of solution of the film, keep the film thin, and thus permit electropolishing to be carried out in less time. It is noticed (Fig. 3) that at the lowest temperature not only was the range found to be considerably more narrow than at 25° and 53° but also that electropolishing could be effected in only the most concentrated solutions available at that temperature. No polishing at all was obtained in the 5.4 *N* potassium hydroxide at 0° C. That is, the rate of solution of the film is so slow at 0° C. that only in the most concentrated solution is the film kept thin and mechanically loose enough to be effective.

*Cation Effect*

The range of electropolishing conditions in sodium hydroxide is considerably larger than in the same concentration of potassium hydroxide (Fig. 5), and the range in lithium hydroxide falls in between the ranges in sodium hydroxide and potassium hydroxide. This is shown in Fig. 6. Differences must be attributed to differences in the properties of $Li^+$, $Na^+$, and $K^+$ since the weighed equivalent concentrations of $OH^-$ are all the same. The fact that zinc electropolishes in much less time in 5 *N* sodium hydroxide than in 5 *N* potassium hydroxide at the same current density is interpreted as resulting from a thinner and more efficient film being formed in sodium hydroxide than in potassium hydroxide. The anodic film formed in lithium hydroxide is apparently less efficient than that formed in sodium hydroxide, but is more efficient than the anodic film formed in potassium hydroxide of the same concentration, at the same current density and temperature. Hence the rate of removal of

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the film formed in sodium hydroxide must be greater than that of the film formed in lithium hydroxide, and this in turn must be greater than the rate of removal of the film formed in potassium hydroxide. Since the removal of the surface film is probably by means of the chemical process,

$$Zn(OH)_2 + 2\ MOH \rightarrow M_2ZnO_2 + 2H_2O,$$

the rate of removal of the film might be controlled by (1) the diffusion of MOH toward the anode, the diffusion of $M_2ZnO_2$, in whatever form, away from the anode into the solution, or the diffusion of water or MOH through the film; or (2) the chemical reaction of the dissolution process. In terms of Fick's law and rate theories (4), the rate of diffusion of MOH into, or reaction products away from, the film–solution interface depends upon the concentration gradient between the interface and the bulk solution, upon molecular or ionic size and weight, the nature and extent of hydration, and upon molecular and ionic cross-bonding or association in the solution. The rate of the chemical process would depend upon the activity of MOH at the interface and upon the exact composition of the film, strength of molecular and ionic association, and cross-linking in the film. The rate of diffusion of water, or MOH through the film depends on the concentration gradients and on the tightness of binding in the film itself. In each case the rate would depend upon those factors which determine the activation free energy for the process.

That the rate of diffusion of MOH into the interface from the bulk solution probably does not determine the thickness of the film is indicated by the fact that diffusion coefficients for the 1 *N* MOH in aqueous solution (figures for higher concentrations are not available) in order of decreasing value are KOH > NaOH > LiOH (7), and the mobilities of the cations decrease in the same order, $K^+ > Na^+ > Li^+$(15). Thus the effects noted above, namely the efficiency of electropolishing in NaOH > LiOH > KOH, must be attributed to (1) diffusion of $M_2ZnO_2$, in some form, away from the anode, or the diffusion of MOH or water through the film, or (2) the differences between the rates of the chemical reactions of dissolution of zinc hydroxide in sodium hydroxide, potassium hydroxide, and lithium hydroxide.

*Detailed Analysis*

A kinetic analysis of the data for zinc in potassium hydroxide solutions establishes some apparent trends and provides further information on the processes involved. For this purpose let us define a "percentage electropolished" to replace the qualitative descriptions, and let 100% electropolished be the equivalent of the qualitative term "electropolished" used above. "Slightly electropolished" would be translated into < 100 percentage units. Since each of the curves in Figs. 2, 3, 4, and 5 refers to the quality "electropolished", each point on the curves refers to a surface of quality 100 E.P.U. Hence, if 100 E.P.U. is achieved in time $t$, then the average rate at which the surface is being polished is [100 (E.P.U.)]/$t$; or average rate = (100/$t$) E.P.U./minute. That the definition and use of such a term as average rate is justified is seen when one considers that once the steady state in the anodic process has been established—and this takes only seconds in this case—

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further radical changes in the characteristics of the surface film would not be expected.

Table I shows average rates of polishing at different current densities,

TABLE I

| $I$, amp. cm.$^{-2}$ | Temp., ° C. | Concentration of KOH, normality | $t_{100}$ E.P.U., min. | Rate of polishing, E.P.U./min. |
|---|---|---|---|---|
| 0.18 | 53.0 | 5.36 | 25.5 | 3.9 ± 0.3 |
| | | 12.0 | 12.6 | 7.9 ± 1.0 |
| | | 19.0 | 7.5 | 13. ± 2. |
| | | 25.0 | 4.0 | 25. ± 3. |
| | 25.0 | 5.4 | 34.0 | 3.0 ± 0.5 |
| | | 12.0 | 20.5 | 4.9 ± 0.6 |
| | | 19.0 | 11.5 | 8.7 ± 0.7 |
| | 0.0 | 8.0 | $\gg$100 | $\ll$1.0 |
| | | 12.0 | 65 | 1.6 ± 0.3 |
| 0.32 | 53.0 | 5.36 | 22.0 | 4.5 ± 0.3 |
| | | 12.0 | 8.0 | 12.5 ± 1.5 |
| | | 19.0 | 5.0 | 20. ± 3. |
| | | 25.0 | 1.8 | 55. ± 10. |
| | 25.0 | 5.4 | 25.0 | 4.0 ± 0.3 |
| | | 12.0 | 10.5 | 9.5 ± 1.0 |
| | | 19.0 | 7.5 | 13. ± 1.0 |
| | 0.0 | 8.0 | ~100 | ~1.0 |
| | | 12.0 | 35 | 2.9 ± 0.3 |
| 1.0 | 53.0 | 2.0 | ~100 | ~1.0 |
| | | 5.36 | 18 | 5.6 ± 0.5 |
| | | 12.0 | 4.0 | 25. ± 6. |
| | | 19.0 | 2.0 | 50. ± 10. |
| | | 25.0 | 0.9 | 110. ± 25. |
| | 25.0 | 5.4 | 19.7 | 5.1 ± 0.5 |
| | | 12.0 | 4.3 | 23. ± 5. |
| | | 19.0 | 3.1 | 32. ± 7. |
| | 0.0 | 8.0 | 22.0 | 4.5 ± 0.4 |
| | | 12.0 | 8.0 | 12.5 ± 1.2 |

temperatures, and concentrations of potassium hydroxide. Times of anodic treatment and maximum probable errors were taken from the experimental points. Fig. 8 shows the dependence of the average rate of polishing on the concentration of potassium hydroxide. It is seen that at the low current density in concentrations of potassium hydroxide up to about 16 $N$ the rate of polishing appears to be linear; that is, the film-determining process seems to be first order with respect to potassium hydroxide. However, at current density 0.32 amp. cm.$^{-2}$ there are slight indications of curvature even below 16 $N$. At the high current density (1.0 amp. cm.$^{-2}$) the deviation from linearity is quite definite.

Table II lists average rates, taken from the experimental data, at the three

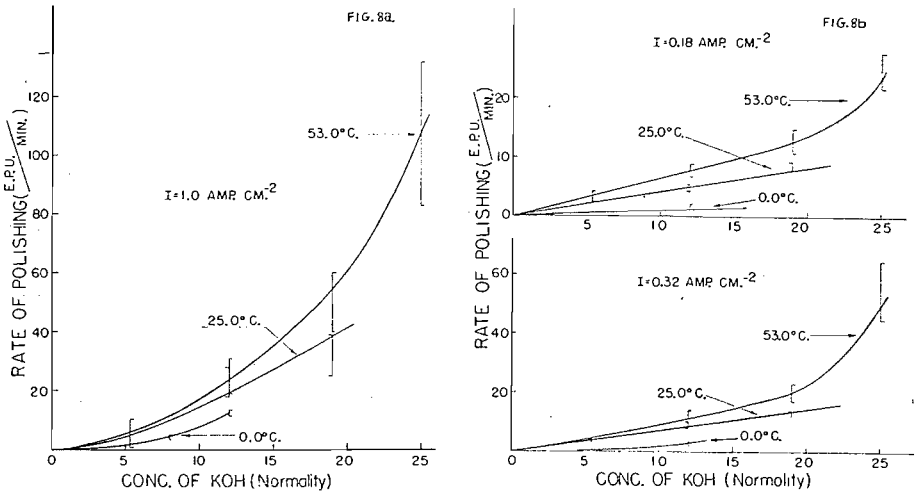



FIG. 8, (*a*) and (*b*). Average rate of polishing vs. concentration of potassium hydroxide for different current densities.

TABLE II

| Concentration of KOH, normality | *I*, amp. cm.$^{-2}$ | Temp., ° C. | Rate of polishing, E.P.U./min. | log rate | $(1/T) \times 10^3$, ° K.$^{-1}$ |
|---|---|---|---|---|---|
| 12 | 0.18 | 0.0 | 1.6 ± 0.3 | 0.20 ± 0.08 | 3.66 |
| | | 25.0 | 4.9 ± 0.6 | 0.69 ± 0.04 | 3.35 |
| | | 53.0 | 7.9 ± 1.0 | 0.90 ± 0.05 | 3.07 |
| | 0.32 | 0.0 | 2.9 ± 0.3 | 0.46 ± 0.05 | 3.66 |
| | | 25.0 | 9.5 ± 1.0 | 0.98 ± 0.04 | 3.35 |
| | | 53.0 | 12.5 ± 1.5 | 1.10 ± 0.05 | 3.07 |
| | 1.0 | 0.0 | 12.5 ± 1.0 | 1.10 ± 0.03 | 3.66 |
| | | 25.0 | 23. ± 5. | 1.36 ± 0.09 | 3.35 |
| | | 53.0 | 25. ± 6. | 1.40 ± 0.09 | 3.07 |
| 19 | 0.18 | 25.0 | 8.7 ± 0.7 | 0.94 ± 0.03 | 3.35 |
| | | 53.0 | 13. ± 2. | 1.11 ± 0.07 | 3.07 |
| | 0.32 | 25.0 | 13. ± 1. | 1.11 ± 0.04 | 3.35 |
| | | 53.0 | 20. ± 3. | 1.30 ± 0.06 | 3.07 |
| | 1.0 | 25.0 | 32. ± 7. | 1.51 ± 0.08 | 3.35 |
| | | 53.0 | 50. ± 10. | 1.70 ± 0.08 | 3.07 |

current densities, in 12 *N* and in 19 *N* potassium hydroxide solution. Arrhenius plots of log rate vs. $1/T$ for these data are shown in Fig. 9. In the Curves *a*, *b*, and *c*, a definite curvature is noted. Tangents to the curves at 0.0° C. and 53.0° C. show the activation energies for the process to decrease with increasing current density and decrease with increasing temperature:

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| $I$ (amp. cm.$^{-2}$) | $E^*$ (cal./mole) | |
|---|---|---|
| | 0.0° C. | 53.0° C. |
| 0.18 | 9800 | 3000 |
| 0.32 | 8100 | 2200 |
| 1.00 | 4300 | 1800 |

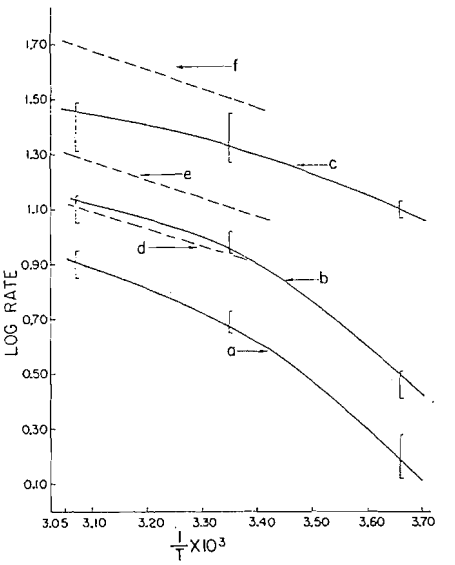



FIG. 9. Arrhenius plots for rate of polishing at various temperatures. *a*, *b*, and *c* 12 *N* potassium hydroxide; *d*, *e*, and *f* 19 *N* potassium hydroxide.

The low values at higher temperature suggest that a liquidlike diffusion process ultimately determines the characteristics of the layer at higher temperatures. The higher values at the lower temperature might refer equally well to the increasing importance of (1) diffusion through a much tighter film at the low temperature, or (2) the rate of the chemical process of dissolution. For the concentration 19 *N* the activation energies were taken from data for 25° and 53° only, since the poor solubility of potassium hydroxide at 0° C. makes the experiment impossible. However, the values were seen to be all about 3200 cal./mole, indicating that even at these higher concentrations the characteristics of the film are controlled by some physical process, probably diffusion.

This temperature and concentration information has suggested the following picture of the anodic processes of film formation and maintenance:

(1) At the low current densities the activation energies for the polishing process show that the heavy black deposit noted on the surface must be very tight at 0° C., much more porous at 53° C. Since the film is tight, penetration of the film is probably quite slow. Since the concentration of free potassium hydroxide in the film in this case would be expected to be quite

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small, dissolution of the film must take place mostly at the film–solution interface, and loosening of the film due to internal dissolution by potassium hydroxide must be negligible. Thus, the rate of polishing would be expected to be linear with respect to potassium hydroxide concentration below that concentration at which internal dissolution of the film becomes important. This is verified by the data of Fig. 8*b*. Indications are that at low current densities the rate of polishing is ultimately controlled by diffusion of the potassium hydroxide through the film toward the anode for precipitation of the fresh zinc ions. That is, the film is built up at the anode–film interface and removed mostly at the film–solution interface.

(2) At higher current densities, when the continuous destroying and rebuilding of the surface layer is much more rapid, the concentration of the potassium hydroxide in the film becomes increasingly important. The rate of penetration of potassium hydroxide to any point in the film, expressed by Fick's law, is proportional to the product of the concentration gradient and the diffusion coefficient. When the higher concentrations of potassium hydroxide are present in the film, internal dissolution of the film becomes appreciable, and the strength of binding in the film decreases. Thus, both the concentration gradient and the diffusion coefficient are increasing functions of the potassium hydroxide concentration. Therefore, since the binding in the film ultimately depends upon the concentration of potassium hydroxide in the film, the rate of supply of potassium hydroxide (and hence the rate of polishing) must depend upon some power of potassium hydroxide concentration greater than unity. That this is so is shown especially in the higher current density curves of Fig. 8: the rate deviates from linear dependence on potassium hydroxide concentration toward the parabolic, although the activation energies for the process under these conditions are still about 3200 cal./mole. At the higher current densities some oxygen was liberated, and the stirring so obtained probably aided the supply of potassium hydroxide to the interface and provided some additional mechanical loosening of the film.

(3) At the very high current densities the film was broken mechanically by the oxygen bubbles, no film could exist, and an electroetch was the result.

It is suggested from this interpretation of the results that the primary function of the film is to provide a loose, though tenuous, structure through which the passage of reaction products is by diffusion alone, convection and small eddy currents in the immediate vicinity of the anode having been minimized or eliminated.

*Other General Considerations*

The results on aluminum and zinc indicate that there probably exists for each temperature an optimum range of concentration of electrolyte for anodic polishing. Thus the work on zinc has shown that at any temperature there is a minimum concentration below which electropolishing is not feasible because of the necessarily extended lengths of time of anodic treatment. The work on aluminum indicates that aluminum hydroxide dissolves so fast in 5 *N* potassium hydroxide solution that the film is not formed at all at reasonable

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current densities, but that in lower concentrations of potassium hydroxide removal of the film is slower, and the film grows to a thickness which permits efficient electropolishing. Hence, a minimum concentration of potassium hydroxide for efficient electropolishing was found for zinc, and a maximum concentration for efficient electropolishing was found for aluminum.

In those cases in which electropolishing could not be obtained, viz. bismuth and tin, and antimony and lead only partially, a combination of effects is probably responsible. The oxides of lead and antimony immediately on the surface seem thin, and too tightly bound to be easily removed in the potassium hydroxide solutions used, and no polishing was obtained even though a second heavier film was formed above that immediately on the surface. The tin oxide is brittle, probably because of strong cross-bonding within the film and slow penetration of water and potassium hydroxide. The rate of solution of the film would be slower, the film thick, very highly resistive, and inefficient for electropolishing. Hence the concentration range for electropolishing tin is apparently toward higher concentrations of potassium hydroxide, beyond the limits of solubility of potassium hydroxide.

## SUMMARY AND CONCLUSIONS

Thus a kinetic analysis of data on the electrolytic polishing of zinc in alkali hydroxide solutions has established some trends and generalizations which seem to fit a proposed qualitative theory of the anodic processes taking place during the electrolytic polishing of metals. An anodic surface layer is pictured whose electrical and mechanical properties vary radically with metal, electrolyte, concentration of electrolyte, current density through the anode, temperature, and time of anodic treatment. The electrical and mechanical properties of the film determine the nature of the resulting surface. The experimental results are interpreted in terms of the theory, and the interpretation permits a rather detailed description of the anodic processes occurring in the film.

This condition of the surface after the metal has been made the anode of an electrochemical cell offers an additional fact relating to the polarizations of the anode. In any such experiment this fact is "measured" automatically, and, if interpreted in terms of the qualitative ideas presented herein, provides considerable useful additional information concerning the nature of the anodic processes involved. Some success has already been achieved along this line during work on another problem.

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# DEPENDENCE OF MOLECULAR PROPERTIES OF CONJUGATED COMPOUNDS ON THE STATE OF ELECTRONIC EXCITATION[1]

By C. Sándorfy

ABSTRACT

Reasons are given for the belief that many new chemical reactions may be obtained in the excited electronic states of the molecules. By the examples of nitrobenzene, *trans* → *cis* isomerization of stilbene and azobenzene, by an interpretation of experimental results concerning acidity and basicity of certain bodies in the excited states, and the evaluation of the charges and dipole moments of the C = N group in different excited states, it is shown how the chemical and physicochemical properties of the molecule may vary from one state to another.

## INTRODUCTION

Every molecule, in addition to its ground state, possesses a series of quantized excited states, into which it may pass by absorption of a photon.

The majority of photochemical reactions studied to date involve ions or free radicals.

We do not intend to concern ourselves with such reactions here. Instead, we wish to present arguments showing that these reactions constitute only a special case of possible reactions, involving the excited states of the molecules.

From work in theoretical chemistry published in recent years, we know that chemical reactivity is associated with the distribution of the electrons in the molecules. In particular, the case of molecules containing a conjugated system of $\pi$ electrons has been studied in great detail.

Now, any method of quantum chemistry shows the distribution of the electrons to be different in the different states.

The establishment of this fact presents the possibility of making the molecules participate in reactions in which they would not take part in their ground level or of increasing the speed of reactions that do take place.

It follows that if some convenient way were found of making the molecules react in their excited states, a scarcely exploited field would be opened to chemistry. To accomplish this it would only be necessary to keep a large number of molecules in their excited states during a reaction by the use of a sufficiently intense radiation. A favorable case would be the excitation to states which have a very long lifetime. This is the case for forbidden transitions, especially where a molecule is excited to its first triplet level. Lewis and Kasha have insisted on the importance of the phosphorescence spectra from this point of view (12, 13, 15).

## REACTIONS IN THE EXCITED STATES

Daudel and Pullman (7) appear to have been the first to evaluate a molecular diagram which describes the charge distribution in an excited state for a conjugated molecule. They did this for cyclopentadiene. Crawford and

[1] *Manuscript received December 12, 1952.*
*Contribution from Centre de Chimie Théorique de France, 155 rue de Sèvres, Paris.*



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Coulson (4) then took up the dimerization of acenaphthylene under the influence of light, and Sándorfy (20) studied the photooxidation and photodimerization of the acenes.

We do not intend to discuss these examples further here.

Chemical reactivity, as it appears in theoretical chemistry, depends on a fairly large number of factors: the charge, the bond order, the free valence number, the "autopolarizability" (3), the activation energy, and the stability of the end products (see for example (8)). For the excited states, their evaluation presents some difficulties.

We shall try here to present some examples in which one of these quantities appears to be of preponderant importance, thus making the study of the problem easier.

However, we shall not confine ourselves to the problems of chemical reactivity. It is clear that other physicochemical properties may vary from one state to another along with the distribution of the electrons.

(A) *Modification of the Orienting Effect of Substituents*

It is well known that, in the case of benzene, substituents exercise a certain orienting effect with respect to a second substitution. For example, the nitro-group orients a second electrophilic substituent in the meta position (during a nitration, for example), and this is explained by the fact that in meta position the positive charge is smallest and repels least the attacking group, which is a positive ion.

It is not possible to obtain ortho- or paradinitrobenzene by direct nitration in any appreciable amount.

Would it be possible to do this by means of a reaction carried out under the influence of light?

Fernandez (9) has evaluated the molecular diagrams of the first three excited states of nitrobenzene by a refined LCAO treatment.

These three levels lie close to one another and will probably be excited simultaneously, if a light source emitting continuous radiation is employed (about 4500–3500 Å in this particular case).

On examining the three corresponding diagrams we note that everywhere the meta position ceases to be the most favored one with respect to an electrophilic reagent (Fig. 1– effective charges given in electron units).

It can therefore be predicted that the formation of ortho- or paradinitrobenzene in appreciable quantities would be possible in the excited states.

Rumpf (19) has studied the possibility of verifying these predictions experimentally.

(B) *Photoisomerization*

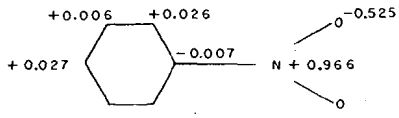
The bond order (3) appears to be the most important quantity in the case which we are now going to discuss.

We are concerned with *trans* → *cis* isomerization due to the effect of light (also *cis* → *trans*, although more rarely).

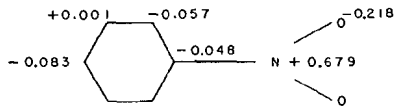
Smakula and Wassermann (22, 23) studied the problem in connection with the absorption spectrum of stilbene, and they came to the conclusion that in

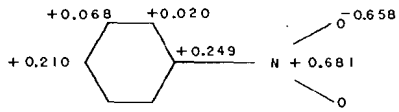
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GROUND STATE




EXCITED STATES



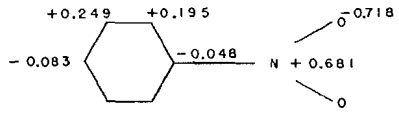
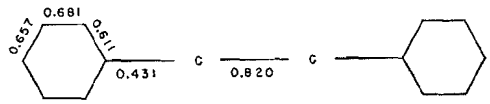




FIG. 1

order to obtain isomerization it was not necessary to remove the $\pi$ component of the ethylenic bond, but only to excite the electrons in this bond. Later Lewis, Magel, and Lipkin (16) again took up the problem.

Smakula thought that the transition must be due to the electrons of the ethylenic bond. To-day we know that such a localization is not admissible, in principle, in a conjugated system. It is necessary to study the levels of the $\pi$ electrons of stilbene. This has been done for the fundamental state by Buu-Hoï, Coulson, P. and R. Daudel, Martin, and A. and B. Pullman (1). We have evaluated the bond orders of the first allowed excited level (2). Here are the results:

GROUND STATE




EXCITED STATE

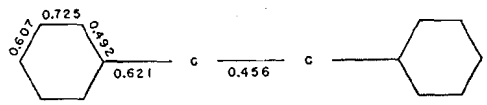



FIG. 2

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It is noted at once that there is a large decrease in the bond order of the ethylenic bond ($\Delta p = 0.384$).

For azobenzene the case is quite similar.

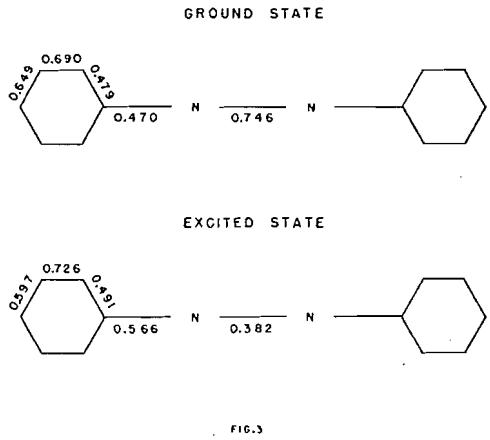



FIG. 3

Here $\Delta p = 0.364$.

All this suggests that in the excited state, in conformity with Smakula's idea, the bond about which an isomerization occurs, although it remains a "double bond", becomes less "double". It can be imagined, therefore, that a rotation will occur more easily about it in the excited state than in the fundamental state.

Mulliken and Roothaan (17) and Parr and Crawford (18) carried out calculations on the variation of the energy of the ethylene molecule, on twisting the plane of one $CH_2$ group relative to that of the other about the C = C axis for various electronic states, and obtained results in satisfactory agreement with experiment.

(C) *Modification of Electrolytic Dissociation Constants*

The tendency of an acid such as phenol to lose a proton is greatest when there is a high positive charge on the oxygen, and the concentration of the protons in the medium is low.

On the other hand a base such as aniline will attract a proton and liberate an hydroxyl ion all the more easily when the negative charge on the nitrogen is great (or its positive charge small), and the concentration of the protons in the medium is high (see for instance (24)) (provided other things, such as changes in resonance energy, are equal).

Förster drew attention to the fact that if the acid or base absorbs a photon and passes into an excited state, the distribution of the charges is profoundly altered, and consequently the acidity or basicity is likewise altered (10).

In order to demonstrate this phenomenon, he studied the absorption spectra and fluorescence spectra of certain acids and bases, in which the pH of the medium varied from 0 to 14. The absorption spectra depend on the state of dissociation of the ground level, the fluorescence spectra on that of the excited level.

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We intend to follow up these experiments with some theoretical calculations. We shall evaluate the charges due to the $\pi$ electrons in all cases by the usual method of molecular orbitals, and we shall take into account the charges due to polarization of the $\sigma$ electrons by means of the charge effect method (5, 14) of Daudel.

We shall consider aniline and phenol as models for the study of larger molecules on which these phenomena were observed.

In the case of aniline, the nitrogen carries a charge equal to $-0.13$ electron in the ground level. (The Coulomb integral is $\alpha_N = 0.61$.) It will be understood, therefore, that even in a solution of low acidity it will be able to attract a proton (Fig. 4*a*).

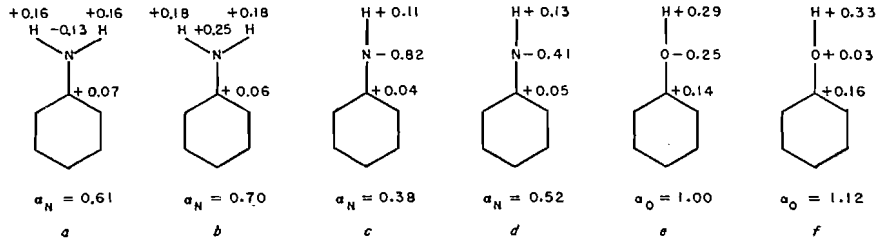



FIG. 4.

Thus the conjugation between the benzene nucleus and the nitrogen is reduced and instead of the aniline absorption spectrum (first band at 2860 Å) only the "benzenic" spectrum (2550 Å) will be found (see 11).

The greater the number of aniline molecules which acquire a third proton, the more intense the "benzenic" band will become at the expense of the "anilinic", and this number will depend on the pH. The "anilinic" band will disappear entirely if the solution is sufficiently acid.

It is a case of the intensity of one band increasing while that of another decreases; there is no question of a band being displaced towards shorter or longer waves.

We have taken the mean value of the charges appearing on the first two close-lying excited levels, and we have found +0.25 on the nitrogen (Fig. 4*b*).

This is a considerable modification. Simply by absorbing a photon the aniline becomes much less basic. Since it has a positive charge it will tend to repulse protons. Consequently, the "anilinic" band will disappear at a much more acid pH value in fluorescence than in absorption.

According to Förster (10), in a very basic solution the hydroxyl ions of the solution may separate a proton from the amino group. The remainder of the molecule, in the ground and excited levels, will have the diagrams in Figs. 4*c* and 4*d*. In the ground level, even if this second proton is lost, the molecule will readily acquire another proton because of the high negative charge of the nitrogen.

Therefore we may expect that this form will appear rather in the excited state (i.e., in fluorescence) where the positive charge of the nitrogen in

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$C_6H_5NH_2$ is higher, and where once the second proton is lost its negative charge is lower.

The corresponding band will be located at longer wave lengths owing to the decreased electronegative character of the nitrogen.

For phenol, the diagrams of Figs. 4*e* and 4*f* are obtained.

The proton, indeed, can be separated more easily when the molecule is at the excited level. The corresponding band will appear at longer wave lengths in fluorescence at a less basic pH value.

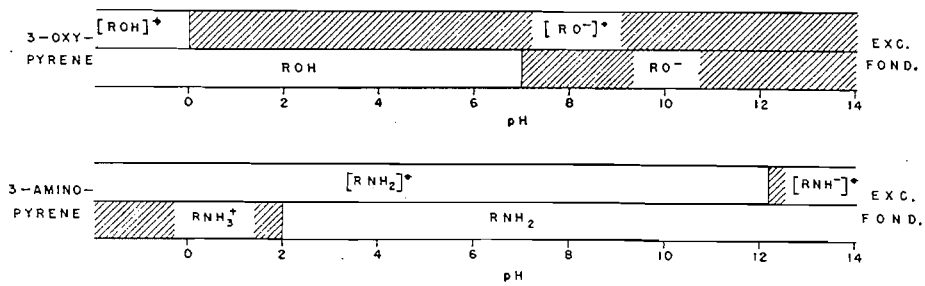



FIG. 5.

The experimental results (10) obtained in the case of 3-amino and 3-oxypyrene, summarized in Fig. 5 (taken from Ref. 10), are quite similar to those which would be expected for aniline and phenol according to our calculations.

Experiments on the $\alpha$ and $\beta$ naphthols and on the $\alpha$ and $\beta$ naphthylamines lead to similar observations (10).

We evaluated the molecular diagrams of the $\alpha$ and $\beta$ naphthols by the method of molecular orbitals, taking $\alpha_O = 1$ for the Coulomb integral of oxygen and $\alpha_C = 0.1$ for the carbon to which it is linked.

We present them here for the ground states and for the first excited states (Fig. 6). The most important fact which may be observed is again the considerable increase of the positive charge on the oxygen due to excitation, and certain important reversals of the values of the charges on other atoms which should not fail to have their effect on the chemical reactivity. We quickly discover atoms, for example, which constitute preferred places for the attack of an electrophilic reagent in the ground level, and which will be preferred places for the nucleophilic reagents in the excited states. Fig. 6 shows also the diagram for the charges of the second excited state of $\beta$ naphthol.

It is interesting to see that the increase of the positive charge is not as great here as for the first excited state, and that the charges of the two carbons next to the one bound to the oxygen are completely reversed compared with those of the first excited state.

From this it may be predicted that it is quite possible to find higher excited states, in which the change in chemical reactivity, relative to that of the ground level, is not as great as for a lower excited state, and it is even possible that the reactivities of certain atoms of a molecule are of an entirely different character for different excited states.

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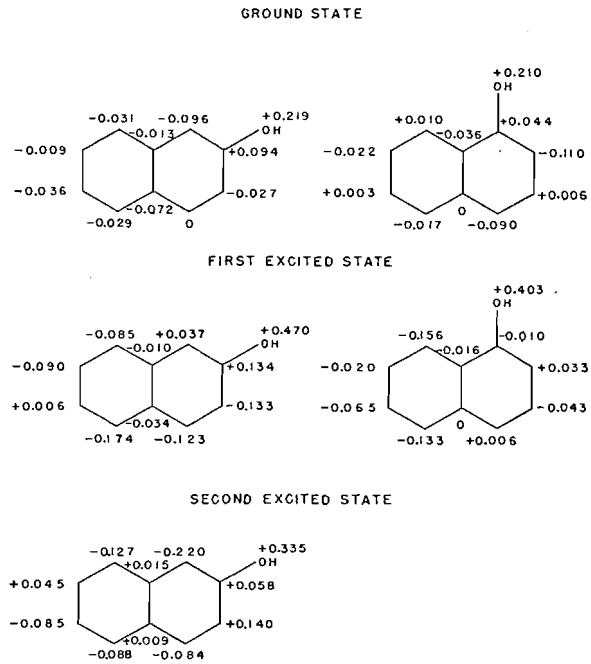



FIG. 6

(D) *Modification of the Polar Moments*

With the aid of definitions recently proposed by Daudel and Laforgue (6) it is possible to evaluate the charges on the atoms, taking into account configurational interaction.

This has been done for the imaginary group C = N (choosing $\alpha_N = 0.5$ as the supplementary Coulomb integral of nitrogen (21)*).

These are the charges for the three states $N$, $V$, and $Z$:

| Excitation energies | Charges |
|---|---|
| $N$ | $-0.01$ C ——— $+0.01$ N |
| $N \rightarrow V$ 11.56 ev. $V$ | $-0.52$ C ——— $+0.52$ N |
| $N \rightarrow Z$ 15.86 ev. $Z$ | $+0.51$ C ——— $-0.51$ N |

The extent to which conditions may vary from one state to another is clearly evident. Owing to the effect of a photon which takes this group from the $N$ state to the $V$ state the carbon will become very open to attack by an electrophilic reagent, but if, by means of a photon of higher energy, the group is made to pass to the $Z$ state it will become easily attacked by the nucleophilic

* *Certain numerical results have been changed from the values given in (21) owing to a different choice of an integral.*

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reagents. All this may be interesting from the point of view of Schiff's bases, $C_6H_5-CH=N-C_6H_5$, for example, where an electronic transition affecting principally the CH = N group (19) probably will be found.

The part of the dipole moment due to the $\pi$ electrons also varies widely according to the state.

| | |
|---|---|
| $N$ | $-0.06\ D$ |
| $V$ | $-3.16\ D$ |
| $Z$ | $3.08\ D$ |

## CONCLUSIONS

These few examples seem to point to the fact that the chemical and physicochemical properties of the molecules, in general, must vary in quite an important way depending on the state of energy in which the molecules find themselves.

A more detailed study of the chemical and physicochemical properties of the molecules by both theoretical and experimental methods in their excited states would therefore be very desirable.

There will no doubt be serious technical difficulties to overcome before such experiments can be carried out.

However, there is no reason to believe that these are insurmountable, and, in the event of success, the theory will have opened up a new field to experimentation.

## ACKNOWLEDGMENTS

I wish to thank Dr. R. Daudel and Dr. P. Rumpf for many valuable discussions. It is hoped that the experiments undertaken by the latter will confirm the theoretical predictions set forth in the present paper.

The manuscript of this article was completed during my tenure of a National Research Council of Canada Postdoctorate Fellowship.

I wish to acknowledge my gratitude to Dr. R. N. Jones for the interest he has shown in this work, to Dr. D. W. Davidson for assistance in the preparation of the manuscript, and to Mr. D. A. Sinclair for the English translation.

## RÉSUMÉ

On donne des raisons de penser qu'un grand nombre de réactions chimiques nouvelles pourraient être réalisées aux états excités des molécules. On montre par les exemples du nitrobenzène, de l'isomerisation *trans* → *cis* du stilbène et de l'azobenzène, par une interprétation des résultats expérimentaux concernant l'acidité et la basicité de certains corps à l'état excité et l'évaluation des charges et des moments dipolaires du groupe C = N à ces différents états, comment les propriétés chimiques et physico-chimiques des molécules peuvent varier d'un état d'energie à un autre.

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# BETATRON IRRADIATION OF WATER SATURATED WITH BENZENE[1]

By G. R. Freeman, A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

The oxidation of benzene to phenol in dilute aqueous solution by $Co^{60}$ gamma rays and betatron X-rays (23 Mev. peak energy) is compared with the oxidation of $Fe^{++}$ to $Fe^{+++}$ under similar conditions. The ratio $\frac{\text{yield of phenol}}{\text{yield of } Fe^{++} \text{ oxidized}}$ was the same for $Co^{60}$ and betatron radiations. The yield for the $Co^{60}$ radiations was about 10% greater than the apparent yield for the betatron radiations, the difference probably being attributable to dose determination at high energies (> 1 Mev.). It is concluded that both reactions are independent of energy and dose rate over the ranges investigated.

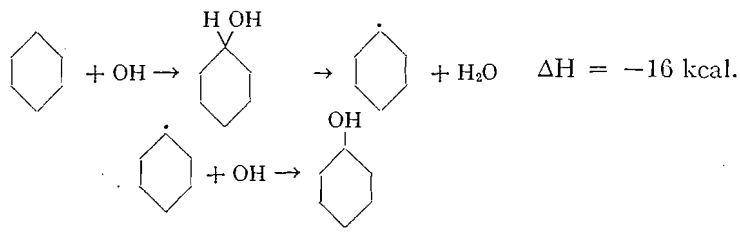
## INTRODUCTION

It has been found that when a saturated aqueous solution of benzene is irradiated with X- or $\gamma$-rays, phenol, hydrogen, biphenyl, and terphenyl are formed (9, 10). When an n-$\gamma$-ray source was used to irradiate the solutions, catechol and products originating from the opening of the benzene ring were produced in addition to those listed above. These products (catechol, etc.) are presumably due to the higher free radical concentration caused by the recoil protons (from neutrons hitting hydrogen atoms) (9).

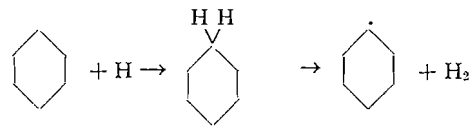
Similar products are obtained by the irradiation of dilute aqueous solutions of sodium benzoate (9, 10).

The latest mechanism (10) advanced for the hydroxylation of benzene on irradiation of its aqueous solution with X-rays is:

$$H_2O \rightsquigarrow H + OH$$

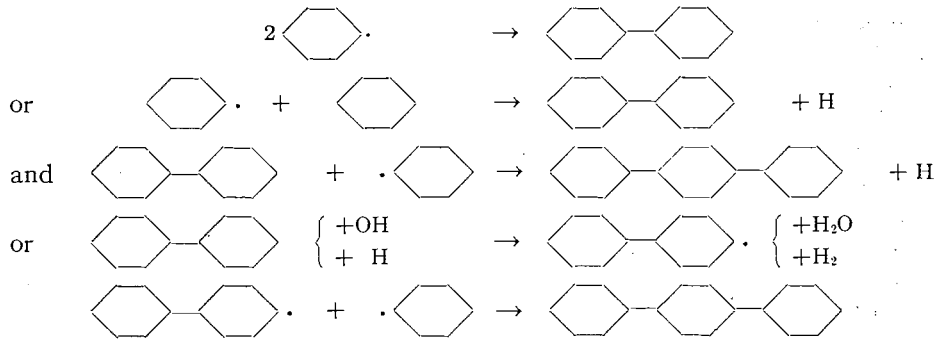



Phenyl radicals may also be formed to a small extent by the reaction:




The phenyl radicals also react to form di- and terphenyl:

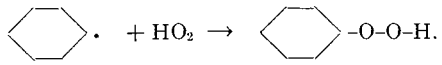
[1] *Manuscript received December 1, 1952.*
*Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*



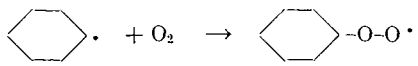

When oxygen is present in the solution, $HO_2$, formed by the reaction

$$H + O_2 \rightarrow HO_2,$$

is also capable of hydroxylating benzene (10, 3),




This may eventually result in the formation of phenol. Similarly, oxygen may react with the phenyl free radical (3),




which may eventually form phenol.

The yield of phenol in aerated solution is five times as great as the yield in deaerated solution (10).

The yield of phenol is not critically dependent on pH, concentration, temperature, or wave length of incident radiation (10, 3). The yield increases slightly at high ($> 10$) and low ($< 4$) pH and decreases by 20% for a 10-fold dilution of the saturated solution (10).

In aerated saturated aqueous benzene solution, the yield of phenol varies directly with the dose up to about 60 kiloroentgens (depending on the amount of oxygen present in the solution and probably also on the dose rate, since oxygen diffuses into the solution from the air above it), beyond which there is a sharp drop in yield, due to the virtual absence of oxygen (10, 3).

The purpose of the present experiments was to carry out the irradiation of aerated saturated aqueous benzene solutions with $\gamma$-rays from $Co^{60}$ and with 23 Mev. peak energy X-rays from a betatron. Parallel experiments were carried out on the oxidation of ferrous sulphate solutions so that the ratio of the yield of phenol produced to the yield of $Fe^{++}$ oxidized could be compared for the two different energy sources.

## MATERIALS

The water used in the benzene solutions and in all analytical reagents used in phenol analyses was prepared by distilling tap water once from alkaline potassium permanganate in an all-Pyrex still.

The water used in the ferrous sulphate solution and in all analytical reagents

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concerned with iron analyses was prepared by distilling tap water once from alkaline potassium permanganate and then once from alkaline manganous hydroxide suspensions (each time in an all-Pyrex still).

The Pyrex test tubes, and ground glass stoppers, used to contain the solutions during irradiation were cleaned with hot chromic acid cleaning solution, rinsed at least three times with tap water, and then at least three times with water distilled from alkaline potassium permanganate.

The benzene used was thiophene-free reagent grade, further purified by shaking once with an equal volume of concentrated sulphuric acid (two minutes) and seven times with equal volumes of distilled water (one minute each time).

The phenol used in the preparation of the standard curve was purified by vacuum distillation from zinc dust.

The Folin-Denis phenol reagent and the standard phenol solution were prepared as in *Colorimetric Methods of Analysis*, Vol. 2, by F. D. Snell. However, it was found that in the phenol standardization, only 10 cc. of normal iodine were necessary to precipitate the triiodophenol (50 cc. of normal iodine solution are prescribed in Snell).

The sulphuric acid used was purified by distilling from potassium dichromate.

## EXPERIMENTAL PROCEDURES

### *Determination of Phenol*

Standard phenol solution (0.1 ml.) (5.63 gm./l.) was diluted to 5 ml. with water, and 3 ml. Folin-Denis reagent was added. After thorough mixing, 15 ml. 20% sodium carbonate solution was added, and the blue color was allowed to develop for 20 min. A transmittance curve was then run on the solution in a model DU Beckman spectrophotometer. Maximum absorption occurs at $\lambda = 750$ m$\mu$ (see Fig. 1.)

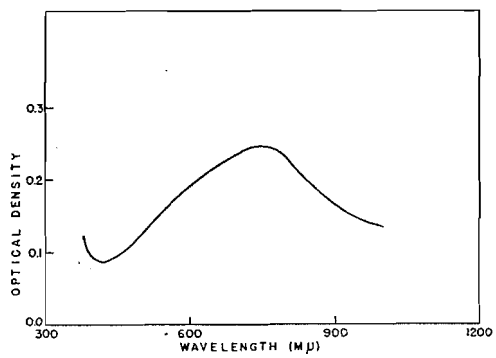



FIG. 1. Transmittance curve for phenol-Folin complex.

The phenol standard curve was obtained by treating solutions of various phenol concentrations (made by diluting standard solution) with Folin reagent and sodium carbonate solution and reading the optical density after 20–25 min. ($\lambda = 750$ m$\mu$, slit 0.015 mm.) using a water blank. The solutions obeyed the

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Beer-Lambert Law, and the extinction coefficient was 12,256 l./mole/cm. Optical density is defined by the equation: $D = kcd = (-\log_{10}(T/100))$, where $D$ = optical density, $k$ = extinction coefficient, $c$ = concentration of sample in solutions, $d$ = light path length of cell; $T$ = % transmission (1).

To determine the amount of phenol produced, 1 ml. Folin reagent was added to the irradiated solution, and after thorough mixing, 5 ml. 20% sodium carbonate solution was added. These amounts were used because larger amounts sometimes produced a turbidity. The optical density was read 20–25 min. after the addition of the sodium carbonate. The color was found to be stable for at least one hour after sodium carbonate addition. The irradiated solution did not appear to change its phenol content if allowed to stand 23 hr., after irradiation, before analysis.

*Determination of $Fe^{++}$*

The *o*-phenanthroline, sodium citrate colorimetric method was used (7). The irradiated solution was shaken with 5 ml. of 0.1% *o*-phenanthroline, 1 ml. saturated sodium citrate solution was added, and the optical density read in the model DU Beckman spectrophotometer at $\lambda = 510$ m$\mu$, using a water blank.

It was found that the citrate and/or *o*-phenanthroline complexes of $Fe^{+++}$ ion also absorb light at $\lambda = 510$ m$\mu$. Although the absorption is small compared to that of the $Fe^{++}$ ion complex, it must be corrected for in the irradiated solution. The absorption for the $Fe^{+++}$ complexes is plotted in Fig. 2.

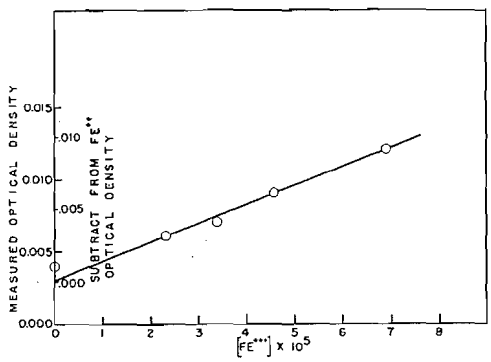



FIG. 2. $Fe^{+++}$-citrate – *o*-phenanthroline calibration curve.

The standard ferric ion solution used in preparing the curve was made by dissolving ferric ammonium sulphate in 0.8 $N$ sulphuric acid. Various concentrations of $Fe^{+++}$ were obtained by diluting this standard solution with 0.8 $N$ sulphuric acid.

The optical density of the solution containing everything but iron was about 0.003. This was constant for all solutions measured, and since the $\mu$m./l. of $Fe^{++}$ oxidized was measured by subtracting the $[Fe^{++}]$ present in the irradiation solution from the $[Fe^{++}]$ in the original solution, no error was introduced in the final result. However, the ferric ion concentration varied with the dosage, and hence had to be corrected for. This correction was obtained by

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subtracting 0.003 from the optical density of the $Fe^{+++}$ complex solution. (The $[Fe^{+++}]$ could be calculated accurately enough from the uncorrected optical densities.) The value thus obtained was subtracted from the optical density of the $Fe^{++}$ solution and the $[Fe^{++}]$ was calculated from the net results. For example, an original $Fe^{++}$ ion solution diluted three times had an optical density of 0.299, corresponding to $[Fe^{++}]$ of 26.0 $\mu$m./l. After irradiation the solution, diluted three times, had an optical density of 0.097, corresponding to $[Fe^{++}]$ of 8.4 $\mu$m./l. (7). Thus, the approximate $[Fe^{+++}]$ was $26.0 - 8.4 = 17.6$ $\mu$m./l. From Fig. 2 this corresponds to an optical density correction of 0.002. Therefore, the corrected optical density of the irradiated solution was $0.097 - 0.002 = 0.095$, corresponding to $[Fe^{++}]$ of 8.1 $\mu$m./l. The true $[Fe^{+++}]$ was then $26.0 - 8.1 = 17.9$ $\mu$m./l. Taking the dilution factor into consideration, $3 \times 17.9 = 53.7$ $\mu$m./l. of $Fe^{++}$ ion were oxidized.

As the oxidation of $Fe^{++}$ ion approaches completion, the correction becomes more significant.

*Irradiation with $\gamma$-Rays from $Co^{60}$*

Samples (3 ml.) of water saturated with benzene (0.082% at 22° C. (6)) were placed in glass stoppered test tubes in a cylindrical lucite block and irradiated with a 2 curie $Co^{60}$ source (see Fig. 3).

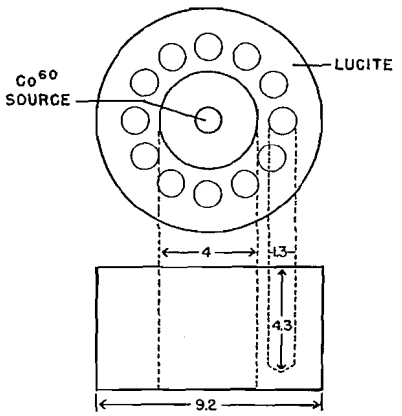



FIG. 3. Lucite block for irradiation with 2 curie $Co^{60}$ source (dimensions in cm.).

Samples (3 ml.) of aqueous ferrous ammonium sulphate solution (0.8 *N* in sulphuric acid) were irradiated in the same way.

The dose rate in roentgens/minute (r./min.) received by each hole in the block was determined using a Victoreen Condenser r.-meter Model 70. The bakelite thimble of a 25 r. chamber was replaced with a lucite one equal in size to the volume of the irradiated solution. It was calibrated against a standard 25 r. chamber using a 1100 curie $Co^{60}$ source. The usual temperature and pressure corrections and the 2% for changing "lucite roentgens" to "air roentgens" at 1.25 Mev. energy must also be applied (7).

*Irradiation with X-rays from the Betatron Using 23 Mev. Peak Energy*

Samples (2 ml.) of water saturated with benzene, in glass stoppered test

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tubes were placed in a cylindrical lucite block which was shielded by cadmium (for details, see Ref. (7)).

Samples (2 ml.) of ferrous ammonium sulphate solution (0.8 *N* in sulphuric acid) were irradiated simultaneously with the benzene solutions.

All samples were placed in the outer ring of holes in the block and the rest of the holes contained test tubes of water. After each sample was removed, a test tube of water was placed in the hole to keep irradiation conditions constant throughout the block.

The dose rate was determined using a 100 r. Victoreen chamber. The Victoreen results were corrected for energy dependence (8% at 23 Mev. peak) and for temperature and pressure (7).

## EXPERIMENTAL RESULTS

All results from the irradiation of $Fe^{++}$ and benzene solutions were treated statistically, and the best fitting straight lines were determined using the method of least squares. The yields are listed with their respective probable errors.

### *Irradiation with $Co^{60}$ $\gamma$-Rays*

#### *Water Saturated with Benzene*

The initial pH of all the benzene solutions was 6.7 (unbuffered). The pH decreased with irradiation to 4.42 at 145 kiloroentgens. This variation is within the pH independent region.

The average temperature was 22.5° C. The dose rate was about 1100 roentgens per hour. The results are plotted in Fig. 4. The average yield of phenol was 2.94 ± 0.08 μmoles/l./kr.

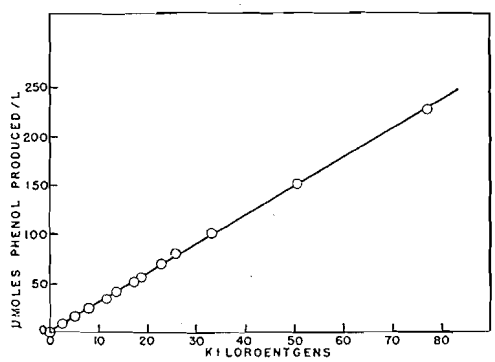



FIG. 4. Irradiation of water, saturated with benzene, with $Co^{60}$ $\gamma$-rays.

#### *Ferrous Ammonium Sulphate Solutions (in 0.8 N Sulphuric Acid)*

The initial ferrous ion concentration was $7.80 \times 10^{-5}$ molar. The temperature was 24° C. The dose rate was about 1100 roentgens per hour. The results are plotted in Fig. 5. The average yield of $Fe^{++}$ oxidized to $Fe^{+++}$ by $Co^{60}$ $\gamma$-rays was 16.8 ± 0.2 μmoles/l./kr. Complete oxidation of $Fe^{++}$ to $Fe^{+++}$ was observed.

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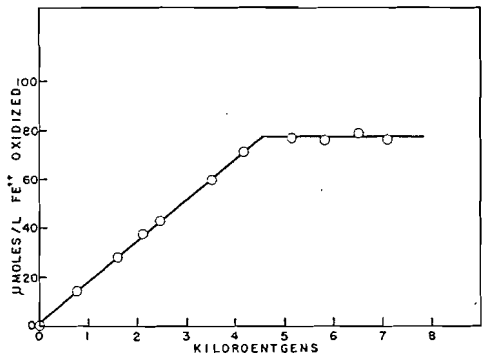



FIG. 5. Irradiation of ferrous sulphate solutions with $Co^{60}$ $\gamma$-rays.

*Irradiation with Betatron X-rays—23 Mev. Peak Energy*

*Water Saturated with Benzene*

The solutions were exactly similar to those used in the $Co^{60}$ $\gamma$-irradiations. The average temperature was 27° C. The dose rate was about 20,000 roentgens per hour. The results are plotted in Fig. 6. The average yield of phenol was 2.64 ± 0.08 μmoles/l./kr.

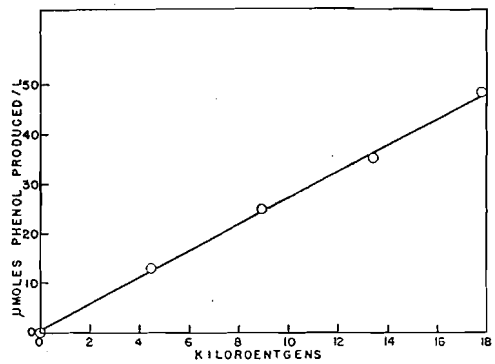



FIG. 6. Irradiation of water, saturated with benzene, with betatron X-rays, 23 Mev. peak energy.

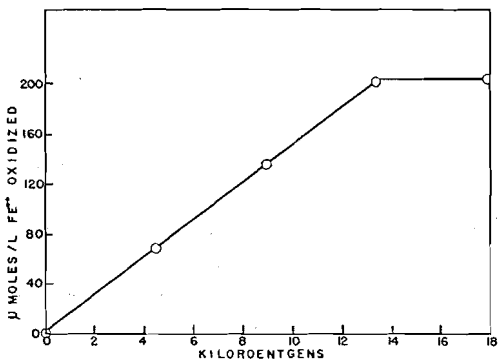



FIG. 7. Irradiation of ferrous sulphate solutions with betatron X-rays, 23 Mev. peak energy.

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*Ferrous Ammonium Sulphate Solutions (in 0.08 N Sulphuric Acid)*

The initial ferrous ion concentration was $2.04 \times 10^{-4}$ molar. The average temperature was 27° C. The dose rate was about 20,000 roentgens per hour. The results are plotted in Fig. 7. The average yield of $Fe^{++}$ oxidized to $Fe^{+++}$ was 15.0 ± 0.2 μmoles/l./kr. Complete oxidation of $Fe^{+++}$ was observed.

The results are summarized in Table I.

TABLE I

SUMMARY OF RESULTS OBTAINED WITH BENZENE SOLUTIONS AND IRON SOLUTIONS USING $Co^{60}$ γ- AND BETATRON X-RAYS

| Radiation source | Solution | Yield (μM./l./kr.) | Yield G(molecules/100 ev.) |
|---|---|---|---|
| $Co^{60}$—Average energy 1.25 Mev. γ-rays | Benzene | 2.94 ± 0.08 | 3.05 ± 0.08 |
| | $Fe^{++}$ | 16.8 ± 0.2 | 17.4 ± 0.2 |
| Betatron—23 Mev. peak energy X-rays | Benzene | 2.64 ± 0.08 | 2.74 ± 0.08 |
| | $Fe^{++}$ | 15.0 ± 0.2 | 15.6 ± 0.2 |

Stein and Weiss (10) using 200 kv. X-rays obtained M/N 0.75 for air saturated solutions of benzene.

## DISCUSSION

From Table I it is seen that the ratio $\frac{\text{yield of phenol}}{\text{yield of } Fe^{++} \text{ oxidized}}$ for equal doses of $Co^{60}$ γ-rays is 2.94/16.8 = 0.175. The same ratio for betatron X-rays with 23 Mev. peak energy is 2.64/15.0 = 0.176. The difference between these two values is not significant, and it thus appears that the $Fe^{++}$ and benzene solutions behave in the same manner with respect to the particular combined variation in the dose rate and energy of incident radiation in the present experiments. These ratios are independent of Victoreen errors and corrections made in converting "lucite roentgens" to air roentgens, since the only requirement is that the doses be equal. With the $Co^{60}$ source equal doses may be obtained by placing samples in the same geometry for equal periods of time. With the betatron, equal doses may be obtained by irradiating the samples simultaneously in the rotating lucite block used in these experiments.

The actual values of the yields (μM./l./kr.) of phenol, and of $Fe^{++}$ oxidized, by irradiation of aqueous solutions of benzene and ferrous ion, respectively, indicate that there is about a 10% difference in the results obtained from the $Co^{60}$ γ-irradiations and from the betatron X-irradiations at 23 Mev. peak energy. This difference could be due to any one or combination of four factors: (1) Victoreen dose determination at high energy (> 1 Mev.), (2) energy of incident radiation, (3) dose rate, (4) the betatron X-rays are emitted in pulses of about 4μsec. duration and frequency of 180 per second. Thus, the dose rate in each pulse is extremely high, and might enhance the ordinary dose rate effect.

The median energy of the photons from the betatron at 23 Mev. peak is about 9 Mev. (calculated from a theoretical Schiff distribution curve for

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maximum photon energy of 23 Mev. which has been modified by absorption of donut, monitor, and lucite). At this high energy, uncertainties in the Victoreen dose determination may account for all or most of the variation; thus, it would appear that both the ferrous and benzene systems are independent of dose rate and energy of incident radiation over the range investigated. This conclusion is supported further by the fact that the ferrous system was found to be independent of dose rate over the range 500–1500 r./hr. by Dewhurst (5) and over the range 72–3600 r./hr. by Miller (8). Since both the benzene and ferrous systems may be regarded as being essentially water, the energy absorbed per roentgen would be the same, i.e., 93 ergs/gm./r.

The fact that the ratios: $\frac{\text{yield phenol}}{\text{yield } Fe^{++} \text{ oxidized}}$ are the same for the $Co^{60}$ and betatron irradiations, probably indicates that the water is the main factor affected, and this effect is relatively independent of the solute. Thus, an indirect reaction mechanism is indicated, and reaction is probably due to activated water molecules or water products such as OH, $HO_2$, etc., and not due to a direct hit on the solute. Of course, this conclusion holds only for the dilute solutions described above and may not apply to concentrated solutions. The possibility that secondary radiation from water may have an effect should also be mentioned (2, 4).

ACKNOWLEDGMENTS

We wish to express our appreciation to the Defence Research Board of Canada for financial support and to the Physics Department of the University of Saskatchewan for use of the betatron. One of us (G.R.F.) is holder of a bursary from the National Research Council of Canada.

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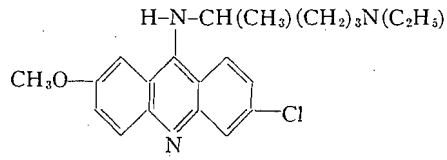
# STUDIES IN THE PREPARATION OF ANTIMALARIALS FROM PYRIDINE[1]

By Henry Gilman and John T. Edward[2]

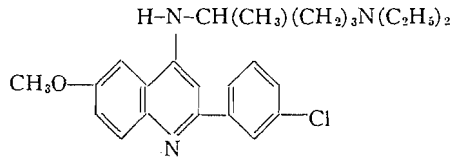
ABSTRACT

The addition of aryllithium compounds to pyridine followed by air oxidation gives satisfactory yields of several 2-arylpyridines. These are readily oxidized by perbenzoic acid to 2-arylpyridine-N-oxides, from which 2-aryl-4- and 6-chloropyridines may be obtained. 2-Arylpyridines and aryllithiums give low yields of 2,6-diarylpyridines. From three different 2-arylpyridines three antimalarials modelled after the plasmoquin type have been prepared.

In earlier investigations in this laboratory (8, 9, 14, 15) it was found that certain "open models" of atebrin (I) such as 2-(3′-chlorophenyl)-4[(α-methyl-δ-diethylaminobutyl)-amino]-6-methoxyquinoline (II) were active against

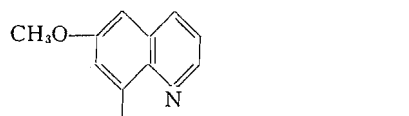



I

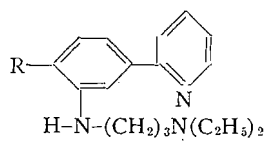



II

experimental avian malarial infections. Consequently, three open models of plasmoquin (III) having the basic side chain on the phenyl group of a 2-phenylpyridine have been prepared. Of these,




III

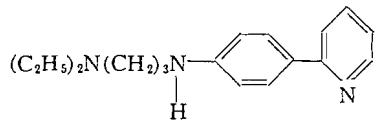



IV

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V

2-(3′-[γ-diethylaminopropyl]-amino-4′-methoxyphenyl)-pyridine (IV; R = $OCH_3$) and 2-(3′-[γ-diethylaminopropyl]-amino-4′-methylphenyl)-pyridine (IV; R = $CH_3$) proved inactive, while 2-(4′-[γ-diethylaminopropyl]-aminophenyl)-pyridine (V) showed slight activity. Somewhat surprisingly, 2-*p*-tolylpyridine also gave indications of activity. It may be significant that the active compounds are vinylogues of α-picoline and a 2-aminopyridine, in both of which there exists the possibility of a tautomeric shift of hydrogen to the hetero nitrogen atom (19, pp. 32, 91); such a possibility has been suggested in explaining the antimalarial activity of atebrin (23) and other compounds (4).

The general method of synthesis of these plasmoquin models is illustrated by the example below. The aryllithium was prepared in all cases by direct interaction of the appropriate aryl bromide with lithium. It has been observed that *p*-anisyllithium metalates *p*-bromoanisole so that the reaction of the latter with lithium ordinarily yields a mixture of *p*-anisyllithium and 2-methoxy-5-bromophenyllithium (10). However, if the *p*-anisyllithium is prepared very rapidly, the extent of metalation is slight and relatively pure *p*-anisyllithium is obtained.

The addition of an aryllithium to pyridine gives an N-lithiodihydropyridine (VI), which hitherto has been converted to the desired 2-arylpyridine (VII) by heating above 100° and splitting out lithium hydride (5, 25, 26, 27). Oxidation of the N-lithiodihydro intermediate with dry air gives, particularly in the cases of 2-*o*-anisyl- and 2-*p*-anisylpyridine, significantly improved yields, though in the case of the *o*-anisyl compound the yield is still low.

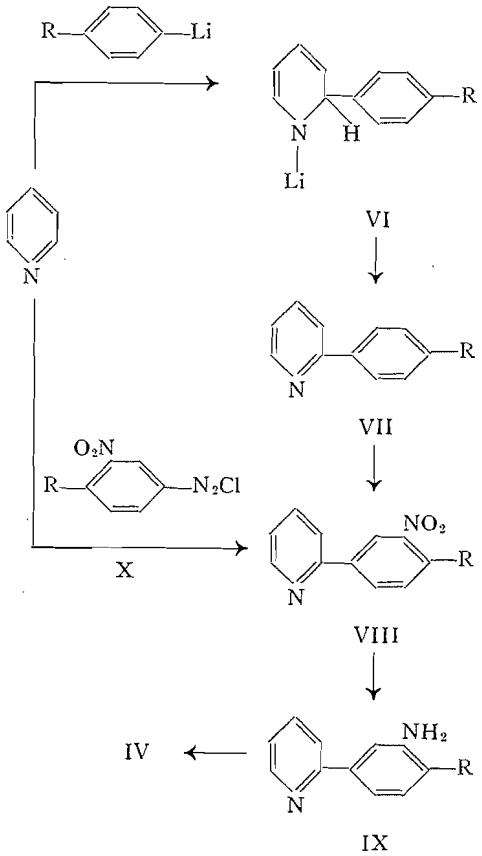
Since this work was completed, the preparation of 2-phenylpyridine in 60% yield by oxidation with nitrobenzene of 2-phenyl-1,2-dihydropyridine (produced from (VI; R = H) when the reaction mixture is poured into water) has been reported (7).

The attempt to prepare 2-phenylpyridine by coupling 2-bromopyridine with phenyllithium gave only a low yield of the desired compound; the isolation of pyridine from the hydrolyzed reaction mixture indicates that a halogen–metal interconversion reaction took place, giving bromobenzene and 2-pyridyllithium. A similar reaction with 3-bromopyridine, using *n*-butyllithium, has been described by Gilman and Spatz (12).

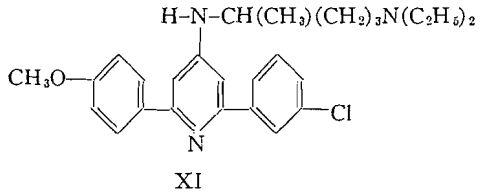
The nitration of 2-phenyl- and 2-*p*-anisylpyridine gave nitro compounds of known orientation (6, 16); however, it was necessary to establish the position of nitration of 2-*p*-tolylpyridine (VII; R = $CH_3$). This was done by an independent synthesis of the product, 2-(3′-nitro-4′-methylphenyl)-pyridine (VIII; R = $CH_3$), by the reaction of diazotized 2-nitro-4-aminotoluene (X) with pyridine. This reaction gave, besides (VIII), two other compounds, presumably the isomers formed by substitution at the 3- and 4-positions of pyridine.

The synthesis of open models of atebrin (e.g. XI) was also envisaged,

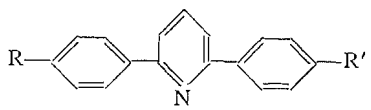
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through the stages 2,6-diarylpyridine → N-oxide → 4-chloropyridine → 4-(basic alkylamino)-pyridine. However, only low yields of 2,6-diarylpyridines (e.g. XII; R = R′ = H; R = $(CH_3)_2N$, R′ = H; and R = $(CH_3)_2N$, R′ = $CH_3$) were obtainable from aryllithiums and 2-arylpyridines.




XI




XII

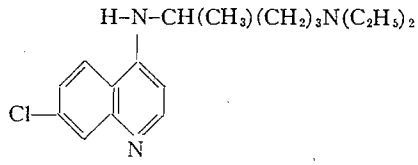
The best yields were obtained by conducting the reaction above 100° and forcing the addition of the aryllithium to the sluggish 2-arylpyridine.

The oxidation of 2,6-diphenylpyridine by a large excess of perbenzoic acid gave a low yield of the N-oxide (cf. 20). On the other hand, 2-phenylpyridine and 2-*p*-anisylpyridine gave good yields of their N-oxides. The introduction of phenyl groups is known to decrease the basicity of the pyridine nucleus (19, p. 71); evidently with two or more of these electron-withdrawing groups

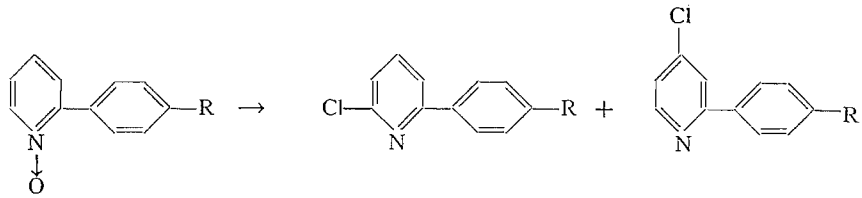
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substituted in pyridine the availability of the unshared electron pair of the nitrogen for co-ordination with oxygen is sharply decreased.

The possibility of preparing open models of the highly active 4-(α-methyl-δ-diethylaminobutyl)-amino-7-chloroquinoline (SN 7618) (XIII) was next




XIII




XIV XV XVI

considered. It is known that the N-oxides of pyridine (2), quinoline (1, 20), and similar compounds, on treatment with sulphuryl chloride or phosphorus oxychloride, yield mixtures of the 2- and 4-chloro bases. These may be separated because of the greater basicity of the 4-chloro compounds (e.g. 18). 2-Phenylpyridine-N-oxide (XIV; R = H) and 2-*p*-anisylpyridine-N-oxide (XIV; R = $OCH_3$) also gave in this way a mixture of chlorinated compounds; the more basic were assumed to be the 4-chloro derivatives (XVI; R = H and $OCH_3$), and were isolated as picrates; the less basic, which did not form picrates, to be 2-chloro derivatives (XV; R = H and $OCH_3$). These compounds contain reactive halogen atoms (19, p. 78) which should be easily replaced by the basic side chain to give open models of XIII.

In searching for an alternative synthesis of 2-aryl-6-chloropyridines, 2-chloropyridine was treated with phenyllithium, but no reaction occurred. Evidently the chlorine deactivates the pyridine nucleus (cf. Gilman and Spatz (13) ).

## EXPERIMENTAL

### *2-Phenylpyridine*

This compound was prepared essentially in accordance with the procedure of Evans and Allen (5), except that the dihydro intermediate was oxidized with air instead of being heated to 110° C. in toluene. Five minutes after addition of slightly more than an equivalent amount of pyridine to phenyllithium, the green color in Gilman's Colour Test I (11), indicative of phenyllithium, had given place to a red color, possibly owing to the dihydro intermediate. The mixture was maintained a further 10 min. under nitrogen, and then dry air was passed over the stirred mixture. The completion of oxidation, indicated when the red color was no longer given, required from 6 to 24 hr.,

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depending on the size of the run. Yields, which did not seem to be much affected by varying the temperature of this oxidation between 0° and 35° C., varied from 40% to 57%, about the same as the yields (40–50%) obtained by Evans and Allen.

*Reaction of Phenyllithium with 2-Bromopyridine*

Phenyllithium (0.065 mole) in 50 cc. of ether was added dropwise over two hours to a stirred solution of 10.2 gm. (0.065 mole) of 2-bromopyridine in 50 cc. of ether. After hydrolysis, the ether layer gave on distillation 3.5 gm. of a yellow liquid boiling at 35–50° C. (20 mm.), which consisted of a water-insoluble liquid and of pyridine, identified by the formation of its picrate (m.p. and mixed m.p.); and 0.5 gm. (5% of theory) of 2-phenylpyridine, b.p. 80° (0.5 mm.), forming a picrate, m.p. 173° to 174° C. (25).

*2-(p-[γ-Diethylaminopropyl]-aminophenyl)-pyridine (V)*

2-Phenylpyridine was nitrated by a solution of potassium nitrate in sulphuric acid, and the mixture of 2-*m*- and 2-*p*-nitrophenylpyridine separated by the procedure of Forsyth and Pyman (6). Reduction of 2-*p*-nitrophenylpyridine to 2-*p*-aminophenylpyridine was accomplished either with tin and hydrochloric acid (6), or by dissolving in 10 parts of ethanol and heating on the steam bath for seven hours with 10 parts of a saturated aqueous sodium sulphide solution (64% yield). 2-*p*-Aminophenylpyridine (4.1 gm.; 0.024 mole) was heated with 6.7 gm. (0.036 mole) of γ-diethylaminopropyl chloride hydrochloride to 130° C. for four hours, and to 190° C. for 12 hr. The brown glassy melt which formed was dissolved in dilute hydrochloric acid. When the solution was made alkaline a brown oil separated, which was taken up in ether, dried, and distilled. The 2-(*p*-[γ-diethylaminopropyl]-aminophenyl)-pyridine was obtained as a viscous yellow oil, b.p. 185–190° C. (1 mm.), $n_D^{25}$ 1.6166, $d_{25}^{25}$ 1.0482; observed molar refraction $R_D$ (from the Lorenz-Lorentz equation), 94.55. Calc. (from constants of Vogel (24)) 89.35*. The yield was 5.1 gm. or 68%. Calc. for $C_{18}H_{25}N_3$: N, 14.83%. Found: N, 14.90%.

The compound gave with picric acid a red oil which could not be crystallized.

*2-m-Aminophenylpyridine*

Seven grams of 2-*m*-nitrophenylpyridine dissolved in 70 cc. of ethanol was heated for seven hours on a steam bath with 70 cc. of aqueous saturated sodium sulphide solution. The solution was filtered from a small amount of colored material and diluted with water. The red oil which separated was taken up in benzene, and the extract dried and distilled. Three grams (50% yield) of yellow oil, b.p. 145–147° C. (0.1 mm.), which crystallized on standing to a solid melting at 72–73° C., was obtained. Calc. for $C_{11}H_{10}N_2$: N, 16.48%. Found: N, 16.38%.

Since the completion of this work, this compound has been described by Cook, Heilbron, and Reed (3) who report a m.p. of 72–74° C.

* *The exaltation of molar refraction noted here and in later examples occurs when the pyridine ring is attached to an aromatic nucleus; when it is attached to alkyl groups, the difference between the observed and calculated molar refractions is less than 1%.*

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The *picrate*, crystallized from ethanol, melted at 219–220° C. Calc. for $C_{17}H_{13}O_7N_5$: N, 17.54%. Found: N, 17.70%.

*p-Anisyllithium*

This compound was prepared from the reaction of 18.7 gm. of *p*-bromoanisole with 1.9 gm. of lithium following the conventional techniques, except that the time of addition of *p*-bromoanisole was reduced to 12 min. and the total time of the reaction to 17 min. This was achieved by having the lithium in very small pieces about 0.5 mm. in thickness, and by cooling the reaction flask with ice water once refluxing of ether had commenced. Carbonation with solid carbon dioxide gave anisic acid melting at 175–184° C. (using a Fisher-Johns heated metal block). Pure anisic acid melted at 185° C.; the admixture of 10% of 2-methoxy-5-bromobenzoic acid lowered the m.p. to 150° C. Hence the m.p. of the carbonation product indicated that it contained probably less than 5% of 2-methoxy-5-bromobenzoic acid.

*2-p-Anisylpyridine* (*VII; R = $OCH_3$*)

The addition of *p*-anisyllithium to pyridine, followed by air oxidation of the dihydro intermediate, gave an oily solid boiling at 120–135° C. (0.1 mm.). This was crystallized from petroleum ether to give a 35% yield of 2-*p*-anisylpyridine, melting at 47–50° C.; its picrate melted at 189° C. and did not depress the m.p. of an authentic specimen prepared by the method of Haworth, Heilbron, and Hey (16). These authors report a m.p. for the base of 50–51° C. and a m.p. for the picrate of 191–192° C. Their b.p. (160–190° C. at 0.1 mm.) is about 40° higher than ours.

When 2-*p*-anisylpyridine was prepared by the method of Evans and Allen (5), a smaller yield of a more impure product was obtained, which gave on repeated recrystallization from ligroin a 6% yield of base melting at 46–49° C.

*2-o-Anisylpyridine*

Addition of *o*-anisyllithium to pyridine was very slow, and even after refluxing the ethereal solution for eight hours Colour Test I gave a faint green color. (Gilman and Spatz (14) found the addition of *o*-anisyllithium to quinoline less complete than the addition of other aryllithiums.) The mixture was then air oxidized and worked up in the usual way to give an 18% yield of yellow oil boiling at 120–140° C. (0.1 mm.), which formed a picrate melting at 152–155° C. Haworth, Heilbron, and Hey (16) report a m.p. for the picrate of 155–156° C.; again their b.p. (160–190° C. at 0.1 mm.) appears to be about 40° too high.

When *o*-anisyllithium was allowed to react with pyridine and the reaction mixture then treated according to the procedure of Evans and Allen, no 2-*o*-anisylpyridine was formed. The fraction of the product boiling at 120–140° C. (0.1 mm.), treated with picric acid, gave an unidentified yellow picrate, m.p. 167–175° C., and considerable amounts of tar; none of the other fractions gave any crystalline derivative with picric acid.

*2-(3′-Amino-4′-methoxyphenyl)-pyridine* (*IX; R = $OCH_3$*)

2-*p*-Anisylpyridine, nitrated in accordance with the procedure of Haworth,

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Heilbron, and Hey (16), gave 2-(3′-nitro-4′-methoxyphenyl)-pyridine (VIII; R = $OCH_3$). This material was then reduced with aqueous sodium sulphide solution in the same way as 2-*m*-nitrophenylpyridine. After removal of most of the ethanol by distillation, a 95% yield of 2-(3′-amino-4′-methoxyphenyl)-pyridine crystallized out. The crude material melted at 92–94° C.; recrystallization from methanol–water gave pale tan needles melting at 94–95° C. Calc. for $C_{12}H_{12}ON_2$: N, 14.00%. Found: N, 14.25%. The *picrate*, crystallized from methanol, melted at 219–220° C. Calc. for $C_{18}H_{15}O_8N_5$: N, 16.32%. Found: N, 16.29%.

*2-(3′-[γ-Diethylaminopropyl]-amino-4′-methoxyphenyl)-pyridine (IV; R = $OCH_3$)*

Six grams (0.030 mole) of 2-(3′-amino-4′-methoxyphenyl)-pyridine and 8.4 gm. (0.045 mole) of γ-diethylaminopropyl chloride hydrochloride were heated together at 150° C. for nine hours. The glassy melt was worked up in the manner described above for V. A heavy yellow oil, reddening slowly on contact with air, and almost setting to a glass at room temperature, was obtained; b.p. 195–200° C. (0.5 mm.), $n_D^{25}$ 1.5859. The yield was 4.3 gm. (46%). Calc. for $C_{19}H_{27}ON_3$: N, 13.42%. Found: N, 13.65%. No crystalline picrate could be formed.

*2-p-Tolylpyridine (VII; R = $CH_3$)*

This compound was prepared in 62% yield by the action of *p*-tolyllithium on pyridine, using the air oxidation method as described for 2-phenylpyridine. It was a yellow oil, b.p. 93–98° C. (1 mm.), $d_{25}^{25}$ 1.055, $n_D^{25}$ 1.6107. $R_D$ observed 55.66, calc. 53.02. Calc. for $C_{12}H_{11}N$: N, 8.28%. Found: N, 8.14%.

The picrate melted at 181–182° C. Calc. for $C_{18}H_{14}O_7N_4$: N, 14.07%. Found: N, 14.28%.

*2-(3′-Nitro-4′-methylphenyl)-pyridine (VIII; R = $CH_3$)*

A. *By the Nitration of 2-p-Tolylpyridine*

To a stirred solution of 42 gm. (0.25 mole) of 2-*p*-tolylpyridine in 35 cc. of sulphuric acid, cooled by an ice bath, was added dropwise a solution of 25 gm. (0.25 mole) of potassium nitrate in 100 cc. of sulphuric acid. The mixture was stirred for 10 min. at room temperature, and for 30 min. at 100° C. It was cooled, poured on ice, and neutralized with ammonium hydroxide. The brown flocculent precipitate, on crystallization from methanol, gave 38.9 gm. (73%) of brownish needles, melting at 58–61° C. and a second crop of 3.5 gm. (6.5%), m.p. 55–59° C. Recrystallization from methanol, after decoloration with Norit, gave white needles, m.p. 60–61° C. Calc. for $C_{12}H_{10}O_2N_2$: N, 13.09%. Found: N, 13.40%. The *picrate* crystallized from methanol in small, yellow prisms, m.p. 184–184.5° C. Calc. for $C_{18}H_{13}O_9N_5$: N, 15.80%. Found: N, 16.24%.

B. *By the Action of Diazotized 2-Nitro-4-aminotoluene (X; R = $CH_3$) on Pyridine*

2-Nitro-4-aminotoluene (7.6 gm.; 0.05 mole), prepared by a modification of the procedure of Nölting and Collin (21), was dissolved in 25 cc. (0.25 mole) of concentrated hydrochloric acid and 12 cc. of water, and diazotized by

3.4 gm. (0.05 mole) of sodium nitrite in 10 cc. of water. The solution of diazotized amine was then added dropwise with stirring to 100 cc. (1.24 mole) of pyridine, over a period of 45 min. A mildly exothermic reaction maintained the temperature at 40–45° C. The reaction mixture was stirred for 30 min. while being heated on a steam bath, and then worked up by the methods employed in similar reactions by Haworth, Heilbron, and Hey (16). Three grams of a yellow oil boiling at 155–160° C. (0.1 mm.) was obtained. This was treated with picric acid in methanol, and the yellow solid obtained was subjected to systematic fractional crystallization from acetone and from ethanol to yield three different picrates. The least soluble, m.p. 217–219° C., crystallized from ethanol–acetone (4: 1) in lemon-yellow, woolly tufts of fine needles, and was probably the picrate of *4-(3′-nitro-4′-methylphenyl)-pyridine*. Calc. for $C_{18}H_{13}O_9N_5$; N, 15.80%. Found: N, 15.65%.

The more soluble fraction was separated into a small amount of a yellow solid, m.p. 240–250° C., probably the impure picrate of 3-(3′-nitro-4′-methylphenyl)-pyridine, and hard canary-yellow prisms melting at 183–185° C., which were shown by mixed m.p. to be identical with the picrate of the *2-(3′-nitro-4′-methylphenyl)-pyridine* prepared by the nitration of 2-*p*-tolylpyridine.

*2-(3′-Amino-4′-methylphenyl)-pyridine* (*IX; R = $CH_3$*)

Reduction of the nitro compound with sodium sulphide was accomplished in the same manner as the reduction of 2-*m*-nitrophenylpyridine. A yield of 88.5% of long yellowish needles, m.p. 109–110° C., was obtained. Recrystallization from methanol failed to raise the melting point. Calc. for $C_{12}H_{12}N_2$: N, 15.22%. Found: N, 15.43%. The *picrate* crystallized from methanol in tufts of needles, m.p. 186–187° C. Calc. for $C_{12}H_{15}O_7N_5$: N, 16.95%. Found: N, 17.10%.

*2-(3′-[γ-Diethylaminopropyl]-amino-4′-methylphenyl)-pyridine* (*IV; R = $CH_3$*)

2-(3′-Amino-4′-methylphenyl)-pyridine (4.5 gm.; 0.024 mole) and 6.9 gm. (0.037 mole) of γ-diethylaminopropyl chloride hydrochloride were fused together at 160° C. for four hours, and the glassy melt was worked up in the same way as for V. A yellow oil was obtained, b.p. 185–190° C. (0.5 mm.), $d_{25}^{25}$ 1.0272, $n_D^{25}$ 1.5887, $R_D$ observed 97.54, calc. 94.00, weighing 4.6 gm. (63% yield). Calc. for $C_{19}H_{27}N_3$: N, 14.14%. Found: N, 14.38%. No crystalline picrate could be formed.

*2,6-Diphenylpyridine* (*XII; R = R′ = H*)

When 2-phenylpyridine was allowed to react with an equivalent amount of phenyllithium in ethereal solution at 35° C. under nitrogen, addition was still incomplete after 80 min., as shown by a pale blue color given by the reaction mixture in Colour Test I. Air oxidation and working up in the usual manner gave a large recovery of 2-phenylpyridine, boiling at 85–90° C. (0.1 mm.), and identified by forming the picrate melting at 174° C. (25), and some 2,6-diphenylpyridine distilling at 195–200° C. (1 mm.). Crystallization of the latter from petroleum ether gave a 13.5% yield of solid melting at 79–81° C.; by repeated recrystallization from ethanol the melting point was raised to 81° C.;

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m.p. of picrate 169° C. Scholtz (22) reports the same melting points for the base and picrate.

On attempting to force addition of phenyllithium to 2-phenylpyridine by refluxing the mixture in ether–toluene at 60° C. under nitrogen it was found that even after 90 min. Colour Test I was pale blue. The mixture was air oxidized and worked up as before to give a 16% recovery of 2-phenylpyridine (isolated as pure picrate from the fraction boiling at 85–100° C. (0.1 mm.)) and 30% yield of impure 2,6-diphenylpyridine; after one crystallization from methanol the yield was 24%, m.p. 79–81° C.

When 2-phenylpyridine was reacted with phenyllithium and the procedure of Evans and Allen (5) followed, a 34% yield of crude 2,6-diphenylpyridine was obtained, but still about 10% of 2-phenylpyridine was recovered.

*2,6-Diphenylpyridine-N-oxide*

A 350 cc. chloroform solution of 20 gm. (0.087 mole) of 2,6-diphenylpyridine and 0.176 mole of perbenzoic acid was kept in an ice box for 18 hr., and at room temperature for three days. Titration then showed that only 0.031 mole of perbenzoic acid remained. The chloroform solution was extracted with sodium hydroxide solution and dried over sodium sulphate. Evaporation of the solution at reduced pressure gave a yellow oil. On addition of a small amount of ether–ligroin to the oil, 7 gm. of white crystals, m.p. 80–115° C., separated out; the filtrate on being cooled to −10° C. gave a further 5 gm., m.p. 60–70° C. These crops were extracted twice with ether, which served to remove 2,6-diphenylpyridine, of which 3.3 gm. (16%) was recovered in this manner. The extracted solid melted at 105–123° C.; crystallization twice from chloroform – petroleum ether gave 1.2 gm. (5.6%) of pure 2,6-diphenylpyridine-N-oxide, m.p. 125–126° C.; and a second crop (1.8 gm.; 8.4%) melting at 121–126° C. Calc. for $C_{17}H_{13}ON$: N, 5.67%. Found: N, 5.84%. The *picrate* crystallized from ethanol in yellow prisms, m.p. 161–162° C. Calc. for $C_{25}H_{16}O_8N_4$: N, 11.75%. Found: N, 11.92%.

*2-p-Dimethylaminophenylpyridine (VII; R = $(CH_3)_2N$)*

This compound was prepared from the reaction of *p*-dimethylaminophenyllithium with pyridine essentially in accordance with the procedure of Evans and Allen (5). It distilled as a yellow oil, b.p. 160–162° C. (0.1 mm.), which set to a solid melting at 87–92° C. (63% yield). Repeated recrystallization from ligroin and from aqueous acetone gave white crystals, m.p. 97–98.5° C. Calc. for $C_{13}H_{14}N_2$: N, 14.15%. Found: N, 13.96%. The *picrate* crystallized from acetone in long fibrous orange needles, m.p. 194–195° C. Calc. for $C_{19}H_{27}O_7N_5$: N, 16.39%. Found: N, 16.30%.

*2-p-Dimethylaminophenyl-6-phenylpyridine (XII; R = $(CH_3)_2N$, R′ = H)*

The reaction of *p*-dimethylaminophenyllithium with slightly more than an equivalent amount of 2-phenylpyridine according to the method of Evans and Allen (5) gave 2-*p*-dimethylamino-6-phenylpyridine, b.p. 230–240° C. (0.1 mm.). After crystallization from benzene and from benzene–methanol, a 13% yield of white needles melting at 172–173° C. was obtained. Calc. for

$C_{19}H_{18}N_2$: N, 10.22%. Found: N, 10.22%. The *picrate* was more soluble in methanol than the free base and separated as fluffy, orange crystals, m.p. 143–144° C., with one molecule of methanol of crystallization. Calc. for $C_{25}H_{21}O_7N_5.CH_4O$: N, 13.09%. Found: N, 12.93, 13.15%.

*2-p-Dimethylaminophenyl-6-p-tolylpyridine* (*XII; R* = $(CH_3)_2N$, *R'* = $CH_3$)

The reaction of *p*-tolyllithium with 2-*p*-dimethylaminophenylpyridine, following the procedure of Evans and Allen (5), gave a 23% yield of impure solid, b.p. 257° C. (0.5 mm.). Decolorization in benzene solution with Norit followed by recrystallization from benzene and benzene–methanol gave a 9% yield of white crystals, m.p. 196–197° C. Calc. for $C_{20}H_{20}N_2$: N, 9.72%. Found: N, 9.78%. The *picrate* was more soluble in methanol than the free base. It crystallized as a fluffy, orange solid melting at 157–158° C.

*2-Phenylpyridine-N-oxide* (*XIV; R = H*)

A 350 cc. chloroform solution containing 20 gm. (0.13 mole) of 2-phenylpyridine and 0.167 mole of perbenzoic acid was left in the refrigerator for 40 hr. It was then extracted with sodium hydroxide solution, dried over sodium sulphate, and evaporated down to a volume of 60 cc. On dilution with 50 cc. of petroleum ether and cooling, 10.7 gm. (48% yield) of white needles melting at 153–155° C. separated. Concentration of the mother liquors gave a further 4.2 gm. (19% yield) melting at 145–155° C. Recrystallization from benzene raised the m.p. to 155–155.5° C. Calc. for $C_{11}H_{19}ON$: N, 8.19%. Found: N, 8.4%.

When the mole ratio of perbenzoic acid to base was increased from 1.28 to 1.66, the total yield rose from 67% to 77%.

The *picrate* of 2-phenylpyridine-N-oxide crystallized in yellow prisms from benzene, m.p. 150–152° C. Calc. for $C_{17}H_{12}O_8N_4$: N, 14.00%. Found: N, 13.95%.

*Chlorination of 2-Phenylpyridine-N-oxide*

2-Phenylpyridine-N-oxide (4.2 gm.; 0.025 mole) protected from moisture and cooled in an ice bath was treated with 46 gm. (0.34 mole) of sulphuryl chloride. The amine oxide dissolved almost immediately. After standing for a few minutes at room temperature, the solution was refluxed gently for five hours. It was then cooled, added to 200 gm. of cracked ice, and made strongly alkaline with ammonia. The oil separating was taken up in ether and treated with alcoholic picric acid to give the picrate of *2-phenyl-4-chloropyridine* (XVI; R = H), m.p. 177–182° C. The yield was 4.5 gm. (43%). Crystallization from methanol gave yellow prisms, m.p. 180–182° C. Calc. for $C_{17}H_{11}O_7N_4Cl$: N, 13.39%. Found: N, 13.73%.

The solvent was removed from the filtrate of the picrate, and the resultant oil treated with 30 cc. of 5% sodium hydroxide solution to remove excess picric acid. It was then taken up in ether and distilled to give 1.7 gm. (35%) of 2-phenyl-6-chloropyridine (XV; R = H), b.p. 124–125° C. (0.1 mm.), m.p. 31° C. Leben (17) reports a m.p. of 34° C.

When 4.2 gm. (0.025 mole) of 2-phenylpyridine-N-oxide was boiled with

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30.7 gm. (0.20 mole) of phosphorus oxychloride for 30 min., the yield of 2-phenyl-4-chloropyridine picrate was 3.0 gm. (29%), and of 2-phenyl-6-chloropyridine 1.4 gm. (29%).

*2-p-Anisylpyridine-N-oxide (XIV; R = $OCH_3$)*

This compound was prepared in essentially the same manner as 2-phenylpyridine-N-oxide from the reaction of 30.5 gm. (0.165 mole) of 2-*p*-anisylpyridine with 0.275 mole of perbenzoic acid. A first crop of 17.0 gm. (51.5% yield) of the amine oxide, m.p. 132–136° C., and a second crop of 8.0 gm. (24%), m.p. 127–136° C., were obtained. Recrystallization from benzene gave white needles, m.p. 135–136° C. Calc. for $C_{12}H_{11}O_2N$: N, 6.97%. Found: N, 7.16 and 7.30%.

The *picrate* crystallized from methanol in long silky yellow needles, m.p. 136–138° C. Calc. for $C_{18}H_{14}O_9N_4$: N, 13.02%. Found: N, 13.10 and 13.31%.

*Chlorination of 2-p-Anisylpyridine-N-oxide*

Phosphorus oxychloride (24.5 gm.; 0.16 mole) was added to 4.0 gm. (0.02 mole) of 2-*p*-anisylpyridine-N-oxide. After standing for 10 min. at room temperature, the mixture was refluxed for 30 min. It was hydrolyzed with 200 gm. of cracked ice and made barely acid to Congo red. A pale tan solid, assumed to be 2-*p*-anisyl-6-chloropyridine (XV; R = $OCH_3$), melting at 87–100° C. was filtered off. It crystallized from methanol in pale tan flakes, m.p. 99–100° C. weighing 1.5 gm. (30% yield). A second crop (0.2 gm.; 4% yield) melted at 92–97° C. Calc. for $C_{12}H_{10}ONCl$: N, 6.38%. Found: N, 6.35%.

Both the aqueous and methanolic mother liquors of the solid, on being made strongly alkaline, became turbid. However, the compound which separated did not solidify on standing, and so was extracted with ether and treated with picric acid. A yellow solid, believed to be the *picrate of 2-p-anisyl-4-chloropyridine* (XVI; R = $OCH_3$) separated. It crystallized from methanol in tiny rods forming a feltlike mat, m.p. 167–168° C. The yield was 0.5 gm. (5%). Calc. for $C_{18}H_{13}O_8N_4Cl$; N, 12.48%. Found: N, 12.44%.

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## NOTE

### 4-BROMOVERATROLE*

By R. A. B. Bannard and G. Latremouille

4-Bromoveratrole has been prepared in one step from veratrole bromination with air-diluted bromine vapor in glacial acetic acid (2), with bromine in carbon tetrachloride (4), and with N-bromosuccinimide in carbon tetrachloride (1). The latter method appeared to be the most desirable since the mild brominating action of the bromoimide should eliminate or minimize two disadvantages of the other methods, namely, demethylation and/or dibromination of the aryl ether. However, Buu-Hoï's procedure (1) was not entirely satisfactory because more than a 100% excess of veratrole had been used. The process was thereby made wasteful of veratrole and an unnecessary complication in isolation of the product introduced. The method was modified (*a*) by using equimolar quantities of reactants, and (*b*) by decreasing the volume of solvent relative to bromoimide. These modifications have increased the yield of 4-bromoveratrole to 83-86% of theoretical from 61% (1), as described in the experimental section. A small quantity of 4,5-dibromoveratrole (3) is formed as by-product.

*Experimental*

Sixty-nine gm. (0.50 mole) of veratrole (Eastman Kodak #274), 80 ml. of carbon tetrachloride (Merck Reagent), and 89 gm. (0.50 mole) of N-bromosuccinimide (Matheson #6123) were placed in a 500 ml. round-bottomed flask equipped with a reflux condenser protected by a calcium chloride drying-tube. The mixture was heated under reflux on the steam-bath for six hours and allowed to stand overnight at room temperature. The succinimide was separated from the deep red solution by suction filtration, using a medium porosity fritted-glass funnel, and washed with three 20 ml. portions of carbon tetrachloride. The carbon tetrachloride was removed from the combined filtrate and washings by distillation at atmospheric pressure. The residue was fractionated *in vacuo* yielding 93 gm. (86%) of 4-bromoveratrole as a colorless to pale yellow oil, b.p. 117-119.5° C. at 5 mm. (256.5° C. at 761 mm.); $n_D^{20}$ 1.5722-1.5730. After distillation was complete and the system had cooled, a small quantity of pale yellow material crystallized on the upper walls of the still pot. A portion of this substance, on recrystallization from 95% ethanol, was identified as 4,5-dibromoveratrole by m.p. 88-90° C. alone and m.p. 90-92° C. in admixture with an authentic specimen of m.p. 91-92° C. (3).

Refractionation of a portion of the 4-bromoveratrole gave a colorless product, b.p. 116.5-117.5° C. at 4.5-5 mm.; $n_D^{20}$ 1.5730; $d_4^{20}$ 1.5068, 1.5069.

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# THE PREPARATION OF D-α-FRUCTOHEPTOSE[1]

BY R. J. WOODS[2] AND A. C. NEISH

ABSTRACT

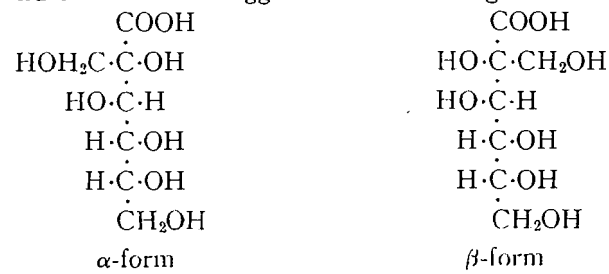
Crystalline D-α-fructoheptose (2-C-hydroxymethyl-D-glucose) has been obtained by the sodium amalgam reduction of D-α-fructoheptonic lactone. Some crystalline derivatives of the sugar are described and also the crystalline heptacetate of D-fructoheptitol (1,1-C-di(hydroxymethyl)-D-arabitol).

## INTRODUCTION

During the course of his work upon the configuration of the sugars, Kiliani (5) condensed fructose with hydrogen cyanide and isolated a crystalline cyanhydrin which he hydrolyzed to a heptonic acid and subsequently reduced to 2-methyl hexanoic acid, thus establishing the position of the carbonyl group in fructose.

The crystalline cyanhydrin and the heptonic acid derived from it were made the subject of further research by Kiliani and Düll (2, 6, 7, 8, 9), the acid being characterized by the formation of several salts (see also 11) and a crystalline lactone, m.p. 126–130° C. Later, the acids obtained by hydrolysis of the crystalline fructose cyanhydrin and by hydrolysis of the whole of the fructose – hydrogen cyanide addition product were examined by Schmidt and Weber-Molster (12). The crystalline cyanhydrin was found to yield only the heptonic acid obtained by Kiliani while the hydrolyzate of the total addition product gave a mixture of acids, which were separated, one as the brucine salt and the other as the phenylhydrazide. The former gave a lactone identical with that obtained by Kiliani while the latter gave the epimeric acid which could be dehydrated to a crystalline anhydro lactone. The two acids were designated D-α- and D-β-fructoheptonic acid respectively, following the order of their isolation.

By comparison of the rotations shown by the free acids, the sodium salts, the amides, and the phenylhydrazides, Schmidt and Weber-Molster showed that the *alpha* and *beta* acids behaved similarly to gluconic and mannonic acids respectively and on this basis suggested the following structures:




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If these structures are correct the sugar obtained by reduction of the alpha lactone is 2-C-hydroxymethyl-D-glucose; the trivial name D-α-fructoheptose is used in this paper.

Fischer (3) noted in an early paper on the sodium amalgam reduction of sugar lactones that fructoheptonic lactone could be reduced to a sugar by this method, though he isolated no pure products. He stated that further work was in progress but we have not been able to find any subsequent references to the preparation of D-α-fructoheptose. We have repeated the reduction of D-α-fructoheptonic lactone with sodium amalgam to give solutions containing D-α-fructoheptose in up to 65% of the theoretical yield.

In the first instance the sugar was obtained as a syrup or amorphous, very deliquescent, solid from which it was very difficult to isolate any pure derivative. However, 2: 5-dichlorophenylhydrazine was found to give a hydrazone that formed readily and was easily purified. Regeneration from this derivative led to a sugar syrup that finally crystallized, subsequent reductions yielding the crystalline sugar directly on seeding. The crystalline sugar was stable and nondeliquescent. Neither the α-fructoheptonic lactone nor the sugar itself showed any evidence of anhydride formation as described for the β-lactone. Assuming aqueous D-α-fructoheptose solutions to mutarotate similarly to the straight chain sugars, the change in rotation to give a less dextrorotatory solution indicated that the crystalline sugar isolated was an α-D-anomer (4). No evidence concerning the ring size was obtained.

The sugar was catalytically hydrogenated to give the corresponding sugar alcohol, isolated as the crystalline heptacetate. The free alcohol has not yet crystallized.

## EXPERIMENTAL

Melting points were determined on a heating stage microscope and, unless otherwise stated, are corrected.

### *Fructose Cyanhydrin*

The method of Zervas and Sessler (16) was followed. It proceeded smoothly once seeds of the cyanhydrin had been obtained to promote crystallization of the condensation product. The fructose cyanhydrin was washed with cold methanol and dried in a vacuum desiccator for 18–20 hr. over calcium chloride before being hydrolyzed. It was obtained as a white crystalline solid, m.p. 108–109° C. (uncorr.), in yields of 50 to 65%; usually one mole was prepared at a time.

### D-α-*Fructoheptonic Lactone*

The cyanhydrin was hydrolyzed by hydrochloric acid and the product worked up essentially as described previously (8, 12). Removal of the hydrogen chloride was greatly expedited by use of an evaporator similar to that described by Bartholomew (1), arranged to recycle automatically. Remaining inorganic materials were removed as previously described (12) and final traces of cations by passage through a column of ion-exchange resin (Amberlite IR-120). Yields of heptonic acid of 85–90% (by titration) were obtained with

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a hydrolysis period of two and one-half hours and yields of 68–78% with a hydrolysis period of four hours. A purified acid was obtained, by regeneration from the once-recrystallized brucine salt, and lactonized by heating to 130° C. for five hours. The syrup crystallized on cooling to give the lactone, m.p. 118–119° C. (uncorr.) in 57% over-all yield (two and one-half hours hydrolysis). One crystallization from ethanol raised the melting point to 129.5° C., unchanged by further crystallization.

*Reduction* D-α-*Fructoheptonic Lactone*

A solution of sodium hydrogen oxalate was prepared by dissolving oxalic acid dihydrate (126 gm.) in warm water (1100 ml.) and adding sodium hydroxide solution (100 ml.; 10 *N*). D-α-Fructoheptonic lactone (180 gm.; m.p. 118–119° C.) was added and the solution cooled to 5° C. Sodium amalgam (2800 gm.; 3%) was stirred into the solution in four equal portions, keeping the temperature below 15° C. and keeping the pH below 4.0 by the addition of powdered oxalic acid. The mixture was then stirred for 45 min. and filtered while still cold. The solid was washed with a little cold water and the filtrate treated with an excess of calcium acetate, the precipitated calcium oxalate being filtered off and the filtrate passed through a column of cation exchange resin (Amberlite IR-120). The amount of aldose present in the solution, estimated by the reduction of hypoiodite, corresponded to a 65% yield of the required sugar. The solution was concentrated under reduced pressure.

The crude reduction mixture could not be crystallized and did not form any derivatives readily. Phenylhydrazine and *as*-diphenylhydrazine did not give solid hydrazones although a crystalline derivative was later obtained with 2: 5-dichlorophenylhydrazine.

Reduction of D-α-fructoheptonic lactone with sodium borohydride by a method similar to that described by Wolfrom and Wood (14), but in the presence of a sodium hydrogen oxalate buffer, gave a solution containing 49% of the theoretical quantity of aldose, estimated by hypoiodite. Since this reagent appeared to offer no advantage over the use of sodium amalgam the reduction employing it was not studied further.

D-α-*Fructoheptose 2,5-Dichlorophenylhydrazone*

The syrupy D-α-fructoheptose obtained above was dissolved in methanol (750 ml.) (cf. Mandl and Neuberg (10)) and treated with an excess (15%) of 2,5-dichlorophenylhydrazine. The crude derivative was washed with ethanol and water and crystallized once from aqueous pyridine (201 gm., m.p. 188° C., uncorr.), further crystallization gave the pure *hydrazone* as white plates, m.p. 190° C. Found: C, 42.45; H, 5.05; Cl, 19.25. $C_{13}H_{18}O_6N_2Cl_2$ requires: C, 42.3; H, 4.9; Cl, 19.2%, $[\alpha]_D^{22.2°}$ 7.9° (*c*, 3.6 in pyridine) changing to $[\alpha]_D^{22.3°}$ 5.05°.

D-α-*Fructoheptose*

A solution of the sugar 2,5-dichlorophenylhydrazone (178 gm.; obs. m.p. 188°) in ethanol (1500 ml.) and water (2500 ml.) was refluxed with benzaldehyde (500 ml.) and benzoic acid (50 gm.) for 18 hr. (cf. Sowden and Fischer (13)). After cooling, the aqueous layer was separated and thoroughly washed

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with chloroform and ether and evaporated to give the sugar as a pale yellow syrup (79 gm.), which crystallized from an ethanolic solution after several weeks as needles (70.5 gm.), m.p. 171.5° C. A sample was recrystallized by dissolving it in a minimum of water and adding glacial acetic acid or ethanol (about five volumes). The pure *sugar* separated slowly as sweet white needles, very soluble in water, m.p. 172.5–173.5° C. Found: C, 40.0; H, 6.7. $C_7H_{14}O_7$ requires: C, 40.0; H, 6.7%, $[\alpha]_D^{18.2°}$ 51.9° (*c*, 5 in water) mutarotating to $[\alpha]_D^{20.5°}$ 42.95°.

In later experiments, in which seed was available, the sugar could be crystallized directly from the syrupy reduction product by diluting with several volumes of glacial acetic acid and seeding. About 80% of the sugar present crystallized directly and the greater part of the remainder could be recovered by treating the mother liquors with 2,5-dichlorophenylhydrazine.

An attempt to regenerate the sugar by treating the hydrazone above with acetaldehyde, as suggested by Mandl and Neuberg (10), was unsuccessful and neither the sugar nor the hydrazone could be recovered.

*Other Hydrazones of* D-α-*Fructoheptose*

The pure sugar formed a *phenylhydrazone*, obtained as unstable, transparent plates from methanol, m.p. 144.5°. Found: C, 52.2; H, 6.75; N, 9.4. $C_{13}H_{20}O_6N_2$ requires: C, 52.0; H, 6.7; N, 9.35%, $[\alpha]_D^{22.2°}$ 9.81° (*c*, 1.6 in ethanol) changing to $[\alpha]_D^{22.2°}$ 1.46° after 40 hr. No osazone could be detected under the usual conditions of osazone formation. The *p-nitrophenylhydrazone* crystallized from water as golden plates and needles, discoloring slightly in light, m.p. 178.5° C. Found: C, 45.3; H, 5.5; N, 12.10. $C_{13}H_{19}O_8N_3$ requires: C, 45.2; H, 5.55; N, 12.15%, $[\alpha]_D^{22.2°}$ −26.3° ± 0.8° (*c*, 0.5 in water) changing to $[\alpha]_D^{21.5}$ −21.6° ± 0.4° after 95 hr. The melting point fell to 150° when the derivative was stored in the dark for six weeks. Though the phenylhydrazone and *p*-nitrophenylhydrazone decomposed on keeping the 2,5-dichlorophenylhydrazone appeared to be quite stable.

D-*Fructoheptitol Heptacetate*

Crystalline D-α-fructoheptose (20 gm.) in water (60 ml.) was shaken in an atmosphere of hydrogen in the presence of a Raney nickel catalyst (1–2 gm.) until the uptake of hydrogen ceased (four hours at 100° C. and 2500 lb./sq. in.). The catalyst was filtered off and the filtrate concentrated to give a pale yellow syrup (21.7 gm.) containing less than 5% aldose (estimated by hypoiodite).

A portion of the syrupy alcohol (13.3 gm.) was refluxed with anhydrous sodium acetate (12 gm.) and acetic anhydride (150 ml.) for three and one-half hours. The gummy acetate, isolated by chloroform extraction, was dissolved in benzene (30 ml.) and filtered through a column of activated aluminum oxide (400 gm.; Merck, washed with 10% acetic acid and water and dried at 180°) and eluted with the same solvent. Fractions (50 ml.) were collected and evaporated, those constituting the main band solidified and were crystallized from ethanol to give D-*fructoheptitol heptacetate* as white needles (24.8 gm.) m.p. 70.5° C. Found: C, 49.85; H, 6.05; $CH_3.CO$, 59.25. $C_{21}H_{30}O_{14}$ requires: C, 49.8; H, 5.95; $CH_3.CO$, 59.5%, $[\alpha]_D^{24.2}$ 31.6° (*c*, 7 in chloroform). The chro-

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matographic purification could be omitted in later preparations in which the crude acetate solidified on seeding.

Acetylation in pyridine solution gave a mixture of products from which the heptacetate could be isolated by chromatography, though in poorer yield than described above.

D-*Fructoheptitol* [*1,1-C-di(hydroxymethyl)*-D-*arabitol*]

The alcohol was regenerated from the heptacetate (15.0 gm.) by solution in anhydrous methanol (70 ml.) containing a little sodium (0.05 gm.) (15). The solution was evaporated under reduced pressure after standing at room temperature (23° C.) overnight and yielded a colorless syrup (7.23 gm.), $[\alpha]_D^{21.8}$ −5.69° (*c*, 11 in water).

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# THE SYNTHESIS OF SYRINGALDEHYDE FROM VANILLIN[1]

By J. M. Pepper and J. A. MacDonald

ABSTRACT

Syringaldehyde has been synthesized in high yields from vanillin. The process consists of the iodination of vanillin, followed by the interaction of the resultant 5-iodovanillin with sodium methoxide in anhydrous methanol at temperatures of 130 ± 4° C. for one hour in the presence of a copper catalyst. Along with the syringaldehyde, small amounts of unchanged 5-iodovanillin and vanillin were always found in the reaction mixture. Analysis of the final product was made by an initial separation of the components by downward paper chromatography using a mixture of petroleum ether (b.p. 100–120° C.), di-*n*-butyl ether, and water (10: 1: 1) as the developing agent for a period of 10 hr. The separated compounds were extracted from the paper and their concentrations in alcoholic alkaline solutions determined spectrophotometrically.

Under conditions by which 5-iodovanillin was converted to syringaldehyde in better than a 95% yield, 5-bromovanillin gave only a 61% yield and 5-chlorovanillin gave no detectable amounts of syringaldehyde.

In connection with an investigation into the fundamental nature of isolated lignins and their degradation products from angiosperms (poplar wood and cereal straws), it was important to have available many reference compounds of known structure. For such work the compounds required are, for the most part, of two types: those containing the guaiacyl (4-hydroxy-3-methoxyphenyl) nucleus and those containing the syringyl (4-hydroxy-3,5-dimethoxyphenyl) nucleus. Many derivatives having the former structure have been synthesized from vanillin (4-hydroxy-3-methoxybenzaldehyde) which is readily available as an oxidation product of gymnosperm lignin or its derivatives. Much less work has been reported on the chemistry of compounds having the syringyl nucleus. A logical starting material for their syntheses would be the corresponding aldehyde, syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde). Even though the oxidation of lignified angiosperm material gives rise to a mixture of both vanillin and syringaldehyde, the separation and recovery of each is not readily accomplished, so another source of this latter aldehyde is preferred.

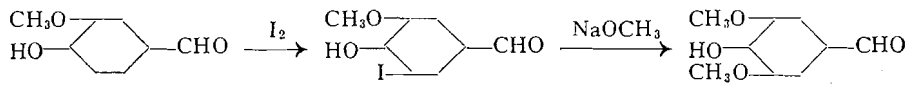
Many syntheses, as outlined by Pearl (9), have been reported, and a laboratory procedure has appeared in Organic Syntheses (1). The main starting material in these procedures is either 1,3-dimethylpyrogallol or gallic acid, the conversion of either of which to the aldehyde involves many separate steps and therefore low over-all yields. A recent publication (10) describes a new synthesis involving the conversion of vanillin to 5-hydroxyvanillin, complete methylation followed by selective demethylation of the 4-methoxy group to give syringaldehyde in good yield. These authors also report that their attempts at the conversion of 5-halovanillin to syringaldehyde were universally unsuccessful. Some time ago an investigation was begun in these laboratories to study this same synthesis of syringaldehyde from vanillin by the introduction

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*Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. This paper constitutes part of a thesis submitted by J. A. MacDonald in partial fulfillment of the requirements for the degree of Master of Science in Chemistry and was presented at the 34th Annual Conference of the Chemical Institute of Canada, Winnipeg, June 1951.*

of a methoxy grouping. One value of such a method would be the possibility of thereby converting a mixture of the aldehydes obtained by the oxidation of hardwoods into pure syringaldehyde should a valuable use be found for this chemical.

In a previous communication (8) it was reported that preliminary experiments on the two-step synthesis: vanillin → 5-bromovanillin → syringaldehyde, appeared promising. By treatment of the 5-bromovanillin with sodium methoxide in anhydrous methanol in the presence of copper turnings at temperatures of 160–200° C., small yields of syringaldehyde were obtained along with other reaction products. Because of the well known reactivity of halogen substituted aromatic compounds increasing from chloro- through bromo- to iodo-derivatives in nucleophilic substitution reactions (3), it was thought that the use of 5-iodovanillin in a similar synthesis would be more suitable. Excellent yields of syringaldehyde (II) have now been obtained from vanillin (I) by this method according to the following equations:




I II

Preliminary runs were carried out in which 5-iodovanillin, anhydrous methanol, sodium methoxide, and a copper catalyst were heated together in a rocking autoclave at temperatures ranging from 72° C. to 180° C. and for reaction times of from one to eight hours. After dilution of the orange to dark red reaction mixture with water and filtration to remove the copper, the products were extracted into chloroform and then treated as follows. First they were separated into bicarbonate-soluble and bicarbonate-insoluble fractions, and then each of these was subdivided into sodium bisulphite-soluble and sodium bisulphite-insoluble portions. It was often noticed that complete acidification of the original alkaline reaction mixture caused any unchanged 5-iodovanillin to precipitate. This insolubility of 5-iodovanillin in acidic aqueous methanol permitted its ready separation from the other components of the reaction mixture. Support was found in these experiments for an observation reported earlier (11) that, from "neutral" lignin fractions, compounds having a syringyl nucleus were isolated. In this case the incomplete liberation of phenolic compounds by the exhaustive carbonation of a strongly alkaline solution was borne out by finding phenolic aldehydic products in both the bicarbonate-soluble and bicarbonate-insoluble portions.

The aqueous residues from the various runs were analyzed for iodide ion by a standard method (12). These results along with the amount of unchanged 5-iodovanillin recovered are given in Table I, where iodide ion is expressed as the corresponding weight of 5-iodovanillin. The values reported for the iodide ion determinations are averages of duplicate analyses which agreed within one per cent and are minimum values since, prior to the analyses, the aqueous solutions had been acidified and extracted several times with chloroform. It

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TABLE I

PRELIMINARY EXPERIMENTS USING 5-IODOVANILLIN[a]

| Run No. | Average temp., ° C. | Reaction time, hr. | Nonaldehydic fraction[b], gm. | Syringaldehyde containing fraction[c], gm. | Percentage of original 5-iodovanillin | | |
|---|---|---|---|---|---|---|---|
| | | | | | Recovered unchanged | Converted to iodide | Total accounted for |
| 1 | 179 | 1.0 | 8.8 | 2.0 | Nil | — | — |
| 2 | 154 | 5.0 | 7.1 | 0.8 | Nil | 96.0 | 96.0 |
| 3[d] | 72 | 7.5 | 0.3 | 0.6 | 82.4 | 7.8 | 90.2 |
| 4 | 137 | 1.25 | 3.9 | 3.9 | Nil | 93.4 | 93.4 |
| 5 | 110 | 1.0 | — | 4.8 | 36.9 | 48.3 | 85.2 |
| 6 | 123 | 1.2 | 0.3 | 6.2 | 19.2 | 77.6 | 96.8 |
| 7 | 118 | 1.0 | 1.0 | 4.9 | 25.4 | 68.0 | 93.4 |
| 8 | 118 | 6.25 | — | 7.2 | Nil | 92.8 | 92.8 |
| 9 | 123 | 8.5 | 3.0 | 6.0 | Nil | 93.4 | 93.4 |
| 10 | 116 | 8.0 | 0.4 | 4.3 | 13.0 | 81.0 | 94.0 |

[a] *For each run, 5-iodovanillin (13.0 gm.), anhydrous methanol (250 ml.), sodium (10.0 gm.) (with the exception of Run 1 in which 5.0 gm. were used), and copper catalyst A (12.8 gm.) were reacted.*

[b] *Bicarbonate-insoluble, sodium bisulphite-insoluble.*

[c] *Combined bicarbonate-insoluble, sodium bisulphite-soluble, and bicarbonate-soluble fractions.*

[d] *Run carried out at atmospheric pressure under reflux.*

seems reasonable to conclude that, under the conditions employed, all or nearly all of the 5-iodovanillin which reacts loses iodine.

Varying small amounts of syringaldehyde were isolated by crystallization and sublimation from many of the fractions obtained in these preliminary experiments, but the amounts given in Table I represent only the weight of the crude products shown to contain syringaldehyde. It appears that, with such a reaction mixture, increasing temperatures lead to an increase in the syringaldehyde-containing fractions until a temperature of 135° C. is reached and that above this temperature the yield of the nonaldehydic fraction becomes more and more appreciable. The chemical nature of this derivative, referred to as the "Unknown" in Fig. 1, has not as yet been determined but qualitative tests show that it is phenolic and contains no iodine.

In an analysis of the reaction product of Run 10 by a chromatographic method, an appreciable quantity of vanillin (28%, based on 5-iodovanillin) along with syringaldehyde was detected. The presence of vanillin, characterized by the comparison of its ultraviolet absorption spectrum and chromatographic behavior with an authentic sample, is not surprising. The reductive cleavage of aryl halides is not uncommon under similar alkaline conditions (3, 10).

The lack of a single fraction containing all of the syringaldehyde, and the detection of vanillin in the reaction product, indicated that a new method of determining yields was required. A method of analysis similar to that used by Stone and Blundell (13) proved satisfactory. The use of a 10: 1: 1 mixture of petroleum ether (b.p. 100–120° C.), di-*n*-butyl ether, and water as the developing solvent gave an adequate separation of syringaldehyde, vanillin, 5-iodovanillin, and the unidentified reaction product on a paper strip (Fig. 1).

The positions of the various phenolic compounds were determined by

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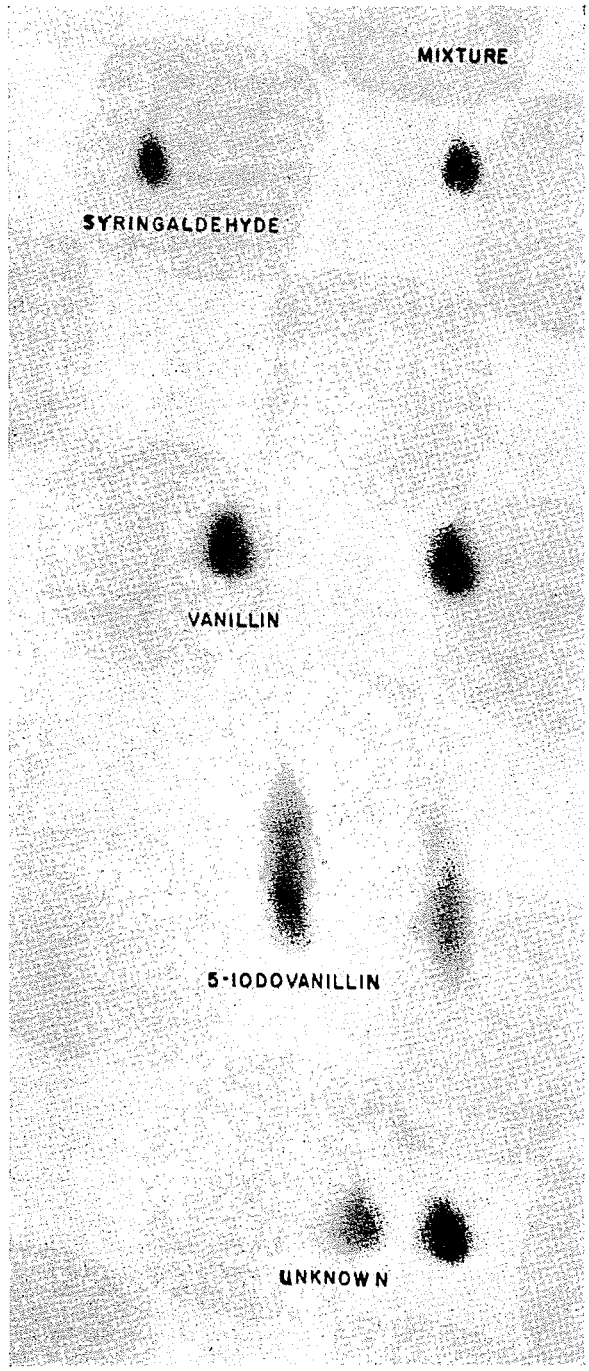



FIG. 1. Chromatographic separation of syringaldehyde, vanillin, 5-iodovanillin, and an unidentified phenolic reaction product. Chromatogram developed for 10 hr. using petroleum ether (b.p. 100–120° C.), butyl ether, and water (10.1.1).

spraying test strips of the chromatogram with a ferric chloride – potassium ferricyanide mixture (2). The separated bands were then extracted with ethanol and the concentrations of the extracts determined spectrophotometrically. Such analyses of known mixtures showed that an average of 7.6% of the syringaldehyde, 18.0% of the vanillin, and a negligible amount of 5-iodovanillin were lost during the analysis. The results of subsequent analyses were corrected for these losses.

A second series of experiments was then carried out and the products analyzed by this preferred method. The results are given in Table II. The results of Runs 11 and 12 indicate that a copper catalyst is necessary in this reaction. It was thought that the extreme variations in yields of products of Runs 11, 13, 14, and 15 were not due primarily to the slight temperature differences recorded but rather to differences in the catalyst, a fresh batch of which had

TABLE II

CONVERSION OF 5-IODOVANILLIN TO SYRINGALDEHYDE[a]

| Run No. | Copper catalyst[b] | Average temp., °C.[c] | Analysis of reaction mixture | | | Total yield, % |
|---|---|---|---|---|---|---|
| | | | Component[d] | Duplicate analyses, gm. | Mean yield, % | |
| 11 | A | 122 | SA | 5.39 5.38 | 63.2 | |
| | | | V | 1.30 1.26 | 18.0 | |
| | | | 5IV | 2.35 2.40 | 18.3 | 99.5 |
| 12 | — | 122 | SA | 0.52 0.52 | 6.1 | |
| | | | 5IV | 12.7 12.3 | 96.3 | 102.4 |
| 13 | A | 128 | SA | 7.50 7.32 | 87.0 | |
| | | | V | 0.28 0.25 | 3.7 | |
| | | | 5IV | 1.61 1.64 | 12.5 | 103.2 |
| 14 | A | 133 | SA | 6.38 6.59 | 76.2 | |
| | | | V | 0.88 0.92 | 12.7 | |
| | | | 5IV | 1.39 1.30 | 10.4 | 99.3 |
| 15 | A | 128 | SA | 7.10 7.02 | 83.0 | |
| | | | V | 0.92 0.98 | 13.4 | |
| | | | 5IV | 0.18 0.12 | 1.5 | 97.9 |
| 16 | B | 126 | SA | 8.42 8.44 | 98.9 | |
| | | | V | 0.14 0.18 | 2.2 | |
| | | | 5IV | 0.31 0.33 | 2.5 | 103.5 |
| 17 | B | 129 | SA | 8.41 8.26 | 97.9 | |
| | | | V | 0.20 0.20 | 2.8 | |
| | | | 5IV | 0.25 0.25 | 1.9 | 102.6 |

[a] *For each run 5-iodovanillin (13.0 gm.), sodium (10 gm.), anhydrous methanol (250 ml.), and copper catalyst (12.8 gm.*) were used; reaction time one hour at elevated temperature.*

[b] *Catalyst A prepared by precipitating copper from copper sulphate solution with zinc; catalyst B was British Drug Houses' precipitated copper powder, reagent grade.*

[c] *Maximum temperature variation, ±4° C.*

[d] *Abbreviations: SA for syringaldehyde, V for vanillin, and 5IV for 5-iodovanillin.*

* *Some later work has indicated that under similar conditions this amount of copper may be reduced to 2.0 gm. without serious decrease in percentage conversions and also that yields of around 50% of syringaldehyde may be obtained if 0.5 gm. iodine are used in place of the metallic copper catalyst.*

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been prepared for each run. Using catalyst portions taken from the same source (Catalyst B), reproducible results were obtained (Runs 16 and 17). Furthermore, the high yields of syringaldehyde obtained indicated that the British Drug Houses precipitated copper powder was the preferred catalyst for this reaction. Subsequently, many runs similar to Runs 16 have been made and pure syringaldehyde readily recovered and recrystallized as light yellow needles from Skellysolve "C", m.p. 109–110° C. in yields of 85% or better.

The possibility of converting either of the cheaper 5-chloro- or 5-bromovanillin to syringaldehyde under similar conditions was investigated. Both these 5-halovanillins moved further than vanillin or syringaldehyde under the previously used chromatographic conditions and hence did not interfere with the analyses. Using 5-bromovanillin, runs carried out at 130° C. and 140° C. gave rise in each case to products representing a 61% conversion to syringaldehyde. Under similar conditions using 5-chlorovanillin at any of 130° C., 140° C., or 175° C., no syringaldehyde was detected. This decreased conversion of the 5-halovanillins to syringaldehyde from 5-iodo- through 5-bromo- to 5-chloro- is in agreement with the known reactivities of halogen substituted aromatic compounds.

This method for the preparation of large amounts of syringaldehyde has since been used very successfully in our laboratories.

## EXPERIMENTAL*

*Reagents.*—The 5-halovanillins were prepared according to the following previously reported procedures: 5-iodovanillin (m.p. 178.5–179.5° C.) by the method of Erdtman (6)**; 5-bromovanillin (m.p. 164° C.) by McIvor and Pepper (8), and 5-chlorovanillin (m.p. 160.5–162° C.) according to Hopkins and Chisholm (7).

*Copper Catalyst A.*—The early experiments were carried out using a copper preparation prepared by the addition of zinc to copper sulphate solution according to the method of Brewster and Groening (4). The catalyst was prepared immediately prior to each run and washed with 10 portions of absolute methanol before use.

*Copper Catalyst B.*—British Drug Houses' precipitated copper powder, Reagent Grade, was used in the later experiments.

*Apparatus.*—All the reactions were carried out in a stainless steel liner, capacity 1080 ml., of an Aminco high pressure hydrogenator, Model No. 406-01 DA. This apparatus served as a rocking autoclave. A Brown Indicating Controller (0–600° C.) coupled with an Aminco variable voltage transformer inserted into the automatic heating circuit permitted temperature control to within ±4° C. A Beckmann Model DU spectrophotometer was used to obtain the ultraviolet absorption data.

### *Procedure Employed in Runs 11–17*

These runs (Table II) were maintained at the stated reaction temperatures for one hour, after which the bomb was cooled slowly. In each case the product

* *All melting points are corrected.*
** *It appears that the 0.2 N sodium hydroxide reported should read 2.0 N sodium hydroxide.*

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was diluted with water (500 ml.) and filtered to remove the copper. The filtrate, which varied in color from yellow to orange red, was analyzed by the chromatographic–spectrophotometric method.

The chromatography was carried out according to the method of Stone and Blundell (13). Strips of Whatman No. 1 filter paper, 22 in. × 6 in., were spotted along a base line with the alkaline reaction mixture. The volumes of the drops were measured by a 1 ml. capacity Emil Greiner ultramicroburette which was graduated in 0.001 ml. divisions. After acidification of the material on the paper using acetic acid vapor, the development was conducted in a descending manner in an apparatus similar to that described by Consden *et al.* (5). Water was placed in the bottom of a tall glass cylinder and the organic phase from a 10: 1: 1 mixture of petroleum ether (b.p. 100–120° C.), di-*n*-butyl ether, and water was placed in the small trough near the top and also in a small beaker placed on the bottom of the tightly closed vessel which was allowed to stand for one-half hour prior to putting the paper in place. After development for 10 hr., the paper strips were removed, and the test strip cut off and sprayed with a 1% solution of ferric chloride followed by a 1% solution of potassium ferricyanide, which indicated, by pronounced blue spots, the position of the phenolic compounds (2). The main chromatogram was then cut into horizontal strips, each of which contained only one compound which was separately extracted with ethanol in Soxhlet extractors for two hours. Each extract was transferred to a 50 ml. volumetric flask containing 4 ml. of 0.2 *N* potassium hydroxide in ethanol, and made up to 50 ml. with ethanol.

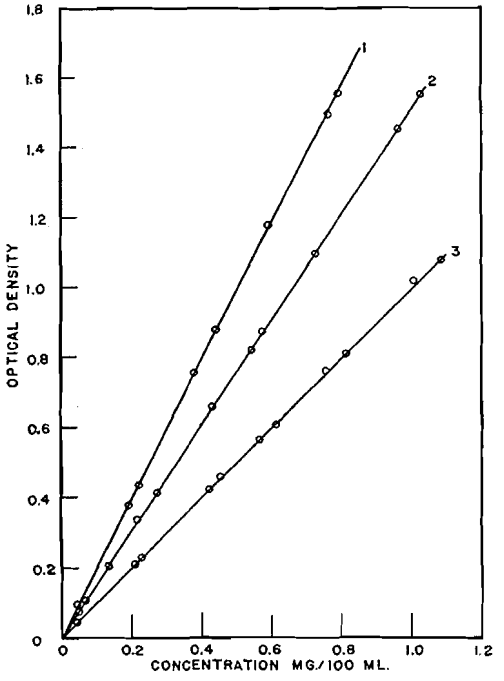



FIG. 2. Concentration vs. optical density curves in alkali-ethanol for (1) vanillin, (2) syringaldehyde, and (3) 5-iodovanillin.

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The concentration of the extract was then determined by the measurement of its optical density and by making use of previously determined optical density versus concentration curves (Fig. 2). The wave lengths used were those determined by an examination of the ultraviolet absorption spectra of the compounds in alcoholic potassium hydroxide and were 368, 352, and 356 mμ for syringaldehyde, vanillin, and 5-iodovanillin, respectively.

*Syringaldehyde.*—Run 16 serves to illustrate a typical preparation of syringaldehyde by this method. Sodium (10.0 gm.) was dissolved in anhydrous methanol (250 ml.). This solution together with 5-iodovanillin (13.0 gm.) and British Drug Houses' precipitated copper powder catalyst (12.8 gm.) was heated in the rocking autoclave at 124–128° C. for one hour. After cooling, the reaction product was diluted with water (500 ml.), filtered to remove the copper, and acidified with hydrochloric acid. A small amount of unchanged 5-iodovanillin precipitated and was removed by filtration. The filtrate was extracted with chloroform (5 × 200 ml.) and the chloroform extract back extracted first with a few milliliters of sodium thiosulphate, to remove any free iodine, and then with water (2 × 10 ml.). After drying over anhydrous sodium sulphate the chloroform solution was concentrated to a small volume by distillation. The residue was crystallized from Skellysolve "C", yielding light yellow needles (7.28 gm.) (85.5%), m.p. 109–110° C. A mixed melting point with authentic syringaldehyde prepared according to Pearl (9) showed no depression. A similarly obtained product, recrystallized several times from Skellysolve "C" and twice from water, melted at 109.8–110.2° C. Calc. for $C_9H_{10}O_4$: C, 59.32; H, 5.53%. Found*: C, 59.33, 59.20; H, 5.59, 5.55%.

## ACKNOWLEDGMENTS

The authors wish to thank the Saskatchewan Research Council for the award of two Graduate Research Fellowships to one of them (J.A.M.) and for other summer financial assistance. Grateful acknowledgment is made to the Howard Smith Chemicals Limited for their kind donation of the vanillin used in this research.

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* *Analyses by Dr. R. U. Lemieux, National Research Council Laboratory, Saskatoon, Sask.*

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# THE EFFECT OF RELATIVE HUMIDITY ON THE REACTION OF NINHYDRIN WITH AMINO ACIDS ON PAPER CHROMATOGRAMS[1]

By Eunice F. Wellington[2]

ABSTRACT

The effect of different relative humidities at 20° C. on the colored product of ninhydrin with amino acids on paper chromatograms has been investigated. It has been shown that there is only a very narrow range of humidity (35–40%) within which maximum color development for most amino acids can be expected (aspartic acid behaves anomalously), and that the color intensity falls off rapidly on both sides of this maximum.

## INTRODUCTION

Earlier workers (2) attempting to use paper chromatography as a quantitative tool for analysis of amino acids by the ninhydrin reaction found that there was considerable day-to-day variability in color yields. This variability was assumed to result from changing temperature and humidity, although no definite tests of this assumption were made.

Later, Thompson *et al.* (3) showed that a constant temperature was necessary for reproducible results. They also controlled the humidity by developing the color in special tanks containing an atmosphere of carbon dioxide and ethyl alcohol. However, they reported no experiments on the direct effect of relative humidity on the reaction of amino acids with ninhydrin.

Wellington (4) recently showed that reproducible results could be obtained by a simpler technique than that of Thompson *et al.* The technique required that the papers be allowed to stand for 30 hr. at 20 ± 1° C. and 40 ± 3% relative humidity after having been sprayed with ninhydrin. Since air-conditioning equipment is not available in most laboratories however, the effect of humidity on the color yield of the reaction of amino acids with ninhydrin has been evaluated more critically, and a simple apparatus affording the necessary degree of control has been developed.

## MATERIALS AND METHODS

Two-dimensional paper chromatograms of standard amounts of amino acids were carried through according to the method previously described (4), with the exception that different levels of relative humidity were tested during color development. The sprayed chromatograms were hung in separate cylinders, in each of which the atmosphere was held for 30 hr. at a constant relative humidity by means of a glycerine–water mixture in the bottom of the cylinder. Layering of the atmosphere above these mixtures was prevented by passing a rapid stream of compressed air into the cylinders through gas-washing bottles filled with corresponding glycerine–water mixtures. Thus, the air was kept at a constant humidity throughout each tank.

[1] *Manuscript received January 8, 1953.*
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The glycerine–water mixtures were prepared according to Carson's table (1). Since the table was prepared for glycerine–water mixtures at 25° C., and the present work was done at 20° C., the relative humidity actually obtained with each of these mixtures was measured during the tests with paired wet and dry thermocouples and a potentiometer.

## RESULTS AND DISCUSSION

The following amino acids were tested: cysteic acid, glutamic acid, aspartic acid, serine, glycine, threonine, alanine, valine, leucine, histidine, arginine, and lysine. All these except aspartic acid were affected in the manner illustrated by glutamic acid, serine, and lysine (Fig. 1) with maximum development

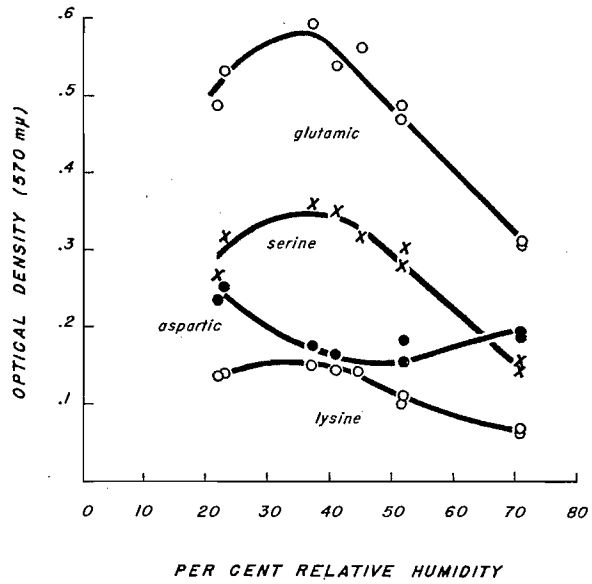



FIG. 1. The effect of relative humidity at 20° C. on the intensity of the colored product formed by the reaction of amino acids with ninhydrin on paper chromatograms (glutamic acid 26γ, serine 13γ, aspartic acid 23γ, and lysine 8γ).

of the colored ninhydrin product in the range of 35–40% relative humidity. Aspartic acid behaves in an anomalous manner, giving a minimum yield of the colored compound near the range where the other amino acids give a maximum.

It is obvious that variations in relative humidity between 40 and 70%, a condition common in laboratories not equipped with air-conditioning, are sufficient to explain the day to day variability in the ninhydrin reaction reported by earlier workers. This variability, together with the fact that earlier workers were using a spray containing 1/5 to 1/20 the concentration of ninhydrin required to give maximum color yields (4), made quantitative determinations of amino acids on paper chromatograms practically impossible.

These results confirm the necessity for the rigid control of humidity previously emphasized (4). In laboratories without air-conditioning, the chromatograms may be hung in a box through which compressed air is blown. The

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compressed air should be brought to at least 35% R.H. by bubbling it from a sintered glass filter through a 60-cm. column of glycerine–water mixture (specific gravity 1.234–1.235). Pure glycerine*–water mixture is particularly suitable since, in contrast with some of the salt and acid solutions tried for this purpose, it has no effect on the development of the ninhydrin color. Furthermore, if the compressed air is originally drier than 35% R.H., only small amounts of water have to be added to the mixture after each run to bring it back to correct proportions.

Fig. 2 shows the details of the apparatus used. The compressed air is passed

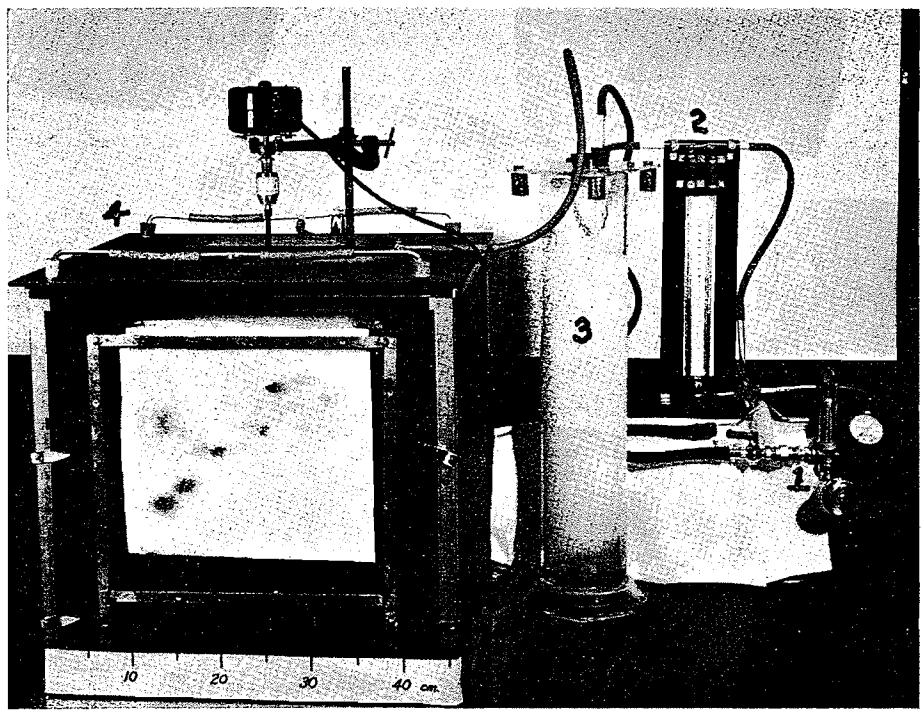



FIG. 2. Apparatus for the color development of amino acids on paper chromatograms under conditions of controlled relative humidity:
1—compressed air source with reducing valve;
2—flowmeter;
3—glycerine–water mixture to control relative humidity;
4—development box, black front cover removed to show interior.

through the first sintered-glass filter to remove any dirt particles and then it passes over an air flow gauge (flow regulated to approximately 8 liters per min.) through a second filter into the glycerine–water mixture. The conditioned air then passes into a 45 cm. square blackened glass box through inlets at each corner, and a 20 cm. fan underneath the papers keeps the air in the box well mixed. A light metal frame inside the box holds 10 papers, each 25.5 × 27.5 cm.

With such an apparatus, the relative humidity can easily be held within ±1%. Furthermore, undesirable fumes are more easily kept away from the

* *Some batches of reagent glycerine are not satisfactory for this purpose since they contain impurities that cause the mixture to foam badly.*

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papers. (As previously mentioned (4), exposure of the papers to even small amounts of hydrochloric acid fumes between the completion of the second chromatographic run and the elution of the colored ninhydrin product will cause anomalous results. Extremely small amounts of this vapor produce variations in color intensity, larger amounts cause the color to change from purple to pink, and still larger amounts prevent the development of the color entirely.)

Previous work (4) showed that it was essential that relative humidity be kept constant for repeatable quantitative results. The present results demonstrate for the first time that there is only a very narrow range of humidity within which maximum color development for most amino acids can be expected, and that the color intensity falls off rapidly on both sides of this maximum.

ACKNOWLEDGMENTS

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# THE BIOGENESIS OF ALKALOIDS

## VIII. THE ROLE OF METHIONINE IN THE FORMATION OF THE N-METHYL GROUPS OF THE ALKALOID HORDENINE[1]

By T. J. Matchett,[2] Léo Marion, and Sam Kirkwood[2]

ABSTRACT

L-Methionine labelled with $C^{14}$ in the methyl group was fed to sprouting barley and hordenine and choline were isolated from the plants. These two molecules proved to be labelled solely in their N-methyl groups. A comparison of formate and methionine methyl as precursors of hordenine methyl shows that the latter was more efficient. The fact that choline methyl does not serve as a precursor of hordenine methyl was confirmed and it was shown that bicarbonate is also ineffective as a methyl precursor. The significance of these findings to the over-all methylation process of the plant is discussed.

Recently the labile methyl metabolism of the higher plants has come under scrutiny in connection with investigations into the origin of the N- and O-methyl groups of the plant alkaloids. It has been shown that formate carbon serves as a precursor of the methyl groups of both hordenine and choline in the barley plant (8). Since choline did not serve as a methyl donor in the formation of hordenine methyl, it was assumed that these methyls did not arise through a process of transmethylation but were produced by a formylation reaction followed by a reduction. This reasoning was based on the fact that in animal metabolism there is a reversible transfer of methyl between choline and methionine. If this reaction occurred in the barley plant, both choline and methionine should have been labelled when labelled choline was fed. Since under these conditions the hordenine methyl was not labelled it was assumed that it did not arise as a result of a transmethylation reaction. Subsequently it was shown by Brown and Byerrum (2) that the methyl carbon of methionine and formate carbon serve as precursors of the N-methyl group of the alkaloid nicotine and that the former is the more efficient precursor. Brown and Byerrum postulate that methionine methyl is transmethylated to nicotine and that formate serves as a precursor of methionine methyl. Dubeck and Kirkwood (3) have shown that methionine methyl serves as a precursor of both the N- and O-methyl groups of the alkaloid ricinine which is synthesized by germinating beans of *Ricinus communis*. In this case both formate and choline methyl failed to serve as precursors of these methyl groups. All of this evidence focuses attention on the central role of methionine in processes involving labile methyl. In view of this we have investigated the role of methionine in the origin of hordenine methyl. We have also reinvestigated the failure of choline to serve as a precursor of hordenine methyl.

[1] *Manuscript received January 22, 1953.*
*Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, and the Department of Chemistry, McMaster University, Hamilton, Ontario. Issued as N.R.C. No. 2967.*
[2] *Present address: Department of Chemistry, McMaster University, Hamilton, Ontario.*

## EXPERIMENTAL

### *Measurement of Radioactivity*

All radioactive compounds were measured in a "Q"-gas counter and appropriate corrections were made.

### *Labelled Compounds*

$C^{14}$-methyl labelled choline chloride was prepared by the method of du-Vigneaud *et al.* (5). L-$C^{14}$-methyl-labelled methionine was synthesized by the method of Melville, Rachele, and Keller (10). $C^{14}$-labelled sodium formate was prepared by a modification of the method of Melville *et al.* (10). $C^{14}$-labelled sodium bicarbonate was prepared by adjusting the pH of a solution of $C^{14}$-labelled sodium carbonate. All syntheses started from $C^{14}$-labelled sodium carbonate supplied by Atomic Energy of Canada, Limited.

### *Germination of Barley and Administration of Labelled Materials*

A 720 gm. sample of Charlottetown No. 80 barley was evenly divided among twelve 20 × 25 cm. Pyrex trays. The seeds were watered twice daily and on the sixth day of germination the labelled compounds were added, dissolved in water. The barley was harvested on the 11th day of germination and worked up for the isolation of the desired compounds.

### *Isolation and Degradation of Hordenine*

Hordenine was isolated from the roots as described previously (7). It was purified to constant specific activity by precipitation as the reineckate followed by decomposition of the salt according to Kapfhammer and Bischoff (6). This procedure effectively separates hordenine from the N-methyl tyramine which occurs along with it in Charlottetown No. 80 barley (9). The resulting hordenine hydrochloride was diluted with inactive hordenine (2.000 gm. in hydrochloric acid solution) and this aqueous solution was basified with concentrated ammonia and extracted continuously with ether for 48 hr. The ether was removed *in vacuo* and the residue converted to the methiodide as described previously (9). The methiodide was converted to the reineckate, its specific activity was checked, and the reineckate was converted to the methochloride by the procedure of Kapfhammer and Bischoff. The methochloride was then converted to the O-methyl derivative by the following procedure which gives a more complete O-methylation than that described previously (9). This results in considerably improved yields in the Hofmann degradation.

Hordenine methochloride (1.80 gm.) was dissolved in a 10% aqueous solution of sodium hydroxide (13.5 ml.) and dimethyl sulphate (9.5 ml.) was added dropwise with stirring. Acetic acid (7.9 ml.) and sodium acetate (3.9 gm.) were then added and the stirring continued for five hours and the solution left overnight. The 2-(*p*-methoxyphenyl)ethyltrimethylammonium ion was precipitated as the reineckate and its specific activity was checked. The reineckate was converted to the corresponding chloride by the method of Kapfhammer and Bischoff and this in turn was converted to the hydroxide with moist silver oxide. The quaternary hydroxide was then submitted to the Hofmann degradation as described by Leete *et al.* (9). The second product

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of the degradation, *p*-vinylanisole, gave rise on oxidation to homoanisaldehyde, isolated in 26% yield as the oxime. These substances were purified to constant specific activities which are shown in Table I.

*Isolation of Choline*

Choline was isolated, separately, from the roots and stems of the barley as described previously (8). It was purified to constant specific activity through its reineckate salt and also through its chloroplatinate. The specific activities of these substances are reported in Table I.

*Absorption of Choline Chloride by Sprouting Barley*

A possible explanation of the failure of choline methyl to serve as a precursor of hordenine methyl would be that the plant does not absorb it or that it is destroyed by bacterial action before it can be utilized by the plant. In order to show that the plants were capable of absorbing choline chloride intact and translocating it throughout the plant, the following experiment was carried out.

Approximately 100 five-day-old barley seedlings were threaded through a wire screen (5 × 5 mm. mesh) in such a fashion that the stems were supported in an upright position. This prevented any possibility of the stems being externally contaminated with the labelled choline fed to the roots. The plants were fed a solution of choline chloride (2 mgm.) dissolved in water (10 ml.). The choline was labelled in the methyl group with $C^{14}$ and the total activity fed was $5.0 \times 10^5$ counts per minute. After five days, activity could be detected in the stem tips, and radioautographs showed a distribution of activity decreasing toward the tip. The leaves were clipped off above the screen and hydrolyzed in 1 *N* aqueous–alcoholic potassium hydroxide solution (100 ml.) containing unlabelled carrier choline chloride (143 mgm.). Choline was isolated from the hydrolyzate as described previously (8) and purified by repeated precipitation as the reineckate (in aqueous acid) and as the chloroplatinate (in ethanol). It retained its radioactivity and held a constant specific activity ($1.2 \times 10^4$ counts/min./millimole). The total activity was shown by degradation to be confined to the N-methyl groups.

This experiment demonstrates clearly that choline is absorbed by the barley root and is translocated to all parts of the plant. This translocated choline is labelled in the same fashion as the choline fed showing that there has been no randomization of activity in the absorbed molecules.

## DISCUSSION

It is evident from the results in Table I that methionine methyl not only serves as a precursor of hordenine methyl but that it is more efficient in this respect than is formate. This supports the idea of Brown and Byerrum that formate serves as a precursor of methionine methyl. The previous report that choline fails to serve as a precursor of hordenine methyl is confirmed (8). This result is not an artifact caused by the exclusion of the choline by the roots or by the destruction of choline by bacteria before it could be absorbed by the roots, since choline is absorbed by the barley root and translocated to all parts of the plant. There can be no doubt, then, that there is no transfer of methyl from choline to methionine in the barley plant. It is beginning to

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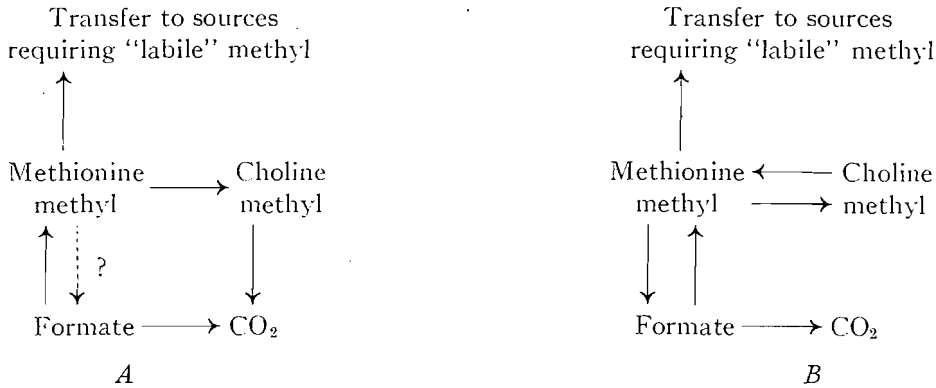
TABLE I

SPECIFIC ACTIVITIES

| Metabolite administered | | | Specific activity in c.p.m. per mM.* | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Weight, mgm. | Total activity | Hordenine | Trimethylamine from degradation of hordenine | Homoanisaldehyde oxime from degradation of hordenine | Choline from root | Trimethylamine from degradation of root choline | Choline from stem | Trimethylamine from degradation of stem choline |
| L-Methionine | 50 | $7.3 \times 10^6$ | $3.9 \times 10^4$ | $3.7 \times 10^4$ | 0 | $5.3 \times 10^4$ | $4.9 \times 10^4$ | $1.1 \times 10^4$ | $1.1 \times 10^4$ |
| Choline chloride | 50 | $2.5 \times 10^7$ | $< 0.1 \times 10^4$ | – | – | – | – | – | – |
| Sodium formate | 10 | $5.0 \times 10^7$ | $4.2 \times 10^4$ | Not degraded | – | $4.7 \times 10^3$ | Not degraded | Not isolated | – |
| Sodium bicarbonate | 18 | $5.0 \times 10^7$ | $< 0.1 \times 10^4$ | – | – | $< 0.1 \times 10^4$ | – | Not isolated | – |

**All specific activities are for carrier-free material.*

appear that this may be a general property of the higher plants since it has also been shown to be true in germinating *Ricinus communis* (3) and in mature *Dicentra* species (12). This gives the following picture of synthesis and transfer of labile methyl groups in the higher plants (*A* in Scheme 1) as contrasted with the process known to occur in animals (*B* in Scheme 1).




Scheme 1. Synthesis and transfer of labile methyl in plants (*A*) and in animals (*B*).

This picture is not totally unexpected. Work with enzyme preparations from animal tissues shows that in the animal labile methyl is synthesized in the form of methionine methyl and is then transmethylated to choline (1). It has further been shown that in animals choline must first be oxidized to betaine before its methyls can be transferred back to methionine (4,11). The reason for this difference between the higher plants and the animals may be that the plant has no need to metabolize its labile methyl groups back through methionine since it has a steady supply available through its synthetic process. The animal is almost wholly dependent on its diet for its supply of labile methyl and since a good portion of this supply must be in the form of choline methyl, the possession of a mechanism for utilizing this supply has obvious "survival" value. It would appear that the animal has developed this mechanism to utilize, efficiently, the available labile methyl supply in its diet. This mechanism would appear to consist of the enzymes necessary to carry out the oxidation of choline to betaine and a "methylpherase" to carry out the transmethylation from betaine to methionine.

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# THE DEPENDENCE OF THE HYDROLYSIS OF DIAZOACETIC ESTER ON THE HYDROGEN ION CONCENTRATION[1]

By A. V. Willi[2] and R. E. Robertson

ABSTRACT

The catalytic constants of the $H_3O^+$ catalyzed hydrolysis of diazoacetic ester in aqueous solutions containing sodium perchlorate have been determined at three different ionic strengths. A spectrophotometric method was used to follow the rate. The results indicate a strong positive salt effect. Measurements at the ionic strength $\mu = 0.110$ were carried out in the pH region from 1.97 to 5.19. For solutions containing less than $10^{-3}$ $N$ perchloric acid the pH data were taken from measurements with a glass electrode in the kinetic cell. Within the limits of experimental error no deviations from proportionality between rate and $[H_3O^+]$ were found. This result is important in connection with our findings for the benzalaniline hydrolysis since it tests the methods applied and proves that the benzalaniline example with deviations from linearity between rate and $[H_3O^+]$ is a special case. The diazoacetic ester hydrolysis is not catalyzed by acetic acid molecules.

According to Brönsted's concept the rate of an acid-catalyzed reaction is determined by the sum of the catalytic effects of the different proton donators present in solution. This is formulated as:

$$k = k_0 + k_{H^+} [\text{H Solv}^+] + k_A [\text{A}]$$

where $k_0$ is the coefficient of the spontaneous reaction, $k_{H^+}$ is the catalytic constant for the solvated proton (in aqueous solution the ion $H_3O^+$), and $k_A$ is the constant for the catalysis of the undissociated acid.

If the reaction under consideration can only be catalyzed by hydroxonium ions or if no other catalyst except H Solv$^+$ is present, that is, if $k_A = 0$, or if $[A] = 0$, the simplified equation

$$k = k_{H^+} [\text{H Solv}^+] + k_0 \qquad [2]$$

can be applied. Furthermore, $k_0$ can often be neglected. While this equation has been tested for very many reactions (1), most of the experimental data for $k_{H^+}$ have been determined in solutions of strong acids in the concentration range between 1 $N$ and $10^{-3}$ $N$. It is generally assumed that Equation [2] is also valid for smaller $H_3O^+$ concentrations and consequently the same value for $k_{H^+}$ as found in those strongly acidic solutions must be obtained at high pH values if only salt effects and medium effects can be excluded. Although this assumption may be very reasonable from the theoretical point of view, deviations from Equation [2] in unbuffered solutions have been found for the hydrolysis of benzalanilines (9) and for the decomposition of diazoacetate ion (7). In the benzalaniline example the rate was followed by a spectrophotometric method and at the same time the pH was measured with a glass electrode and a silver chloride half-cell directly introduced into the kinetic cell. The liquid junction potential of this system was considered to be negligible.

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According to our knowledge, rate measurements of this type for hydrogen ion catalyzed reactions in unbuffered solutions have never been carried out before. In fact, it is generally recognized (1, p. 66) that most rate data obtained in buffer solutions of weak acids cannot be related to hydrogen ion concentrations. This is because the concentration acidity constant for the buffer at the particular ionic strength was not known and the hydrogen ion concentrations of the solutions could not be determined by potentiometric measurements since the liquid junction potentials could not be excluded. It occurred to us that deviations from linearity for the dependence of the rate on $H_3O^+$ in the intermediate pH range may have been observed by others, but could not be clearly established because it was not known whether their pH measurements contained systematic errors due to liquid-junction potentials. These difficulties were rendered negligible by the method applied in our study (9). Accordingly we decided to investigate a standard reaction showing acid catalysis in order to test Equation [2] for pH values higher than 3 in buffered and in unbuffered solutions. For this purpose we selected the hydrolysis of diazoacetic ester and carried out a kinetic study of the reaction $N_2CHCOOC_2H_3 + H_2O \rightarrow HOCH_2COOC_2H_5 + N_2$ for different ionic strengths in dilute aqueous solutions of perchloric acid and in buffered solutions. This reaction was studied for the first time by Fraenkel (5) and an extended investigation at different temperatures had been done by Moelwyn-Hughes and Johnson in 1941 (8). Both workers had applied the gasometric method.

## EXPERIMENTAL

Diazoacetic ester was synthesized by the method given in "Gattermann" (6). Instead of the steam distillations and the subsequent vacuum distillations, we carried out only one vacuum distillation in a modified Bower-Cooke column (2).

Since diazoacetic ester has a high ultraviolet absorption band at 250 m$\mu$ ($\epsilon \approx 10{,}000$) (10), it was convenient to study the kinetics of the reaction by a spectrophotometric method as described in the preceding paper. The initial concentration of diazoacetic ester was $10^{-4}$ $M$ or smaller and the amount of nitrogen evolved during the complete run (in a 240 cc. reaction cell) was therefore smaller than $\frac{1}{2}$ cc. and gas bubbles could not seriously influence the light absorption measurements.

The method for the pH measurements was the same as used in the preceding study for the benzalaniline hydrolysis in unbuffered solutions: a glass electrode and a silver chloride half-cell were directly introduced into the kinetic cell.

Moelwyn-Hughes and Johnson (8) have reported the formation of chloroacetic ester as a side reaction in the presence of chloride ions, consequently sodium perchlorate was used in place of potassium chloride to keep a constant ionic strength.

The Ag-AgCl half-cell contained 0.100 $N$ sodium perchlorate and 0.0100 $N$ potassium chloride. The ionic strength of the solutions to be measured was $\mu = 0.110$. The unbuffered solutions contained 0.110 $M$ sodium perchlorate and the acetate buffer 0.100 $M$ sodium perchlorate, 0.0100 $M$ sodium acetate,

and some acetic acid. Calibration of the glass electrode was carried out in a separate temperature controlled cell containing a solution of $5.50 \times 10^{-3}$ $M$ perchloric acid and 0.1045 $M$ sodium perchlorate with the pH of 2.26. The pH data obtained by this method refer to $H_3O^+$ concentrations and not to activities. The liquid-junction potentials could be neglected because the concentration differences of the various salts in both half-cells are small. Our results confirm that this assumption is justified.

## RESULTS

Table I and Fig. 1 give the experimental data obtained for $k_{H^+} = k/[H_3O^+]$ in the presence of perchloric acid and sodium perchlorate at three different ionic strengths. Within each series, the $k_{H^+}$ values agree well for different acid concentrations.

TABLE I

SALT EFFECT ON THE ACID CATALYZED HYDROLYSIS OF DIAZOACETIC ESTER IN WATER AT 20.00°C. ( ± 0.03°)

| No. | $C_{HClO_4} = [H_3O^+]$ (moles l.$^{-1}$) | $C_{NaClO_4}$ (moles l.$^{-1}$) | $\mu$ (moles l.$^{-1}$) | $k$ (min.$^{-1}$)* | $k_{H^+}$ (min.$^{-1}$moles$^{-1}$l.) | Average |
|---|---|---|---|---|---|---|
| 1 | $10.68 \times 10^{-3}$ | 0.100 | 0.110 | 0.1198 | 11.22 | |
| 2 | $5.34 \times 10^{-3}$ | 0.105 | 0.110 | 0.0600 | 11.24 | 11.22 |
| 3 | $2.862 \times 10^{-3}$ | 0.1075 | 0.110 | 0.03205 | 11.20 | |
| 4 | $1.431 \times 10^{-3}$ | 0.109 | 0.110 | 0.01607 | 11.23 | |
| 5 | $4.30 \times 10^{-3}$ | 0.0400 | 0.0443 | 0.0438 | 10.19 | |
| 6 | $2.862 \times 10^{-3}$ | 0.0411 | 0.0440 | 0.0287 | (10.03) | 10.20 |
| 7 | $1.431 \times 10^{-3}$ | 0.0426 | 0.0440 | 0.01459 | 10.20 | |
| 8 | $1.431 \times 10^{-3}$ | 0.0206 | 0.0220 | 0.01433 | 10.01 | 9.98 |
| 9 | $2.150 \times 10^{-3}$ | 0.0200 | 0.0221 | 0.0214 | 9.95 | |

**Our k values are calculated with the aid of decadic logarithms. They are defined by the formula* $-(d[E]/dt) = 2.303\, k[E]$.

The primary salt effect of sodium perchlorate is surprisingly large for an example of a reaction between an ion and an uncharged molecule (1, p. 23). Addition of 0.1$N$ has been found in the present study to increase the rate at 20°C. by 11.4%, while in previous studies, at 15°C., (3) an increase of 14.8% was observed. It is noted that the special acid-catalyzed hydrolysis of dimethylacetal also exhibits a large (13%) primary salt effect of sodium perchlorate (4).

Moelwyn-Hughes and Johnson (8) investigated the diazoacetic ester reaction at different temperatures by application of the gasometric method. They found a value of $k_{H^+} = 0.3892$ [ln sec.$^{-1}$]* $= 10.14$ [log$_{10}$, min.$^{-1}$]* at 293.39°K. in $10^{-3}$–$10^{-2}$ $N$ solutions of nitric acid without salt addition. Interpolation to 293.20°K. gives a value of $k_{H^+} = 9.94$ [log$_{10}$, min.$^{-1}$] which agrees within the experimental error with the value obtained by extrapolation of our data to zero ionic strength (9.75).

**Moelwyn-Hughes's data are defined by the equation* $-(d[E]/dt) = k[E]$*; our definition for k is different (see Table I).*

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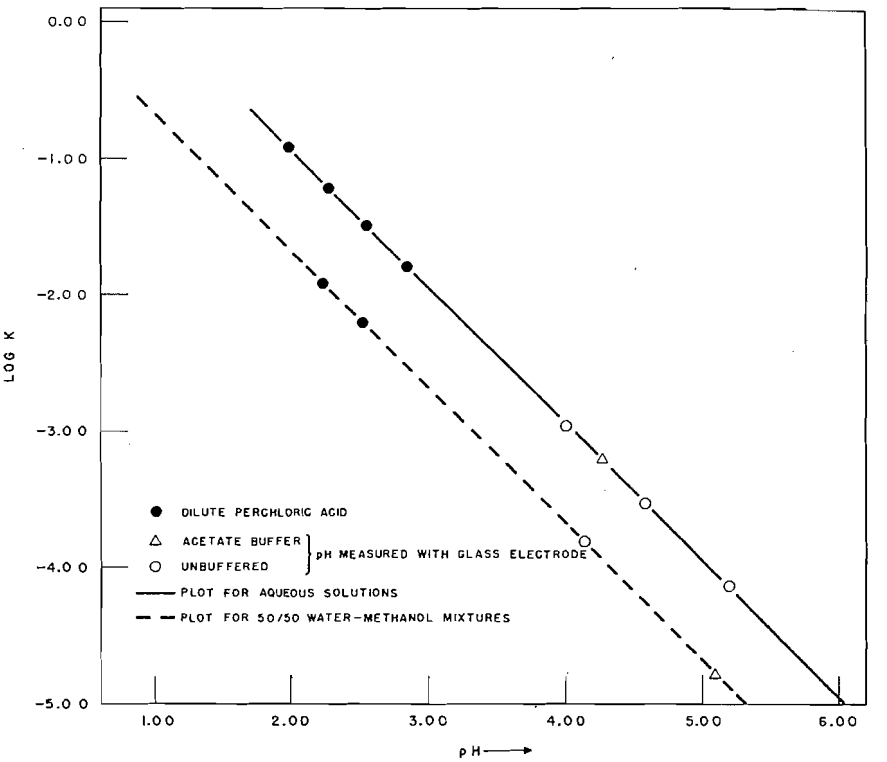



FIG. 1. The pH dependence of the rate constant for the hydrolysis of diazoacetic ester at the ionic strength $\mu = 0.110$ and 20.00°C.

TABLE II

HYDROLYSIS OF DIAZOACETIC ESTER IN ACETATE BUFFERS AND IN UNBUFFERED AQUEOUS SOLUTIONS
$\mu = 0.110$ AT 20.00°C.

| No. | Solute | pH (measured) | $k$ (min.$^{-1}$)* | $k$/[H Solv$^+$] (min.$^{-1}$moles$^{-1}$ l.) |
|---|---|---|---|---|
| 10 | 0.110 *M* $NaClO_4$<br>Trace $HClO_4$ | 4.00 | $1.08 \times 10^{-3}$ | 10.8 |
| 11 | 0.100 *M* $NaClO_4$<br>0.0100 *M* NaAc<br>0.01947 *M* HAc | 4.26 | $6.15 \times 10^{-4}$ | 11.2 |
| 12 | 0.110 *M* $NaClO_4$<br>Trace $HClO_4$ | 4.58 | $2.90 \times 10^{-4}$ | 11.03 |
| 13 | 0.110 *M* $NaClO_4$<br>Trace $HClO_4$ | 5.19 | $7.3 \times 10^{-5}$ | 11.3 |

*See Table I.

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The data for the rates of decomposition of diazoacetic ester in unbuffered solutions and in acetate buffer at $\mu = 0.110$ are given in Table II and in Fig. 1. Division of the observed rate by the $H_3O^+$ concentration (measured with the glass electrode) gives also within the experimental error the same value for $k_{H^+}$ as determined in the presence of $10^{-2}$–$10^{-3}N$ perchloric acid at $\mu = 0.110$. For these data, an error of at least 2% may be expected because the pH could not be determined more accurately than to 0.01 units. Nevertheless, it can be concluded from these results that the equation $k = k_{H^+}[H_3O^+]$ is very well fulfilled in the pH range 2–5.2. Also in the presence of acetic acid (experiment No. 11) the observed rate is in agreement with this equation which indicates that catalysis by acetic acid is absent or negligible.

The deviations from Equation [2] for the benzalaniline reaction reported in the preceding paper were observed in a 50/50 methanol–water mixture. In order to check whether the deviations were due to the special solvent, we carried out a few experiments in the same solvent mixture on the diazoacetic ester reaction. From the data in Table III and Fig. 1 it is clear that there is also a linear relation between the rate and the concentration of the solvated protons in a 50/50 methanol–water mixture.

TABLE III

HYDROLYSIS OF DIAZOACETIC ESTER IN 50/50 w/w METHANOL–WATER MIXTURE
$\mu = 0.110$ AT 20.00°C.

| Solute | pH measured | [H Solv$^+$] (moles l.$^{-1}$) | $k$ (min.$^{-1}$)* | $k$/[H Solv$^+$] (min.$^{-1}$moles$^{-1}$ l.) |
|---|---|---|---|---|
| 0.104 $M$ $NaClO_4$<br>$5.87 \times 10^{-3}$ $M$ $HClO_4$ | | $5.87 \times 10^{-3}$ | $1.23 \times 10^{-2}$ | 2.10 |
| 0.107 $M$ $NaClO_4$<br>$2.93 \times 10^{-3}$ $M$ $HClO_4$ | | $2.93 \times 10^{-3}$ | $6.33 \times 10^{-3}$ | 2.16 |
| 0.110 $M$ $NaClO_4$<br>Trace $HClO_4$ | 4.13 | $7.4 \times 10^{-5}$ | $1.56 \times 10^{-4}$ | 2.11 |
| 0.100 $M$ $NaClO_4$<br>0.0100 $M$ NaAc<br>0.01947 $M$ HAc | 5.08 | $8.32 \times 10^{-6}$ | $1.71 \times 10^{-5}$ | 2.06 |

*See Table I.

These results indicate that either proportionality between rate constants and [H Solv$^+$] also exists at low hydrogen ion concentrations for a constant ionic strength, or the deviations of the rate from proportionality to [H Solv$^+$] are equal in sign and magnitude to the errors involved in our method of pH measurement. It is highly improbable that these two completely different things, the deviation of the rate from proportionality to [H Solv$^+$] and the liquid-junction potential, could be identical for a change of the independent variable by a factor of 1000. Therefore, it is justifiable to conclude: the rate is actually proportional to [H Solv$^+$] and the liquid-junction potential is in fact negligible or cancels out. The second conclusion is also important with

respect to our results obtained for the hydrolysis of benzalanilines in unbuffered solutions. It indicates that our findings for the pH dependence of that reaction are not due to deficiencies of the method of pH measurement applied in both studies.

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# REFRACTIVE INDICES OF SOME SATURATED AND MONOETHENOID FATTY ACIDS AND METHYL ESTERS[1]

By B. M. Craig[2]

ABSTRACT

The refractive indices for a number of saturated and monoethenoid fatty acids and their corresponding methyl esters have been determined. Equations have been calculated to obtain the refractive index at any given temperature. Significant differences have been found for the temperature coefficients of refractive index within an homologous series and between the free fatty acid and the corresponding methyl ester.

The literature contains few references to systematic studies on the refractive indices of the fatty acids and their esters, particularly the variation in refractive index with temperature. Dorinson, McCorkle, and Ralston (1) have reported refractive indices for the saturated fatty acids from caproic to stearic at five degree intervals of temperature. Wyman and Barkenbus (8) determined the refractive indices of the methyl esters of this series of fatty acids at 45°C. and this work was extended by Mattil and Longenecker (5) who determined the variation in refractive index as a function of temperature. The latter workers computed equations to calculate the refractive indices at any intermediate temperatures. More recently Krewson (3) has published data on the refractive indices of the methyl esters of the saturated acids up to and including methyl octacosanoate at temperatures of 50°C. and 80°C.

Data on refractive indices of unsaturated acids and esters are more meager than for the corresponding saturated series. Wood *et al.* (7) have reported on the refractive indices of oleic, elaidic, linoleic, and linolenic acids at 50°C. McCutcheon (4) determined the refractive indices of ethyl linoleate and ethyl linolenate over the range 20°C. to 60°C.

In the course of some work on rapeseed oil the saturated and monoethenoid acids and esters of the $C_{16}$ to $C_{22}$ series were purified, and a refractive index study was made on these materials. Equations were calculated from the data expressing the refractive index as a function of temperature.

## MATERIALS AND METHODS

Crude commercial stearic acid was used as a source for methyl palmitate and methyl stearate. The crude acid was hydrogenated to a negligible iodine value and converted to methyl esters by conventional procedures. The crude esters were distilled in a Podbielniak "Heli-Grid" distillation column. The methyl palmitate and methyl stearate fractions were redistilled and fractionally crystallized to yield pure esters. Methyl oleate was obtained by converting olive oil to the methyl esters and distilling the esters. The $C_{18}$ fraction was repeatedly crystallized from acetone until the precipitates and filtrates agreed in refractive index. The purified methyl oleate was then redistilled in

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the Podbielniak column. Methyl eicosenoate and methyl erucate were prepared from rapeseed oil in the same manner. Methyl behenate and methyl arachidate were prepared from the corresponding monoethenoid esters by hydrogenation with Raney nickel followed by fractional crystallization.

The pure fatty acids were obtained by saponification of the corresponding pure methyl esters and fractional crystallization. The physical and chemical constants of the esters and acids are given in Table I. Iodine values were

TABLE I

PHYSICAL AND CHEMICAL CONSTANTS FOR FATTY ACIDS AND METHYL ESTERS

| | Acids | | | | Esters | | | |
|---|---|---|---|---|---|---|---|---|
| | I.V. | Theor. I.V. | M.P. | Reported M.P. | I.V. | Theor. I.V. | M.P. | Reported M.P. |
| Oleic | 89.90 | 89.87 | — | — | 85.63 | 85.62 | — | — |
| Eicosenoic | 81.62 | 81.75 | 24.2 | 23–24 | 78.15 | 78.22 | — | — |
| Erucic | 74.81 | 74.98 | 33.0 | 33.5 (6) | 71.91 | 71.99 | — | — |
| Palmitic | 0 | 0 | 63.3 | 62.9 (2) | 0 | 0 | 29.9 | 30.6 (2) |
| Stearic | 0 | 0 | 70.1 | 69.6 (2) | 0 | 0 | 39.1 | 39.1 (2) |
| Arachidic | 0 | 0 | 75.4 | 75.35 (2) | 0 | 0 | 46.9 | 46.6 (2) |
| Behenic | 0 | 0 | 80.7 | 79.95 (2) | 0 | 0 | 53.3 | 53.3 (2) |

determined by the Wijs method, one hour reaction time and 0.1 *N* solution. Melting points were measured by the Wiley method using a Bureau of Standards thermometer and applying stem emergence corrections. Diene and triene acid contents of the unsaturated esters and acids were determined according to the standard A.O.C.S. procedure. No measurable quantities were found in any of the monoethenoid esters or acids.

A Bausch and Lomb Abbe type refractometer equipped with a circulating water bath controlled to $\pm$ 0.005°C. was used to measure the refractive indices. A thermometer calibrated against a Bureau of Standards thermometer was used to read the temperature in the prism and stem emergent corrections were applied to the thermometer reading. No prism corrections were applied to the refractive index values. The refractive indices were measured at five degree intervals over the temperature range at which the material under study was in the liquid state from 20°C. to 85°C. The refractometer was carefully calibrated with the test piece supplied by the manufacturer and checked with purified ethyl oxalate and ethyl citrate.

## RESULTS

Equations for calculation of refractive indices of the esters and acids at any given temperatures are listed in Table II. The equations were calculated by the method of least squares and the error of estimate for the equation and the standard error of the regression coefficient are included. The errors of estimate of the equations listed in Table II are of the same order as the error of measurement of refractive index credited to the instrument used in the

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TABLE II

EQUATIONS FOR CALCULATION OF REFRACTIVE INDICES

| | | Standard error of estimate | Standard error of regression coefficient |
|---|---|---|---|
| Methyl oleate | R.I.t = 1.45968 − 0.000377t | 0.00005 | 0.000,001 |
| Methyl eicosenoate | R.I.t = 1.46134 − 0.000372t | 0.00005 | 0.000,001 |
| Methyl erucate | R.I.t = 1.46288 − 0.000369t | 0.00009 | 0.000,002 |
| Methyl palmitate | R.I.t = 1.44830 − 0.000379t | 0.00008 | 0.000,002 |
| Methyl stearate | R.I.t = 1.45149 − 0.000375t | 0.00006 | 0.000,001 |
| Methyl arachidate | R.I.t = 1.45363 − 0.000366t | 0.00005 | 0.000,001 |
| Methyl behenate | R.I.t = 1.45554 − 0.000358t | 0.00007 | 0.000,002 |
| Oleic acid | R.I.t = 1.46677 − 0.000354t | 0.00009 | 0.000,002 |
| Eicosenoic acid | R.I.t = 1.46805 − 0.000351t | 0.00008 | 0.000,001 |
| Erucic acid | R.I.t = 1.46892 − 0.000346t | 0.00008 | 0.000,002 |
| Palmitic acid | R.I.t = 1.45589 − 0.000355t | 0.00006 | 0.000,004 |

*R.I. t = Refractive index at temperature t°C.*

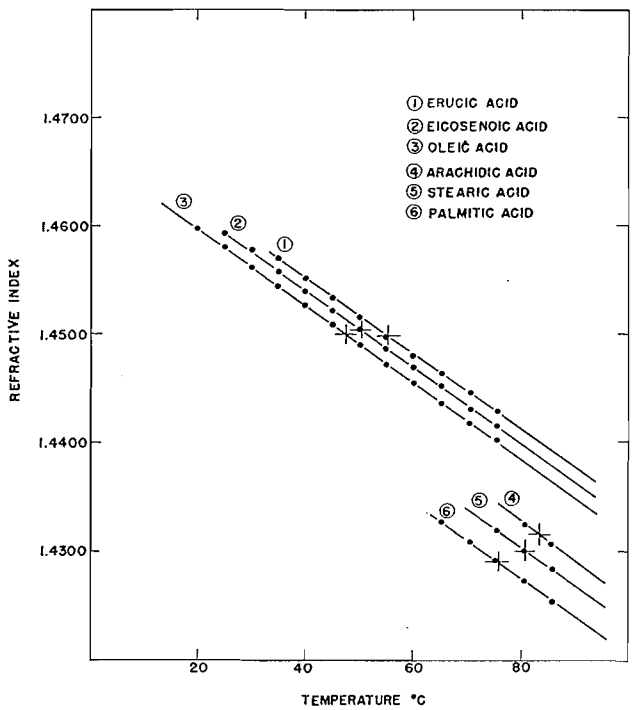



FIG. 1. Refractive indices of fatty acids at different temperatures.

study. Lines representing the equations and the experimental values for refractive indices are presented graphically in Figs. 1 and 2.

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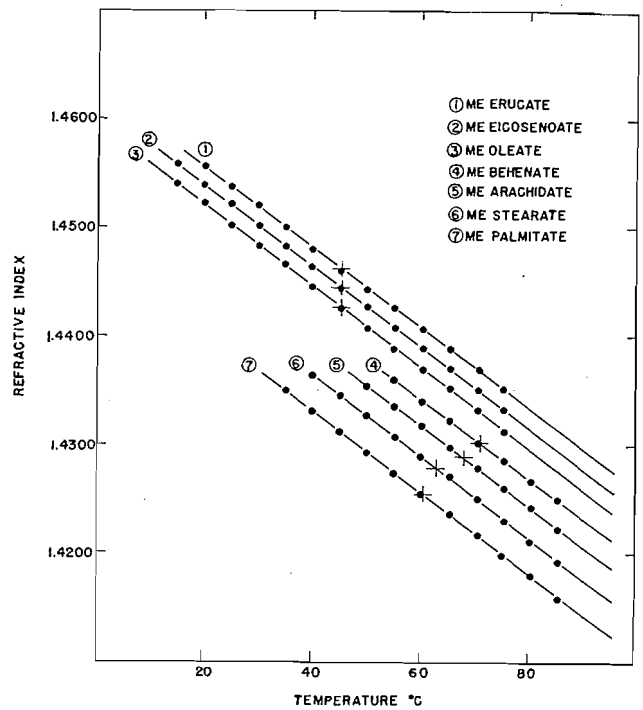



FIG. 2. Refractive indices of methyl esters of fatty acids at different temperatures.

Table III shows a comparison of the values obtained experimentally and those calculated from the equations given in Table II. Experimental values are included for stearic, arachidic, and behenic acids where there were insufficient data to calculate the necessary equations.

The refractive indices for acids and esters given in this study agree quite well with those reported by other workers. The equations which are given in Table II represent an accurate and convenient means for calculating refractive indices at any temperature and are a definite advantage where temperatures other than those reported in the literature are used to measure refractive index. It is interesting to note that the temperature coefficients of refractive index given in the equations in Table II vary in a regular manner within an homologous series of acids or esters. Statistically the difference may not be significant between any two consecutive members of the series, e.g. methyl palmitate (0.000379) and methyl stearate (0.000375), but the difference is significant between two members such as methyl palmitate (0.000379) and methyl behenate (0.000358). It must also be noted that there are significant differences between the temperature coefficients of refractive index for the methyl esters and the corresponding free fatty acids. The practice of using the general figure 0.00038 as the temperature coefficient of refractive index will lead to an error, the magnitude of which will depend on the temperature being used.

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TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL REFRACTIVE INDICES

| | Experimental | Calculated |
|---|---|---|
| | $n_D^{35}$ | |
| Methyl oleate | 1.44656 | 1.44650 |
| Methyl eicosenoate | 1.44833 | 1.44832 |
| Methyl erucate | 1.44977 | 1.44977 |
| | $n_D^{60.2}$ | |
| Methyl palmitate | 1.42549 | 1.42550 |
| Methyl stearate | 1.42897 | 1.42892 |
| Methyl arachidate | 1.43165 | 1.43160 |
| Methyl behenate | 1.43391 | 1.43399 |
| | $n_D^{35}$ | |
| Oleic acid | 1.45442 | 1.45438 |
| Eicosenoic acid | 1.45574 | 1.45576 |
| Erucic acid | 1.45674 | 1.45681 |
| | $n_D^{85.6}$ | |
| Palmitic acid | 1.42545 | 1.42550 |

| | Experimental refractive indices | | |
|---|---|---|---|
| | $n_D^{75.5}$ | $n_D^{80.5}$ | $n_D^{85.6}$ |
| Stearic acid | 1.43202 | 1.43012 | 1.42830 |
| Arachidic acid | — | 1.43247 | 1.43066 |
| Behenic acid | — | — | 1.43257 |

The differences in the coefficient for the monoethenoid methyl ester and the corresponding saturated methyl esters, e.g. methyl oleate (0.000377), methyl stearate (0.000375), do not seem to be statistically significant. However reasoning in the same manner as for the homologous series given above, the difference might be shown to be significant if this study were extended to include diethenoid and triethenoid acids and esters of the same chain lengths.

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# THE REACTION OF METHYL RADICALS WITH ISOBUTANE[1]

By M. H. Jones[2] and E. W. R. Steacie

ABSTRACT

An investigation is reported of the reaction of methyl radicals, produced in the photochemical decomposition of azomethane, with isobutane. The energy of activation of this process was found to be 6.7 ± 0.8 kcal./mole, assuming that the combination of methyl radicals has an activation energy of zero. From some experiments with *n*-butane, a value of 9 ± 1 kcal./mole was obtained.

## INTRODUCTION

A recent study of the photolysis of azomethane (5) has shown that it may be used as a source of methyl radicals for an investigation of reactions of the type

$$CH_3 + RH \rightarrow CH_4 + R$$

where RH is any hydrogen containing compound. The choice of suitable compounds is, however, limited as the activation energy of hydrogen abstraction from azomethane itself is low. Since the method of investigation involves the determination of rate differences, the velocities of the two competitive reactions must be of roughly the same order of magnitude if quantitative results are required. Isobutane was chosen in the first instance as a simple hydrocarbon containing a tertiary carbon–hydrogen bond, where there is greater ease of abstraction (6, 7) than from a corresponding primary or secondary bond.

## EXPERIMENTAL

The apparatus and analytical procedure have been described elsewhere (5). The nitrogen-methane and ethane fractions were analyzed by the mass spectrometer and there was no evidence that the latter were contaminated with isobutane.

The light source was a Hanovia S-500 medium pressure mercury arc and the collimated light beam had a volume within the quartz reaction cell of 110 cc. The cell volume was 170 cc. Two filters were used to cut out the short ultraviolet wave lengths. Filter A, a Corning filter No. 2–37 or 586, was opaque to wave lengths below 3150 Å and had a transmission such that 96% of the absorbed radiation was the 3660 Å lines. Filter B was a Corning filter No. 0–53 or 774 and limited the incident radiation to wave lengths greater than 2800 Å.

The azomethane was a sample that had been prepared previously (5). It was kept as a liquid at −78° C., vapor pressure 6.6 mm., in a trap darkened to exclude daylight. Research Grade isobutane, obtained from the Phillips Petroleum Company, was found to contain traces of methane and ethane (~ 0.05 mole %) which were sufficient to cause errors of several per cent in the analysis of the reaction products. The samples used were, therefore, intro-

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[2] *National Research Council of Canada Postdoctorate Fellow, 1950–1952.*



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duced into the analysis system and these impurities pumped off at −165° C. The *n*-butane, also a Research Grade product of the Phillips Company, was treated in the same manner.

## RESULTS AND DISCUSSION

The rates of formation of the gaseous products in the photolysis of azomethane may be described by the reaction scheme

$$CH_3N{=}NCH_3 + h\nu \rightarrow N_2 + 2CH_3 \quad [1]$$

$$CH_3 + CH_3N{=}NCH_3 \rightarrow CH_4 + CH_2N{=}NCH_3 \quad [2]$$

$$CH_3 + CH_3 \rightarrow C_2H_6\,. \quad [3]$$

In the presence of isobutane we have the additional methane producing reaction

$$CH_3 + C_4H_{10} \rightarrow CH_4 + C_4H_9\,. \quad [4]$$

From reactions [2] and [3] it follows that, when $R_{CH_4}$ and $R_{C_2H_6}$ are the rates of formation of methane and ethane, for azomethane alone

$$R_{CH_4} = k_2\,[CH_3]\,[\text{Azo}]$$

$$R_{C_2H_6} = k_3\,[CH_3]^2.$$

The other terms in the rate equations have their usual significance. Hence, applying the normal stationary state conditions,

$$(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_A = k_2\,[\text{Azo}]/k_3^{\frac{1}{2}}$$

and for the photolysis of a mixture of azomethane and isobutane,

$$(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_{A+B} = k_2\,[\text{Azo}]/k_3^{\frac{1}{2}} + k_4\,[C_4H_{10}]/k_3^{\frac{1}{2}}$$

where the subscripts $A$ and $B$ refer to the reactants. As the quantities $(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_{A+B}$ and $(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_A$ may be determined over a range of temperatures for known concentrations of azomethane and isobutane on the one hand, and azomethane on the other, we have a method of obtaining values of $(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_B/[C_4H_{10}]$ i.e. $k_4/k_3^{\frac{1}{2}}$. Thus expressing the rate coefficients in terms of the Arrhenius parameters,

$$k_4/k_3^{\frac{1}{2}} = (A_4/A_3^{\frac{1}{2}})\,\exp[-(E_4 - \tfrac{1}{2}E_3)/RT]\,.$$

Such a kinetic treatment is dependent on the condition that methane is formed only by reactions [2] and [4] and ethane only by reaction [3].

The values of $(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_B/[C_4H_{10}]$ at temperatures between 24° C. and 169° C. are given in Table I. The values of $(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_A/[\text{Azo}]$ required in these calculations have been taken from the experimental Arrhenius curve for azomethane which was found to deviate from linearity at temperatures below 80° C. The choice of the experimental rather than the extrapolated curve in this region is considered justified by the fact that the resultant Arrhenius plot for isobutane is linear over the whole temperature range. The set of experiments, runs 111–127, on which the azomethane plot is based were conducted immediately following those quoted in Table I with Filter A and immediately prior to those with Filter B, using the same sample of azomethane. The optical system was undisturbed.

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TABLE I

ABSTRACTION OF HYDROGEN ATOMS BY METHYL RADICALS FROM ISOBUTANE AND *n*-BUTANE

| Run No. | Temp., °K. | [Azo].$10^6$ mole/cc. | [$C_4H_{10}$].$10^6$ mole/cc. | $R_{N_2}.10^5$ | $R_{CH_4}.10^5$ | $R_{C_2H_6}.10^5$ | $(R_{CH_4}/R^{1/2}_{C_2H_6})_{A+B}.10^3$ | $\frac{(R_{CH_4}/R^{1/2}_{C_2H_6})_B}{[C_4H_{10}]}.10^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| | | | | cc. at N.T.P./min. | | | | |
| *Filter A* | | | | | | | | |
| Isobutane | | | | | | | | |
| 104 | 298 | 3.22 | 3.38 | 50.2 | 6.91 | 35.8 | 3.66 | 2.87 |
| 107 | 300 | 2.25 | 4.59 | 35.0 | 6.02 | 26.2 | 3.72 | 3.75 |
| 99 | 319 | 2.13 | 2.37 | 39.0 | 6.50 | 22.1 | 4.36 | 5.87 |
| 103 | 334 | 2.81 | 3.16 | 42.4 | 12.8 | 22.6 | 8.53 | 9.37 |
| 100 | 345 | 2.55 | 2.64 | 44.6 | 12.6 | 14.9 | 10.3 | 14.2 |
| 109 | 356 | 2.37 | 2.58 | 42.8 | 14.3 | 11.9 | 13.1 | 19.6 |
| 101 | 373 | 2.73 | 2.57 | 48.9 | 19.1 | 7.40 | 22.2 | 26.5 |
| 110 | 384 | 2.63 | 2.67 | 44.5 | 21.4 | 4.51 | 31.8 | 43.8 |
| 106 | 404 | 2.13 | 2.89 | 41.3 | 22.2 | 2.85 | 41.5 | 54.3 |
| 102 | 406 | 2.51 | 2.34 | 46.2 | 22.6 | 2.36 | 46.5 | 58.5 |
| 105 | 427 | 2.17 | 2.13 | 42.8 | 24.7 | 1.45 | 64.8 | 93.0 |
| 108 | 442 | 2.12 | 2.20 | 40.4 | 26.7 | 1.09 | 81.2 | 98.6 |
| *Filter B* | | | | | | | | |
| Isobutane | | | | | | | | |
| 128 | 328 | 2.85 | 3.03 | 222.9 | 31.9 | 155.1 | 8.10 | 10.6 |
| 130 | 349 | 2.53 | 2.59 | 215.9 | 43.5 | 123.3 | 12.4 | 20.0 |
| 142 | 354 | 2.71 | 2.65 | 242.8 | 44.0 | 118.5 | 12.8 | 15.4 |
| 137 | 375 | 2.71 | 2.36 | 218.0 | 67.1 | 83.4 | 23.2 | 30.9 |
| 125 | 384 | 2.33 | 2.47 | 218.5 | 78.4 | 55.8 | 33.2 | 61.9 |
| 132 | 411 | 2.50 | 2.51 | 228.8 | 102.4 | 26.2 | 63.3 | 106. |
| 135 | 438 | 2.38 | 2.35 | 221.0 | 123.4 | 17.5 | 93.5 | 134. |
| *n*-Butane | | | | | | | | |
| 141 | 352 | 2.37 | 2.77 | 210.5 | 32.7 | 112.5 | 9.76 | 9.28 |
| 136 | 375 | 2.45 | 3.03 | 204.4 | 57.3 | 75.6 | 20.8 | 21.1 |
| 133 | 411 | 2.42 | 2.61 | 221.9 | 87.8 | 26.8 | 53.5 | 69.0 |
| 134 | 435 | 2.73 | 2.83 | 254. | 122.5 | 15.8 | 97.2 | 111. |

As the rates have been given in cc. of gas at N.T.P./min. and the concentrations in mole/cc., the $(R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6})_B/[C_4H_{10}]$ values must be multiplied by the factor $1.11.10^{-15}/V^{\frac{1}{2}}$ where $V$ is the reaction volume, in order to express $k_4/k_3^{\frac{1}{2}}$ in the more conventional units (molecule/cc.)$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$

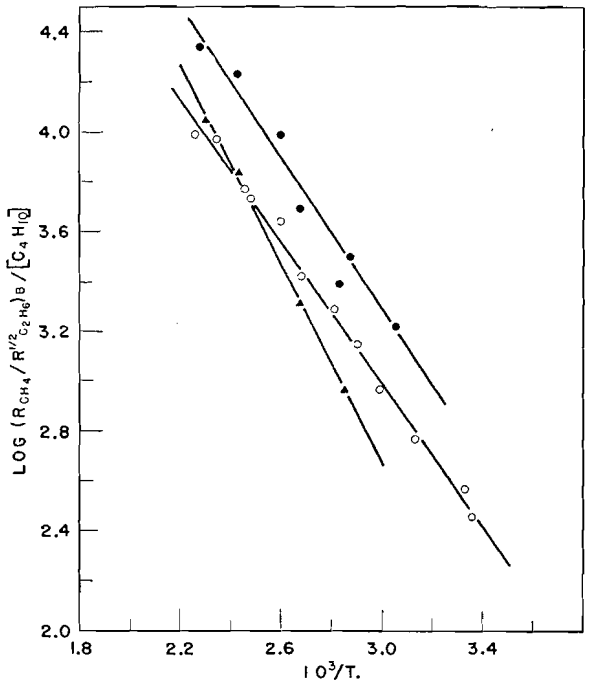



FIG. 1. Arrhenius plots for the reaction of methyl radicals with the butanes. The results for isobutane with Filter B have been displaced upwards 0.2 units in the ordinate scale.
Filled Circles—isobutane—Filter B.
Open Circles—isobutane—Filter A.
Triangles—*n*-butane.

The Arrhenius curves for isobutane appear in Fig. 1 together with that obtained from four experiments with *n*-butane. The activation energy differences, $E_4 - \frac{1}{2}E_3$, calculated by the method of least squares are recorded in Table II. These are the values for the hydrogen abstraction reaction if it is assumed that the combination of methyl radicals does not require activation (3). The difference between the two results for isobutane is not considered significant. Thus, taking the mean, a value of 6.7 ± 0.8 kcal./mole is obtained, and for the reaction of methyl with *n*-butane, 9 ± 1 kcal./mole. Although the standard errors quoted above are greater than those determined from the experimental scatter (see Table II), we consider that they represent a more conservative estimate of the errors inherent in the system. The ratio of the steric factors, $P_4/P_3^{\frac{1}{2}}$, calculated from simple collision theory ($A = PZ$ in the Arrhenius expression) are $10^{-4}$ and $10^{-3}$ respectively for isobutane and *n*-butane, assuming the collision diameters $CH_3 = 3.5.10^{-8}$ cm., iso-$C_4H_{10}$ $= 5.8.10^{-8}$ cm., and *n*-$C_4H_{10} = 5.9.10^{-8}$ cm.

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TABLE II

COMPARISON OF RESULTS OBTAINED IN VARIOUS INVESTIGATIONS FOR THE REACTION OF METHYL RADICALS WITH ISOBUTANE AND *n*-BUTANE

| Compound | Methyl source | $E_4 - \frac{1}{2}E_3$, kcal. | $P_4/P_3^{\frac{1}{2}}$ | $k_4/k_3^{\frac{1}{2}}.10^{13}$ at 100°C., molecule$^{-\frac{1}{2}}$.cc$^{\frac{1}{2}}$.sec.$^{-\frac{1}{2}}$ | Reference |
|---|---|---|---|---|---|
| Isobutane | Azomethane. Filter A | $6.5 \pm 0.2$ | $\sim 10^{-4}$ | 3.0[a] | This work |
| Isobutane | Azomethane. Filter B | $6.9 \pm 0.5$ | $\sim 10^{-4}$ | 4.0[a] | This work |
| Isobutane | Acetone | 7.6 | $3.10^{-4}$ | 6.2 | Trotman-Dickenson, Birchard, and Steacie (7) |
| Isobutane | Mercury dimethyl | (4.2) | | | Smith and Taylor (6) |
| *n*-Butane | Azomethane. Filter B | $9.1 \pm 0.3$ | $\sim 10^{-3}$ | 2.2[a] | This work |
| *n*-Butane | Acetone | 8.3 | $3.10^{-4}$ | 2.7 | Trotman-Dickenson, Birchard, and Steacie (7) |
| *n*-Butane | Mercury dimethyl | (5.5) | | | Smith and Taylor (6) |
| *n*-Butane | Mercury dimethyl | 8.4 | | | Gomer (2) |

[a] *The values of $k_4/k_3^{\frac{1}{2}}$ have been calculated on the assumption that the effective reaction volume is that of the light beam i.e. 110 cc.*

Also included in Table II are the activation energies for the abstraction of a hydrogen atom from the two butanes by methyls produced in the photolysis of acetone (7) and mercury dimethyl (6, 2). Except for the earlier values of Smith and Taylor, which are inaccurate since they were based on the rate of methane formation only, assuming the ethane rate remained sensibly constant, there is fair agreement in the results. It may be concluded, therefore, as is to be expected, that the reaction is independent of the nature of the methyl source. Since the method of kinetic analysis is identical when azomethane and acetone are used as the radical source, it is possible to make a comparison of the ratio of the rate coefficients, $k_4/k_3^{\frac{1}{2}}$, which does not reflect compensating error in $E$ and $A$. Here there is also good agreement, particularly in the case of *n*-butane.

Trotman-Dickenson and Steacie (8) have demonstrated that the facility with which a hydrogen atom may be abstracted from a hydrocarbon increases in the order primary, secondary, and tertiary. In a compound containing more than one type it is at once apparent that the measured $E$ is a composite activation energy. However, even for isobutane, which possesses only one tertiary and nine primary hydrogen atoms, the abstraction is predominately tertiary and at temperatures below 200° C. a simple calculation shows that the deviation in the energy of activation lies within the experimental accuracy. The same is true of *n*-butane where the abstraction is mainly secondary.

The radicals resulting from reaction [4] are the tertiary butyl and secondary butyl. As these are stable thermally up to 250° C. (1, 4) it can be supposed that they disappear either by combination with each other

$$2C(CH_3)_3 \rightarrow (CH_3)_3C - C(CH_3)_3 \qquad [5]$$

and

$$2CH_3CH_2CHCH_3 \rightarrow CH_3CH_2(CH_3)CH - CH(CH_3)CH_2CH_3 \qquad [6]$$

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or with methyl radicals

$$(CH_3)_3C + CH_3 \rightarrow (CH_3)_3C\ CH_3 \quad [7]$$

and $$CH_3CH_2CHCH_3 + CH_3 \rightarrow CH_3CH_2CH(CH_3)_2\,. \quad [8]$$

Evidence for a reaction analogous to [7] and [8] accounting for the fate of the radical $CH_2N = NCH_3$ was obtained in the study of the photolysis of azomethane alone (5). A disproportionation reaction between butyl radicals may also occur although indirect evidence suggests that the corresponding unsymmetrical process involving a methyl does not take place (7). As the latter is a methane producing reaction, the kinetic method described above would be invalidated if it occurred to any appreciable extent.

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## UNIT CELL, SPACE GROUP, AND X-RAY POWDER DIFFRACTION DATA FOR LYCOCTONINE MONOHYDRATE, $C_{25}H_{39-41}O_7N.H_2O$[1]

By W. H. Barnes and Maria Przybylska*

Recently we have had occasion to take X-ray powder photographs of crystals of lycoctonine monohydrate, $C_{25}H_{39-41}O_7N.H_2O$ (2), provided by Dr. L. Marion, and extracted from *Delphinium consolida* L. (3) and from *Delphinium Brownii* Rydb. (4), respectively. The diffraction patterns were identical but it was difficult to compare our photographs directly with the prints reproduced by Cook and Beath (1) for a specimen isolated from *Delphinium barbeyi* H., and for one prepared by the basic hydrolysis of ajacine. Dr. W. B. Cook, however, very kindly supplied a sample of his lycoctonine monohydrate from *D. barbeyi*, and a powder photograph confirmed its identity with the specimens from *D. consolida* and from *D. Brownii*.

In order to obtain additional X-ray crystallographic data for lycoctonine monohydrate, the unit cell constants and space group have been determined from precession photographs with filtered Cu radiation ($\lambda(K_\alpha) = 1.5418$Å).

Lycoctonine monohydrate is monoclinic sphenoidal and crystallizes from aqueous alcohol as colorless needles, elongated in the direction of the $b$ axis. Radial aggregates are common. The most prominent forms observed were $\{110\}$, $\{10\bar{1}\}$, and $\{100\}$. The crystals are strongly piezoelectric. The unit cell dimensions are $a = 14.95 \pm 0.03$Å, $b = 7.92 \pm 0.02$Å, $c = 10.98 \pm 0.02$Å, $\beta = 103°6'$. The space group is $P2_1$ ($C_2^2$) and there are two molecules per cell. The molecule of lycoctonine monohydrate, therefore, is asymmetric.

The density, as found by flotation in aqueous potassium iodide solutions, was 1.26 gm. per ml. at room temperature. That calculated for $C_{25}H_{39}O_7N.H_2O$ is 1.267 gm. per ml. while that for $C_{25}H_{41}O_7N.H_2O$ is 1.273 gm. per ml., thus precluding a choice between $H_{39}$ and $H_{41}$ on this basis unless relatively large clear crystals, suitable for very accurate density measurements, can be grown. The observed density, however, supports evidence (4) that the crystals are the monohydrate since the calculated density of the dihydrate ($H_{39}$ or $H_{41}$) is approximately 1.31 gm. per ml.

X-ray powder diffraction data are given in Table I. Lines corresponding to $d > 3.20$Å have been indexed on the basis of the unit cell constants. The powder patterns were obtained with Co radiation ($\lambda(K_\alpha) = 1.790$Å), filtered with Fe foil, in a 114.6 mm. diameter camera using Straumanis film mounting. The longest interplanar spacing measurable with the apparatus used (i.e., the "cutoff") was 20Å. Film shrinkage corrections were only about 0.13% and, therefore, were not applied. Relative intensities ($I/I_1$) were estimated visually.

[1] *Issued as N.R.C. No. 2955.*

* *National Research Council Postdoctorate Fellow, now with the Division of Applied Chemistry, National Research Council, Ottawa, Canada.*

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR LYCOCTONINE MONOHYDRATE

| $I/I_1$ | $d$(Å) Obs. | $d$(Å) Calc. | $hkl$ | $I/I_1$ | $d$(Å) Obs. | $d$(Å) Calc. | $hkl$ |
|---|---|---|---|---|---|---|---|
| 80 | 14.5 | 14.56 | 100 | | | 3.57 | 003 |
| 10 | 10.6 | 10.70 | 001 | 15 | 3.48 | 3.53 | 121, 20$\bar{3}$ |
| 80 | 9.69 | 9.74 | 10$\bar{1}$ | | | 3.50 | 212 |
| 85 | 7.79 | 7.81 | 101 | | | 3.48 | 220 |
| 50 | 7.29 | 7.28 | 200 | 30 | 3.40 | 3.42 | 22$\bar{1}$ |
| 100 | 6.94 | 6.96 | 110 | | | 3.39 | 40$\bar{2}$ |
| — | — | 6.77 | 20$\bar{1}$ | | | 3.32 | 11$\bar{3}$ |
| 50 | 6.36 | 6.37 | 011 | 5 | 3.31 | 3.31 | 410 |
| 40 | 6.10 | 6.14 | 11$\bar{1}$ | 15 | 3.20 | | |
| — | — | 5.56 | 111 | 2 | 3.06 | | |
| | | 5.47 | 201 | 5 | 3.00 | | |
| 30 | 5.37 | 5.43 | 10$\bar{2}$ | 20 | 2.85 | | |
| | | 5.36 | 210 | 20 | 2.68 | | |
| | | 5.35 | 002 | 1 | 2.59 | | |
| 25 | 5.14 | 5.15 | 21$\bar{1}$ | 5 | 2.54 | | |
| 12 | 4.85 | 4.87 | 20$\bar{2}$ | 5 | 2.49 | | |
| | | 4.85 | 300, 30$\bar{1}$ | 4 | 2.43 | | |
| 3 | 4.68 | 4.69 | 102 | 2 | 2.37 | | |
| 30 | 4.44 | 4.50 | 211 | 4 | 2.32 | | |
| | | 4.48 | 11$\bar{2}$ | 3 | 2.25 | | |
| | | 4.43 | 012 | 3 | 2.22 | | |
| 50 | 4.13 | 4.15 | 21$\bar{2}$ | 2 | 2.17 | | |
| | | 4.14 | 310, 31$\bar{1}$ | 4 | 2.15 | | |
| 12 | 4.03 | 4.08 | 301, 30$\bar{2}$ | 2 | 2.07 | | |
| | | 3.96 | 020 | 1 | 2.05 | | |
| 1 | 3.92 | 3.91 | 202 | 2 | 1.94 | | |
| 20 | 3.81 | 3.82 | 120 | 1 | 1.88 | | |
| — | — | 3.71 | 021, 40$\bar{1}$ | 5 | 1.83 | | |
| | | 3.67 | 12$\bar{1}$ | 1 | 1.78 | | |
| 10 | 3.65 | 3.66 | 10$\bar{3}$ | | | | |
| | | 3.64 | 400 | | | | |
| | | 3.63 | 311 | | | | |

1. COOK, W. B. and BEATH, O. A. J. Am. Chem. Soc. 74: 1411. 1952.
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## THE OXIDATION OF FERROUS SULPHATE SOLUTIONS BY $\gamma$-RAYS—THE EFFECT OF SURFACE/VOLUME RATIO OF POLYSTYRENE CELLS ON THE YIELD[1]

BY T. J. HARDWICK

A serious discrepancy exists between the results of various workers on the yield of ferric ion in the oxidation of air-saturated ferrous sulphate solutions in 0.8 $N$ sulphuric acid by $\gamma$-rays. Hochanadel (5) found a value of $G$ (mols. ferric ion produced per 100 ev. absorbed) = 15.5, using a calorimetric method to determine the rate of energy absorption. Using air wall equivalent ion chambers for the measurement of energy absorbed, Miller (6) found $G$ = 20.4, while Hardwick (3) obtained $G$ = 20.8.

A possible reason for this anomaly was that while Hochanadel carried out his irradiations in glass vessels, Miller and Hardwick used plastic (polystyrene)

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TABLE I

X-RAY POWDER DIFFRACTION DATA FOR LYCOCTONINE MONOHYDRATE

| $I/I_1$ | $d$(Å) Obs. | $d$(Å) Calc. | $hkl$ | $I/I_1$ | $d$(Å) Obs. | $d$(Å) Calc. | $hkl$ |
|---|---|---|---|---|---|---|---|
| 80 | 14.5 | 14.56 | 100 | | | 3.57 | 003 |
| 10 | 10.6 | 10.70 | 001 | 15 | 3.48 | 3.53 | 121, 20$\bar{3}$ |
| 80 | 9.69 | 9.74 | 10$\bar{1}$ | | | 3.50 | 212 |
| 85 | 7.79 | 7.81 | 101 | | | 3.48 | 220 |
| 50 | 7.29 | 7.28 | 200 | 30 | 3.40 | 3.42 | 22$\bar{1}$ |
| 100 | 6.94 | 6.96 | 110 | | | 3.39 | 40$\bar{2}$ |
| — | — | 6.77 | 20$\bar{1}$ | | | 3.32 | 11$\bar{3}$ |
| 50 | 6.36 | 6.37 | 011 | 5 | 3.31 | 3.31 | 410 |
| 40 | 6.10 | 6.14 | 11$\bar{1}$ | 15 | 3.20 | | |
| — | — | 5.56 | 111 | 2 | 3.06 | | |
| | | 5.47 | 201 | 5 | 3.00 | | |
| 30 | 5.37 | 5.43 | 10$\bar{2}$ | 20 | 2.85 | | |
| | | 5.36 | 210 | 20 | 2.68 | | |
| | | 5.35 | 002 | 1 | 2.59 | | |
| 25 | 5.14 | 5.15 | 21$\bar{1}$ | 5 | 2.54 | | |
| 12 | 4.85 | 4.87 | 20$\bar{2}$ | 5 | 2.49 | | |
| | | 4.85 | 300, 30$\bar{1}$ | 4 | 2.43 | | |
| 3 | 4.68 | 4.69 | 102 | 2 | 2.37 | | |
| 30 | 4.44 | 4.50 | 211 | 4 | 2.32 | | |
| | | 4.48 | 11$\bar{2}$ | 3 | 2.25 | | |
| | | 4.43 | 012 | 3 | 2.22 | | |
| 50 | 4.13 | 4.15 | 21$\bar{2}$ | 2 | 2.17 | | |
| | | 4.14 | 310, 31$\bar{1}$ | 4 | 2.15 | | |
| 12 | 4.03 | 4.08 | 301, 30$\bar{2}$ | 2 | 2.07 | | |
| | | 3.96 | 020 | 1 | 2.05 | | |
| 1 | 3.92 | 3.91 | 202 | 2 | 1.94 | | |
| 20 | 3.81 | 3.82 | 120 | 1 | 1.88 | | |
| — | — | 3.71 | 021, 40$\bar{1}$ | 5 | 1.83 | | |
| | | 3.67 | 12$\bar{1}$ | 1 | 1.78 | | |
| 10 | 3.65 | 3.66 | 10$\bar{3}$ | | | | |
| | | 3.64 | 400 | | | | |
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cells. It has been shown that traces of organic material seriously interfere with the oxidation of ferrous ion by radiation, generally causing an increase in yield (1,2,4). It was therefore a possibility that the bombardment of the plastic interface by the electrons produced within the wall might pollute the solution sufficiently to cause a change in the measured yield.

The existence of such an effect could be checked if irradiations were made in plastic cells with varying surface/volume ratios. The amount of impurity going into solution would be dependent on the surface area only. Under conditions of constant surface area and varying volume, any effect arising from the plastic walls would be greatest in the smallest volume.

Three sets of well-type cells were constructed of polystyrene, an identical pair to each set. The general features are shown in Fig. 1; a more detailed

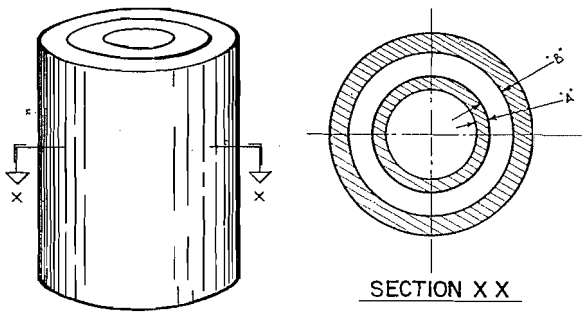



FIG. 1. Well-type cell used for irradiations.

description has been reported previously (3). The dimension $A$ refers to the thickness of plastic between the source and the irradiation chamber, while $B$ refers to the width of the annulus comprising the irradiation volume. All other dimensions were the same in all cells.

TABLE I

| Cell No. | Dimension $A$, mm. | Dimension $B$, mm. | Surface, cm.$^2$ | Volume, cm.$^3$ | $\frac{\text{Surface}}{\text{Volume}}$, cm.$^{-1}$ | Yield, mols./100 ev. |
|---|---|---|---|---|---|---|
| 1 | 2.37 | 3.89 | 61.03 | 10.80 | 5.65 | $20.8 \pm 0.3$ |
| 2 | 3.85 | 2.41 | 62.14 | 7.07 | 8.79 | $20.5 \pm 0.5$ |
| 3 | 4.66 | 1.60 | 62.64 | 4.83 | 10.97 | $20.2 \pm 0.8$ |

The method of using one of each pair of cells for ion chamber measurements and the other for solution irradiations has been described previously (3). The results are shown in Table I. The values of the yield are based on at least 10 ferrous ion oxidations each and as many ion current measurements. The standard deviation becomes greater at smaller volumes owing to the technical difficulty in working with such small annuli. Clearly there is no marked effect of the surface volume ratio on the yield. Pollution of the solution by the walls, if it occurs, does not appear to affect the yield. Another explanation must be sought for the discrepancies between the two methods of determining the yield in this chemical system.

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## UNIT CELL, SPACE GROUP, AND X-RAY POWDER DIFFRACTION DATA FOR THE ALKALOID LUPANOLINE, $C_{15}H_{24}N_2O_2$, AND FOR LUPANOLINE MONOHYDRATE, $C_{15}H_{24}N_2O_2.H_2O$[1]

BY W. H. BARNES AND MARIA PRZYBYLSKA*

In connection with X-ray crystallographic studies of the $C_{15}$ lupin alkaloids (3), lupanoline, $C_{15}H_{24}N_2O_2$, was examined at a time when the possibility of its identity with hydroxylupanine was under consideration. Recently (2) the former has been fully characterized chemically as an isomer of the latter. During an exploratory X-ray investigation, it became apparent that crystals from two authentic specimens of lupanoline were not structurally identical. They have now been identified as anhydrous lupanoline and lupanoline monohydrate. Unit cell, space group, and X-ray powder diffraction data are presented as an aid to their differentiation.

Work was commenced with crystals of a specimen that may be designated lupanoline A, and a few preliminary X-ray precession photographs were obtained. Owing to the pressure of other matters, however, some months elapsed before the study of lupanoline was continued with another, presumably identical, group of crystals. Precession photographs showed, however, that the crystals of this second specimen (lupanoline B) were not structurally the same as those of lupanoline A. The problem temporarily became more confused by the discovery that three or four selected single crystals of lupanoline B that had been stored in a separate vial had become opaque and gave, without crushing, excellent *powder* diffraction patterns. X-ray photographs taken before and after exposure of lupanoline B crystals to heat, sunlight, and mechanical grinding showed that no polymorphic change could be induced by these agencies. In the meantime, attempts to determine the density of lupanoline B by flotation of the clear crystals in aqueous potassium iodide solutions had been troublesome, and it was observed that these crystals also had become opaque. Immersion of clear single crystals of lupanoline B in distilled water, and simple exposure to water vapor in a closed vial, provided the answer. Single crystals of lupanoline B take up water of hydration very readily to form hydrate pseudomorphs consisting of sufficiently large numbers of submicroscopic crystals in completely random orientation to give almost ideal X-ray diffraction powder patterns even without rotation of the specimen. Apart from opacity, the sharply defined faces of the original crystals are retained and the pseudomorphs exhibit no marked evidence of friability.

The identity of the hydrate of lupanoline B with lupanoline A was estab-

[1]*Issued as N.R.C. No. 2960.*

**National Research Laboratories Postdoctorate Fellow, now with the Division of Applied Chemistry, National Research Council, Ottawa, Canada.*

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lished by a series of powder photographs of both substances after wetting, and after drying at about 60°C., care being taken to prevent loss, or gain, of water until each photograph had been obtained.

That lupanoline B is anhydrous, and is not merely a lower hydrate, is evident from the analytical results for the sublimed alkaloid (1). The degree of hydration of lupanoline A was difficult to determine because, although water can be removed at a relatively low temperature, the crystals vaporize readily. Through the courtesy of Dr. L. Marion a determination of C and H was obtained on a sample (3.856 mgm.) of lupanoline (A) that had been exposed for 48 hr. to an atmosphere saturated with water vapor. The results are shown in Table I where they may be compared with those found for

TABLE I
LUPANOLINE

| | Found (%) | | Calculated (%) | | |
|---|---|---|---|---|---|
| | A | B | Dihyd. | Monohyd. | Anhyd. |
| C | 62.6 | 69.0 | 60.0 | 63.8 | 68.1 |
| H | 8.94 | 8.85 | 9.33 | 9.28 | 9.15 |

sublimed lupanoline (B) and those calculated for anhydrous $C_{15}H_{24}O_2N_2$, for the monohydrate, and for the dihydrate.

The analytical results for lupanoline A are low probably owing to the presence of excess water which was difficult to remove completely without danger of partial dehydration of the hydrate. There is no doubt, however, that lupanoline A is lupanoline monohydrate and that lupanoline B is anhydrous.

Anhydrous lupanoline (B) and lupanoline monohydrate (A) both crystallize from acetone as clear, colorless, monoclinic prisms elongated in the direction of the *b* axis, and as flat rectangular plates tabular on $(10\bar{1})$. Both are strongly piezoelectric. Their densities were difficult to measure owing to the small size of the crystals, but that of anhydrous lupanoline was estimated to be less than 1.23 gm. per ml. by flotation in solutions of ethylene dichloride and amyl acetate, and that of lupanoline monohydrate as approximately 1.25 gm. per ml. by flotation in solutions of amyl bromide and methyl iodide.

Unit cell and space group data, obtained from precession photographs, are given in Table II. Both Mo (Zr filtered), $\lambda$ ($K_\alpha$) = 0.7107 Å, and Cu (Ni

TABLE II
UNIT CELL AND SPACE GROUP DATA FOR LUPANOLINE AND FOR LUPANOLINE MONOHYDRATE

| | Lupanoline (anhydrous) | Lupanoline monohydrate |
|---|---|---|
| *a* | 11.97 ± 0.02 Å | 10.59 ± 0.02 Å |
| *b* | 12.20 ± 0.02 Å | 8.06 ± 0.02 Å |
| *c* | 10.73 ± 0.02 Å | 9.03 ± 0.02 Å |
| $\beta$ | 114°9′ | 105°14′ |
| S.G. | $P2_1$ ($C_2^2$) | $P2_1$ ($C_2^2$) |
| Mols./cell | 4 | 2 |
| Density (calc.) | 1.226 gm./ml. | 1.260 gm./ml. |

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TABLE III

X-RAY POWDER DIFFRACTION DATA FOR LUPANOLINE AND FOR LUPANOLINE MONOHYDRATE

| Lupanoline (anhydrous) | | | | Lupanoline monohydrate | | | |
|---|---|---|---|---|---|---|---|
| $I/I_1$ | $d$(Å) Obs. | $d$(Å) Calc. | $hkl$ | $I/I_1$ | $d$(Å) Obs. | $d$(Å) Calc. | $hkl$ |
| 4 | 10.8 | 10.92 | 100 | 20 | 10.2 | 10.23 | 100 |
| — | — | 9.78 | 001 | 30 | 8.73 | 8.70 | 001 |
| 90 | 9.45 | 9.46 | 10$\bar{1}$ | 30 | 7.70 | 7.70 | 10$\bar{1}$ |
| 15 | 8.11 | 8.14 | 110 | 100 | 6.30 | 6.33 | 110 |
| 20 | 7.62 | 7.63 | 011 | 40 | 5.90 | 5.91 | 011, 101 |
| — | — | 7.47 | 11$\bar{1}$ | 50 | 5.53 | 5.57 | 11$\bar{1}$ |
| 25 | 6.13 | 6.14 | 101 | 85 | 5.09 | 5.12 | 200 |
| | | 6.10 | 020 | | | 5.02 | 20$\bar{1}$ |
| — | — | 5.91 | 20$\bar{1}$ | 40 | 4.76 | 4.76 | 111 |
| 10 | 5.50 | 5.49 | 111 | 10 | 4.45 | 4.45 | 10$\bar{2}$ |
| | | 5.46 | 200 | — | — | 4.35 | 002 |
| 20 | 5.35 | 5.36 | 10$\bar{2}$ | 25 | 4.30 | 4.32 | 210 |
| — | — | 5.32 | 21$\bar{1}$, 120 | | | 4.26 | 21$\bar{1}$ |
| 100 | 5.15 | 5.18 | 021 | 10 | 4.00 | 4.03 | 020 |
| | | 5.13 | 12$\bar{1}$ | | | 3.98 | 201 |
| | | 4.99 | 210 | 15 | 3.89 | 3.90 | 11$\bar{2}$ |
| 35 | 4.90 | 4.91 | 11$\bar{2}$ | 5 | 3.82 | 3.85 | 20$\bar{2}$ |
| | | 4.89 | 002 | | | 3.83 | 012 |
| 1 | 4.72 | 4.73 | 20$\bar{2}$ | 2 | 3.72 | | |
| 15 | 4.55 | 4.54 | 012 | 20 | 3.66 | | |
| — | — | 4.41 | 21$\bar{2}$ | 18 | 3.56 | | |
| 5 | 4.32 | 4.33 | 121 | 5 | 3.48 | | |
| 10 | 4.23 | 4.24 | 22$\bar{1}$ | 40 | 3.32 | | |
| | | 4.11 | 201 | 30 | 3.15 | | |
| 25 | 4.08 | 4.07 | 220 | 5 | 2.97 | | |
| | | 4.03 | 12$\bar{2}$ | 10 | 2.77 | | |
| — | — | 3.99 | 30$\bar{1}$ | 2 | 2.70 | | |
| 7 | 3.90 | 3.91 | 102 | 15 | 2.64 | | |
| | | 3.89 | 211 | 1 | 2.56 | | |
| 30 | 3.73 | | | 10 | 2.51 | | |
| 12 | 3.56 | | | 5 | 2.44 | | |
| 5 | 3.41 | | | 10 | 2.36 | | |
| 5 | 3.34 | | | 5 | 2.29 | | |
| 12 | 3.26 | | | 25 | 2.25 | | |
| 3 | 3.12 | | | 2 | 2.22 | | |
| 3 | 3.07 | | | 2 | 2.20 | | |
| 1 | 2.97 | | | 5 | 2.16 | | |
| 15 | 2.90 | | | 2 | 2.10 | | |
| 10 | 2.82 | | | 2 | 2.04 | | |
| 1 | 2.73 | | | 3 | 1.95 | | |
| 10 | 2.65 | | | 1 | 1.91 | | |
| 1 | 2.58 | | | 8 | 1.87 | | |
| 20 | 2.50 | | | 3 | 1.78 | | |
| 7 | 2.36 | | | 1 | 1.75 | | |
| 8 | 2.32 | | | 1 | 1.71 | | |
| 2 | 2.26 | | | 2 | 1.66 | | |
| 7 | 2.20 | | | 2 | 1.51 | | |
| 1 | 2.12 | | | | | | |
| 3 | 2.08 | | | | | | |
| 1 | 2.04 | | | | | | |
| 7 | 2.00 | | | | | | |
| 2 | 1.94 | | | | | | |
| 2 | 1.87 | | | | | | |
| 1 | 1.77 | | | | | | |
| 1 | 1.72 | | | | | | |

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filtered), $\lambda$ ($K_\alpha$) = 1.5418 Å, radiations were employed and measurements were corrected for film shrinkage. An interesting feature of the unit cell data is the presence of four molecules per cell in anhydrous lupanoline. Since the maximum number of asymmetric units per cell in $P2_1$ is 2, two molecules of lupanoline must occupy one set of general positions and two molecules must occupy another set of general positions. The asymmetric unit, therefore, may be considered as comprising two molecules of lupanoline.

X-ray powder diffraction data are shown in Table III. The photographs were taken with Co radiation ($\lambda$ ($K_\alpha$) = 1.790 Å), filtered with Fe foil, in a camera of 114.6 mm. diameter, and with Straumanis film mounting. The longest interplanar spacing measurable with the apparatus used (i.e., the 'cut-off') was 20 Å. Film shrinkage corrections were $< 0.2\%$ and were not applied. Relative intensities ($I/I_1$) were estimated visually. Lines having values of $d > 3.8$ Å have been indexed on the basis of the single crystal data given in Table II.

We are indebted to Mrs. H. M. Sheppard for assistance with the powder investigations.

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## SYNTHESIS OF $C^{14}$ LABELED DDT

BY R. MACDONALD AND B. E. BAKER

Barry (1) described a method for preparing DDT which involved the coupling of acetic anhydride with chlorobenzene by the use of aluminum chloride catalyst to yield *p*-chloroacetophenone. The 1-(*p*-chlorophenyl)-2,2,2-trichloroethanone, which was obtained by direct chlorination of *p*-chloroacetophenone, yielded the corresponding alcohol on reduction with aluminum isopropoxide in dry isopropyl alcohol. The alcohol was condensed with chlorobenzene to give DDT.

This note describes the adaptation of this method to the preparation of $C^{14}$ labeled DDT.

### EXPERIMENTAL

The complete synthesis was carried out with inactive materials and the biological toxicity of the product was compared with an authentic sample of the insecticide. The biological tests showed that the probability of the two materials being different was approximately 1 in 100. It may be concluded that the materials were practically identical so far as their biological effects in these tests were concerned. A mixed melting point of the two materials remained unchanged.

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*Preparation of Sodium Acetate-1-$C^{14}$*

Labeled barium carbonate was prepared by the technique described by Henneberry and Baker (2). Forty milliliters of sodium carbonate ($C^{14}$) solution, having an activity of 0.211 mc. per ml., along with 203 mgm. of inactive sodium carbonate, was added to 50 ml. of saturated barium hydroxide solution. The water and alcohol used to wash the barium carbonate were combined and set aside for measurement of radioactivity (A). The yield of barium carbonate ($C^{14}$) was 1.976 gm.

Labeled sodium acetate was prepared from the barium carbonate following the procedure of Van Bruggen *et al.* (5). The barium carbonate (1.976 gm.) was transferred to the reaction vessel by means of acetone (B) which was subsequently evaporated. At the end of the reaction the ether and residual carbon dioxide were removed by a stream of nitrogen gas. The flushing gas was bubbled through 1*N* sodium hydroxide (C). The residue (D), left in the reaction vessel after the acetic acid had been removed by distillation, was also kept for measurement of radioactivity. The yield of anhydrous sodium acetate was 0.6080 gm.

*Preparation of Acetic Anhydride-1-$C^{14}$ and p-Chloroacetophenone-carbonyl-$C^{14}$*

A mixture of sodium acetate-1-$C^{14}$ (0.6080 gm.) and *p*-toluene sulphonyl chloride (1.62 gm.) was heated at 180–200°C. for 30 min. This method of preparing acetic anhydride from sodium acetate was described briefly by Shantz and Rittenberg (4). The acetic anhydride which distilled off (residue E) was heated at 100°C. for 18 hr. with anhydrous aluminum chloride (2.4 gm.) and chlorobenzene (1.40 gm.). At the end of this heating period, ice (4 gm.) and concentrated sulphuric acid (4 ml.) were added and the temperature was reduced to 50–60°C. The *p*-chloroacetophenone-carbonyl-$C^{14}$ was recovered from the reaction mixture by steam distillation (residue F). It was extracted from the aqueous layer (G) with ether and was distilled under reduced pressure. The ether forerun and the residue were combined and kept for measurement of radioactivity (H).

*Preparation of 1-(p-Chlorophenyl)-2,2,2-trichloroethanol-1-$C^{14}$*

The 1-(*p*-chlorophenyl)-2,2,2-trichloroethanone-1-$C^{14}$, which was obtained by the chlorination at 210°C. of labeled *p*-chloroacetophenone, was mixed with anhydrous isopropanol (8 ml.) and aluminum isopropoxide (2.16 gm.). The temperature of the reaction mixture was maintained sufficiently high to remove the acetone as it was formed. When a negative test (2,4-dinitrophenylhydrazine reagent) for acetone in the distillate was noted, the reaction mixture was refluxed for 15 min. and the distillation was then continued. The cycle of distillation, refluxing, and distillation, was repeated until the test for acetone in the distillate (I) was no longer positive. Ice (3 gm.), followed by concentrated sulphuric acid (3 ml.), was added to the reaction mixture and the product was extracted with ether and then was distilled under reduced pressure. The residue (J) was kept for measurement of radioactivity.

*Preparation of 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane-1-$C^{14}$*

Chlorobenzene (0.6 gm.) and sulphuric acid (3.84 ml., 99.1% pure) were added to the flask which contained the labeled 1-(*p*-chlorophenyl)-2,2,2-

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trichloroethanol. The reaction vessel was surrounded by an ice bath and the reactants were stirred for six hours. The reaction was quenched by the addition of ice (1 gm.) and the DDT was extracted with four 5-ml. portions of chloroform. The acid layer (K) was kept for measurement of radioactivity. The DDT solution was evaporated (distillate L) to dryness at 60° at 1 mm. The crude DDT was purified by three successive recrystallizations from ethanol. There was obtained 197 mgm. of DDT melting at 108°–108.7° (corr.) and having a specific activity of 62,000 counts per min. per mgm. The mother liquors (M), from the recrystallization, were combined and set aside for measurement of radioactivity.

The oxidation mixture of Lindenbaum *et al.* (3) was found to be inadequate for the complete combustion of DDT. Reproducible results were obtained when 20 ml. of a solution containing 69 gm. of chromic trioxide, 200 ml. of fuming sulphuric acid (30% $SO_3$), and 100 ml. of syrupy phosphoric acid was used for each sample.

The residues, distillates, washings, etc., which were obtained during the synthesis, were dissolved in appropriate solvents, and aliquots were oxidized with the modified Lindenbaum mixture. The distribution of activity in the various by-products, as well as the DDT, is shown in the table.

DISTRIBUTION OF $C^{14}$ IN THE PRODUCTS OF THE DDT SYNTHESIS

| Sample | A | B | C | D | E | F | G | H | I | J | K | L | M | DDT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Distribution, % | 1.13 | 0.79 | 1.51 | 18.50 | 9.51 | 16.66 | 0.72 | 9.18 | 1.09 | 10.91 | 22.16 | 0.43 | 1.08 | 4.76 |

The authors wish to thank Dr. W. F. Oliver for his help with the radioactive measurements and Dr. F. O. Morrison for carrying out the biological tests.

The authors are indebted to the National Research Council of Canada for a grant to the Macdonald College Tracer Committee which made this research possible.

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# KINETICS OF SILVER–SILVER ION EXCHANGE[1]

BY A. BAERG AND C. A. WINKLER

## ABSTRACT

The kinetics of silver–silver ion exchange have been studied with etched silver foils. The results indicate that several different rates of reaction occur on a single specimen. This may be interpreted to indicate the presence of crystal faces of different orientations, each of which exchange at a given rate. Interchange of ions in solution with radioactive ions adsorbed on the metal surface was not distinguishable from exchange between ions in solution and active atoms of the metal. When adsorbed silver ions were electrodeposited, the resulting metal surface exhibited a completely heterogeneous character with respect to exchange.

## INTRODUCTION

In previous studies in this laboratory (1), the extent of exchange between silver foils and radioactive silver ion in solution showed no quantitative correlation with Bowden-Rideal area measurements of the surfaces. The exchange behavior was interpreted in terms of the theories of crystal growth, from which, in turn, it was anticipated that several rates of exchange might occur on individual crystalline specimens, depending on the orientations of the crystal faces exposed on the surface. An investigation has now been made of the exchange kinetics on etched silver surfaces, with the results outlined below.

## EXPERIMENTAL AND RESULTS

For greatest accuracy in measuring the radioactivity changes it was necessary to observe the activity on the metal surface rather than that in the solution. This necessitated a technique which would permit continuous activity measurements without removing the metal specimen from the exchange solution. To meet these requirements the metal was allowed to exchange with a thin film of radioactive silver nitrate solution which flowed over the specimen from a circulation system. The relatively high energy gamma radiation emitted by the silver isotope made it possible to follow the reaction by counting through the solution film.

A cross-sectional diagram of the exchange cell is shown in Fig. 1 (lower section). It was made from a solid lucite rod 2 in. in diameter and 2 in. long. One end was machined flat with a 0.020 in. depression, 0.75 in. in diameter, in the center. Capillary holes were drilled obliquely from the circumference into the lucite block to meet the depression as shown. They were enlarged at the outer end to accommodate glass capillary tubes (*G*, *H*) through which

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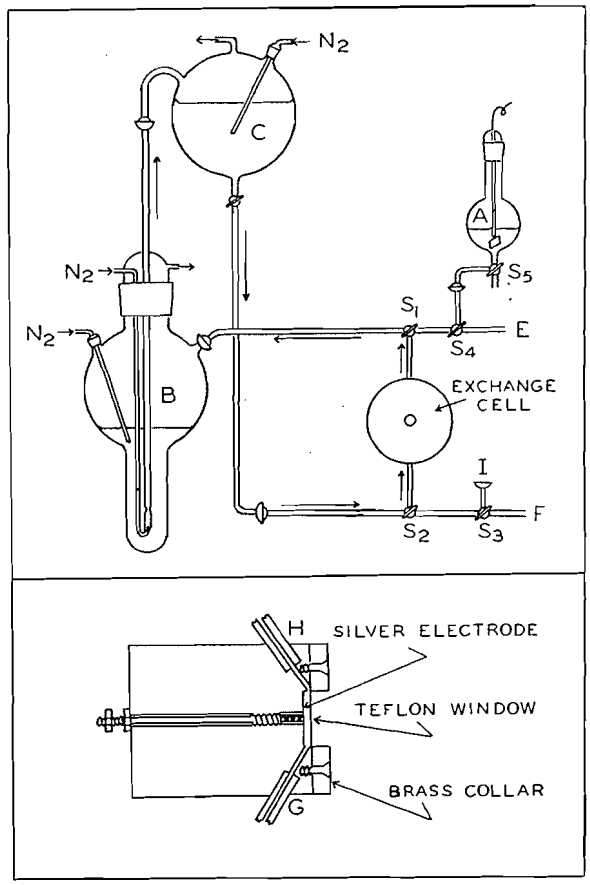



FIG. 1. Diagram of apparatus.

the exchange solution was circulated. The etched silver specimen, a disk 2.5 cm.$^2$ in area and 0.004 in. thick, was fixed firmly in the depression by slightly wetting the lucite with a drop of chloroform. When necessary, electrical contact with the silver was made through a silver spring and brass rod which ran through the middle of the block. A Teflon sheet, 0.0015 in. thick, was placed over the front face of the block to cover the depression. This served as a "window" through which to count the radioactivity on the metal, using a well shielded end-window Geiger tube. The Teflon sheet was held in place by a flat brass collar tightened with six brass screws.

The circulation system, in relation to the cell, is also shown in Fig. 1 (upper section). It was made entirely of glass and to preclude the possibility of contamination of the silver by grease films no lubrication was used in the stopcocks and joints. The exchange solution was placed in the 200 ml. vessel, *B*, and pumped to the upper reservoir, *C*, by a "gas lift" (based on a design by Mason and Rochow (6)), using purified nitrogen. From *C* the solution flowed through the tubes leading to the lower inlet of the exchange cell. After passing through

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the cell and into the vessel, $B$, it was again pumped up to $C$, thus maintaining continuous circulation.

It was desirable to reverse the reaction after a period of "forward exchange" with the active solution. For this purpose a parallel circulation system, similar to the one described, and which contained inactive silver nitrate solution, was connected at $E$ and $F$, through $T$-stopcocks.

Each of the systems contained 200 ml. of $10^{-5}$ $N$ silver nitrate solution which was maintained oxygen-free by bubbling pure nitrogen through them. The active solution contained radioactivity equivalent to about 0.04 mc. The entire apparatus was mounted in an air thermostat from which light was excluded.

To remove any oxide which might remain on the silver surface after etching, the metal was rendered cathodic with $N/5$ sulphuric acid in the cell, using a current of $10^{-4}$ amp. The acid was admitted to the cell and an anode compartment, $A$, through the inlet, $I$, and stopcock, $S_3$. The acid was subsequently flushed out of the anode compartment drain, $S_5$, using inactive silver nitrate solution. Circulation of the solution was continued for an additional two or three hours to equilibrate the surface before exchange with the active solution was commenced.

The reaction was followed by operating the counter continuously during the experiment. The cumulative count recorded on a register was noted at one minute intervals and plotted against the time. The counts per minute at any instant were obtained by evaluation of tangents at various points on the count–time curve, or directly from the average counts per minute over a short time interval. Suitable corrections for background and the count from the solution in the exchange cell were made from the data of a blank experiment in which the silver specimen was replaced by a thin glass slide. The magnitude of the corrections was about 1500 counts per minute while the exchange gave about 1000 counts per minute per apparent atomic layer exchange.

Initial experiments indicated a rapid exchange at first, followed by a much slower reaction which continued indefinitely. When the reaction was reversed, however, using inactive solution, the activity on the metal was reduced to an essentially constant value in several hours but a part of the acquired activity was not removable. This was taken to indicate that the slow process was due largely to local cell action and subsequent experiments were restricted to three hours' duration to study the rapid reaction which was presumably concerned with a reversible process.

It was a simple matter to repeat forward and reverse reaction cycles indefinitely with the same silver specimen. The applicability of the first order rate law to typical data of two exchange cycles for one etched specimen is shown in the upper two graphs of Fig. 2. The equation used was:

$$-2.3 \log F = kt$$

where $k$ is a constant, $t$ the time of reaction,

$F = (x_3 - x)/x_3$ for the forward exchange (active solution)

and $F = (x - x_3)/(x_0 - x_3)$ for the reverse exchange (inactive solution)

in which $x_3$ is the value of the exchange activity, $x$, at the end of three hours

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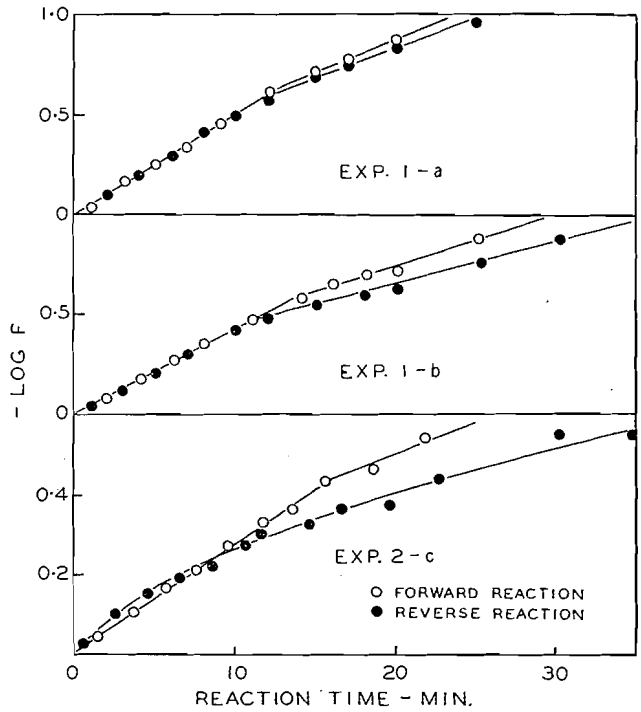



FIG. 2. Applicability of first order rate law.

reaction, and $x_0$ is the initial (zero time) activity for the reverse exchange. The segmented appearance of the graphs indicates several different rates of reaction and discloses the heterogeneous character of the metal surface. While some of the plotted data showed slight tendency toward curvature, most of the results gave segmented graphs as in Fig. 2.

From earlier work (1) it was realized that some of the observed activity on the metal was probably present in an adsorbed ionic double layer. With another silver specimen this was further investigated. As found previously it was not possible to remove such activity by a simple water wash. Oxygen-free water flowing through the cell for one hour failed to reduce the activity acquired by the metal during a three hour "forward" exchange. In another reaction cycle, about 10 ml. of $N/5$ sulphuric acid was run through the cell and into the anode compartment, following the forward reaction. The metal was then rendered cathodic to deposit the adsorbed silver ions. In the subsequent exchange with inactive solution, 31% of the activity acquired with active solution remained on the metal even after 20 hr. In contrast, only 7% was not removable in the previous exchange cycle. Equally interesting is the kinetic behavior of the exchange following the cathodic treatment. A plot with a definite curvature was obtained from the data for the reverse reaction (Experiment 2–*c*, Fig. 2), which indicates a surface structure of a completely heterogeneous character and suggests random, "out-of-lattice", deposition of the ions. Although a curved plot was obtained for a still further exchange cycle, recrystallization of the

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deposited activity appeared to take place since the count was noticeably reduced when exchange with inactive solution was continued for several days.

The over-all results of the experiments described above are summarized in Table I.

TABLE I

RESULTS OF CONTINUOUS EXCHANGE

| Experiment (cycle) | Reaction temp., °C. | | Initial rate, min.$^{-1}$ | $\Delta x$, apparent atomic layers | Deep seated exchange |
|---|---|---|---|---|---|
| 1–*a* | f | 31 | 0.11 | 1.95 | 15% |
| | r | 31 | 0.11 | 1.66 | |
| 1–*b* | f | 40 | 0.098 | 1.74 | 19% |
| | r | 40 | 0.098 | 1.44 | |
| 1–*c* | f | 19.5 | 0.10 | 1.78 | 11% |
| | r | 19.5 | ? | 1.58 | |
| 1–*d* | f | 31 | 0.11 | 2.10 | 17% |
| | r | 31 | 0.13 | 1.70 | |
| 2–*a* | f | 25 | 0.09 | 6.17 | 18% |
| | r | 25 | 0.06 | 5.05 | |
| 2–*b* | f | 25 | 0.055 | 4.43 | 7% |
| | r | 25 | 0.055 | 4.15 | |
| 2–*c* | f | 25 | 0.063 | 4.73 | Cathodic treatment |
| | r | 25 | ? | 3.2 | 31% |
| 2–*d* | f | 25 | ? | 3.9 | 2% |
| | r | 25 | ? | 3.8 | |

The forward and reverse reactions are designated by *f* and *r* respectively. Approximate values of the initial rates of exchange are given as 2.3 times the negative slopes of the linear sections of the plotted data. Included also are the values of the total extent of exchange, $\Delta x$, for each reaction of the various cycles, in terms of the apparent atomic layers involved. "Deep seated" exchange is given in per cent of the activity acquired in the forward reaction which was not removed in the reverse exchange. A pronounced difference in $\Delta x$ is observed between the two silver specimens studied, even though they were both obtained from the same stock and both prepared by etching with nitric acid. The initial rates of exchange, although they can only be regarded as approximate, also differ by a factor of as much as 2 for the two specimens. It may be remarked that the specimen of Experiment 2 had a dull, more heterogeneous appearance than did the other and possibly exhibited a quite different surface structure. The graphs, in addition, showed considerable variation in shape between cycles, for the same specimen. However, this is perhaps not surprising in view of surface structural changes which must occur as a result of slow recrystallization during the deep seated exchange. Any influence of the temperature on the reaction rate was doubtless obscured by this effect.

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## DISCUSSION

In the previous report (1) on silver–silver ion exchange the theories of crystal growth were invoked to arrive at an exchange mechanism which might explain the results obtained. According to these theories the well known phenomena of dissimilar chemical reactivity and growth rate among the faces of single crystals may be attributed to differential bonding along the principle directions within the crystal lattice. Similarly, differences in exchange rate may be expected and the results obtained here appear to substantiate these views.

The different faces exposed on the surface of the silver specimens may be regarded as constituting the local cells which result in the deep seated exchange during reaction with active solution, as pointed out previously (1). While both the rate and extent of exchange will be affected by the local cell action in the forward exchange the rate only can be altered in the reverse exchange. The ions in solution were then essentially all inactive and deposition on cathodic regions (faces of higher binding energy) would have negligible effect on the observed change in activity. However, a net dissolution from anodic regions (faces of lower binding energy) can only result in a decrease of surface activity of somewhat greater rate than that corresponding to reversible exchange.

In the earlier work some evidence was noted which appeared to indicate a decreased rate of exchange due to the presence of adsorbed ionic material on the metal surface. It has not been possible to investigate this further with the apparatus used. The manner in which an adsorption layer might affect the rate of reaction is not clear. Zimens (7) has reasoned that the reaction rate should increase with increasing adsorption, i.e. with increased concentration. He suggests that the variation of exchange rate with concentration should obey a law of a form similar to an adsorption isotherm, and that the rate should attain a maximum value at complete coverage of the surface with adsorbed material. However, qualitative observations by Hevesy and Blitz (4) and by Kolthoff (5) indicate that the rate actually decreases with increased adsorption.

A possible line of speculation is that secondary adsorption of anions or solvent molecules constitutes a barrier to "exchange" with underlying silver ions and metallic atoms. While electrodeposition of adsorbed silver ions indicated (1) that they would account for 20 to 25% of the observed exchange, the initial reaction rate observed here was constant to about 60% reaction (Expt. 1). It must then be concluded that "exchange" with adsorbed ions cannot be distinguished from reaction with exchangeable surface atoms. This would imply that exchange of adsorbed ions with surface atoms is comparatively rapid and that the over-all rate on any one crystal face is governed by other factors, possibly adsorbed anions. A similar suggestion has been made to explain the dependence of exchange rate on the type of anion in solution, as observed by Haissinsky (3).

Since preferential adsorption of both constituents may occur on certain crystal faces (2), it might seem that the effect would be to equalize the binding energy of the atoms among different crystal faces so that the exchange rate should be equal for all faces. No evidence for behavior of this kind has appeared for equilibrium exchange reactions or for nonequilibrium reactions like crystal

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growth. However, modification and even inversion of relative growth rate among faces at appropriate concentrations of adsorbates have been observed (2).

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# A NEW SYNTHESIS OF β-GLUCOPYRANOSIDES[1]

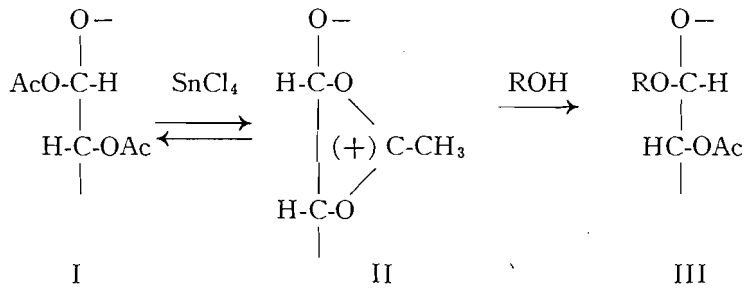
By R. U. Lemieux and W. P. Shyluk[2]

ABSTRACT

Reaction of equivalent amounts of pentaacetyl-β-D-glucopyranose and methanol in benzene or chloroform solution in the presence of 0.5 or more moles of stannic chloride per mole of methanol gave 50-60% yields of methyl tetraacetyl-β-D-glucopyranoside. α-Acetochloroglucose was a by-product of the reaction. The mechanism of the reaction is discussed. The method was applicable for the preparation of phenyl tetraacetyl-β-D-glucopyranoside.

## INTRODUCTION

Lemieux and Brice (3) have shown that the treatment of pentaacetyl-β-D-glucopyranose (I) with stannic chloride in chloroform solution resulted in a rapid dissociation of the Cl to acetoxy group bond to yield carbonium ions of which the resonance stabilized 1,2-cyclic ion (II) is the predominant type. Treatment of 1,2,3,4-tetraacetyl-β-D-glucose under these conditions yielded the internal glucoside, triacetyl-D-glucosan ⟨1, 5⟩β⟨1, 6⟩ (3). Thus, it was reasonable to expect that treatment of pentaacetyl-β-D-glucopyranose with stannic chloride in chloroform containing an alcohol would lead to glucoside formation. Since the ion II would predominate and the reaction of this ion with the alcohol under the prevailing acidic conditions would be accompanied by an inversion of the anomeric center, it was expected that the initial reaction




I II III

product would be the acetylated β-D-glucopyranoside (III). Since pentaacetyl-β-D-glucopyranose was found to be rapidly dissociated by stannic chloride (3), it was anticipated that the β-glucoside would be formed rapidly at the boiling point of the reaction mixture. Pacsu (8) has shown that stannic chloride can catalyze the anomerization of methyl tetraacetyl-β-D-glucopyranoside only slowly. Consequently, it was expected that the reaction of pentaacetyl-β-D-glucopyranose with methanol in the presence of stannic chloride would afford a good yield of methyl tetraacetyl-β-D-glucopyranoside. Lindberg (5) has shown that the rate of anomerization of a β-glucopyranoside depends greatly on the nature of the aglucon.

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[2] *The experimental work was carried out by W. P. Shyluk toward an M.A. thesis, University of Saskatchewan, to be presented in 1953.*

Consequently, it was not possible to predict the success of the method for the preparation of other alkyl β-glucopyranosides. It is well known that aryl β-glucopyranosides are highly resistant to acid catalyzed anomerization (6, 7). This paper is concerned mainly with the reaction using methanol as reagent to produce methyl tetraacetyl-β-D-glucopyranoside.

The preceding predictions were substantiated in all respects. Reaction of pentaacetyl-β-D-glucopyranose with an equivalent of methanol catalyzed by at least half a mole of stannic chloride per mole of methanol proceeded rapidly at the boiling point to give 50-60% yields of methyl tetraacetyl-β-D-glucopyranoside. The rate of reaction was measured at 40°C. A convenient method for gaining an approximate measure of the glucoside content of a reaction product was based on the analysis for reducing sugar in a saponified sample. The curves in Fig. 1 show that the reaction rate was dependent on the catalyst

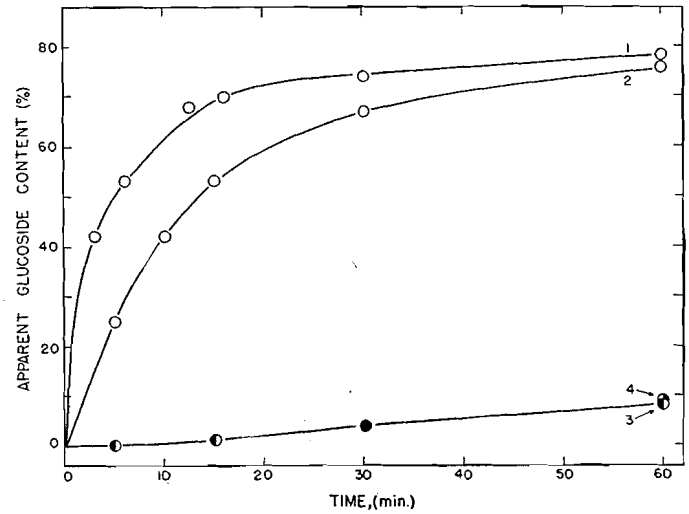



FIG 1. Effect of stannic chloride and methanol concentrations on rate of glucoside formation in benzene at 40°C.

| Curve | β-Glucose pentaacetate | Methanol | Stannic chloride |
|---|---|---|---|
| 1 | 0.1 *M* | 0.1 *M* | 0.1 *M* |
| 2 | 0.1 *M* | 0.1 *M* | 0.05 *M* |
| 3 | 0.1 *M* | 0.2 *M* | 0.05 *M* |
| 4 | 0.1 *M* | 0.1 *M* | 0.025 *M* |

concentration. However, the decrease in the rate of glucoside formation on decreasing the catalyst concentration from 0.05 *M* to 0.025 *M* was much greater than was expected. A marked decrease in the rate of glucoside formation was observed (see Fig. 1) when the methanol concentration was increased from 0.1 *M* to 0.2 *M* and the stannic chloride concentration was kept at 0.05 *M*. Thus, the ratio of methanol to stannic chloride molecules has a profound effect on the reaction rate. This can be due to the lowering of the catalytic efficiency of stannic chloride by neutralization with methanol. Thus, it is apparent that while $SnCl_4.2CH_3OH$ is highly effective in catalyzing the reaction, $SnCl_4.4CH_3OH$

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TABLE I

EFFECT OF METHANOL ON THE REACTION RATE USING 0.1 *M* β-GLUCOSE PENTAACETATE AND 0.05 *M* STANNIC CHLORIDE IN BENZENE AT 40°C.

| Methanol concentration, *M* | Reaction time, min. | % Crude yield of substance isolated | |
|---|---|---|---|
| | | β-glucose pentaacetate | β-methyl glucoside tetraacetate |
| 0.1 | 30 | — | 43 |
| 0.1 | 60 | — | 55 |
| 0.2 | 30 | 76 | — |
| 0.2 | 180 | — | 22 |

is very inefficient. The results listed in Table I are in support of the above kinetic data.

Fig. 2 shows the effect of changes in stannic chloride and methanol concentration on the rate of reaction measured polarimetrically. In each case the trend was toward higher dextrorotation. Since the main product, methyl tetraacetyl-β-D-glucopyranoside, is levorotatory, the trend toward higher dextrorotation indicates that the main reaction was accompanied by side reactions which led to highly dextrorotatory by-products. A study of the product from the reaction of β-glucose pentaacetate (0.1 *M*), methanol (0.1 *M*), and stannic chloride

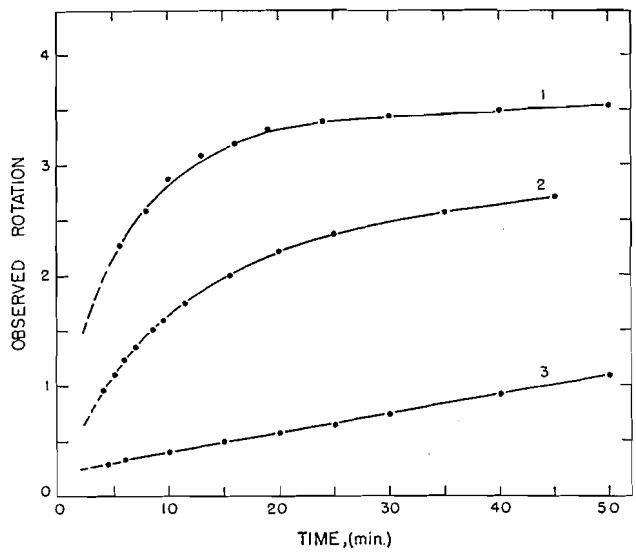



FIG. 2. Effect of stannic chloride and methanol concentrations on the polarimetric rate in benzene at 40°C.

| Curve | β-Glucose pentaacetate | Methanol | Stannic chloride |
|---|---|---|---|
| 1 | 0.1 *M* | 0.1 *M* | 0.1 *M* |
| 2 | 0.1 *M* | 0.1 *M* | 0.05 *M* |
| 3 | 0.1 *M* | 0.2 *M* | 0.05 *M* |

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(0.05 *M*) in benzene at 40°C. for 60 min. was made to establish the nature and extent of the side reactions. Methoxyl estimation indicated the presence of 61.9% methyl tetraacetyl glucoside, and isotopic dilution analysis showed the presence of 60% methyl tetraacetyl-β-D-glucopyranoside. Therefore, it was apparent that little of the α-anomer was formed. A 50% yield of essentially pure methyl tetraacetyl-β-D-glucopyranoside was isolated by crystallization. The reaction product possessed a chlorine content which would correspond to 16.4% acetochloroglucose. The material, $[\alpha]_D$ +33° (chloroform), was treated under the conditions of the Koenigs-Knorr reaction to convert the acetochloroglucose to methyl tetraacetyl-D-glucoside. The resultant product, $[\alpha]_D$ +4.9° (chloroform), possessed a methoxyl content equivalent to 78% methyl glucoside tetraacetate and crystallization gave a 65.5% yield (based on the weight of sirup) of methyl tetraacetyl-β-D-glucopyranoside. The decrease in specific rotation and the increased content of methyl tetraacetyl-β-D-glucopyranoside effected by the Koenigs-Knorr reaction established the presence of about 16% α-acetochloroglucose in the reaction product. Isotopic dilution analysis for α- and β-glucose pentaacetate in the mother liquors from the Koenigs-Knorr reaction indicated the presence of little if any of the α-anomer and about 9% of the starting material in the original reaction product. The analyses therefore accounted for approximately 85% of the reaction product. A consideration of the contributions to the rotation of the product which would be made by the substances identified indicated that the unidentified portion was strongly dextrorotatory. This fraction was undoubtedly composed to some extent of methyl tetraacetyl-α-D-glucopyranoside.

The reaction of β-glucose pentaacetate with phenol in the presence of stannic chloride in boiling benzene solution gave a 40% yield of phenyl tetraacetyl-β-D-glucopyranoside. Bretschneider and Beran (1) have reported the preparation of aryl tetraacetyl-β-D-glucopyranosides by reaction of pentaacetyl-β-D-glucopyranose in benzene solution with uni- or bivalent phenols in the presence of boron trifluoride as catalyst.

Treatment of 0.1 *M* pentaacetyl-α-D-glucopyranose in benzene with equivalent amounts of methanol and stannic chloride for 10 min. at reflux temperature resulted in little reaction and the α-acetate was recovered in 82% yield. Lemieux and Brice (3) have shown that pentaacetyl-α-D-glucopyranose is only very slowly dissociated by stannic chloride. Thus, it was not surprising that the α-pentaacetate was unsuitable as starting material for the synthesis of β-glucosides using stannic chloride as catalyst.

In 1929, Zemplen (10) discovered that treatment of α-octaacetylcellobiose with ferric chloride in chloroform which contained a small amount of ethanol yielded ethyl heptaacetyl-α-cellobioside. Under the same conditions β-octaacetylmaltose yielded ethyl heptaacetyl-α-maltoside. These reactions in all probability possess mechanisms analogous to that proposed above for the preparation of glucosides with stannic chloride as catalyst. However, in the case of the Zemplen reaction, the initial product formed was probably the β-glucoside which subsequently underwent rearrangement to the α-anomer. Thus, the reaction sequence would be analogous to that demonstrated by Lindberg (4)

for the preparation of acetylated α-glucosides by the interaction of α-acetobromoglucose with an alcohol in benzene solution with mercuric acetate as catalyst. Lindberg has shown (4) that the initial product is the β-glucoside which under the prevailing acidic conditions undergoes anomerization. It is noteworthy that Zemplen (11) found that the reaction of acetobromocellobiose with ethanol in benzene solution in the presence of mercuric acetate gave the α-cellobioside heptaacetate only when the ethanol concentration was low. Thus, it is apparent that high ethanol concentrations resulted in a deactivation of the catalyst in a manner similar to that observed for the effect of methanol on stannic chloride.

## EXPERIMENTAL

### *Reagents*

The dry chloroform was prepared immediately before use. Reagent grade chloroform was washed several times with water, dried over calcium chloride, refluxed over phosphorus pentoxide, and distilled. Thiophene-free benzene was dried by distillation. Except where otherwise stated, the stannic chloride was purified by distillation in a dry atmosphere. The methanol was dried by treatment with magnesium and distillation.

### *Methods*

The rotations were measured at room temperature, 23-28°C. The experiments conducted at constant temperature were thermoregulated by means of a bath controlled to within ± 0.1°C. The radioactive samples were converted to barium carbonate for counting at infinite thickness (3). The melting points are corrected.

### *Methyl Tetraacetyl-β-D-glucopyranoside*

Pentaacetyl-β-D-glucopyranose, 9.75 gm., 25 mM., was dissolved in 200 ml. of benzene which contained 0.80 gm., 25 mM., of dry methanol. The mixture was warmed to 40°C. and 50 ml. of a benzene solution which contained 1.5 ml., 3.35 gm., 12.9 mM., of Merck Reagent Grade stannic chloride. After one hour at 40°C., the benzene solution was washed with cold water, then with sodium bicarbonate and twice more with water. After drying over sodium sulphate, the benzene was removed *in vacuo* to yield 9.04 gm. of a partially crystalline sirup. The material was stirred at room temperature with 15 ml. of dry methanol. Crystallization was rapid and after standing at room temperature for several minutes the mixture was kept at − 10°C. for seven hours. Filtration gave 5.12 gm., 57% yield, of crude product, m.p. 98-102.5°C., $[\alpha]_D$ −9.8° in chloroform. Recrystallization from 5 ml. of methanol gave 4.79 gm., 53% yield, of essentially pure methyl tetraacetyl-β-D-glucopyranoside, m.p. 104-105°C., $[\alpha]_D$ −17° (*c*, 2.8 in chloroform).

The following experiment was designed to test the reaction of pentaacetyl-α-D-glucopyranose under conditions where the β-anomer reacted almost completely. A solution of pentaacetyl-α-D-glucopyranose, 2.25 mM., methanol, 2.25 mM., and stannic chloride, 2.25 mM., in 22.5 ml. of benzene was refluxed for 10 min. The product was crystallized from 5 ml. of ethanol to yield 0.72 gm., 82%, of starting material, m.p. 110-111°C.

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The following experiments were performed in an effort to characterize and analyze the products formed on the reaction of 0.1 *M* methanol, 0.1 *M* β-glucose pentaacetate, and 0.05 *M* stannic chloride in benzene at 40°C. for one hour. At zero time, a solution of 20 mM. of β-glucose pentaacetate in 50 ml. of benzene warmed to 40°C. was added to 150 ml. of benzene solution kept at 40°C. which contained 20 mM. of methanol and 10 mM. of stannic chloride. After one hour, the reaction mixture was poured into 200 ml. of cold water. The benzene layer was washed successively with sodium bicarbonate solution and water. The aqueous solutions were extracted successively with chloroform and the chloroform extract was combined with the benzene solution. After drying over sodium sulphate the mixture was diluted to 500 ml. with chloroform. Portions of this solution were examined as follows. A 25 ml. portion was evaporated to sirup, 0.345 gm., $[\alpha]_D$ +33° (*c*, 1.3 in chloroform) which contained 5.3% methoxyl and 1.59% chlorine. These values correspond to 61.9% methyl glucoside tetraacetate and 16.4% acetochloroglucose. A 200 ml. portion was evaporated *in vacuo* to sirup which was crystallized from 7 ml. of methanol at −10°C. to yield 1.45 gm., 50% yield, of crude methyl tetraacetyl-β-D-glucopyranoside, m.p. 101.5-103°C. Methyl tetraacetyl-β-D-glucopyranoside, 100 mgm., labelled in the methoxyl group with carbon-14, 33,100 c.p.m., was added to 20 ml. of the solution. Evaporation gave a sirup which was crystallized from 1 ml. of methanol. Three recrystallizations from methanol gave pure methyl tetraacetyl-β-D-glucopyranoside, m.p. 104.5-105°C., 13,000 c.p.m. The dilution in radioactivity required that the reaction product contain 60% methyl tetraacetyl-β-D-glucopyranoside. A 250 ml. portion of the solution was evaporated to sirup, 3.45 gm., which was dissolved in 50 ml. of dry methanol and treated with 2.0 gm. of silver carbonate at 40°C. for three hours. The product, 2.99 gm., isolated in the usual manner, possessed a specific rotation 4.9° (*c*, 1.7 in chloroform) and a methoxyl group content, 6.69%, which corresponded to 78% methyl glucoside tetraacetate. The material, 2.90 gm., was crystallized from 6 ml. of methanol at − 10°C. to yield 1.90 gm. of crude methyl tetraacetyl-β-D-glucopyranoside, m.p. 102-104°C. The yield was 65.5% on the basis of the weight of sirup crystallized. The substance was recrystallized and the mother liquors were combined with those of the first crystallization. Evaporation gave a sirup which was thoroughly dried. Radioactive α-glucose pentaacetate, 12,900 c.p.m., labelled in the carboxyl of the Cl-acetoxy group, 123.7 mgm., was added to 83.4 mgm. of the sirup. After four recrystallizations from ether–petroleum ether, α-glucose pentaacetate, m.p. 112.3-112.8°C., was obtained which gave 13,000 c.p.m. Thus, the reaction product contained less α-glucose pentaacetate than could be detected by this method. Another sample of the sirup, 498.5 mgm., and 100 mgm. of radioactive β-glucose pentaacetate, 13,900 c.p.m., labelled in the carboxyl of the Cl-acetoxy group were mixed and recrystallized six times from ethanol to yield β-glucose pentaacetate, m.p. 131-131.5°C., 6400 c.p.m. Therefore the Koenigs-Knorr product contained about 9% β-glucose pentaacetate. This value should be in fairly good agreement with the amount in the original reaction product.

The experiments which are summarized in Table I were carried out in the

usual manner. The yields are based on crude products which were identified by mixed melting point determination and by further purification.

The following experiments were carried out to determine the effect of prolonged reaction time and high stannic chloride concentration on the yield of methyl tetraacetyl-β-D-glucopyranoside. Pentaacetyl-β-D-glucopyranose, 1.17 gm., 3 mM., was dissolved in 30 ml. of chloroform which contained 0.096 gm., 3 mM., of methanol and 1.56 gm., 6 mM., of stannic chloride. The solutions were refluxed for the various times given below and the products, isolated in the usual manner, were dissolved in 1.5 ml. of methanol for crystallization at −10°C. for several hours. The yield of crude methyl tetraacetyl-β-D-glucopyranoside obtained after a reflux period of five minutes was 0.60 gm., 55%, m.p. 100-102°C.; after 15 min., 0.65 gm., 60%, m.p. 100-102°C.; after 30 min., 0.57 gm., 53%, m.p. 100-102°C.; and after 60 min., 0.44 gm., 41%, m.p. 99-101.5°C.

*Phenyl Tetraacetyl-β-D-glucopyranoside*

Pentaacetyl-β-D-glucopyranose, 7.80 gm., 20 mM., was added to a solution of 3.76 gm., 40 mM., phenol and 2 ml., approximately 17.1 mM., of Merck Reagent Grade stannic chloride. The solution was refluxed for 10 min., washed three times with cold water, three times with saturated aqueous bicarbonate solution, once more with water, and dried over sodium sulphate. Evaporation *in vacuo* yielded a sirup which was stirred at room temperature with 12 ml. of ethanol. Crystallization began immediately. After cooling overnight at −10°C., the crystalline product was collected by filtration and washed with cold ethanol. The yield of crude phenyl tetraacetyl-β-D-glucopyranoside, m.p. 124-125°C., $[\alpha]_D$ −19.9° (*c*, 2.4 in chloroform), was 3.36 gm. or 40%. The pure compound melts at 125-126°C., $[\alpha]_D$ −22.5° (*c*, 2 in chloroform) (7).

*Determination of Reaction Rates*

The volumes of 0.45 *M* solutions of methanol and stannic chloride in benzene required to give the desired concentrations in the final reaction mixture were measured at room temperature, added to a 50 ml. flask and the volume adjusted to 30 ml. by the addition of benzene. The solution was warmed to 40°C. and the desired amount of β-glucose pentaacetate in 15 ml. of benzene solution warmed to 40°C. was added at zero time. After shaking, the solution was either added to a water-jacketed 2 dm. polarimeter tube kept at 40°C. for polarimetric rate determination or 5 ml. aliquots of the reaction mixture were distributed by means of syringe among 10 ml. glass-stoppered tubes kept at 40°C. After each time interval, the reaction was stopped by pouring the contents of a tube into 50 ml. of water and shaking the mixture vigorously. The product was isolated in the usual manner and dried *in vacuo* at 60°C. for one day before analysis.

The following procedure was devised as a means for the rapid estimation of the methyl glucoside content of a sample. Samples of the sirup, equivalent in reducing power to 3-5 mgm. of β-glucose pentaacetate, were added to 2.4 × 20 cm. test tubes. The samples were dissolved in 2 ml. of methanol and 3 ml. of 0.1 *N* aqueous sodium hydroxide and 5 ml. of the Somogyi reagent (9) containing potassium iodate was added. The tubes were heated on the steam bath for 15

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min., cooled, and the iodine liberated on the addition of 1 ml. of 2.5% aqueous potassium iodide and 1.5 ml. of 0.2 *N* aqueous sulphuric acid was determined by titration (9). Different quantities of β-glucose pentaacetate were treated in the same manner and a pair of reagent blanks were prepared for each batch of runs. Within the limits of 2-7 mgm. of β-glucose pentaacetate, direct proportionality prevailed between the amounts of β-glucose pentaacetate and the amounts of copper reduced. Since the reaction product was not composed entirely of acetylated methyl glucoside and glucose pentaacetate, it was not possible to calculate the percentage of methyl glucoside in the sample from the reducing value. However, the apparent methyl glucoside tetraacetate content, which was calculated on the basis of the assumption that the reducing power measured for a reaction product was derived from glucose pentaacetate and the remainder was methyl glucoside tetraacetate, was checked in several instances by methoxyl estimation and the agreement was usually well within ±3%. Acetochloroglucose was a by-product in the glucoside synthesis. It has been suggested (2) that alkaline hydrolysis of this substance may lead to the formation of levoglucosan. This may account for the apparent glucoside contents being usually somewhat higher than the methyl glucoside content determined by methoxyl group estimation.

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# COMPARISON OF METHOXYMERCURIALS DERIVED FROM CYCLOPENTENE AND CYCLOHEXENE[1]

By A. G. Brook, R. Donovan, and George F Wright

ABSTRACT

The α- and β-2-methoxycyclopentylmercuric chlorides, bromides, and iodides have been prepared. The X-ray powder patterns, dipole moments, and thermal analyses among each series have been compared with the homologous methoxycyclohexyl derivatives. In both of the series the dipole moments of the β-diastereomers are greater than those of the corresponding α-isomers. In both series the α- and β-diastereomers seem to comprise isostructural series among the three halides. This isostructural relationship seems to be reflected in the melting point composition diagrams.

The three diastereomeric pairs of 2-methoxycyclopentylmercuric chlorides, bromides, and iodides have been prepared. The α-diastereomer of each is, by definition, the one obtained by treatment of cyclopentene with mercuric acetate and methanol, followed by treatment with sodium chloride, bromide, or iodide after the formation of the 2-methoxycyclopentylmercuric acetate is complete. The β-diastereomers have each been obtained by treatment of the α modification with hydrazine hydrate (5). Cautious addition of the requisite halogen acid to the diastereomeric mixtures thus obtained has served to decompose the α-isomer much more rapidly than the β form. Therefore the β-diastereomers are more stable toward halogen acids than the α-mercurials, and thus resemble the homologous group which has been obtained from cyclohexene (6, 4, 2).

It has been reported (1) that the two diastereomeric sets of crystalline 2-methoxycyclohexylmercuric halides are isostructural among each set. The powder diagrams have now been determined (Table I) for these α and β series; they do not contradict the isostructural designation. Of course one would expect that mixture melting points between the α and β series would be reliable, since the two series are not mutually isostructural. On the other hand, mixture melting points within each series would be suspect as criteria of identity. In the same sense one might doubt the reliability of melting point as a criterion of purity if the compound were one of an isostructural series.

Melting point composition diagrams among members of each series have been determined (Fig. 1). These thermal analyses confirm the unreliability of melting points as criteria of purity and identity, especially among the α-2-methoxycyclohexylmercuric halides. Among the β series there is more evidence of eutectic composition (especially between β-2-methoxycyclohexylmercuric chloride and bromide), but the eutectic lowering does not extend over the entire range of compositions.

The similarities among the powder diagrams of the methoxycyclohexylmercurials are also found among those shown in Table II for the methoxycyclopentylmercurials. Also similar (Fig. 2) are the melting point composition diagrams. In some instances (αCl vs. αBr, βBr vs. βI, βCl vs. βI) there is some

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*Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.*



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TABLE I*

POWDER PATTERNS USING Cu, $K_\alpha$, Ni-FILTERED RADIATION (1.5405 Å)
2-METHOXYCYCLOHEXYLMERCURIC HALIDES

| α | | | | | | β | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Chloride | | Bromide | | Iodide | | Chloride | | Bromide | | Iodide | |
| d (Å) | $I/I_1$ | d (Å) | $I/I_1$ | d (Å) | $I/I_1$ | d (Å) | $I/I_1$ | d (Å) | $I/I_1$ | d (Å) | $I/I_1$ |
| 10.52 | 1.0 | 10.64 | 1.0 | 10.52 | 1.0 | 9.50 | 1.0 | 9.60 | 1.0 | 9.50 | 1.0 |
| 7.25 | 0.2 | 7.49 | 0.3 | 7.43 | 0.2 | 6.36 | 0.8 | 7.89 | 0.1 | 8.04 | 0.3 |
| 5.98 | 0.1 | 6.80 | 0.1 | 5.53 | 0.3 | 5.90 | 0.3 | 7.43 | 0.8 | 5.90 | 0.2 |
| 5.71 | 0.2 | 5.78 | 0.2 | 5.24 | 0.2 | 5.50 | 0.2 | 5.90 | 0.4 | 4.79 | 0.2 |
| 5.47 | 1.0 | 5.57 | 0.7 | 4.77 | 0.3 | 5.24 | 0.8 | 5.57 | 0.3 | 4.48 | 0.2 |
| 5.18 | 0.4 | 5.43 | 0.2 | 4.00 | 1.0 | 4.72 | 0.3 | 5.30 | 0.8 | 3.98 | 0.6 |
| 4.84 | 0.4 | 5.27 | 0.3 | 3.77 | 0.5 | 4.48 | 0.3 | 4.74 | 0.4 | 3.72 | 0.6 |
| 4.19 | 0.2 | 4.87 | 0.3 | 3.52 | 0.9 | 4.019 | 0.5 | 4.50 | 0.5 | 3.56 | 0.1 |
| 3.91 | 1.0 | 4.19 | 0.1 | 3.41 | 0.5 | 3.914 | 0.2 | 4.02 | 0.8 | 3.45 | 0.3 |
| 3.75 | 0.1 | 3.98 | 0.7 | 3.19 | 0.3 | 3.782 | 0.1 | 3.93 | 0.1 | 3.18 | 0.5 |
| 3.66 | 0.4 | 3.735 | 0.5 | 3.025 | 0.5 | 3.674 | 0.2 | 3.80 | 0.2 | 3.03 | 0.5 |
| 3.56 | 0.1 | 3.65 | 0.2 | 2.966 | 0.1 | 3.545 | 0.1 | 3.72 | 0.3 | 2.89 | 0.4 |
| 3.41 | 0.2 | 3.490 | 0.5 | 2.910 | 0.5 | 3.398 | 0.3 | 3.56 | 0.2 | 2.79 | 0.4 |
| 3.35 | 0.2 | 3.398 | 0.5 | 2.882 | 0.5 | 3.066 | 0.4 | 3.40 | 0.4 | 2.67 | 0.4 |
| 3.28 | 0.1 | 3.324 | 0.1 | 2.769 | 0.1 | 2.957 | 0.1 | 3.206 | 0.8 | 2.53 | 0.1 |
| 3.19 | 0.2 | 3.206 | 0.2 | 2.554 | 0.2 | 2.846 | 0.1 | 3.108 | 0.1 | 2.31 | 0.3 |
| 3.129 | 0.1 | 3.045 | 0.3 | 2.526 | 0.2 | 2.619 | 0.2 | 3.045 | 0.1 | 2.20 | 0.3 |
| 3.025 | 0.2 | 2.986 | 0.3 | 2.421 | 0.5 | 2.540 | 0.1 | 2.986 | 0.1 | 2.10 | 0.5 |
| 2.986 | 0.2 | 2.900 | 0.7 | 2.348 | 0.5 | 2.506 | 0.1 | 2.947 | 0.1 | 1.97 | 0.1 |
| 2.919 | 0.2 | 2.769 | 0.1 | 2.302 | 0.2 | 2.330 | 0.1 | 2.855 | 0.2 | 1.88 | 0.1 |
| 2.855 | 0.8 | 2.680 | 0.1 | 2.205 | 0.2 | 2.274 | 0.1 | 2.786 | 0.1 | 1.82 | 0.5 |
| 2.786 | 0.1 | 2.533 | 0.3 | 2.164 | 0.2 | 2.220 | 0.2 | 2.627 | 0.3 | 1.80 | 0.1 |
| 2.728 | 0.1 | 2.493 | 0.1 | 2.074 | 0.1 | 2.199 | 0.2 | 2.533 | 0.2 | 1.74 | 0.1 |
| 2.642 | 0.1 | 2.440 | 0.1 | 2.000 | 0.2 | 2.056 | 0.1 | 2.354 | 0.2 | 1.67 | 0.1 |
| 2.519 | 0.2 | 2.340 | 0.5 | 1.905 | 0.1 | 1.955 | 0.1 | 2.302 | 0.1 | | |
| 2.466 | 0.1 | 2.268 | 0.1 | 1.850 | 0.1 | 1.796 | 0.4 | 2.236 | 0.4 | | |
| 2.404 | 0.2 | 2.210 | 0.1 | | | 1.685 | 0.1 | 2.070 | 0.2 | | |
| 2.336 | 0.6 | 2.092 | 0.2 | | | 1.520 | 0.1 | 1.812 | 0.3 | | |
| 2.307 | 0.1 | 1.979 | 0.2 | | | | | | | | |
| 2.257 | 0.1 | 1.928 | 0.1 | | | | | | | | |
| 2.189 | 0.2 | 1.890 | 0.1 | | | | | | | | |
| 2.102 | 0.1 | 1.850 | 0.1 | | | | | | | | |
| 1.987 | 0.2 | 1.809 | 0.1 | | | | | | | | |
| 1.975 | 0.2 | | | | | | | | | | |
| 1.935 | 0.3 | | | | | | | | | | |
| 1.819 | 0.1 | | | | | | | | | | |
| 1.679 | 0.1 | | | | | | | | | | |
| 1.614 | 0.1 | | | | | | | | | | |

**Intensities determined visually. Largest d value measurable with equipment, about 17Å.*

evidence of eutectic composition. However the chance that these eutectic lowerings would be apparent in a mixture melting point determination is not good. Among the other three thermal analyses (αBr vs. αI, αCl vs. αI, and βCl vs. βBr) there is no apparent eutectic formation. In the extreme case (βCl vs. βBr) the presence of chloromercurial as a contaminant in the bromomercurial could not be detected by melting point determination.

Rough determinations of the dipole moments of the 12 oxymercurials are recorded in Table III. It may be seen that within each series of halides the moment increases in the order $I \gtrsim Cl < Br$. It may also be observed that in every instance, the moment of the α-compound is lower than that of its β-diastereomer. This seems not to be related to the fact that the α-diastereomers are

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TABLE II*

POWDER PATTERNS USING Cu, $K_\alpha$, Ni-FILTERED RADIATION (1.5405 Å)
2-METHOXYCYCLOPENTYLMERCURIC HALIDES

| α | | | | | | β | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Chloride | | Bromide | | Iodide | | Chloride | | Bromide | | Iodide | |
| $d$ (Å) | $I/I_1$ | $d$ (Å) | $I/I_1$ | $d$ (Å) | $I/I_1$ | $d$ (Å) | $I/I_1$ | $d$ (Å) | $I/I_1$ | $d$ (Å) | $I/I_1$ |
| $14.3_2$ | <.1 | $12.3_5$ | 1.0 | $12.3_0$ | 1.0 | $10.0_2$ | 0.1 | $10.7_3$ | 0.1 | $10.1_6$ | 0.1 |
| $12.7_8$ | 1.0 | 9.41 | 0.5 | 9.48 | 0.5 | 9.01 | 1.0 | $10.1_1$ | 0.1 | 9.33 | 1.0 |
| 9.65 | 0.5 | 8.556 | 0.7 | 9.05 | 0.8 | 6.910 | 0.1 | 9.00 | 1.0 | 5.387 | 0.5 |
| 7.412 | 0.3 | 6.154 | 0.2 | 6.964 | 0.4 | 5.760 | 0.6 | 6.986 | 0.5 | 5.151 | 0.2 |
| 6.463 | 0.5 | 5.705 | 0.4 | 6.477 | 0.4 | 5.497 | 0.5 | 6.544 | 0.3 | 4.643 | 0.4 |
| 5.672 | 0.5 | 4.891 | 0.3 | 6.133 | 0.3 | 5.108 | 0.1 | 5.855 | 0.8 | 4.275 | 0.5 |
| 5.181 | 0.4 | 4.705 | 0.5 | 5.948 | 0.3 | 4.828 | 0.5 | 5.562 | 0.7 | 4.103 | 0.2 |
| 4.790 | 0.5 | 4.371 | 0.4 | 5.668 | 0.3 | 4.626 | 0.4 | 4.878 | 0.5 | 3.879 | 0.7 |
| 4.521 | 0.6 | 4.082 | 0.6 | 4.761 | 0.6 | 4.465 | 0.5 | 4.672 | 0.4 | 3.517 | 0.7 |
| 4.227 | 0.7 | 3.603 | 0.5 | 4.037 | 0.7 | 4.135 | 0.3 | 4.467 | 0.3 | 3.437 | 0.3 |
| 4.051 | 0.4 | 3.454 | 0.7 | 3.882 | 0.4 | 3.869 | 0.5 | 4.170 | 0.2 | 3.289 | 0.2 |
| 3.818 | 0.5 | 3.373 | 0.6 | 3.751 | 0.7 | 3.784 | 0.6 | 3.955 | 0.6 | 3.123 | 0.5 |
| 3.651 | 0.4 | 3.215 | 0.4 | 3.590 | 0.6 | 3.712 | 0.4 | 3.865 | 0.8 | 3.033 | 0.6 |
| 3.490 | 0.4 | 3.137 | 0.4 | 3.332 | 0.4 | 3.546 | 0.5 | 3.612 | 0.6 | 2.970 | 0.2 |
| 3.273 | 0.8 | 2.936 | 0.4 | 3.257 | 0.5 | 3.435 | 0.4 | 3.500 | 0.5 | 2.803 | 0.4 |
| 3.127 | 0.3 | 2.871 | 0.3 | 3.172 | 0.5 | 3.250 | 0.4 | 3.296 | 0.5 | 2.688 | 0.4 |
| 3.068 | 0.3 | 2.767 | 0.5 | 3.067 | 0.4 | 3.131 | 0.4 | 3.171 | 0.4 | 2.574 | 0.5 |
| 2.901 | 0.3 | 2.650 | 0.4 | 3.006 | 0.1 | 3.025 | 0.3 | 3.072 | 0.3 | 2.377 | 0.5 |
| 2.837 | 0.3 | 2.554 | 0.4 | 2.840 | 0.4 | 2.948 | 0.5 | 2.980 | 0.6 | 2.311 | 0.3 |
| 2.759 | 0.4 | 2.438 | 0.5 | 2.760 | 0.1 | 2.844 | 0.5 | 2.890 | 0.7 | 2.255 | 0.5 |
| 2.641 | 0.6 | 2.340 | 0.3 | 2.711 | 0.3 | 2.749 | 0.5 | 2.771 | 0.7 | 2.184 | 0.1 |
| 2.522 | 0.5 | 2.298 | 0.3 | 2.663 | 0.3 | 2.634 | 0.3 | 2.659 | 0.2 | 2.118 | 0.4 |
| 2.435 | 0.5 | 2.254 | 0.2 | 2.609 | 0.3 | 2.564 | 0.3 | 2.592 | 0.2 | 2.072 | 0.1 |
| 2.359 | 0.1 | 2.195 | 0.2 | 2.538 | 0.4 | 2.430 | 0.1 | 2.438 | 0.5 | 2.032 | 0.3 |
| 2.250 | 0.1 | 2.133 | 0.2 | 2.470 | 0.2 | 2.409 | 0.1 | 2.342 | 0.8 | 1.936 | 0.4 |
| 2.170 | 0.1 | 2.077 | 0.4 | 2.400 | 0.2 | 2.386 | 0.2 | 2.203 | 0.2 | 1.854 | 0.5 |
| 2.104 | 0.2 | 1.977 | 0.3 | 2.330 | 0.1 | 2.314 | 0.5 | 2.140 | 0.6 | 1.794 | 0.3 |
| 2.033 | 0.6 | 1.789 | 0.5 | 2.294 | 0.1 | 2.131 | 0.5 | 2.085 | 0.5 | 1.753 | 0.1 |
| 1.979 | 0.1 | 1.682 | 0.1 | 2.255 | 0.1 | 2.099 | 0.3 | 2.045 | 0.1 | 1.719 | 0.3 |
| 1.930 | 0.2 | 1.614 | 0.2 | 2.220 | 0.1 | 2.075 | 0.4 | 1.980 | 0.1 | 1.667 | 0.1 |
| 1.872 | 0.2 | 1.574 | 0.2 | 2.169 | 0.2 | 2.004 | 0.2 | 1.927 | 0.3 | 1.640 | 0.1 |
| 1.843 | 0.1 | 1.496 | 0.1 | 2.043 | 0.2 | 1.955 | 0.2 | 1.895 | 0.2 | 1.526 | 0.3 |
| 1.818 | 0.2 | 1.420 | 0.1 | 1.967 | 0.1 | 1.900 | 0.2 | 1.851 | 0.2 | 1.493 | 0.1 |
| 1.678 | 0.2 | | | 1.912 | 0.2 | 1.883 | 0.1 | 1.805 | 0.2 | 1.452 | 0.1 |
| 1.646 | 0.1 | | | 1.857 | 0.1 | 1.819 | 0.1 | 1.771 | 0.3 | 1.415 | 0.2 |
| 1.613 | 0.2 | | | 1.807 | 0.1 | 1.760 | 0.2 | 1.738 | 0.3 | 1.360 | 0.1 |
| 1.568 | 0.1 | | | 1.746 | 0.1 | 1.732 | 0.2 | 1.722 | 0.1 | | |
| 1.512 | 0.1 | | | | | 1.704 | 0.1 | 1.677 | 0.1 | | |
| 1.443 | 0.1 | | | | | 1.617 | <.1 | 1.650 | 0.1 | | |
| 1.404 | 0.1 | | | | | 1.591 | <.1 | 1.626 | 0.1 | | |
| 1.363 | 0.1 | | | | | 1.515 | 0.1 | 1.598 | 0.1 | | |
| | | | | | | 1.483 | <.1 | 1.568 | 0.2 | | |
| | | | | | | 1.455 | 0.1 | 1.527 | 0.3 | | |
| | | | | | | 1.406 | <.1 | 1.481 | 0.1 | | |
| | | | | | | 1.384 | <.1 | 1.463 | 0.2 | | |
| | | | | | | 1.350 | 0.1 | 1.442 | 0.1 | | |
| | | | | | | 1.317 | 0.1 | 1.424 | 0.1 | | |
| | | | | | | | | 1.388 | 0.1 | | |
| | | | | | | | | 1.329 | 0.1 | | |
| | | | | | | | | 1.310 | 0.1 | | |
| | | | | | | | | 1.277 | 0.1 | | |
| | | | | | | | | 1.252 | 0.1 | | |
| | | | | | | | | 1.190 | 0.1 | | |
| | | | | | | | | 1.153 | 0.1 | | |

*Intensities determined visually. Largest $d$ value measurable with equipment about 17Å.

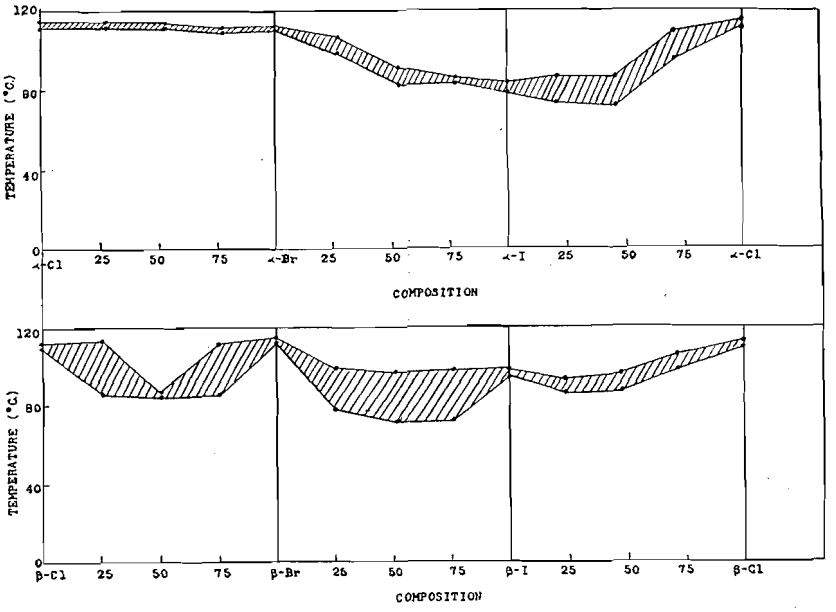



Fig. 1. Mixed melting ranges of the 1-methoxy-2-halomercuricyclohexanes.

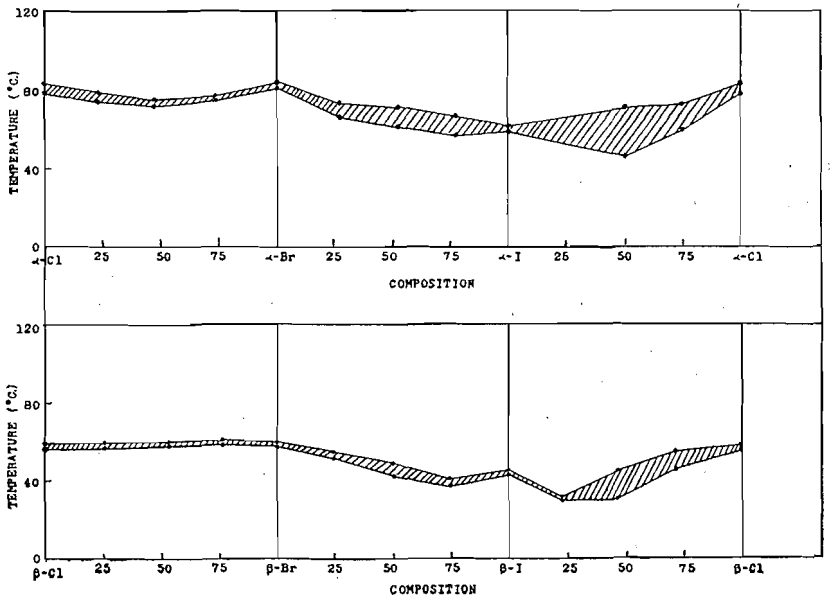



Fig. 2. Mixed melting ranges of the 1-methoxy-2-halomercuricyclopentanes.

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TABLE III

DIPOLE MOMENTS OF MERCURIALS (± 0.2)

| 2-Methoxycyclopentylmercuric halides | | | | 2-Methoxycyclohexylmercuric halides | | | |
|---|---|---|---|---|---|---|---|
| α | | β | | α | | β | |
| Halide | μ | Halide | μ | Halide | μ | Halide | μ |
| Cl | 2.9 | Cl | 4.1 | Cl | 3.8 | Cl | >4 |
| Br | 3.4 | Br | 4.7 | Br | 4.5 | Br | >4 |
| I | 3.2 | I | 3.9 | I | 3.7 | I | >4 |

derived from cyclohexene and cyclopentene, which resemble *cis*-geoisomeric alkenes in a stereochemical sense. Thus the moments of the α-2-methoxy-1, 2-diphenylethylmercuric halides derived from *cis*-stilbene (5) are higher (Cl, 4.3; Br, 4.6; I, 4.0) than the moments of the β-diastereomers (Cl, 3.3; Br, 3.6) derived from *trans*-stilbene. However one correlation among the mercurials derived from cyclohexene, cyclopentene, and stilbene can be drawn, namely, that the oxymercurial with the lowest dipole moment is the one most easily split to the parent alkene by use of hydrochloric acid.

## EXPERIMENTAL

### *α-2-Methoxycyclopentylmercuric Chloride*

A suspension of 89.4 gm. (0.28 mole) of mercuric acetate in 20 ml. (0.226 mole) of cyclopentene (b.p. 44-44.8°) and 400 ml. of methanol became homogeneous after it was stirred for two minutes at 25°C. Titration of several aliquots showed that reaction was complete. After 12 hr. the solution was treated with 78 ml. (0.195 mole) of 10% aqueous sodium hydroxide and the yellow turbidity was removed by filtration. The filtrate was treated with an excess of 5% aqueous sodium chloride. The precipitate (64 gm., 88%), m.p. 76-77°C., was crystallized from 195 ml. of hot 95% ethanol, using Nuchar, m.p. 83.3-83.7°C. It may also be crystallized from butanone-2 (4 ml. per gm.). Calc. for $C_6H_{11}OHgCl$: C, 21.5; H, 3.29. Found: C, 21.3; H, 3.34.

### *α-2-Methoxycyclopentylmercuric Bromide*

An identical procedure using sodium bromide as the precipitant gave a 90% yield of crude product, m.p. 75°C., which was crystallized from hot 95% ethanol (4 ml. per gm.), m.p. 82-82.3°C. Calc. for $C_6H_{11}OHgBr$: C, 19.0; H, 2.93. Found: C, 18.8; H, 2.85.

### *α-2-Methoxycyclopentylmercuric Iodide*

A mixture of 44.7 gm. (0.14 mole) of mercuric acetate, 10 ml. (0.14 mole) of crude cyclopentene and 200 ml. of methanol was allowed to react for seven hours. Then 56 ml. (0.14 mole) of 10% aqueous sodium hydroxide was added to the stirred solution during 15 min. The grayish-yellow precipitate was filtered off, the filtrate being received into a stirred solution of 42 gm. (0.28 mole) of sodium iodide in 300 ml. of water which was maintained at 20°. When the substance is already available, it is well to seed at this point. The crude mercurial was filtered off, 38.5 gm. (65%), m.p. 56°C. This mercurial was crystallized

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from hot methanol (5 ml. per gm.), m.p. 60.5-61°C. Calc. for $C_6H_{11}OHgI$: C, 16.9; H, 2.61. Found: C, 17.0; H, 2.73.

*β-2-Methoxycyclopentylmercuric Chloride*

A solution of 16.7 gm. (0.05 mole) of the α-diastereomer in 80 ml. (0.1 mole) of 5% aqueous sodium hydroxide was heated to incipient boiling. During the next hour, 0.5 ml. (0.008 mole) of 85% hydrazine hydrate was added. The mixture was refluxed for one hour, then cooled and 3.62 gm. (0.0175 atom) of metallic mercury was separated. The aqueous phase was filtered, treated with excess of sodium chloride, and then with gaseous carbon dioxide. The precipitated oil solidified when it was chilled, 9.62 gm., m.p. 30-35°C. This was dissolved in 30 ml. of methanol, and 1.3 ml. (0.013 mole) of concentrated hydrochloric acid for exactly one minute. The whole was poured quickly into 20 ml. (0.05 mole) of 10% alkali. After an hour the mercuric oxide was filtered or centrifuged, and the filtrate was treated with gaseous carbon dioxide. The precipitate (6.1 gm., 40%), m.p. 56-57°C., was crystallized from hot methanol (3 ml. per gm.) with Nuchar, m.p. 59-59.5°C. A mixture melting point with the α-diastereomer was depressed. Calc. for $C_6H_{11}OHgCl$: C, 21.5; H, 3.29. Found: C, 21.7; H, 3.43.

*β-2-Methoxycyclopentylmercuric Bromide*

The residues from crystallization of the α-diastereomer weighed 20 gm. Calculating this residue as α-diastereomer (0.052 mole), it was suspended in 100 ml. (0.125 mole) of 5% aqueous sodium hydroxide and boiled while 0.72 ml. (0.01 mole) of 85% hydrazine hydrate was added during three hours. After cooling, diethyl ether was added and the mercury was separated. Gaseous carbon dioxide was bubbled through the combined etherous and aqueous layers, and the oil which precipitated was dissolved in alkali-washed chloroform. This solution was filtered and evaporated, leaving 8 gm. of oil. The oil was dissolved in 25 ml. of methanol and was treated with 1.5 ml. of 48% hydrobromic acid for exactly one minute at 20°C. The whole was poured into 100 ml. of 5% aqueous sodium hydroxide. This solution was ice-cooled while it was neutralized with hydrobromic acid until the mercuric oxide redissolved. The crude product, m.p. *ca.* 50°C., weighed 5.34 gm. (26%). It was redissolved in 200 ml. of 3% aqueous sodium hydroxide, treated with acetylene black, and acidified with gaseous carbon dioxide. The precipitate (3.95 gm., m.p. 56-58°C.) was crystallized from hot methanol (3 ml. per gm.) with Nuchar, m.p. 59.5-60°C. A mixture melting point with the α-diastereomer was lowered to 37°. Calc. for $C_6H_{11}OHgBr$: C, 19.0; H, 2.93. Found: C, 19.2; H, 2.99.

*β-2-Methoxycyclopentylmercuric Iodide*

A suspension of 13.8 gm. (0.0324 mole) of α-2-methoxycyclopentylmercuric iodide in 80 ml. (0.01 mole) of 5% aqueous sodium hydroxide was heated to boiling while 0.32 ml. (0.051 mole) of 85% hydrazine hydrate was added during 10 min. The suspension was then boiled for one hour to decrease the volume to half that of the original mixture. After cooling and addition of diethyl ether the metallic mercury was separated. The etherous layer was evaporated and the residue was dissolved in 30 ml. of methanol. This solution was heated with 4.7 gm. (0.0015

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mole) of mercuric acetate for 30 min. The methanol was evaporated during this time; the residue was dissolved in water and chloroform. The chloroform layer was evaporated. Most of the residue dissolved in 75 ml. of methanol, and this solution at 20°C. was treated for exactly one minute with 1 ml. of 47% hydriodic acid. The whole was then quickly poured into 20 ml. (0.05 mole) of aqueous sodium hydroxide. The cloudy suspension was saturated with gaseous carbon dioxide. The precipitated oil was dissolved in chloroform, and this solution was filtered to remove mercuric iodide; the filtrate was vacuum-evaporated. The residual oil was dissolved in 10 ml. of ether, chilled to −20°C., and filtered cold to remove 2.50 gm. (18%) of β-diastereomer, m.p. 42-43°C. This product was crystallized from methanol (7 ml. per gm.), m.p. 44.5-45°C. If the crude product has a melting point lower than 40°, it should be re-treated with hydriodic acid rather than purified by crystallization. A mixture melting point of the α- and β-diastereomers was lowered below 25°C. Calc. for $C_6H_{11}OHgI$: C, 16.9; H, 2.84. Found: C, 16.5; H, 2.80.

*Determinations of Dipole Moments*

The dielectric constants of the methoxymercurials were determined in benzene solution ($\epsilon = 2.26$) or dioxane ($\epsilon = 2.27$). Comparable determinations of α-2-methoxycyclopentylmercuric chloride showed identical results within the limits of our precision with the two solvents. The determinations were made with a type 3A dielectric constant meter (Yellow Springs Instrument Co., Yellow Springs, Ohio) at 20° ± 0.05°C. This crude instrument could be used only because the dielectric constants of these mercurials seem to be independent of concentration in the weight fraction range 0.1-0.005-0.0025. The dielectric constants at these three concentrations extrapolated to the constants of the pure solvent ± 0.02. The dipole moments were calculated by the method of Halverstadt and Kumler (3), the atomic and electronic polarizations having been estimated from the refractive indices of the solutions.

*Thermal Analyses*

Thermal analyses were carried out by capillary melting point with a heating rate of 1° per three minutes in a metal block. Three accurately weighed mixtures of each pair of components were dissolved in dioxane and the solutions were evaporated in order to obtain the intermediate compositions in each analysis. The appearance of first liquid and the disappearance of the last crystal are recorded in Figs. 1 and 2.

ACKNOWLEDGMENTS

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# *LYCOPODIUM* ALKALOIDS

## II. SOME REACTIONS OF THE PERMANGANATE OXIDATION PRODUCT OF ANNOTININE[1]

By David B. MacLean and H. C. Prime[2]

ABSTRACT

The permanganate oxidation product of annotinine is shown to be an amide that contains the ether ring of annotinine still intact. The Clemmensen reduction of this compound to the saturated base, $C_{16}H_{23}O_2N$, was re-examined. A number of intermediates were isolated from the system and these were also prepared from the oxidation product by other methods. Analogous reactions of annotinine chlorohydrin were also studied. From these results suggestions are presented regarding the size of the ether ring and its position relative to the nitrogen atom.

Annotinine, $C_{16}H_{21}O_3N$, is one of the major alkaloids isolated from the *Lycopodium* group. Manske and Marion (2) have reported a number of reactions of the base from which a lactone ring, an ether bridge, and a tertiary nitrogen atom were established as the reactive functional groups in the molecule. One of the reactions reported was an oxidation of annotinine with permanganate to the compound $C_{16}H_{19}O_4N$. This compound, hereinafter referred to as the oxidation product, was reported to be an amine, and because of its conversion by Clemmensen reduction to the saturated base, $C_{16}H_{23}O_2N$, it was suggested that it contained two carbonyl groups formed by oxidation at both ends of an ether bridge. Because of the lack of color and general stability of the compound they suggested that the two carbonyl groups were either 1, 4 or 1, 5, and by inference, therefore, established the ether ring as five or six membered. A re-examination of the oxidation reaction revealed that the product was not a base but an amide. Therefore another interpretation of these results was necessary and the present work was designed to this end.

An amide linkage in the oxidation product of annotinine could be formed by the method outlined above. This would fix one end of the ether bridge adjacent to the nitrogen atom. Alternatively, this could be achieved by oxidation of a methylene group adjacent to nitrogen. In the second case the original ether ring would still be present in the oxidation product. The following results indicate that the latter alternative applies.

The oxidation product readily undergoes reaction with concentrated aqueous hydrochloric acid to give a chlorohydrin, $C_{16}H_{20}O_4NCl$ (I) which on prolonged refluxing with the same reagent yields the dehydration product of this chlorohydrin, $C_{16}H_{18}O_3NCl$ (II). II may be prepared in good yield by dehydration of I with phosphorus oxychloride. The formation of I apparently proceeds through fission of an oxide ring with the formation of an hydroxyl and a chloro group.

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*Contribution from the Department of Chemical and Metallurgical Engineering, Nova Scotia Technical College, Halifax, Nova Scotia, with financial assistance from the National Research Council of Canada. A part of this work was taken from the thesis of H. C. Prime submitted to the Department of Graduate Studies in partial fulfillment of the requirements for the Degree of Master of Engineering.*

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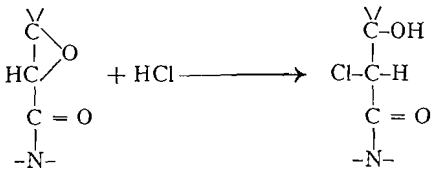
Upon treatment of these compounds with dilute permanganate, II reacted readily but I remained unaffected. This confirms the unsaturation in II and suggests that the hydroxyl group in I is tertiary. I underwent ring closure to reform the oxidation product on refluxing with sodium bicarbonate in acetone. Treatment of I with hydrogen over Adams catalyst resulted in the isolation of two products, $C_{16}H_{21}O_4N$ (III) and $C_{16}H_{21}O_3N$ (IV). In the formation of III the chloro group was eliminated by hydrogenolysis, and in the formation of IV both the chloro and hydroxyl groups were eliminated. A similar treatment of II yielded IV as the sole product, formed by saturation of the double bond and hydrogenolysis of the chloro group.

Both III and IV were resistant to dilute permanganate indicating that both were saturated, and that the hydroxyl group in III was probably tertiary. III underwent dehydration on refluxing with phosphorus oxychloride to yield $C_{16}H_{19}O_3N$ (V). However, III was virtually unaffected after prolonged boiling with concentrated hydrochloric acid. The presence of a double bond in V is indicated by its reaction with permanganate. III was also recovered unchanged after treatment with hydrogen over Adams catalyst indicating that removal of hydroxyl in the similar treatment of I was probably contingent upon the presence of the chloro group.

The reactions of I contrast with those of annotinine chlorohydrin (2). This compound underwent no reaction upon similar treatment with sodium bicarbonate in acetone, concentrated hydrochloric acid, phosphorus oxychloride, and hydrogen over Adams catalyst. Recovery of the starting material was quantitative in three of the four cases. The exception was the treatment with phosphorus oxychloride where the only product recovered was the starting material. There was, however, a considerable loss presumably due to a side reaction involving the lactone ring.

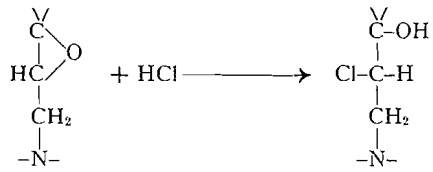
The only structural difference between the two chlorohydrins is the replacement of a $-CH_2-N$ by a $-C(=O)-N$ group. The increased lability of the chloro and hydroxyl groups in the chlorohydrin of the oxidation product must be dependent upon this factor. This suggests that the ether ring is attached adjacent to the carbonyl carbon of the amide group. The effect that the chloro and hydroxyl groups appear to exert on one another, as in the ready removal by hydrogenolysis and Clemmensen reduction of the hydroxyl group in the presence of chlorine, and the ring closure with sodium bicarbonate, suggests that the chloro and hydroxyl group are adjacent. The ether ring would therefore be an epoxide ring.

With these assumptions the addition of hydrochloric acid to the oxidation product would proceed as outlined:



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and to annotinine:



Both additions are considered to proceed *trans* and with inversion at the carbon carrying the chloro group.

According to the accepted theory of *trans* elimination, both compounds would dehydrate with difficulty. The dehydration of the chlorohydrin of the oxidation product can be accounted for by isomerization at the carbon carrying the chloro group because of the lability of the amide linkage in the ionizing media employed. Such isomerization is not possible with annotinine chlorohydrin and dehydration was not brought about by similar treatment. Replacement of chlorine by hydrogen should allow facile dehydration and indeed it does proceed. However, a dehydration product could not be isolated on treatment of III with concentrated hydrochloric acid. Apparently the presence of halogen tends to aid the separation of the proton in the dehydration reaction. The compound from annotinine analogous to III has not been studied. However, Manske and Marion (2) report that annotinine chlorohydrin undergoes hydrogenolysis of the chloro group, and dehydration to an unsaturated base, $C_{16}H_{21}O_2N$, upon treatment with hydrochloric acid and chromous chloride. This reaction is interpreted to proceed through replacement of chlorine by hydrogen followed by dehydration in the acid medium. The hydrogen introduced would have been then in the proper steric relationship to allow facile dehydration.

The lack of reactivity of the tertiary hydroxyl group to displacement reactions with hydrochloric acid and phosphorus oxychloride when dehydration does not occur, suggests that it may be of the type studied by Bartlett (1), where the carbon atom is attached to a rigid ring structure with the hydroxyl group fixed in space. In compounds of this type displacement reactions which proceed through inversion do not occur. Reactions of the type investigated, i.e., treatment with concentrated hydrochloric acid and phosphorus oxychloride, would be expected to proceed through a nucleophilic displacement mechanism with inversion. The unreactivity of the tertiary hydroxyl group can thus be accounted for, and it is not unlikely that such a configuration could exist in this multimembered ring system.

An objection to the postulated epoxide ring in annotinine may be raised on the grounds that the annotinine hydrate of Manske and Marion (2) does not react with periodic acid. This hydrate according to the present theory would be a 1,2-diol. However, it would also be a cyclic *trans*-diol and therefore would oxidize with difficulty. Furthermore, the reaction may be impeded for steric reasons due to the complex ring system which must be present in this molecule. A more serious objection to the whole argument is that it is based in part upon the assumption that dehydration must proceed in the direction of the nitrogen

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atom. Nevertheless, the theories proposed above account very well for the known reactions of annotinine and its oxidation product. Furthermore, they should serve as a guide to further work toward elucidation of the structure.

Examination of the Clemmensen reduction of the oxidation product revealed that besides the saturated base $C_{16}H_{23}O_2N$, compound III was formed in good yield along with a smaller amount of IV. The nonbasic material was formed in much higher yield than the base. Attempts to isolate I proved unsuccessful even after a reaction period of only forty minutes. It is possible, therefore, that oxide fission in this reaction proceeds by hydrogenolysis as well as by the action of hydrochloric acid. The isolation of III and IV suggested that they were possible intermediates in the system and their behavior was therefore examined separately. Both III and IV yielded only small amounts of the saturated base, $C_{16}H_{23}O_2N$, even after prolonged reaction periods.

I and II were also treated under conditions similar to those above. I was rapidly converted to a mixture of III and IV. II was rapidly converted to IV as the sole nonbasic product. Both I and II formed the saturated base $C_{16}H_{23}O_2N$ in poor yield relative to the formation of the nonbasic components.

The results of these reactions indicate that the Clemmensen reduction of these compounds involves a direct reduction of an amide to an amine, a circumstance not usually associated with this type of reaction. The removal of the chloro and hydroxyl groups is not typical of this reaction but has been reported for $\alpha$-chloro acids and $\alpha$-chloro ketones and for $\beta$-hydroxy acids. Furthermore, the reduction of the double bond in the conversion of II to IV by the Clemmensen method finds an analogy in the saturation of the double bond in $\alpha,\beta$-unsaturated acids (3). All of the reactions therefore tend to confirm the supposition that the oxide linkage is 1,2, and, furthermore, that it is situated at the carbon atom, adjacent to the carbonyl group of the amide.

## EXPERIMENTAL

### *Preparation of $C_{16}H_{19}O_4N$*

Annotinine (3.0 gm.) was dissolved in an aqueous solution of 1.0 gm. of oxalic acid in 100 cc. of water. The solution was treated with aqueous potassium permanganate until the color of the permanganate was permanent. The excess reagent and the precipitated manganese dioxide were reduced with sulphur dioxide gas leaving a clear aqueous solution containing a suspended white precipitate of the oxidation product. The suspended solid was removed by shaking with chloroform and the clear solution was extracted several times more with fresh chloroform. The combined extracts were evaporated nearly to dryness and methanol was added whereupon the oxidation product separated in crystalline form. After recrystallization from methanol it melted at 234°C. Yield: 2.1 gm.

### *Treatment of $C_{16}H_{19}O_4N$ with Hydrochloric Acid*

The oxidation product (1.85 gm.) was refluxed with 60 cc. of concentrated hydrochloric acid for forty minutes. The mixture was cooled to room temperature and the separated crystalline solid filtered off. Yield: 1.5 gm. Evaporation of the

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acid filtrate to dryness followed by crystallization of the residue from methanol resulted in the recovery of an additional 0.15 gm. After recrystallization from methanol it melted at 293°C. Calc. for $C_{16}H_{20}O_4NCl$: C, 59.00; H, 6.15; N, 4.30%. Found: C, 59.07, 59.04, H, 6.42, 6.24; N, 4.45, 4.35%.

*Dehydration of $C_{16}H_{20}O_4NCl$ (I)*

(*a*) With phosphorus oxychloride: 1.0 gm. of the chlorohydrin was refluxed for one and one-half hours, with 25 cc. of phosphorus oxychloride. The material entered solution only slowly but was completely dissolved after about one-half hour. The phosphorus oxychloride was removed under reduced pressure and the residue was taken up in water.

The acid solution was extracted several times with chloroform. The chloroform extract was washed, dried, and evaporated to yield a colored residue which crystallized in contact with ether. After two recrystallizations from methanol it melted at 187°C. Yield: 0.7 gm. Calc. for $C_{16}H_{18}O_3NCl$: C, 62.50: H, 5.85%. Found: C, 62.30, 62.27: H, 6.13, 6.10%.

(*b*) With concentrated hydrochloric acid: The chlorohydrin was prepared *in situ* from 0.33 gm. of the oxidation product and 25 cc. of concentrated hydrochloric acid. The mixture was refluxed for a period of seven hours during which the chlorohydrin slowly dissolved. The hydrochloric acid was removed under reduced pressure, water was added, and the solution again taken to dryness to aid in removal of the hydrochloric acid. The residue was taken up in methanol to yield a small amount of the starting material which was separated by filtration. The filtrate was taken to dryness and the residue ether extracted. The other extract was concentrated to yield a crystalline product, 0.11 gm., which, after recrystallization from methanol, melted at 187°C. There was no depression in melting point when this compound was mixed with the product of dehydration of the chlorohydrin with phosphorus oxychloride. The ether insoluble fraction was water soluble and failed to crystallize. It was probably an amino acid chloride although attempts to isolate it as an N-benzene sulphonamide were not successful.

*Treatment of $C_{16}H_{20}O_4NCl$ (I) with Sodium Bicarbonate in Acetone*

Chlorohydrin (0.37 gm.) was taken up in 25 cc. acetone; 0.15 gm. of sodium bicarbonate and 3 cc. of water were added and the mixture was refluxed for four hours. The acetone was then removed by distillation and water added. The white crystalline precipitate which separated was extracted with chloroform and the chloroform extract washed and taken to dryness. The residue was taken up in methanol from which 0.26 gm. of a white crystalline solid separated. It melted at 233-234°C. either alone or in admixture with an authentic sample of the oxidation product. An additional 0.04 gm. of similar material was recovered from the mother liquors.

*Catalytic Reduction of $C_{16}H_{20}O_4NCl$ (I)*

Chlorohydrin (0.6 gm.) was taken up in methanol, 0.1 gm. of Adams catalyst, and a drop of ammonia added, and the mixture shaken for six hours with hydrogen at 40 p.s.i.g. The resulting solution was filtered free of catalyst and

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concentrated to yield 0.2 gm. of a white crystalline solid. The mother liquors were taken to dryness and treated with acetone to yield an additional 0.1 gm. of this product. After recrystallization from methanol it melted at 303°C. Calc. for $C_{16}H_{21}O_4N$: C, 66.00, H, 7.23; N, 4.82%. Found: C, 66.12, 65.91; H, 7.61, 7.47; N, 4.98, 4.90%.

From the acetone mother liquors from the separation above, another material separated in crystalline form. After several recrystallizations from acetone it melted at 176-177°C. Calc. for $C_{16}H_{21}O_3N$: C, 69.81; H, 7.63, N, 5.09%. Found: C, 69.90, 69.73; H, 7.46, 7.59; N, 4.85, 4.9%.

*Catalytic Reduction of $C_{16}H_{18}O_3NCl$ (II)*

The compound was dissolved in methanol, the catalyst and a few drops of ammonia were added, and the mixture was subjected to a hydrogen pressure of 50 p.s.i.g. for two hours. After the pressure was released the solution was filtered free of catalyst and taken to dryness. The residues were taken up in acetone from which a crystalline compound separated which melted at 176-177°C. The melting point showed no depression in admixture with the compound $C_{16}H_{21}O_3N$ described above.

*Dehydration of $C_{16}H_{21}O_4N$ (III)*

(*a*) With phosphorus oxychloride: 0.4 gm. of the compound was refluxed with 20 cc. of phosphorus oxychloride. During the course of the reaction the crystalline starting material disintegrated and a flocculent red precipitate settled out on the sides of the flask. At no time was a homogeneous mixture obtained. After one hour the excess phosphorus oxychloride was removed under reduced pressure and the residue treated with water and made alkaline with ammonia. Extraction with chloroform yielded a colored solution which on evaporation produced a colored crystalline residue. After several recrystallizations from acetone the compound melted sharply at 174-175°C. although the crystals were still slightly discolored. Calc. for $C_{16}H_{19}O_3N$: C, 70.33; H, 6.96, N, 5.12%. Found: C, 70.14, 70.16; H, 6.46, 6.61, N, 5.09, 5.28%.

(*b*) With concentrated hydrochloric acid: 0.52 gm. of $C_{16}H_{21}O_4N$ was taken up in 20 cc. of concentrated hydrochloric, in which it readily dissolved, and refluxed for seven hours. The hydrochloric acid was then removed under reduced pressure and the residue taken up in methanol. Upon concentration of the methanol solution a white crystalline compound separated, 0.27 gm. The mother liquors were concentrated and treated with acetone to yield an additional 0.18 gm. of similar material. The residues from the above separation proved to be water soluble and could not be brought to crystallization. The compound isolated proved to be impure starting material which sintered at 280°C. but failed to melt until 302°C. The melting point was not depressed in admixture with the pure starting material. After one recrystallization from methanol, the product melted at 302-303°C. either alone or in admixture with pure starting material. No other product could be isolated from the reaction mixture by the methods employed.

*Clemmensen Reduction of $C_{16}H_{19}O_4N$*

The oxidation product (0.95 gm.) was refluxed for 40 min. with 10 gm. of zinc amalgam and 20 cc. of 1:1 water and concentrated hydrochloric acid.

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The clear acid solution was filtered free of suspended zinc and taken to dryness on the steam bath under reduced pressure. Addition of water followed by chloroform extraction yielded an extract which deposited 0.23 gm. of a white crystalline solid on evaporation and addition of methanol. An additional 0.12 gm. of the same material was recovered from the mother liquors by treatment with acetone. After recrystallization from methanol the compound melted at 301-303°C. alone or mixed with an authentic sample of $C_{16}H_{21}O_4N$ (III). The acetone mother liquors from the separation of compound III deposited 0.20 gm. of another crystalline substance which melted at 175-177°C. alone or mixed with an authentic sample of $C_{16}H_{21}O_3N$ (IV). There remained 0.07 gm. of acetone soluble noncrystalline residue which was probably impure IV.

The residual acid solution from the chloroform extraction was basified with ammonia and again chloroform extracted. A resinous residue was obtained on evaporation of the washed extract. When this residue was dissolved in methanol and treated with perchloric acid, 0.16 gm. of a crystalline perchlorate separated. After recrystallization from methanol it melted at 254°C. with some decomposition. In admixture with a sample of $C_{16}H_{23}O_2N$, $HClO_4$ prepared by an alternative route (2) there was no depression in melting point. Manske and Marion report a melting point of 282°C. for the compound. The free bases were also prepared and again found identical.

*Clemmensen Reduction of $C_{16}H_{20}O_4NCl$ (I)*

The chlorohydrin (1.0 gm.) was treated for a period of one hour in a fashion similar to the above. The basic extract amounting to 0.13 gm. as perchlorate proved to be identical with the above while the acid extract was worked up to yield the compounds $C_{16}H_{21}O_4N$ (III), 0.23 gm., and $C_{16}H_{21}O_3N$ (IV), 0.36 gm., identified by melting point and mixed melting point with authentic samples.

*Clemmensen Reduction of $C_{16}H_{18}O_3NCl$ (II)*

The reaction was carried out for a period of two hours in a fashion similar to the above. The basic extract was identical with that described above. The acid extract after recrystallization from acetone yielded $C_{16}H_{21}O_3N$ (IV) as the sole product, identified by melting point and mixed melting point with an authentic sample.

*Clemmensen Reduction of $C_{16}H_{21}O_3N$ (IV)*

The reaction was carried out for an eight hour period in a manner similar to the above. Only a small amount of the base $C_{16}H_{23}O_2N$ was formed. The bulk of the starting material was recovered unchanged.

*Clemmensen Reduction of $C_{16}H_{21}O_4N$ (III)*

The reaction was carried out for a two hour period in a manner similar to the above. Only a small amount of the base $C_{16}H_{23}O_2N$ was formed while the bulk of the starting material was recovered unchanged. No other neutral material could be isolated after separation of the starting material.

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# THE REACTIVITY OF CELLULOSE

## II. WATER SORPTION, HEATS OF WETTING, AND THE REACTIONS WITH THALLOUS ETHYLATE IN ETHER, NITRATION MIXTURES, AND HEAVY WATER OF COTTON LINTERS ALTERNATELY WETTED WITH WATER AND DRIED[1]

By W. James Brickman,[2] H. Brian Dunford,[3] Elmer M. Tory,[4] John L. Morrison, and Robert K. Brown

ABSTRACT

Cotton linters dewaxed with benzene and alcohol possess a slightly expanded structure attributed to the swelling effect of the alcohol. Storage causes a partial collapse of the linters especially so when moisture is present. Wetting with water followed by rigorous drying produces a marked reduction in accessibility, but with each additional wetting–drying cycle accessibility of the dried linters increases slightly as measured by reaction with thallous ethylate in ether, a nitration mixture, and in hydrogen–deuterium exchange. Differences in nitration found for limited reaction times are obliterated when these reaction times are extended. Increasing accessibility due to repeated wetting and drying is accompanied by lower water sorption and smaller heats of wetting. This anomaly is due to the fact that cellulose samples obtained by alternately wetting and drying dewaxed linters, when stored with a desiccant, compete for the limited amount of water present and adsorb moisture in proportion to their accessibility. Upon further exposure to water the sample of least accessibility, having adsorbed less water, can now adsorb to a greater extent than do the linters of somewhat greater accessibility.

The evidence indicates that the difference in accessibility occasioned by repeated wetting and drying is of a physical rather than chemical nature.

## INTRODUCTION

The accessibility of cellulose to reagents is a matter of considerable practical and theoretical importance and in recent years has been given a great deal of attention (6, 12, 16, 19, 21, 28). It has been shown quite conclusively that this accessibility is influenced by the previous history of the cellulose sufficiently that uniform reactivity is obtained only by the observation of great care in the choice and processing of the raw material (14, 25).

The association of cellulose with water throughout most of its history has provoked enquiries regarding the influence that water has upon the properties of cellulose. It is generally believed that water itself exercises only a swelling effect, producing nothing more than an increase in the amount of accessible cellulose at the expense of that portion less highly organized. However, recent work indicates that a slight change in dimensions of the unit cell occurs when dry mercerized ramie, spun viscose, or regenerated acetate fibers are wetted (15). Furthermore, lengthy exposure of wet cellulose to oxygen (air) or ozone is reported to produce some degradation of the macromolecule (3, 4). The *removal* of water from cellulose by direct drying methods is accompanied by a decrease

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*Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta. This paper constitutes a part of the theses submitted by W. J. Brickman and H. B. Dunford in partial fulfillment of the requirements for the degree of Master of Science.*
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in accessibility which influences the reactivity unfavorably (5, 14). In fact to avoid this complication pulp is transported in the moist state, in spite of increased cost, to preserve its reactivity (14). Recently it has been shown that purified cotton linters alternately wetted and dried several times exhibited a small but significant improvement in reactivity of the dried linters (23). For example, a technical nitration mixture of sulphuric acid, nitric acid, and water reacting with linters wetted and dried once gave a nitrocellulose containing 10.96% nitrogen whereas the same mixture reacting under identical conditions with the same linters wetted and dried 12 times yielded a nitrate of 11.31% nitrogen. This was borne out by measurements of accessibility to thallous ethylate in ether wherein the accessibility increased from 0.33% to 0.56% after 17 wetting–drying cycles. The enhanced reactivity was attributed to an improved physical arrangement of the fibrils and/or macromolecular chains which permitted better penetration by the reagents during the time allotted for the reaction.

This paper presents further observations on the effect upon the reactivity of purified cotton linters of alternate wetting and drying.

## EXPERIMENTAL

### *Preparation of Cotton Linters*

High grade cotton linters were dewaxed by extraction for 48 hr. in a large Soxhlet apparatus with a 2:1 mixture of benzene and ethanol. The air-dried linters were preserved in glass jars for subsequent experiments.

A portion of the purified linters was immersed for three hours in distilled water at 25°C., then separated from the bulk of the liquid by filtration under mild suction. The slightly moist cotton was then dried for several days with phosphorus pentoxide in a desiccator intermittently evacuated to about 20 cm. of mercury. The material was considered dry when the surface of freshly-added phosphorus pentoxide showed no liquefaction over a 24-hr. period. A 10–20 gm. sample was kept over phosphoric anhydride in a second large desiccator reserved for the preservation of chosen samples while the remainder of the cotton was again wetted and dried as before. In this manner there was obtained a series of dried linters samples which had been given from zero to as many as 25 wetting and drying cycles. These were then kept in the dry atmosphere of the desiccator for at least two more weeks before further treatment or analysis. Several series of samples were prepared in this manner. Any variations in detail will be noted in the discussion of results.

### *Accessibility to Thallous Ethylate*

The thallation procedure was that developed by Assaf, Haas, and Purves (2). Methoxyl analyses were carried out by the method of Hoffman and Wolfrom (13). A Glas-Col heating mantle for the reaction flask was found to give less bumping and better all-round performance than did an ordinary flame. A spherical ground glass joint, rather than a standard taper joint, connected the receiver to the scrubbing unit thus decreasing the rigidity of the system and consequent danger of breakage. Results are reported in Table I and Fig. 1.

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*Nitration of Dried Cotton Linters*

This was accomplished with a technical nitration mixture of water, sulphuric acid, and nitric acid to yield a nitrate containing 10 to 11% nitrogen. Details of the procedure have already been published (5, 23).

*Estimation of Nitrogen*

Some of the nitrates were analyzed for nitrogen by the semimicro Kjeldahl method (5, 23) but since deviations were rather large the remaining analyses were performed with a Du Pont seminicro nitrometer (8). Corrections for moisture sorption during weighing were made on all nitrocellullose samples. This was accomplished by allowing the dried and weighed nitrocellulose to adsorb moisture from the atmosphere until equilibrium was reached (about 24 hr. was satisfactory). From a final weighing the percentage increase in weight due to water was calculated. Portions of this equilibrated nitrocellulose were then weighed out, corrected for moisture content, and analyzed (Tables I and III, Figs. 2 and 3).

*Accessibility by Hydrogen–Deuterium Exchange*

The technique developed by Frilette, Hanle, and Mark (9, 10) permitted the calculation of an empirical value, $F$, which gave a measure of the percentage of hydroxyl groups readily accessible to heavy water. The reference liquids made of a solution of purified technical grade phenanthrene in carefully distilled $\alpha$-methylnaphthalene (Eastman Kodak Co.) were found to discolor and accumulate dark particles unless they were stored in the absence of light. Such solutions were filtered and recalibrated before further use. The results of exchange determinations are recorded in Table IV and Figs. 4 and 5.

*Sorption of Water by Cotton Linters*

About 500 ml. of a water – sulphuric acid mixture, calculated to produce an atmosphere of 45% relative humidity (31), was put into the bottom of a large desiccator. The concentration of the acid was checked before and after sorption experiments and found to be unaltered within experimental error, thus eliminating the necessity for corrections due to change in relative humidity.

Samples (0.5 – 1.0 gm.) of the dried cellulose were weighed in dry, tared, wide-mouthed weighing bottles which were then placed in the desiccator in a dish supported by a porcelain plate. The cover of each weighing bottle was so arranged that it permitted easy access of air to the cellulose yet could be slipped quickly over the mouth of the bottle to exclude atmospheric moisture during the subsequent weighings. The samples were allowed to adsorb moisture and their weights determined periodically. The percentage increase in weight due to adsorbed moisture was based upon the original weight of the dried linters. Results are shown in Table V and Fig. 6.

*Determination of Heat of Wetting of Dried Cotton Linters*

The heat of wetting of the dried cotton linters was measured with a rotating adiabatic calorimeter described in the literature (17, 18) and used by Argue and Maass to determine the heat of wetting of cellulose samples (1). However, a few slight changes were made in the design as follows.

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The thermopile was held only by the shellac placed on the lower junctions, thus eliminating the thin glass supports described for the original apparatus. A stainless steel plug sealed the opening through which water was pipetted into the calorimeter. Vaseline ensured a water-tight seal here as well as on the end flange of the calorimeter. Bolts with wing-type nuts, rather than clamps, held the flange with its Garlock gasket onto the copper jacket containing the calorimeter. All switches were of the mercury commutator type. Finally, a cover shielded the bath from drafts so as to permit better adiabatic control.

For a typical determination the sample of cellulose (2 gm.) was removed from the storage desiccator and put into the weighed inner box of the calorimeter. The sample with its container was then oven-dried at 105°C. for two hours, and then allowed to cool in a desiccator containing phosphoric anhydride. This desiccator was so constructed as to speed up cooling and minimize entrance of outside air when it was opened. (A hollow metal cylinder, 9 in. in diameter and 5 in. deep was covered with a glass plate sealed to the metal with De Khotinsky cement. A hole in this glass top, 4 in. in diameter, covered with an ordinary glass desiccator top allowed access to the container.) When the apparatus had reached room temperature the cover was quickly placed on the cooled inner box and the weight of the cellulose sample then accurately determined. The container with the cellulose was then set into the calorimeter and the heat of wetting determined according to the regular procedure. The results of the measurements are shown in Table VI and Fig. 7.

*Analysis for Water in Dried Cotton Linters*

Water content was measured by the Karl Fischer titration method, the end point being determined electrometrically (24, 26, 30) with the aid of a Model H2 Beckman pH meter equipped with two platinum electrodes. Pure, dried methanol, stirred mechanically, was titrated in an enclosed beaker to the end point with standardized Karl Fischer reagent. An optimum amount (0.6–0.7 gm.) of the dried cotton linters was then immersed in the methanol and the mixture stirred for several minutes whereupon the addition of the Karl Fischer reagent was continued till the end point was reached. This end point is premature unless the linters move freely in the beaker. Results are shown in Table VII.

## DISCUSSION

Five different series of wetted and dried linters samples were prepared for the work described in this paper. Series A, which was given three-hour immersion periods for each wetting followed by drying for an extended period of from 3 to 20 days (depending upon the mass of moist cellulose to be dried) under intermittent vacuum over phosphorus pentoxide, supplied material for determinations of water sorption and of accessibility to thallous ethylate, nitration mixtures, and heavy water. Series B, similarly prepared approximately one year later, permitted corroboration of some results obtained for Series A. Series C and D were given three-hour immersions followed by a preliminary overnight air drying to speed up the process, then further intensive drying for 48 hr. with phosphoric anhydride. Heats of wetting were obtained with the

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linters of Series C while Series D was reserved for measurements of water content. Inadvertently, the temperature of the water during wetting 19 of Series A rose to 70°C. Therefore to support some findings which followed from this rise in temperature a fifth series (Series HT) was prepared, two months after Series A had been completed, but soaked in water for three hours at 80°C. rather than at 25°C. during each wetting. Drying was accomplished as usual with phosphorus pentoxide for periods from 14 to 26 days.

As found previously (23), accessibility to thallous ethylate in ether and to nitration mixtures increased with the number of cycles of wetting and drying (Table I, Figs. 1 and 2).

TABLE I

ACCESSIBILITY OF ALTERNATELY WETTED AND DRIED COTTON LINTERS TO THALLOUS ETHYLATE AND TO NITRATION MIXTURES

Series A

| No. of cycles | Accessibility to thallous ethylate, % | | | | | Average $N_2$ in the nitrates, %[c] | |
|---|---|---|---|---|---|---|---|
| | Determination number[a] | | | Average | After humidifying[b] | Kjeldahl[d] | Nitrometer[d] |
| | 1 | 2 | 3 | | | | |
| 0 | 1.65 | 1.26 | | 1.46 | 0.67 | 10.58(9) | 10.82(6) |
| 1 | 0.43 | 0.54 | | 0.48 | 0.43 | | 10.46(4) |
| 5 | 0.63 | 0.56 | | 0.60 | 0.37 | 10.29(7) | 10.72(4) |
| 9 | 0.67 | 0.57 | | 0.62 | 0.47 | | |
| 13 | 0.84 | 0.57 | 0.48 | 0.63 | 0.53 | 10.49(11) | |
| 17 | 0.82 | 0.56 | 0.56 | 0.65 | 0.49 | | 10.99(4) |
| 21 | 0.64 | 0.67 | 0.64 | 0.65 | 0.44 | | 10.82(4) |
| 25 | 0.87 | 0.67 | 0.74 | 0.76 | 0.39 | 10.86(6) | 11.02(5) |

[a] *Each figure represents the average of three determinations made simultaneously agreeing well within* ±10%.

[b] *Accessibility after exposure of Series A samples to 45% relative humidity and redrying with phosphorus pentoxide.*

[c] *All nitrocellulose samples corrected for adsorbed moisture.*

[d] *Figures in brackets indicate the number of analyses made. Nitrometer values deviated* $< \pm 0.05\%$; *Kjeldahl values deviated much more than this.*

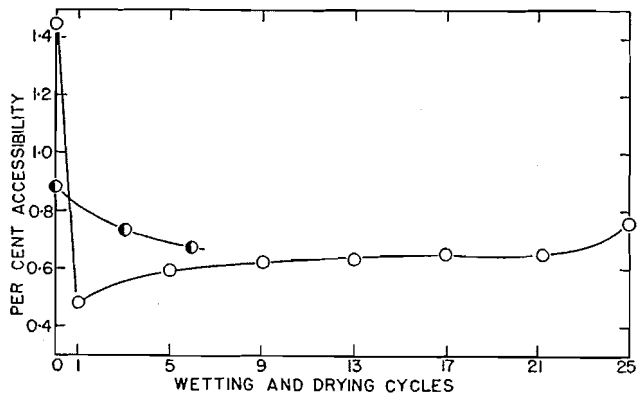



FIG. 1. Thallous ethylate accessibility for Series A samples of wetted and dried cotton linters. ○ – Linters samples wetted at 15°C., then dried. ◐ – Linters wetted at 80°C., then dried.

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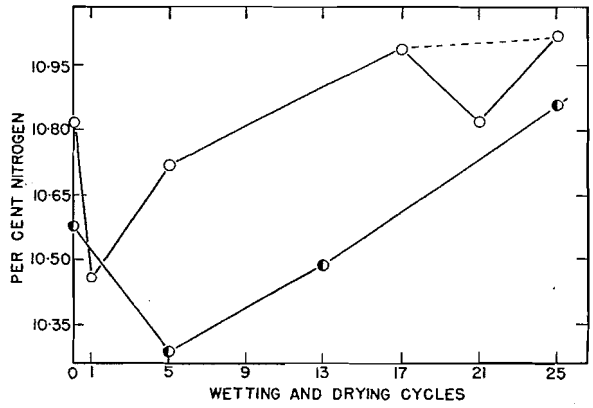



FIG. 2. Nitrogen content of Series A samples nitrated and then analyzed by both Kjeldahl (◐) and nitrometer (○) methods.

The original, dewaxed but unwetted cotton linters (0 cycle) show considerably greater accessibility to both thallous ethylate and the technical nitration mixture than they do when given one wetting and drying cycle, an observation omitted in the previous work (23). This is to be expected since the process of dewaxing with ethanol–benzene should involve some swelling by the polar solvent ethanol. As benzene and ethyl alcohol form an azeotropic mixture, with the proportions of solvents used evaporation of the remaining mixture of solvent during air drying would leave some residual benzene to be finally removed. In effect this constitutes drying by solvent exchange (2, 5, 27) resulting in at least a partial maintenance of the swollen state. The first wetting and drying cycle would therefore show a marked decrease in accessible cellulose.

The accessibility of the sample given 21 cycles is somewhat lower than expected from the shape of the curve (Figs. 1 and 2). Since this followed directly after the accidental rise to 70°C. of the swelling water for wetting number 19, it was felt that the lower value might be of some significance rather than being due to experimental error. This point of view is supported by the observation that portions of the same dewaxed linters used to prepare Series A, when wetted with water at 80°C. and dried, showed a *decrease* in accessibility with increase in the number of wetting and drying cycles (Table II, Fig. 1).

TABLE II

ACCESSIBILITY TO THALLOUS ETHYLATE OF COTTON LINTERS ALTERNATELY WETTED AT 80° AND DRIED

Series HT

| No. of cycles | Accessibility, %[a] |
|---|---|
| 0 | 0.89 |
| 3 | 0.73 |
| 6 | 0.67 |

[a]*Each value represents the average of triplicate analyses agreeing well within 10%.*

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This is not entirely unexpected since wetting and swelling of cellulose is an exothermic reaction (1). However, owing to the insufficient number of measurements (Table II) along with the deviation apparently inherent in the thallation method for accessibility estimation (2) the results *may* not be significant. Unfortunately, measurements of the degree of nitration were not made on these samples. Further study of the effects of high temperature wetting on the reactivity of cellulose is necessary.

The lower accessibility to thallous ethylate of the linters of Series HT given zero wettings (0.89%, Table II) as compared with the same sample for Series A (1.45%, Table I), in spite of the fact that they are both from the same batch of dewaxed but unwetted linters, suggests that the period of storage for the dewaxed linters used for Series HT saw a partial collapse of the ethanol–benzene dewaxed linters. That such a collapse of swollen linters occurs on storage, particularly under conditions where small amounts of moisture prevail, appears indicated by the results obtained when portions of Series A samples were exposed to an atmosphere of 45% relative humidity for 44 days and then dried as usual. The typical differences in, as well as the magnitude

TABLE III

NITROGEN CONTENT OF THE NITRATES OF ALTERNATELY WETTED AND DRIED COTTON LINTERS Series A and B[a]

| No. of cycles | Series A, $N_2$,%[b] | Series B, $N_2$,%[b] | 90 min. nitration of Series B, $N_2$,% |
|---|---|---|---|
| 0 | 10.70 | 10.96 | 11.25 |
| 1 | 10.70 | 10.93 | 11.29 |
| 5 | 10.70 | 10.95 | |
| 9 | 10.88 | 10.97 | |
| 13 | 10.91 | 10.99 | |
| 17 | 10.86 | 11.01 | |
| 21 | 10.96 | 11.04 | |
| 25 | 10.97 | 11.09 | 11.27 |

[a]*All $N_2$ estimations made by nitrometer. $\%N_2$ calculated on dry weight basis.*
[b]*All nitrations of a series carried out in one day; Series B nitrated two weeks after Series A.*

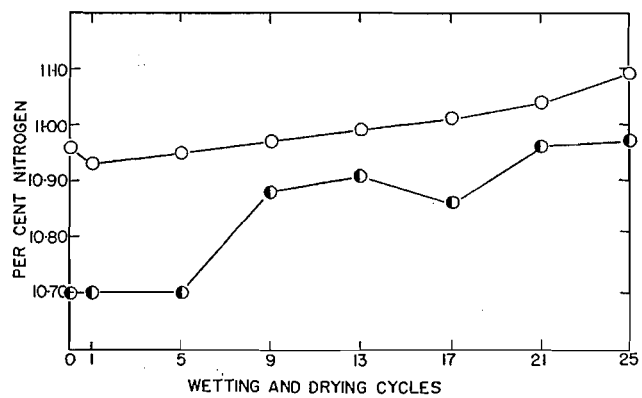



FIG. 3. Comparison of nitrogen content of Series A (◐) and Series B (○). Series A had been stored 13 months before nitration by the same mixture used for Series B.

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of, the accessibility found before were markedly decreased (Table I, column 6).

Series B, prepared one year after some of the work on Series A had been carried out, corroborates the findings regarding accessibility to nitration (Table III, Fig. 3). Since the nitration mixture used for this series was the same one that had been employed for Series A, but had been preserved in a refrigerator, it was felt that for better comparison with Series B the samples of Series A should again be nitrated by this mixture. The values for Series A (second nitration) were found to be from 0.1 to 0.3% lower than those for Series B (Table III, Fig. 3). Although this might again be due to the general collapse suffered by the Series A samples stored for about 13 months before the second nitration, the difference between the two series might also arise from slight differences in reaction conditions between the two sets of nitrations.

The trend of the curves in Figs. 1, 2, and 3 indicates that, although 25 wetting and drying cycles had been made, further cycles should increase accessibility. The preparation of samples with greater than 25 wettings was not attempted. However when the nitration period was extended from the usual 30 min. to 90 min. for three chosen samples of Series B, it was found that a higher degree of nitration is attainable and that the differences found for limited nitration times were obliterated (Table III, column 4). This supports the belief that the changes brought about by repeated wetting and drying are physical rather than chemical (3, 4, 23), and influence the rate of diffusion of the reagent through the cellulose mass. We have shown also that mechanical manipulation during the process of wetting and removal of the water is important. A linters sample, unstirred during water immersion and then pressed firmly to remove water during suction filtration, gave thallous ethylate accessibility of 0.84% while the same linters, stirred during the wetting with water followed merely by gentle suction to remove water prior to drying, possessed thallous ethylate accessibility of 1.02%.

Since the technique of hydrogen–deuterium exchange has been improved to the point where it can be used to measure accessibility (9, 10, 22), and the values of accessibility so obtained on cotton linters are numerically much greater than those obtained by the thallous ethylate procedure (10), it was felt that

TABLE IV

HYDROGEN–DEUTERIUM EXCHANGE MEASUREMENTS OF ACCESSIBILITY IN COTTON LINTERS ALTERNATELY WETTED AND DRIED

Series A

| No. of cycles | Value of $F$ at reaction time, hr. | | | |
|---|---|---|---|---|
| | 0.5 | 1.0 | 4.0 | 24.0 |
| 0 | 0.26 | 0.38 | 0.51 | 0.44 |
| 1 | 0.25 | 0.27 | 0.47 | 0.44 |
| 5 | 0.34 | 0.40 | 0.45 | 0.48 |
| 17 | 0.34 | 0.40 | 0.39 | 0.42 |
| 21 | 0.50 | 0.43 | 0.52 | 0.52 |
| 25 | 0.46 | 0.51 | 0.34 | 0.48 |

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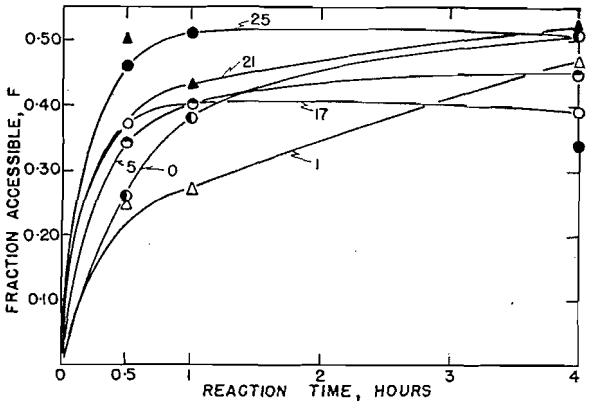



FIG. 4. Hydrogen–deuterium exchange for alternately wetted and dried linters samples of Series A.

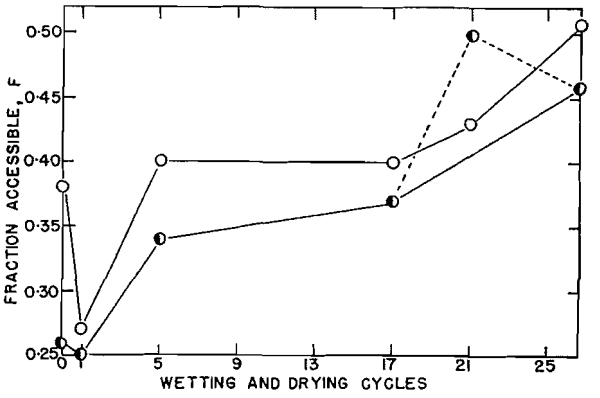



FIG. 5. Hydrogen–deuterium exchange for linters samples of Series A. ◐ – at reaction time of 0.5 hr. ○ – at reaction time of 1 hr.

this method might show greater differences between the members of a series of wetted and dried linters samples. However, the differences were again found to be small but still following the pattern observed before (Table IV, Figs. 4 and 5). The plots of $F$ (the fraction of cellulose possessing greater accessibility) against time (Fig. 4) and $F$ at reaction times of 0.5 hr. and 1.0 hr. versus the number of wetting and drying cycles (Fig. 5) show the drop in accessible cellulose which accompanies the first wetting, followed by the expected increasing values of $F$ with increased cycles.

In view of preferential adsorption of water by the more accessible portion of cellulose (19, 21), a study of the water sorption was carried out to gain more information concerning the differences brought about in cotton linters by alternate wetting and drying. Exposure of 1-gm. portions of the phosphoric anhydride-dried linters of Series A to an atmosphere of 45% relative humidity produced an increase in weight in all samples (Table V, Fig. 6). However, examination of the data reveals that contrary to expectations less moisture

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TABLE V

MOISTURE SORPTION FROM AN ATMOSPHERE OF 45% RELATIVE HUMIDITY OF DRIED COTTON LINTERS ALTERNATELY WETTED AND DRIED

Series A

| No. of cycles | % Weight increase for days | | | |
|---|---|---|---|---|
| | 3 | 8 | 20 | 44 |
| 0 | 4.39 | 4.49 | 4.44 | 4.73 |
| 1 | 5.00 | 5.32(?) | 5.04 | 5.05 |
| 5 | 4.92 | 5.02 | 4.93 | 5.07 |
| 9 | 4.75 | 4.82 | 4.79 | 5.04 |
| 13 | 4.84 | 4.92 | 4.86 | 5.00 |
| 17 | 4.82 | 4.88 | 4.85 | 5.02 |
| 21 | 4.68 | 4.72 | 4.71 | 4.99 |
| 25 | 4.76 | 4.84 | 4.81 | 5.00 |

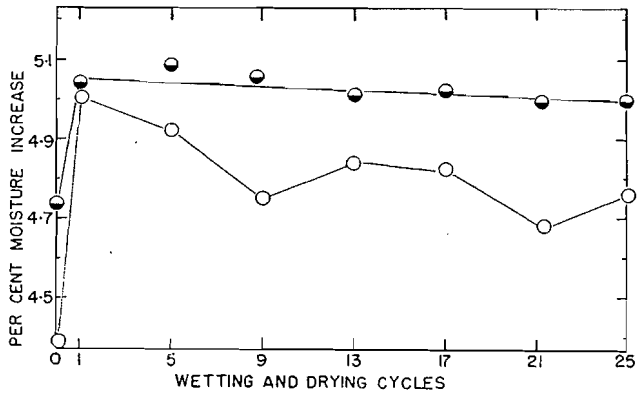



FIG. 6. Water sorption from an atmosphere of 45% relative humidity by dried linters samples of Series A. ○ – Sorption during three days' exposure. ◐ – Sorption during 44 days' exposure.

was adsorbed as the accessibility increased. A second adsorption determination on more of Series A gave much the same results and is therefore not reported.

This characteristic was more pronounced during the initial stages of water sorption, with the differences decreasing as the time of exposure increased (Fig. 6) indicating that the rate of adsorption as well as the amount adsorbed was greatest for that member of the series having the least accessibility (cycle 1). Here again it might be pointed out that sample number 21 adsorbed somewhat less than expected. However, following the reasoning expressed before that increase of accessibility is less when wettings are made at higher temperatures, this sample should adsorb *more* water than do its neighbors in the plot (Fig. 6).

As a means of checking these results on water sorption, heats of wetting were measured on portions of samples from Series C by the method developed by Argue and Maass (1). Preliminary tests, as a check on technique, upon samples of "standard cellulose" (1) gave 10.15 cal./gm. for an average of

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TABLE VI

HEATS OF WETTING OF DRY COTTON LINTERS PREVIOUSLY WETTED AND DRIED SEVERAL TIMES
Series C

| Run No. | No. of cycles | Heat of wetting, cal./gm. | Mean heat of wetting, cal./gm. |
|---|---|---|---|
| 1 | 0 | 10.44 | |
| 6 | | 10.50 | |
| 11 | | 10.57 | 10.50 |
| 10 | 1 (at 25°C.) | 10.84 | |
| 12 | | 10.83 | 10.84 |
| 13 | 3 " | 10.76 | 10.76 |
| 4 | 5 " | 10.67 | |
| 8 | | 10.64 | 10.66 |
| 14 | 9 " | 10.70 | 10.70 |
| 18 | 11 " | 10.62 | 10.62 |
| 2 | 13 " | 10.55 | |
| 5 | | 10.72 | |
| 9 | | 10.66 | 10.64 |
| 15 | 15 " | 10.62 | 10.62 |
| 16 | 17 " | 10.51 | 10.51 |
| 3 | 19 " | 10.50 | |
| 7 | | 10.39 | 10.45 |
| V–0 | 0 | 10.34 | |
| | | 10.43 | 10.38 |
| V–1 | 1 (at 25°C.) | 10.53 | |
| | | 10.64 | 10.58 |
| V–HT | 1 (at 80°C.) | 10.92 | 10.92 |
| Abs. cotton | 0 | 10.74 | |
| | | 10.74 | 10.74 |
| Abs. cotton | 1 (at 25°C.) | 11.04 | |
| | | 11.90 | 10.97 |

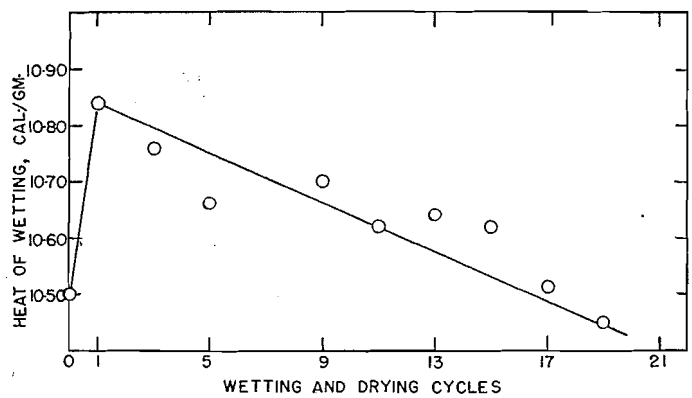



FIG. 7. Heat of wetting of cotton linters samples of Series C.

five determinations, in good agreement with the figure 10.16 cal./gm. found by Argue and Maass.

From Table VI and Fig. 7 it can be seen that differences in heat of wetting do occur between members of Series C and these follow the characteristic form shown for water sorption (Table V, Fig. 6)—the sample with the least accessibility (cycle 1) producing the greatest value for heat of wetting.

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We have also shown that ordinary medical absorbent cotton dried over phosphoric anhydride for two months gave a slightly lower heat of wetting (10.74 cal./gm.) than did the same cotton wetted once and dried thoroughly (10.97 cal./gm.). Furthermore a portion (V-O) of another quantity of the dewaxed linters merely dried gave a heat of wetting of 10.38 cal./gm., a second fraction (V-1) wetted once and dried to reduce accessibility gave 10.58 cal./gm., while a third portion (V-HT) wetted at 80° and dried showed a value of 10.92 cal./gm. (Table VI). All three of these samples of cellulose (V-0,-1,-HT) had been stored in the same desiccator over the drying agent for at least two months before the heats of wetting were obtained. These figures again support the belief that high temperature wetting apparently yields a cellulose of lower accessibility than expected.

The direct proportionality of heats of wetting of cellulose samples to their ability to adsorb moisture from a surrounding atmosphere has been pointed out before (1, 29), hence similarity in results of the heats of wetting and water sorption found in our work indicates that the differences observed are quite significant.

Argue and Maass (1) found that only when a "standard cellulose" was prepared under carefully controlled conditions could reproducible heats of wetting be obtained. These authors pointed out that the heat of wetting is dependent upon the available internal surface, and as different methods of preparation should produce differences in average chain length and micellar structure and thus in the extent of the internal surface, variability in heat of wetting can be expected. Furthermore they found that removal of water from their standard cellulose to a value less than 0.015 gm. per gm. of cellulose caused a reversion of the cellulose to the "dry state" which gave *variable* and somewhat higher figures for the heat of wetting. Since our experiments deal with cotton whose water content had been reduced to values less than 0.015 gm./gm. cellulose, it is likely that the same phenomenon operates. However in a previous article (23) it has been shown that cellulose alternately wetted and merely air dried exhibited the same trend of increased accessibility with increased number of cycles although to lesser degree. It is unlikely that the air-dried cellulose was left with such a small amount of water as 0.015 gm./gm. cotton. Wahba (29) has found that the heat of wetting of a standard cellulose is dependent upon the *time* of immersion, and the ability of the reagent to penetrate the cellulose mass. Thus, differences in technique of manipulating the cellulose during preparation should be reflected in heat of wetting, especially if the duration of the wetting process is limited.

The anomalous behavior of the series of wetted and dried cotton linters in possessing on the one hand increasing accessibility to thallous ethylate, technical nitration mixtures, and hydrogen deuterium exchange yet on the other hand lower water sorption as well as decreased heat of wetting with increase in the number of cycles of wetting and drying can be rationalized. It is known that bone-dry cellulose competes with phosphoric anhydride for available water (7, 20). The attainment, therefore, of perfectly water-free cellulose is difficult and may be all but impossible without decomposition of the

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cellulose. Since our series of linters samples occupied a single desiccator which contained phosphoric anhydride, a competition for any available moisture in the container was set up. The samples of cellulose adsorbed a share of the water proportional to the degree of accessibility in agreement with previous observations (11, 19, 21). Upon further exposure to moisture, the linters sample with low accessibility (e.g., cycle 1), having therefore adsorbed little water while stored with phosphoric anhydride, will now adsorb water at a greater rate and to a larger extent, as well as give a higher value for the heat of wetting than do the more accessible samples. Unless *completely* dried, it appears that cellulose will retain small amounts of moisture to some degree proportional to the extent of accessibility, a characteristic which in turn is determined by its previous history.

This interpretation was strengthened by measurements of residual water content in the dried samples of Series D by means of the Karl Fischer titration method using a Model H2 Beckman pH meter to obtain an electrometric end point. Visual end points were too indefinite for the accuracy required. The results are illustrated in Table VII.

It is difficult to duplicate accurately analyses of properties of cellulose which are so sensitive to variations in technique of preparation. Therefore, since measurements of such small amounts of water are subject to considerable experimental error, the results obtained are reasonably good. They show

TABLE VII

WATER CONTENT OF DRIED LINTERS SAMPLES ALTERNATELY WETTED AND DRIED
Series D

| No. of cycles | Water content, [a] mgm./gm. cellulose | No. of cycles | Water content, mgm./gm. cellulose |
|---|---|---|---|
| 1 | 9.95 (4) | 9 | 12.02 (4) |
| 3 | 11.27 (7) | 11 | 12.68 (6) |
| 5 | 10.78 (8) | 13 | 12.63 (7) |
| 7 | 11.46 (6) | 15 | 12.60 (4) |

[a] *These figures represent average values. The number of determinations is indicated in brackets. The figures for the sample with 11 cycles, 11.50, 14.13, 14.43, 11.59, 10.17, and 14.28 typify the kind of results obtained.*

quite clearly that dried linters in contact with the limited amount of moisture present in a desiccator containing phosphoric anhydride do adsorb moisture in proportion to their degree of accessibility.

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# SYNTHESIS OF 3-HYDROXY-2-ALKYLPYRIDINES[1]

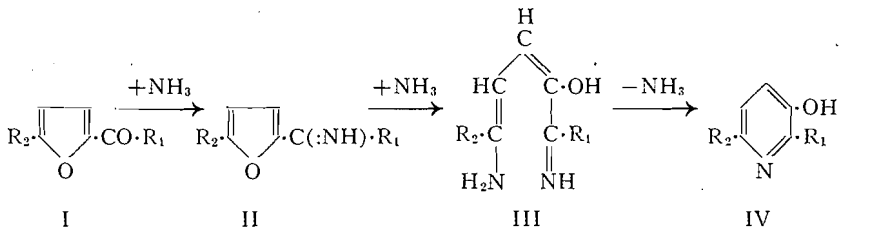
By W. Gruber

ABSTRACT

Aliphatic 2-furylketones rearrange to 3-hydroxy-2-alkylpyridines under the influence of ammonia and heat. The furylketones were prepared by a modified Friedel-Crafts reaction. Conditions to obtain the pyridine derivatives in good yield have been established.

A general method for the synthesis of 3-hydroxy-2-alkylpyridines is the Hofmann degradation of 2-alkylnicotinic acids as was shown by Dornow (1, 2, 3) who demonstrated this synthesis for 3-hydroxy-2-methylpyridine starting from 2-methylnicotinic acid made by the condensation of amino-crotonic ester and beta-ethoxyacrolein diethyl acetal. For the preparation of higher alkylated 3-hydroxypyridines, however, the starting material is more difficult to make, and the difficulties grow with the size of the side-chain. Recently Leditschke (11) has published a synthesis of 3-hydroxy-2-arylpyridines. The simplicity of his method and the good yields obtained suggested a similar procedure for the synthesis of aliphatic substituted pyridines, which are related to derivatives of previous (4, 5, 6) as well as current investigations.

The basic reaction of this synthesis is the rearrangement of 2-alkylfuryl-ketones under the influence of ammonia:




I II III IV

The first step is the formation of the ketimine (II). Further addition of ammonia may bring about ring cleavage to (III), which is immediately transformed into the hydroxypyridine derivative (IV) with a simultaneous splitting off of ammonia. Direct proof of this mechanism is lacking because (III) has not been isolated. However, reaction products other than pyridine derivatives can be expected if primary amines are used instead of ammonia, because the last step (III) to (IV) takes place only with difficulty in the case of primary amines. Experiments have shown that under these conditions the reaction products are in fact not uniform.

The 2-alkylfurylketones used as starting materials were prepared by a Friedel-Crafts type reaction from furan and the corresponding acid anhydrides, using

[1] *Manuscript received March 16, 1953.*
*Contribution from the Division of Chemistry, British Columbia Research Council, Vancouver 8, Canada.*

phosphoric acid or boron-trifluoride-etherate as a catalyst (9, 10). Some of these ketones are new (Table I).

TABLE I

| No. | 2-Furylketones (I) | B.p., °C., mm.Hg | Used method | Ref. |
|---|---|---|---|---|
| 1 | 2-Acetylfuran ($R_1 = CH_3$, $R_2 = H$) | 66–68° 11–12 mm. | A | 7,8,9,10,12 |
| 2 | 2-Propionylfuran ($R_1 = C_2H_5$, $R_2 = H$) | 63–65° 3–4 mm. | A | 10 |
| 3 | 2-*n*-Butyrylfuran ($R_1 = n$-$C_3H_7$, $R_2 = H$) | 75–77° 5–6 mm. | A | 10 |
| 4 | 2-Isobutyrylfuran ($R_1$ = iso-$C_3H_7$, $R_2 = H$) | 51–53° 3–4 mm. | A | |
| 5 | 2-*n*-Valerylfuran ($R_1 = n$-$C_4H_9$, $R_2 = H$) | 72–75° 2–3 mm. | B | |
| 6 | 2-Isovalerylfuran ($R_1 = sec$-$C_4H_9$, $R_2 = H$) | 67–70° 3–4 mm. | A | |
| 7 | 2-*tert*-Valerylfuran ($R_1 = tert$-$C_4H_9$, $R_2 = H$) | 57–60° 2–3 mm. | B | |
| 8 | 2-Propionyl-5-methylfuran ($R_1 = C_2H_5$, $R_2 = CH_3$) | 66–69° 2–3 mm. | A | |
| 9 | 2-Phenacetylfuran ($R_1 = CH_2C_6H_5$, $R_2 = H$) | 155–158° 2–3 mm. | C | |

The rearrangement was best effected by heating the ketone with 2–3 moles of ammonia in alcoholic solution in a sealed tube at 170°C. for 15 hr. The ammonia solution was prepared by saturating absolute ethanol at 0°C. The presence of ammonium chloride increased the yields only slightly. The reaction mixtures were worked up by evaporating the alcohol under reduced pressure, distilling the residue *in vacuo*, and extracting a solution of the distillate in 2 *N* sodium hydroxide with chloroform to remove neutral contaminants. The alkaline solution of the hydroxypyridine was then neutralized and extracted again with chloroform. (Table II.)

While the rearrangement of 2-acetylfuran (I, $R_1 = CH_3$, $R_2 = H$) gave the 3-hydroxy-2-methylpyridine in a yield of only 4.6%, the yield increased rapidly with the size of $R_1$ and reached 74% for 3-hydroxy-2-propylpyridine (IV, $R_1 = C_3H_7$, $R_2 = H$, "*o*-hydroxyconyrine"). Equally satisfactory yields were obtained whether $R_1$ was straight or branched. The rearrangement of 2-benzylfurylketone (I, $R_1 = CH_2C_6H_5$, $R_2 = H$) under the same conditions gave a poor yield and Leditschke's method of heating the ketone with ammonium acetate at higher temperatures would seem advisable.

To investigate the behavior of a 5-alkyl substituted 2-furylketone, 5-methyl-2-propionylfuran (I, $R_1 = C_2H_5$, $R_2 = CH_3$) was treated by this procedure and yielded 85% of 3-hydroxy-2-ethyl-6-methylpyridine (IV, $R_1 = C_2H_5$, $R_2 = CH_3$).

The basic properties of these pyridine derivatives and their tendency to form picrates and chloroplatinates decrease with increasing size of the side-chain. All the compounds are readily soluble in 2 *N* acids and 1–2 *N* alkalies, and give a reddish-brown color reaction with ferric chloride in dilute alcoholic solution. Coupling with diazotized *o*- and *p*-nitroaniline gives brownish-red azo dyes.

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TABLE II

| No. | 3-Hydroxy-2-alkylpyridines (IV) | M.p., °C. | Yield, % | Analytical figures | |
|---|---|---|---|---|---|
| | | | | Calcd., % | Found, % |
| 1 | 3-Hydroxy-2-methylpyridine ($R_1 = CH_3$, $R_2 = H$) | 166–168 | 4.6 | $C_6H_7NO$: | |
| | | | | N 12.84 | 12.6 |
| | Picrate | 203–205 | | N 16.57 | 16.8 |
| | Chloroplatinate | 160–163 | | Pt 29.57 | 29.62 |
| 2 | 3-Hydroxy-2-ethylpyridine ($R_1 = C_2H_5$, $R_2 = H$) | 134–136 | 10 | $C_7H_9NO$: | |
| | | | | N 11.37 | 11.5 |
| | Picrate | 173–175 | | N 15.91 | 16.0 |
| 3 | 3-Hydroxy-2-*n*-propylpyridine ($R_1 = n$-$C_3H_7$, $R_2 = H$) | 133–135 | 74 | $C_8H_{12}NO$: | |
| | | | | N 10.21 | 10.5 |
| 4 | 3-Hydroxy-2-isopropylpyridine ($R_1$ = iso-$C_3H_7$, $R_2 = H$) | 191–192 | 81 | C 70.04 | 70.04; 70.18 |
| | | | | H 8.08 | 8.16; 8.02 |
| 5 | 3-Hydroxy-2-*n*-butylpyridine ($R_1 = n$-$C_4H_9$, $R_2 = H$) | 127–129 | 78 | $C_9H_{13}NO$: | |
| | | | | C 71.49 | 71.47; 71.30 |
| | | | | H 8.67 | 8.64; 8.42 |
| 6 | 3-Hydroxy-2-*sec*-butylpyridine ($R_1 = sec$-$C_4H_9$, $R_2 = H$) | 157–159 | 60 | N 9.26 | 9.55 |
| 7 | 3-Hydroxy-2-*tert*-butylpyridine ($R_1 = tert$-$C_4H_9$, $R_2 = H$) | 199–201 | 71 | | 71.70; 71.45 |
| | | | | | 8.71; 8.50 |
| 8 | 3-Hydroxy-2-ethyl-6-methylpyridine ($R_1 = C_2H_5$, $R_2 = CH_3$) | 170–172 | 80 | $C_8H_{11}NO$: | |
| | | | | C 70.04 | 69.78 |
| | | | | H 8.08 | 8.06 |
| 9 | 3-Hydroxy-2-benzylpyridine ($R_1 = CH_2C_6H_5$, $R_2 = H$) | 189–191 | 5.4 | $C_{12}H_{11}NO$: | |
| | | | | C 77.81 | 77.46 |
| | | | | H 5.99 | 5.72 |
| | | | | N 7.56 | 7.55 |

The 3-hydroxy-3-methylpyridine was also prepared by Dornow's method so that a direct comparison of the products of both methods was possible. They were identical.

## EXPERIMENTAL

Melting points are corrected. Analyses are by Drs. Weiler and Strauss, Oxford.

*Method A. 2-Isopropylfurylketone* (Table I, No. 4)

A well-stirred mixture of 95 gm. (0.6 moles) of isobutyric anhydride and 20.4 gm. (0.3 moles) of furan was warmed to 40°, the heat removed, and 6 gm. of 85% orthophosphoric acid was added at once. This caused a slight rise in temperature which was allowed to subside and the mixture was kept at 60° for two hours. After cooling, 120 ml. of water were added and the mixture

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stirred for one hour. The dark-colored organic layer was shaken for 24 hr. with saturated sodium carbonate solution. The ketone was taken up in chloroform, washed once with water, dried with anhydrous sodium sulphate, and the solvent removed under reduced pressure. The residue was distilled *in vacuo* twice through a short column. B.p. 51–53°C. (3–4 mm.), yield 40.0 gm., i.e. 93% based on furan.

*Method B. 2-tert-Valerylfuran* (Table I, No. 7)

A mixture of 37.2 gm. (0.2 moles) of trimethyl acetic anhydride and 12 gm. (0.177 moles) of furan was cooled in tap water to 15°C. and well stirred. Addition of 3 ml. of redistilled boron-trifluoride-etherate caused a slight rise of temperature. The mixture was kept at 60°C. for three hours, then cooled to 20° and, after adding 200 ml. of water, stirred for two hours. The ketone was taken up with chloroform, washed with 10% sodium carbonate solution, and, after removal of the chloroform, the product distilled *in vacuo* through a column. B.p. 57–60°C. (2–3 mm.) yield 22.0 gm., i.e. 91%.

*Method C. 2-Benzylfurylketone* (Table I, No. 9)

A mixture of 52 gm. (0.204 moles) of phenyl acetic anhydride, 11 gm. (0.162 moles) of furan, and 0.5 ml. of hydriodic acid (sp. gr. 1.7) was heated to 55°C. for three hours with good agitation. The heat was removed, 200 ml. of water added, and stirring was continued for two hours. The organic layer was drawn off and poured into 200 ml. of saturated sodium carbonate solution and allowed to stand for one week with occasional shaking. The ketone was taken up with chloroform and finally distilled *in vacuo*. B.p. 155–158°C. (2–3 mm.), yield 27.0 gm., i.e. 90%.

The following are a few typical examples of the rearrangement procedure.

*3-Hydroxy-2-methylpyridine* (Table II, No. 1)

Twelve grams of 2-acetylfuran and 30 ml. of a saturated solution of ammonia in absolute ethanol were heated with a trace of ammonium chloride in a sealed tube to 150°C. for 15 hr. After evaporating the alcohol under reduced pressure, the residue was digested with 100 ml. of 2 *N* sodium hydroxide solution, filtered through a wetted filter, and neutralized to litmus with 2 *N* hydrochloric acid. The mixture was extracted several times with chloroform, the solvent removed *in vacuo*, and the residue sublimed under a pressure of 0.1 mm. and 110–120°C. bath temperature. Final purification was by repeated crystallization from chloroform under pressure. M.p. 166–168°C., yield 0.560 mgm., i.e. 4.6% (based on 2-acetylfuran). Mixed with a sample prepared by degradation of 2-methylnicotinic acid according to (1), the melting point was not depressed. The *picrate* was prepared by adding an ethereal solution of the base to a solution of picric acid in ether, and the product was recrystallized from ether under pressure to give a yellow powder, m.p. 203–205°C. (dec.). The *chloroplatinate* was obtained by dissolving the base in the minimum amount of 20% hydrochloric acid and adding the calculated amount of chloroplatinic acid. The mixture was evaporated and the residue taken up in methanol and precipitated with ether. M.p. 160–163°C., very soluble even in methanol.

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*3-Hydroxy-2-ethylpyridine* (Table II, No. 2)

Thirteen grams of 2-propionylfuran was sealed in a tube with 30 ml. of saturated alcoholic ammonia solution and heated at 160°C. for 15 hr. After cooling to room temperature there was an appreciable vacuum in the tube, showing the consumption of ammonia. After removal of the solvent, the residue was distilled *in vacuo*, after the forerun was rejected. The sublimated crystals were dissolved in 2 *N* sodium hydroxide (50 ml.) on the water bath and after cooling and diluting with an equal volume of water the solution was filtered and saturated with carbon dioxide. The base was extracted with chloroform and sublimed twice at 0.1 mm. and 120°C. (air bath). Recrystallization from chloroform–ether gave 1.132 gm., i.e. 9%, of white prisms, m.p. 134–136°C., reaction with ferric chloride in dilute alcoholic solution: dark red-brown. The *picrate* was made by mixing ethereal solutions of base and picric acid and recrystallizing from methanol–ether until a constant melting point of 173–175°C. (dec.) was reached; orange needles.

*3-Hydroxyconyrine* (Table II, No. 3)

2-*n*-Butyrylfuran, 11.6 gm., and 30 ml. of alcoholic ammonia solution were heated in a sealed tube to 165°C. for 20 hr. The product was worked up by evaporating the solvent and subliming the residue in a vacuum of 3 mm. almost without forerun. Yield, 8.5 gm. (i.e. 74%), m.p. 127–131°C. An analytical sample was prepared by recrystallization from a mixture of ether and petroleum ether and finally from ether alone, m.p. 133–135°C., thick prisms with the characteristic odor of the hemlock plant.

*3-Hydroxy-2-benzylpyridine* (Table II, No. 9)

2-Phenylacetylfuran, 13.7 gm., was heated with 30 ml. of ammonia solution in a sealed tube to 175°C. for 24 hr. The solvent was distilled off under diminished pressure leaving a liquid residue. Addition of ether produced a precipitate which was filtered off and discarded. The ethereal filtrate was treated first with 10% sodium bicarbonate solution, which was discarded, then five times with 50 ml. of 2 *N* sodium hydroxide solution which was separated and neutralized with 2 *N* hydrochloric acid. The neutral solution was extracted with ether, the solvent removed, and the remaining crystals sublimed in a vacuum of 1 mm. Recrystallization from ether under pressure yielded 0.734 gm. (i.e. 5.4%), m.p. 189–191°C.

This work was carried out under a consolidated grant from the National Research Council of Canada.

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# COEXISTENCE PHENOMENA IN THE CRITICAL REGION

## II. INFLUENCE OF GRAVITY ON THE COEXISTENCE CURVES OF ETHANE, ETHYLENE, AND XENON[1]

By S. G. Whiteway[2] and S. G. Mason

ABSTRACT

Liquid–vapor coexistence curves of ethane, ethylene, and xenon have been measured in the region of the critical point. Impurities present in the ethane and ethylene gave retrograde systems; reduction of the impurities yielded coexistence curves which were flat along the temperature axis to 0.001°C. When the height of the ethylene system was decreased the range of densities over which the curve was flat was diminished. Stirring of the system caused the curve to be rounded. Similar results, confirming those of Weinberger and Schneider, were obtained with xenon. The observed behavior is in good agreement with the hypothesis that the major part of the flat top effect is due to gravitational compression.

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## INTRODUCTION

The question of whether the liquid–vapor coexistence curve of a one-component system is flat over a finite density range at the maximum temperature of coexistence (the critical temperature) has not been satisfactorily resolved, either theoretically or experimentally.

A "flat top" was originally predicted by Harrison and Mayer (10, 11) from a statistical–mechanical treatment of vapor condensation, although Zimm (21) has recently modified the theory so that a rounded top is predicted, similar to that given by the classical Van der Waals equation of state. Rice (15, 16), on the other hand, has outlined a theory based upon a thermodynamic treatment of molecular clusters which predicts a flat top.

The experimental findings have proved to be contradictory. Except for the measurements of Schroer (17), who found evidence of a flat top region, all of the coexistence curves reported in the early literature show rounded tops. More recently, Maass and co-workers (9, 12, 14) found short flat tops for ethane and ethylene, although some of their observations have been questioned (1, 2, 15).

The present experimental study was undertaken in a further attempt to resolve the question, using an experimental method which, unlike that of the earlier measurements (9, 14), made it possible to determine a complete coexistence curve on the same sample, thus eliminating the effect of variable composition. The sensitivity, although not the absolute accuracy, was high.

While this work was in progress, Atack and Schneider (2) reported that the coexistence curve of sulphur hexafluoride had a rounded top. In a later investigation of xenon, however, Weinberger and Schneider (18) found a well-defined flat top; when the vertical height of the system was decreased the flat top portion was substantially reduced, suggesting that the effect was due to gravitational compression. The observed flat top widths were later shown (20) to agree reasonably well with values calculated from compressibility measure-

[1] *Manuscript received February 13, 1953.*
*Contribution from Chemistry Department, McGill University, Montreal, Que.*
[2] *Holder of a Fellowship from the National Research Council of Canada.*

ments on the assumption that the effect was due entirely to gravity. At the same time, a study of the gravity effect in ethane by light scattering carried out in this laboratory (13) pointed to the existence of a flat top region.

The initial measurements were made using ethane and ethylene. In the preliminary experiments, the systems gave rounded tops and exhibited retrograde condensation; when precautions were taken to minimize impurities and to allow equilibrium conditions to be approached, the coexistence curves were found to have flat tops. In view of the contradictory results of Schneider *et al.* (2, 18) on sulphur hexafluoride and xenon, it was decided to extend the present investigation to the latter substance. Excellent confirmation of Weinberger and Schneider's (18) measurements was obtained.

Experiments on the effect of bomb height and stirring confirm previous suggestions (13, 18) that the flat tops are principally due to gravity.

## EXPERIMENTAL

### *Apparatus*

The experimental arrangement used is shown in Fig. 1. The sample was contained in a vertical pyrex bomb of 10 mm. I.D. and 3 mm. wall thickness. The contents could be vigorously stirred by a small perforated iron slug moved up and down by two magnets mounted on a guide rod.

One end of the bomb (the only glass component in the high pressure system) was terminated by a length of capillary sealed to the metal system through the gasket N.

The system was arranged so that the free volume of the bomb could be continuously varied by pushing mercury into the bomb from the stainless steel injector. The injector was a piston–cylinder arrangement in which the shaft B was moved up and down the space in the block D by means of a long screw thread which engaged in A. A, equipped with spokes for turning, had a ball bearing movement on F, the latter being rigidly connected to C by rods. The piston was maintained vacuum and pressure tight by means of a teflon gasket E which sat between two fiber rings and was tightened around the piston shaft by tightly screwing D into C. The bottom of the injector was fitted with an adapter nut to take a standard pressure connector. After careful evacuation the space in D was filled with mercury; failure to outgas both the mercury and the injector carefully before filling caused erratic fluctuations in the mercury column during a run, presumably due to liberation of occluded gases in the injector.

The injector delivered 0.07570 cc./turn. Fractions of a turn could be determined to 2 degrees of arc. Volume changes measurable to 0.0005 cc. were therefore possible. The injector design is essentially that of Keyes (6) and has been used, but never described, by others (3, 8, 13). A description has been included here for future reference.

The injector had a capacity of 6.5 cc. whereas a typical bomb had a total volume of 13 cc. The incorporation of a mercury reservoir R extended the range over which the amount of mercury injected into the bomb, and hence the free volume, could be varied. Additional mercury could be run into the injector from R by closing valve G and opening valve L.

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The mercury injector, bomb, reservoir, and valves G, H, and L (Aminco superpressure with teflon packings) were mounted on a rigid brass insert frame (not shown in Fig. 1) which fitted into a thermostat tank. The valves were operated by rods extending through the top of the bath. This frame also carried the knife heaters, cooling coils, and high speed stirrers of the thermostat.

The thermostat tank was of sheet brass and was equipped on each side with a vertical armor-plate glass window. The tank was enclosed in a wooden box, insulated with rock wool, and containing plexiglass windows. A clear oil (Risella No. 17) was used as the thermostat medium. A fluorescent lamp placed behind the bath provided a uniform field of white light. The bomb contents were thus viewed by transmitted light.

The temperature of the bath could be maintained constant, by manual operation of the knife heaters, to better than 0.001°C., using as a control a high resistance thermistor (Western Electric No. 14A) in a sensitive Wheatstone bridge circuit. Ordinarily, temperatures were measured to a precision of ± 0.001°C., by a Beckmann thermometer, calibrated against a standard thermometer to an absolute accuracy of ± 0.01°C. In comparing temperatures during the course of a run, however, thermistor resistance readings were used. It should be emphasized then, that when "flat tops" are spoken of later, the uncertainty in their flatness is only about ± 0.0005°C.

*Materials*

Ohio Chemical Company "anaesthetic" grade ethane and ethylene were used in the earlier runs. These materials showed retrograde condensation and were, therefore, impure. Some of the impurities were shown to originate from the gasket which was used at the glass–metal seal.

In later experiments, a fiber gasket was substituted for teflon and Phillips Petroleum Company "Research Grade" ethane (99.75 mole % purity) and ethylene (100 mole % purity) were used with greatly improved results.

The xenon was obtained from Linde Air Products Corporation. Impurities were stated as being less than 280 p.p.m.

*Procedures*

The gases, after being fractionated over liquid nitrogen and roughly metered in a glass vacuum system, were introduced into the bomb in one of two ways, designated respectively as the high pressure and the low pressure methods.

In both cases the mercury from the injector was brought to a point between valves G and H (Fig. 1) and with G closed and H opened the system was thoroughly evacuated.

In the high pressure method an excess of gas was condensed into the steel bomb U (Fig. 1) with liquid nitrogen. Valve M was then closed and, with the bath at several degrees below the critical temperature, the liquid in U was distilled into the glass bomb. When the desired amount had been introduced, H was closed, G opened, and the mercury was run up into the glass bomb.

This method allowed the high pressure liquid to come into contact with the valve packings and gasket material for a considerable length of time and to dissolve out impurities. Many of the early failures to obtain pure systems were

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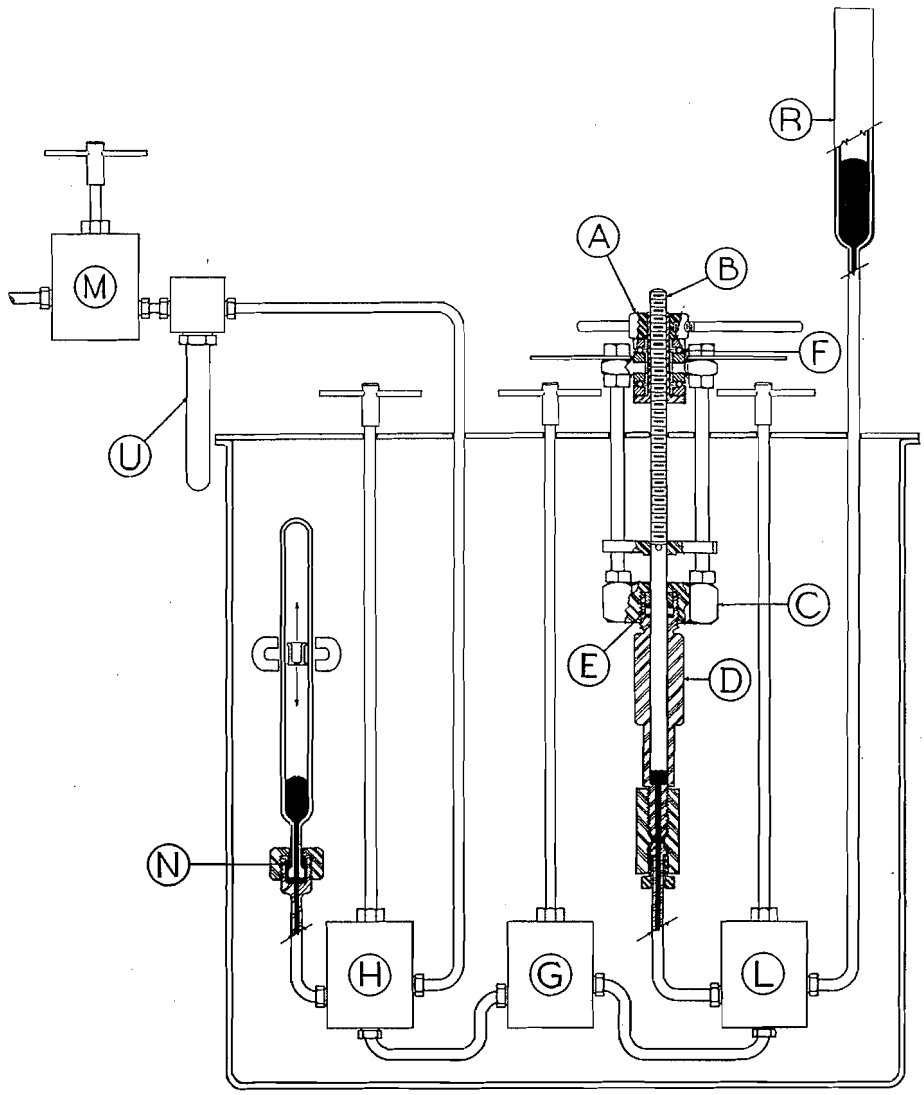



FIG. 1. Experimental arrangement.

attributed to this effect. Weinberger and Schneider (18) have reported similar experiences.

In the low pressure filling method the gas was condensed directly into the glass bomb. Paper drinking cups, with holes cut in their bottoms, were "nested" snugly on the bomb and contained the liquid nitrogen for this purpose. Valve H was closed, G was opened, and the mercury was run up into the bomb before the gas was allowed to warm up. This method led to more consistent behavior.

Mean densities ($\bar{\rho}$) were calculated from the volume and mass. The total volume of the bomb from a datum line on the capillary was measured and during a run this datum was used as a zero for injector readings. From these

measurements the free bomb volume at any injector reading could be determined. After a run, the entire gas sample was condensed into a glass weighing bomb and weighed. Alternatively, the gas could be removed in stages and further experiments made on the residue after additional mercury was run in. In this way the effective height of the system was varied. The portion removed was condensed into glass weighing bombs, and the mass of the residue determined by difference. Absolute densities computed by the weighing method were accurate to 1 part in 500. Relative densities were dependent only on injector readings and, on the basis of a free bomb volume of 10 cc., were precise to 1 part in 20,000.

## RESULTS

### A. *Retrograde Coexistence Curves*

#### *Ethane*

In the preliminary experiments both teflon and fiber gaskets were used in the glass–metal union and the samples were introduced into the bomb under pressure. Of 13 fillings only two had critical temperatures corresponding to the maximum temperature of liquid–vapor coexistence.

The other 11 runs yielded coexistence curves of which that shown in Fig. 2

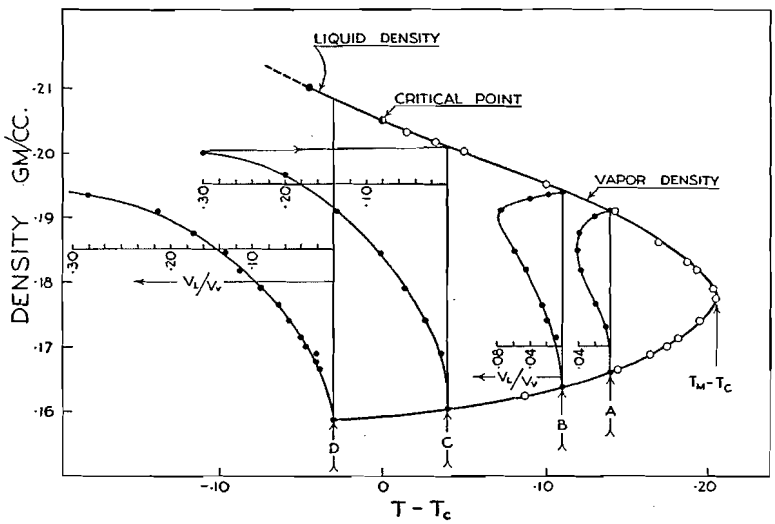



FIG. 2. Coexistence curve of an impure ethane sample showing retrograde condensation of the first kind. The large circles designate temperatures of appearance of the first droplet of liquid (open circles) or bubble of vapor (solid circles) on cooling at constant density. The rise and subsequent fall of the meniscus when the system is compressed isothermally is shown as the ratio of liquid volume to vapor volume (plotted as small solid circles on the auxiliary axes parallel to the temperature axis) for three isotherms (*A*, *B*, and *C*). Nonretrograde behavior occurs below $T_c$ (Isotherm *D*.)

is a typical example. The critical temperature, $T_c$, as characterized by reappearance of the meniscus at the center of the bomb on cooling (and a maximum in opalescence) was 0.205°C. below the maximum coexistence temperature $T_m$. The systems thus exhibited retrograde condensation of the first kind (4, 5, 7) which indicated that they were multicomponent.

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Also shown in Fig. 2 are meniscus positions found on isothermal compression of the system at four different temperatures, three above and one below $T_c$. The results are plotted as the ratio of liquid and vapor volumes ($V_l/V_v$) versus average density. The curves have their respective isotherms as base lines.

On compression of the system isothermally along $A$ ($T - T_c = 0.140$°C.) the first droplet of liquid appeared when the coexistence density of the vapor was reached. On further compression the volume of liquid increased, rose to a maximum, and then decreased. At a density corresponding to the upper part of the coexistence curve the amount of liquid had decreased to zero. Compression along $B$ ($T - T_c = 0.110$°C.) showed the same behavior, although the average density for maximum meniscus height showed a shift toward higher densities. At a temperature corresponding to $C$ ($T - T_c = 0.04$°C.) this shift was so pronounced that the average density for maximum meniscus height differed from the upper coexistence density, where the amount of liquid was zero, by only about 0.001 gm./cc.

This sequence is in contrast to that in a nonretrograde system, i.e., where $T_c = T_m$. In the latter case continued compression increased the amount of liquid until it entirely filled the bomb tube. These systems are discussed later. This behavior is also exhibited in retrograde systems at temperatures below $T_c$. Curve $D$ is such an isotherm ($T - T_c = -0.03$°C.); here $V_l/V_v$ approached infinity as the upper coexistence density was approached.

The various retrograde fillings exhibited critical temperatures ranging from 32.28 to about 33°C. The relation between the critical (or "plait-point" (10)) and maximum (or "critical point of contact") temperatures for eight fillings of Research Grade ethane (which showed a smaller retrograde effect than the Anaesthetic Grade) is shown in Fig. 3. Included are the two fillings where $T_m = T_c \pm 0.0005$°C. These two fillings yielded flat top coexistence curves and are discussed below.

*Ethylene*

Ethylene fillings obtained by the high pressure method also showed retrograde

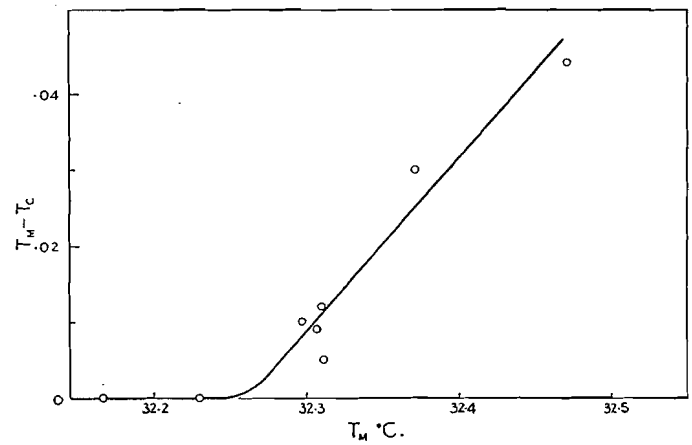



FIG. 3. Variation of ($T_m - T_c$) with maximum coexistence temperature for ethane systems.

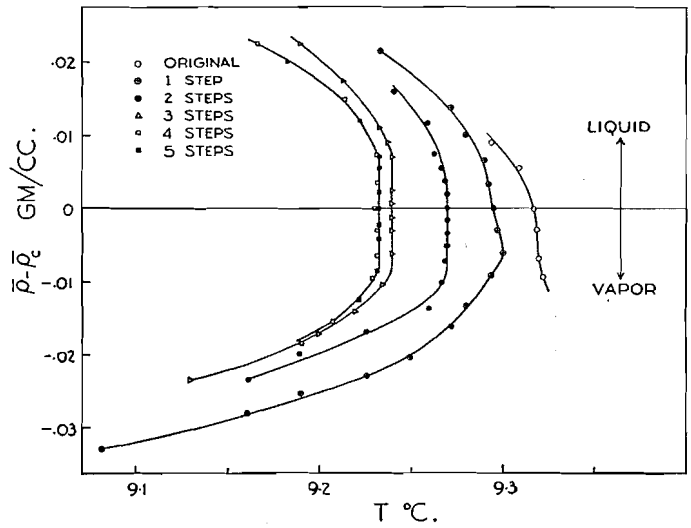



FIG. 4. Transition of coexistence curves of ethylene from retrograde to flat-topped systems by a stepwise removal of portions of the liquid phase.

condensation. Fig. 4 shows a series of coexistence curves obtained after bleeding off small amounts from the original bomb filling as follows. After the first (retrograde) curve was obtained the mercury was withdrawn and the bath was kept at a temperature at which about 10% of the bomb contents was liquid. After the contents were well stirred a small quantity of liquid was allowed to escape from the bomb. When the coexistence curve was again determined, the critical temperature was lower than before. From this it was concluded that a purification had taken place. Additional amounts were removed in steps until there was no further temperature decrease. The last four curves showed flat tops, the temperatures of the final two agreeing to within experimental error at a temperature of 9.23°C.

In this series of runs the mass of each sample removed was determined by pressure measurements in the calibrated glass system. The critical densities agreed within 3%, the limit of accuracy of this method. However, the plot of $\bar{\rho} - \bar{\rho}_c$ makes comparison of the various curves much easier. The low density section of the first retrograde curve could not be obtained. At the lowest determined density the mercury was already withdrawn to the bottom of the bomb.

It is probable that the impurities were more soluble in the liquid than in the vapor, and were progressively removed by extraction. The relationship between $T_m - T_c$ and $T_m$ for this series was similar to that shown for ethane in Fig. 3.

B. *Coexistence Curves Showing Flat Tops*

*Ethane*

Using a fiber gasket in the bomb assembly, the high pressure filling method, and Phillips "Research Grade" gas, one system was obtained showing a flat top at 32.23°C. over a considerable density range. Unfortunately before the weight of material could be determined a leak developed in the metal tubing and the filling escaped.

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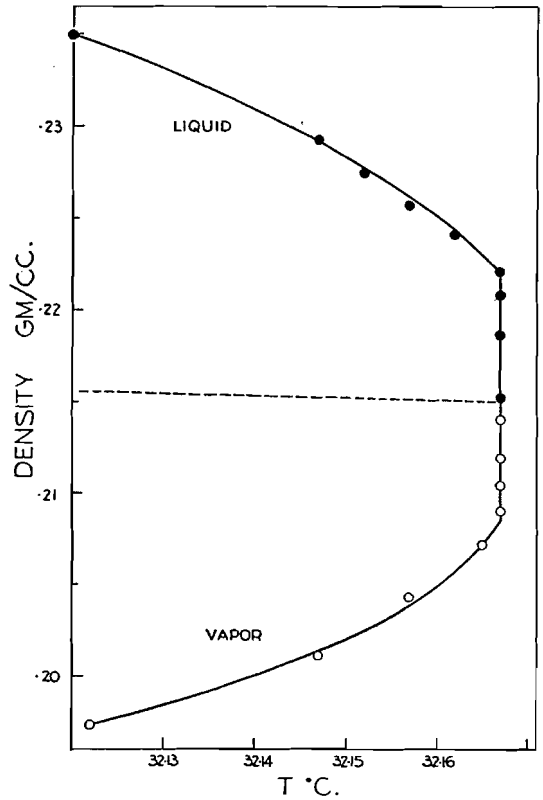



FIG. 5. Flat-topped coexistence curve of ethane in a filling for which the bomb height was 15 cm.

A second filling, having a flat top at 32.167°C., was obtained under the same conditions. The data are shown in Fig. 5 and Table I. The dashed line represents application of the law of rectilinear diameters and extrapolates to the center of the flat top portion at a density of 0.215 gm./cc., designated as $\bar{\rho}_c$. The observed $T_c$ was lower than previously reported values of 32.23 ± 0.01 (1, 12) for carefully purified ethane samples.

Points on all of the coexistence curves thus far discussed (including retrograde fillings) were obtained in the following way. At a fixed injector setting the bomb was slowly heated with continuous stirring to several thousandths of a degree above the point at which all trace of liquid disappeared. The bomb was then cooled in steps of 0.001°C. with stirring between steps. After each temperature decrement the bomb was thermostatted for about ten minutes and observed closely. At low or high densities the coexistence point was precisely defined by the first appearance of a minute droplet of liquid or vapor. At intermediate densities the clear reddish opalescence coagulated suddenly into a grayish-red "wet fog" at the coexistence point and settled out slowly to form a visible meniscus.

If the mean density in a retrograde system was greater than the mean density corresponding to $T_m$, the initial fog of condensation always appeared in the top

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TABLE I

LIQUID–VAPOR COEXISTENCE DENSITIES OF ETHANE
$T_c = 32.17 \pm 0.01$°C.
Bomb height 15 cm.

| Density, gm./cc. | $(T_c - T)$°C. |
|---|---|
| 0.2350 | .047 |
| 0.2293 | .020 |
| 0.2275 | .015 |
| 0.2257 | .010 |
| 0.2241 | .005 |
| 0.2221 | .000 |
| 0.2208 | .000 |
| 0.2186 | .000 |
| 0.2152 | .000 |
| 0.2140 | .000 |
| 0.2119 | .000 |
| 0.2104 | .000 |
| 0.2090 | .000 |
| 0.2072 | .002 |
| 0.2043 | .010 |
| 0.2011 | .020 |
| 0.1973 | .045 |

of the bomb, even though this density range included a region below $\bar{\rho}_c$. As discussed by Murray and Mason (13) this points to the existence of vertical density gradients before condensation takes place.

This phenomenon was also noted in the flat top fillings of ethylene shown in Fig. 4 and ethane shown in Fig. 5. This may constitute a more sensitive test for retrograde characteristics than the relationship between $T_c$ and $T_m$ with the methods of temperature control and measurement employed here. It is, therefore, possible that while the tops were flat within $\pm$ 0.0005°C., they nevertheless possessed a finite slope, i.e., the systems were in fact retrograde.

At this stage of the experimental work, it was noted by Murray and Mason (13) that, near the critical point, settling periods considerably longer than those allowed in the measurements discussed above were required to establish the vertical distribution of opalescence after stirring. Thus there existed the possibility that all of the curves thus far determined were not only retrograde, but also were not true equilibrium curves. In the subsequent experiments on ethylene and xenon (described below) additional precautions were therefore taken to eliminate the retrograde effect and to allow for the establishment of equilibrium.

*Ethylene*

An additional sample of ethylene was introduced into the apparatus, this time using the low pressure filling method. The original filling gave a flat topped curve. Two high pressure bleedings were carried out, as in the earlier ethylene runs. Approximately 10% of the sample was removed during these steps. On determining the new curve the flat top temperature was found to be unchanged within the experimental error. The bomb length at a density corresponding to the mid-point of the curve for this filling was 15 cm.

To allow equilibrium gradients to be established, the following procedure

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was adopted. The system was heated above the temperature of disappearance of liquid, and cooled with continuous stirring to several thousandths of a degree above the expected condensation point. Stirring was then stopped and the temperature was kept constant for periods of one-half to two hours. If there was no condensation the temperature was lowered in steps of not more than 0.001°C. (without intermediate stirring) and the bath thermostatted for 10 min. between each stop, until finally a meniscus formed. In this manner large vertical opalescence gradients similar to those reported by Murray and Mason (13) were established near the critical point.

The meniscus behavior differed somewhat from that observed previously. At densities on the flat top portion greater than $\bar{\rho}_c$ the position of maximum opalescence was towards the top of the bomb; near $\bar{\rho}_c$ the maximum was near the center, while below $\bar{\rho}_c$ it was towards the bottom of the bomb. *Upon condensation, fog initially formed at the point of maximum opalescence* and settled out to form a meniscus at or near the same point. This is evidence not only of a gravity effect but also that $T_c = T_m$, i.e., the system was nonretrograde. The other ethylene system and the xenon systems discussed below showed the same pattern of behavior.

Systems examined as described above have been designated as "unstirred", although it should be borne in mind that they were stirred in the earlier stages of the temperature sequence.

In another type of experiment an attempt was made to prevent density gradients from being established. On cooling from above $T_c$ the contents were stirred every 20 sec. with one upward and one downward stroke of the slug. The temperature was lowered in steps of 0.001°C. spaced about ten minutes apart. The coexistence temperature was taken to be the maximum at which a stable whisp of fog persisted during the downward motion of the stirrer. Systems examined this way are designated as "stirred".

At densities above and below $\bar{\rho}_c$, the coexistence temperatures, which could be reproduced to 0.001°C. except near $\bar{\rho}_c$, *were lower than for the unstirred systems of corresponding density* (Fig. 6 and Table II). The flat top portion was substantially reduced and appeared to have disappeared entirely; the apex of the stirred coexistence curve touched the center of the unstirred flat top at 9.258 $\pm$ 0.002°C. It was difficult to determine precisely the condensation point with stirring near $\bar{\rho}_c$ because of the intense opalescence. It had been found that continuous stirring appeared to have a slight heating effect. When measured condensation temperatures for various rates of continuous stirring were extrapolated to zero stirring rate, the temperature was the same as the condensation temperature found by intermittent stirring. Thus it is presumed that no spurious heating effects were caused by the intermittent stirring employed in these experiments.

After the above measurements were carried out, a portion of the sample was removed at high pressure so that the residue gave a critical filling at a bomb height of 6 cm. The critical temperature was within 0.001°C. of its previous value. Stirred and unstirred coexistence curves were determined as before. The results are shown in Fig. 6 and Table II.

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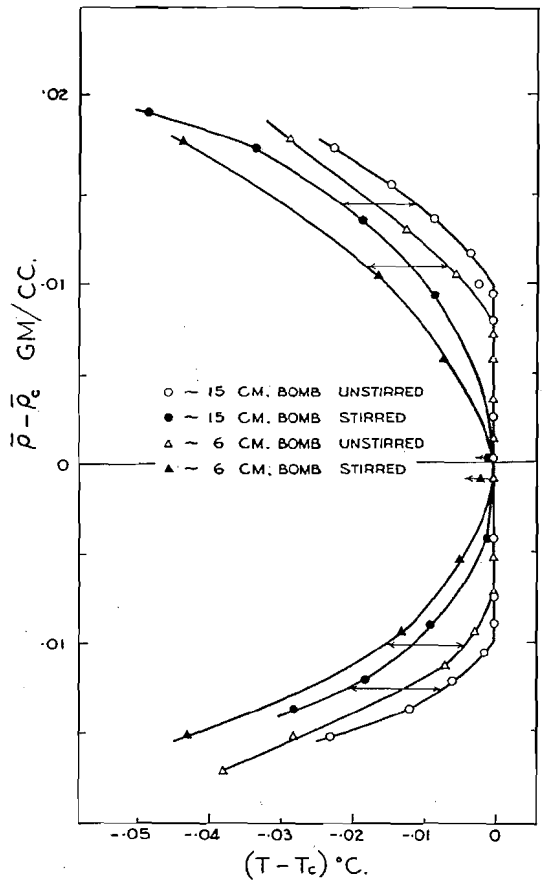



FIG. 6. Coexistence curves of "stirred" and "unstirred" ethylene in systems 6 cm. and 15 cm. in height.

The $\bar{\rho}_c$ values obtained from the two unstirred systems were 0.2091 and 0.2098 gm./cc. for the 15 cm. and 6 cm. bombs respectively; the agreement is therefore within the accuracy of the absolute density determination. By plotting $\bar{\rho} - \bar{\rho}_c$ against $T - T_c$, as has been done in Fig. 6, the centers of the curves can be brought into coincidence to show the influence of bomb height. The range of densities over which the curve was flat was greater ($0.095\ \bar{\rho}_c$) for the 15 cm. filling than ($0.076\ \bar{\rho}_c$) for the 6 cm. filling, as would be expected from the gravity effect (13, 18). The height effect causes the curves to be separated over a temperature interval below $T_c$.

The significant difference between the 15 cm. and 6 cm. stirred fillings indicates clearly that height effect, although reduced, was not eliminated.

*Xenon*

Xenon fillings were obtained by the low pressure distillation method with a fiber gasket in the glass–metal seal.

The first filling gave an unstirred coexistence curve with a flat top. The

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TABLE II

LIQUID–VAPOR COEXISTENCE DENSITIES OF ETHYLENE
$T_c = 9.26 \pm 0.01$°C.

| Bomb height 15 cm. | | | Bomb height 6 cm. | | |
|---|---|---|---|---|---|
| Density, gm./cc. | $(T_c - T)$°C. | | Density, gm./cc. | $(T_c - T)$°C., | |
| | Unstirred | Stirred | | Unstirred | Stirred |
| 0.2285 | | .048 | 0.2333 | .057 | |
| 0.2265 | .022 | .033 | 0.2280 | .027 | .042 |
| 0.2245 | .014 | | 0.2330 | .011 | |
| 0.2225 | .008 | .018 | 0.2205 | .004 | .015 |
| 0.2206 | .003 | | 0.2172 | .000 | |
| 0.2188 | .002 | | 0.2158 | .000 | .006 |
| 0.2183 | .000 | .008 | 0.2135 | .000 | |
| 0.2169 | .000 | | 0.2113 | .000 | |
| 0.2115 | .000 | | 0.2091 | .000 | .000 to .003 |
| 0.2092 | .000 | .000 to .002 | 0.2048 | .000 | .004 |
| 0.2047 | .000 | .000 to .002 | 0.2028 | .000 | |
| 0.2015 | .000 | | 0.2007 | .002 | .012 |
| 0.2000 | .000 | .009 | 0.1988 | .006 | |
| 0.1984 | .002 | | 0.1949 | .027 | .042 |
| 0.1969 | .006 | .018 | 0.1930 | .037 | |
| 0.1953 | .012 | .028 | | | |
| 0.1938 | .023 | | | | |

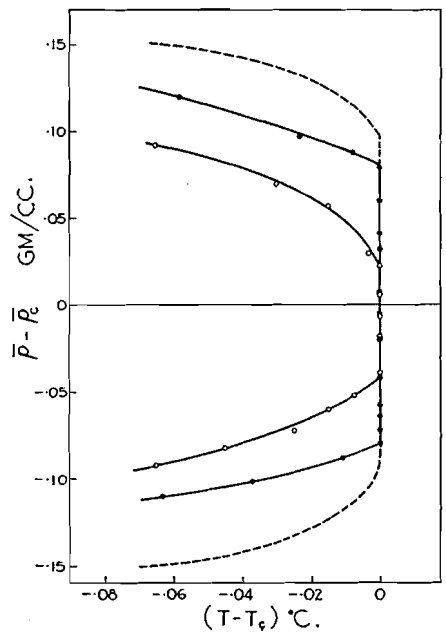



FIG. 7. Coexistence curves of xenon (unstirred) at critical filling heights of 4 cm. (solid circles) and 13 cm. (open circles). The broken line is that obtained by Weinberger and Schneider (18) for a height of 19 cm.

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critical temperature was 16.60 ± 0.01°. However, before the run could be completed, the bomb tube exploded, and densities could not be determined.

Measurements on a second sample whose mean critical density occurred at a bomb height of 13 cm. are shown in Figs. 7 and 8 and Table III. The curve, determined by the procedures described above for ethylene, was flat over a density range of 0.161 $\bar{\rho}_c$ for the unstirred system and was rounded for the stirred system.

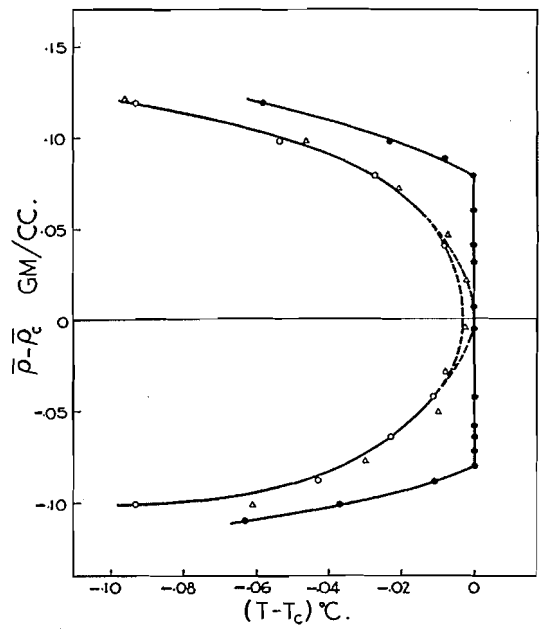



FIG. 8. Stirred (open circles) and unstirred (solid circles) coexistence points of xenon at a bomb height of 13 cm. The triangles are points from Weinberger and Schneider's data (18) at a bomb height of 1.2 cm.

When a portion of the sample was removed so that the mean critical filling existed at a bomb height of 4 cm., the unstirred curve was flat over a density range of only 0.063 $\bar{\rho}_c$. In this case, the stirring data showed considerable scatter, an effect believed to be caused by gross disturbances produced by the stirrer which, in these experiments, occupied a substantial fraction of the total volume. Generally speaking, however, the effect of stirring was the same as before, i.e., the curve was rounded, but a quantitative comparison with the stirred curve at 13 cm. was not possible.

The unstirred data fall into line remarkably well with Weinberger and Schneider's data (18) on a 19 cm. bomb. In their experiments, Weinberger and Schneider cooled in intervals of 0.001°C., with cooling between each step; the settling time after stirring is not clearly stated, but it appears to have been of the order of one-half to one hour. The procedure was thus similar but not identical to the one here used. Both $\bar{\rho}_c$ (1.110 ± 0.002 gm./cc.) and $T_c$ (16.59 ± 0.01) observed here show good agreement with Weinberger and Schneider's values of 1.105 ± 0.002 gm./cc. and 16.590 ± 0.001°C. respectively. When the data are

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TABLE III

LIQUID–VAPOR COEXISTENCE DENSITIES OF XENON
$T_c = 16.59 \pm 0.01$°C.

| Bomb height 13 cm. | | | Bomb height 4 cm. | |
|---|---|---|---|---|
| Density, gm./cc. | $(T_c - T)$°C. | | Density, gm./cc. | $(T_c - T)$°C., |
| | Unstirred | Stirred | | Unstirred |
| 1.229 | .058 | .093 | 1.202 | .065 |
| 1.208 | .023 | .053 | 1.180 | .030 |
| 1.198 | .008 | | 1.167 | .015 |
| 1.189 | .000 | .027 | 1.140 | .003 |
| 1.170 | .000 | | 1.132 | .000 |
| 1.151 | .000 | .008 | 1.116 | .000 |
| 1.142 | .000 | | 1.105 | .000 |
| 1.117 | .000 | | 1.092 | .000 |
| 1.105 | .000 | | 1.071 | .000 |
| 1.090 | .000 | | 1.058 | .007$_5$ |
| 1.068 | .000 | .011 | 1.050 | .015 |
| 1.052 | .000 | | 1.038 | .025 |
| 1.046 | .000 | .023 | 1.028 | .045 |
| 1.038 | .000 | | 1.018 | .065 |
| 1.030 | .000 | | | |
| 1.022 | .011 | .043 | | |
| 1.009 | .037 | .093 | | |
| 1.000 | .063 | | | |

compared on a differential basis by plotting $(\bar{\rho} - \bar{\rho}_c)$ against $(T - T_c)$ to eliminate absolute errors, as has been done in Fig. 7, the three curves assume a regular order.

Weinberger and Schneider (18) also determined the coexistence curve in a bomb arranged horizontally so that the height was 1.2 cm.; as far as can be ascertained from their description of the experiment, the points were determined

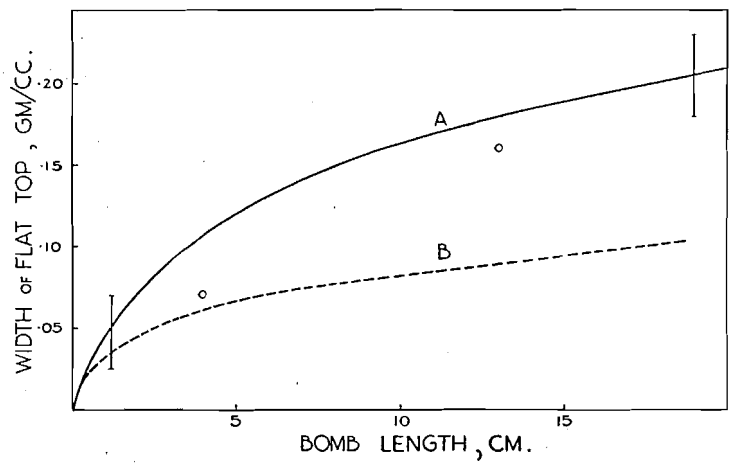



FIG. 9. Width of flat top of xenon coexistence curve as a function of bomb height. Vertical lines are from Weinberger and Schneider. The curves are those calculated by Weinberger, Habgood, and Schneider (20).

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with continuous stirring. The data (Fig. 8) show good agreement with the stirred values observed here in the 13 cm. bomb. In view, however, of the definite height effect observed with the stirred ethylene (Fig. 6) and of differences in the method of stirring between the present experiments and those of Weinberger and Schneider, the agreement between these two curves may be purely fortuitous. It is of interest to note that Weinberger and Schneider consider their curve to have a short flat apex (Fig. 9), although there is no evidence of this in the present stirred systems.

The flat top widths are shown in Fig. 9. The solid curve (*A*) was obtained by Weinberger *et al.* (20) using an experimentally determined critical isotherm for xenon. It was calculated (18) on the assumption that gravitational effects are capable of explaining the whole of the flat top width. Since the isotherm data were obtained in a bomb of finite height, these calculations represent an upper limit for the variation of flat top width with bomb length. Similar calculations, using a classical Van der Waals isotherm, yielded the lower curve (*B*). It would appear that the actual curve is between *A* and *B*. This conclusion might also be inferred from the more recent work of Weinberger and Schneider (19), although here the evidence is not unequivocal.

## DISCUSSION

The foregoing results provide abundant evidence of flat-topped coexistence curves in systems of sufficient purity so that the effect is not masked by retrograde condensation. The increase in flat top width with increasing bomb height, the positions of initial condensation in both retrograde and nonretrograde systems and finally the effect of stirring are all consistent with the hypothesis that the flat top is due principally to gravitational compression (13, 17). It cannot be stated categorically, however, that the flat top effect would be completely eliminated in a bomb of zero height. Proof of this by direct measurement of coexistence densities would involve very great experimental difficulties.

The differences between stirred and unstirred coexistence curves show the importance of establishing equilibrium. It should be emphasized that the procedures used here were somewhat arbitrary and were adopted as matters of practical compromise. The height effect observed in stirred ethylene (Fig. 6) makes it doubtful that the stirring eliminated the gravity effect entirely. Thus the true zero height coexistence curve may be inside the 6 cm. stirred curve. On the other hand, there is no assurance that the settling periods in the unstirred systems were of sufficient duration to establish true equilibrium distributions. It is conceivable that had longer settling times been allowed, greater density differences would have been established with correspondingly wider flat-top regions; this might yield closer agreement with Weinberger, Habgood, and Schneider's calculated curve (Fig. 9) for xenon. Failure to allow adequate settling times may have been the reason why Atack and Schneider (2) did not observe a flat top with sulphur hexafluoride.*

** Added in proof: Dr. D. Atack has recently informed us that in the experiments with sulphur hexafluoride, the system was cooled in steps of 0.001°C. with continuous stirring in the cooling process, and periods from 1 to 24 hr. were allowed for settling before further cooling. The rounded coexistence curve may therefore have been due to retrograde condensation.*

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If the flat top is due solely to gravity, as is indicated, it is of practical but not of fundamental importance in the critical phenomena. The time lags in establishing equilibrium, on the other hand, are believed to be of greater significance and will be discussed in a later paper.

ACKNOWLEDGMENTS

The authors wish to acknowledge their indebtedness to Dr. W. G. Schneider of the National Research Council for providing the injector used in this investigation and to Mr. A. Rezanowich for assistance in construction of the apparatus.

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# CARBODIIMIDES

## PART II.* THE REACTION OF SULPHONIC ACIDS WITH CARBODIIMIDES. A NEW METHOD OF PREPARATION OF SULPHONIC ANHYDRIDES[1]

By H. G. Khorana

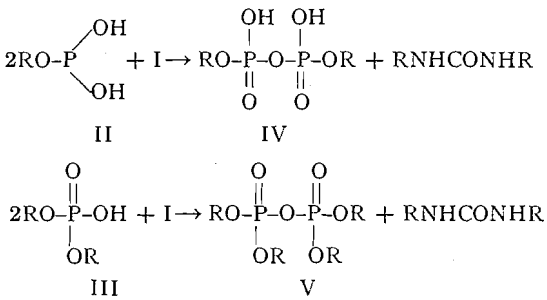
ABSTRACT

Methane, benzene, and *p*-toluene sulphonic acids react instantaneously at room temperature with dicyclohexyl and di-*p*-tolyl carbodiimides to form the corresponding sulphonic anhydrides, VI, and disubstituted ureas, VII. The use of di-*p*-tolyl carbodiimide affords a convenient general method of preparation of sulphonic anhydrides.

Interest in the chemistry of carbodiimides ** (I, R = alkyl or aryl) has been revived during the past decade or so and a very large number have been prepared (8, 13, 14). Among the reactions of these compounds,

$$RN{=}C{=}NR$$
I

those with carboxylic acids have been by far the most studied (12) and have proved to be particularly interesting. This study has recently been extended to the strongly acidic mono- and disubstituted esters (II and III respectively).* It was shown that these acids reacted instantaneously at room temperature



with aliphatic (dicyclohexyl, I, R = *cyclo*hexyl) and aromatic (di-*p*-tolyl, I, R = *p*-tolyl) carbodiimides to form respectively the symmetrical disubstituted and tetrasubstituted esters of pyrophosphoric acid (IV and V respectively). This method has found application in the nucleotide field (3).

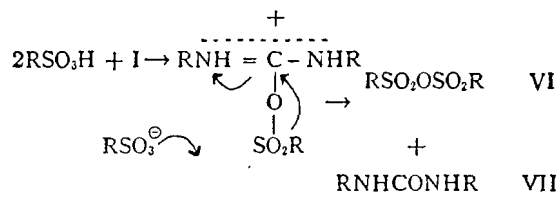
In the present investigation the reactions of sulphonic acids with dicyclohexyl (8, 9) and di-*p*-tolyl carbodiimides (11, 13, 14) have been examined. As expected, these strong acids react analogously to the phosphoric acids (II and III) to form readily and practically quantitatively the corresponding sulphonic anhydrides (VI) and disubstituted ureas (VII). The formation of the sulphonic anhydrides was clearly shown in preliminary experiments through a check

[1] *Manuscript received February 25, 1953.*
*Contribution from the Chemical Laboratory of the British Columbia Research Council, Vancouver 8, B.C.*

**Studies on Phosphorylation. Part XI. The reactions of mono and diesters of phosphoric acid with carbodiimides, by H. G. Khorana and A. R. Todd, J. Chem. Society, London, 1953, in press, is regarded as Part I of this series.*

***The subject has been reviewed recently; H. G. Khorana. Chem. Reviews, 1953. In press.*

of the melting points and their general reactions, particularly that with amines to form the sulphonamides and the amine salts. The latter reaction also serves




as a method of assay of the anhydrides

$$RSO_2OSO_2R + R'NH_2 \longrightarrow RSO_3^{\oplus}NH_3R' + RSO_2NHR'.$$

From a preparative point of view the use of dicyclohexyl carbodiimide was not completely satisfactory because of the difficulty in separating the dicyclohexyl urea from the sulphonic anhydrides. However, through the use of di-*p*-tolyl carbodiimide and benzene as the solvent, the complete removal of di-*p*-tolyl urea was readily achieved, the urea being insoluble in this solvent. In this way, the anhydrides of methane, benzene, and *p*-toluene sulphonic acids have been prepared in excellent yield. These three examples are thought to be sufficient to establish the generality of this convenient method of preparation of alkyl and aryl sulphonic anhydrides.

A recent communication* (4) describes another general method for the production of aromatic sulphonic anhydrides by fusion of the acids with phosphorus pentoxide. The products are, however, rather difficult to isolate in pure form and the yields do not exceed 50%. The present method affords directly excellent yields of pure anhydrides and promises to offer particular advantage where valuable sulphonic acids might be involved.

## EXPERIMENTAL

### *Methane Sulphonic Anhydride*

Methane sulphonic acid (Eastman Kodak Technical) was distilled *in vacuo* and the constant boiling fraction (112° at 2 mm.) was employed for the preparation of the anhydride.

To methane sulphonic acid (3.1 gm.) was added as quickly as possible a solution in anhydrous benzene (30 cc.) of di-*p*-tolyl carbodiimide (4 gm.; *ca.* 10% excess) and the mixture agitated vigorously with exclusion of moisture. Di-*p*-tolyl urea separated from the light yellow solution immediately and was removed (4 gm.) after one hour and washed twice with small amounts of anhydrous benzene. The clear filtrate was evaporated at 30° under reduced pressure. The light yellow crystalline residue was taken up in dry ether (10 cc.) and kept at – 10°. A practically colorless crop of needles (2.3 gm.) was collected after 18 hr. and washed with cold ether. The mother liquor on concentration and standing gave a second crop. Total yield of methane sulphonic anhydride

**The older methods of preparation, notable among which is the reaction of sulphonyl chlorides with silver salts of sulphonic acids, are also summarized in this paper.*

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2.54−2.6 gm. (*ca.* 92%) m.p. 68°−70°. Recrystallization from ether gave pure white material with m.p. 71°−72° (Billeter (1) gives m.p. 71°).

On the addition of aniline (1.2 cc., *ca.* 0.013 mole) to benzene solution (8 cc.) of methane sulphonic anhydride (0.87 gm.; 005 mole), anilinium methane sulphonate separated immediately and was collected after 15 min. and washed with benzene; yield, 0.915 gm.; 97% of theoretical. The clear filtrate was extracted thrice with *N* hydrochloric acid, washed once with water, dried with sodium sulphate, and evaporated. The residue (0.82 gm.; 96%) after crystallization from aqueous ethanol gave the sulphonamide, m.p. 101° (Duguet (2) gives m.p. 99°).

*Benzene Sulphonic Anhydride*

Purification of benzene sulphonic acid (Eastman Kodak Technical) was found to be essential. The direct use of the commercially available sample gave much reduced yields of the anhydride.

The technical sample (sesquihydrate; 8 gm.) was dehydrated by the azeotropic removal of water through continued distillation, in its presence, of portions (*ca.* 50 cc. each) of benzene. Finally, a clear solution (40 cc.) of the acid was obtained. Crystallization was induced by chilling the contents to below 0° (under exclusion of moisture throughout), remelting the solvent, and warming the mixture carefully until most of the separated finely crystalline acid redissolved. Keeping the flask at 0−5° for 12 hr. gave a practically colorless crop of crystals, which after the dark brown mother liquor was poured off was washed with more cold anhydrous benzene and dried *in vacuo* over phosphorus pentoxide (yield 2.85 gm.). This sample was employed in the following experiment.

To the rapidly cooled dry benzene solution (15 cc.) of the acid was added at once with agitation, di-*p*-tolyl carbodiimide (2.4 gm.; *ca.* 15% excess) dissolved in the same solvent (10 cc.). The contents turned light yellow and di-*p*-tolyl urea began to separate almost immediately. After an hour, the urea (2.2 gm.) was removed and washed with benzene. The clear filtrate was concentrated to a small volume in a vacuum with exclusion of moisture (2-3 cc.). Crystallization of benzene sulphonic anhydride began soon after addition of ether (15 cc.). After the flask had been overnight at 0°, stout colorless needles (2.15 gm.) were collected and washed with cold ether; m.p. 88°-91° after previous shrinkage (identical with that given by Field (4)). The mother liquor after concentration and standing gave a further crop (0.15 gm.; total yield, 86%).

*p*-Toluidine (0.5 gm.; *ca.* 2.3 mols.) was added to a dry benzene solution (10 cc.) of the anhydride (0.518 gm.) obtained as above. The *p*-toluidine salt of benzene sulphonic acid soon crystallized on shaking and was removed after 15 min. and washed with benzene (0.46 gm.; theoretical). Benzene sulphon-*p*-toluidide was isolated as described for methane sulphonanilide; (yield 0.400 gm.; 97%). After recrystallization from aqueous ethanol (yield, 0.330 gm.), it melted at 123° (Rabaut (6) gives m.p. 122°; Wallach and Huth (10) give m.p. 120°).

*p-Toluene Sulphonic Anhydride*

*p*-Toluene sulphonic acid monohydrate (recrystallized from concentrated

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hydrochloric acid) (3.8 gm.; 0.02 mole) was dehydrated azeotropically as described for benzene sulphonic acid. To its solution in anhydrous benzene (25 cc.) was added rapidly di-*p*-tolyl carbodiimide (2.4 gm.; *ca.* 0.011 mole) dissolved in the same solvent (10 cc.). Some warming was observed and di-*p*-tolyurea separated immediately. (If considerably more concentrated solutions of the reactants were employed part of the sulphonic anhydride crystallized out along with the urea.) After one hour the urea (2.4 gm.; theoretical) was removed, and anhydrous ether (30 cc.) was added to the clear filtrate and the contents kept at 0°. Colorless stout prisms (1.9 gm.) of *p*-toluene sulphonic anhydride were collected after 18 hr. and the mother liquor was concentrated to a small volume (*ca.* 5 cc.) and diluted again with ether (15 cc.). A second crop (1.1 gm.) of equally pure anhydride was thus obtained, m.p. 134-135° (Field (4) gives m.p. 129.5°-131.5°; Meyer (5) quotes m.p. 125°). Total yield, 92% of theoretical.

On adding 0.63 gm. of *p*-toluidine (*ca.* 2.2 mol.) to the benzene solution (10 cc.) of the sulphonic anhydride (0.82 gm.) the *p*-toluidine salt (0.73 gm.) of *p*-toluene sulphonic acid was deposited. *p*-Toluenesulphon-*p*-toluidide was recovered from the benzene solution in the usual way. One crystallization from aqueous ethanol gave 0.55 gm. (84%) of the substance with m.p. 119°-120°. (Reverdin and Cre'pieux (7) give m.p. 117°.)

In an earlier experiment anhydrous *p*-toluene sulphonic acid (from 3.8 gm. of the hydrated sample) was treated with dicyclohexyl carbodiimide (2.3 gm.; *ca.* 10% excess), also dissolved in ether (15 cc.). The colorless material which separated was collected (4.2 gm.) and washed with ether. The filtrate deposited, on standing at 0°, stout crystals of the sulphonic anhydride (0.5 gm.; m.p. 128°-129°). More anhydride (0.95 gm.) was recovered from the colorless material obtained above by fractional extraction with benzene.

ACKNOWLEDGMENT

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# REACTIONS OF SULPHONIC ESTERS

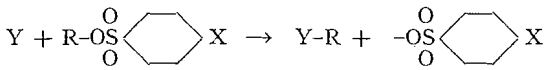
## I. A KINETIC STUDY OF THE EFFECT OF SUBSTITUENTS FOR A SERIES OF SULPHONIC ESTERS[1]

By R. E. Robertson

ABSTRACT

Kinetic data for the solvolysis of parasubstituted methyl, ethyl, and isopropyl benzenesulphonates in ethanol, methanol, methanol–water, and dioxane–water mixtures have been determined. It has been shown that the effect of the ionizing properties of the solvent of $\alpha$-methylation, and of the addition of a strong base show the same general characteristics which for the halides have been considered diagnostic of a change in mechanism from a bimolecular solvolysis to a reaction in which ionization is rate controlling. The changes in the relative effect of para-substituents which accompany the apparent change of mechanism are examined. The greater effect of the para-$NO_2$ substituent over the meta-$NO_2$ substituent for the isopropyl esters under ionizing conditions is attributed to the contribution of resonance stabilization in forming ion.

This is the first paper of a series in which we propose to examine in some detail certain characteristics of reactions involving the displacement of the benzenesulphonate group in the generalized equation



[1]

where Y is a nucleophilic agent which may or may not be charged, R is an alkyl group, and X is a para-substituent.

In this paper we shall report the results of an investigation of the changes in the relative substituent effects for a series of methyl, ethyl, and isopropyl esters in a series of solvents of different ionizing properties, where other evidence has suggested that a possible change in mechanism may occur. Significant changes would be expected in the relative effect of substituents at X if structural changes in R were such as to change the mechanism of the reaction from one having the characteristics of a bimolecular substitution ($S_N2$) to a reaction in which the rate-controlling step is an ionization ($S_N1$) (1, 18).

The evidence that the alkyl benzenesulphonates react by an $S_N2$-$S_N1$ type of mechanism rather than by some alternative mechanism (29), the problems involved in the shift from one mechanism to the other (34), and an investigation of salt effects properly belong to another publication. In this paper we shall limit our discussion of mechanism to the establishment of the correspondence between the kinetic effects of changes in structure, reagent, solvent, and substituents in the benzenesulphonate series with those observed for the organic halides for which the $S_N2-S_N1$ classification was first established (15), and for the alkyl nitrates recently discussed by Baker and Easty (2). The latter show the same evidence for a change of mechanism as the alkyl halides, and like the sulphonates, usually involve the breaking of a C–O bond in the transition state.

Swain and Langsdorf (31), in a recent study of relative effects of para-

[1] *Manuscript received January 6, 1953.*
*Contribution from the Division of Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3004.*

substituents in reactions of aralkyl halides, have concluded that the sign and magnitude of the factor $\rho$ of the Hammett equation

$$\log k_X/k_H = \rho\sigma \quad [2]$$

are a measure of the extent of bond-making and bond-breaking at the transition state. The value of $\rho$ would be large and negative for those reactions in which bond-breaking occurs prior to bond-making ($S_N1$) while smaller values would be characteristic of a bimolecular nucleophilic substitution ($S_N2$) where the two processes occur together. No such grouping of values was observed for the series of organic halide reactions reviewed by them; they therefore concluded that the $S_N2$-$S_N1$ classification of such reactions is not supported by this criterion and suggest that this classification be replaced by one which recognizes a unity of mechanism for halide reactions (28, 30).

It is clear that the study of the relative effects of para-substituents on the rate of solvolysis of benzenesulphonic esters is not strictly analogous to the halide displacements discussed by Swain and Langsdorf (31) since, in our case, the para-substituted group is at C in the general three-center displacement reaction

$$A + BC \rightarrow AB + C \quad [3]$$

while for the halides the substituted group is at B. This should, however, introduce a simplification, since the sign of $\rho$ is easily predicted when the aromatic system is at A or C, whereas when the aromatic system is at B the task is complicated by the fact that any effect favoring bond-making must oppose bond-breaking, and so neither the sign nor the magnitude of $\rho$ can be predicted with certainty (3, 12, 13). Further, the magnitude of the change of the relative substituent effects with a change in mechanism would be expected to be at least as significant when the aromatic system is at C as when it is at B. Thus, the deductions made by Swain and Langsdorf (31) relating mechanism and relative substituent effects should also be valid for the solvolysis of a series of alkyl benzenesulphonates. This is the basic assumption which underlies the following experiments.

While there has been no systematic study of the reactions of the benzenesulphonic esters comparable to the work on the organic halides, on which the $S_N1-S_N2$ classification is based,* it has long been known (9), and generally accepted, that the mechanism of the displacement involves the scission of the C–O bond save in the special case where R (Equation 1) is a phenyl group (9, 4) and this mechanism has been accepted as a basis for comparing the effect of changes in the structure of the alkyl group, or the para-substituent, or the solvent. Elimination in solvolysis of these esters was considered to be negligible for the purpose of this comparison since it was shown in preliminary runs both by a titration method (23) previously calibrated against a known, and by a fractionation of products and estimation of the propylene with a mass spectrograph,** that the amount of elimination in the presence of 0.025 *M* NaOEt was

*This work, largely due to the extensive research of C. K. Ingold, E. D. Hughes, and colleagues, has been summarized by E. D. Hughes (Ref. 18) and recently reviewed in part by Winstein, Grunwald, and Jones (Ref. 34).

**The assistance of Dr. F. P. Lossing, in whose section of these laboratories the mass spectrographic analysis was made, is gratefully acknowledged.

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10–12% for isopropyl *p*-methyl benzenesulphonate in dry ethanol at 50°C.

The general effect of changes in the alkyl group on the rate of alcoholysis of the alkyl benzenesulphonates was known (27) and certain evidence indicated that the shift from $S_N2$ to $S_N1$ occurred more readily for these esters than for the corresponding halides. Winstein and his colleagues (34) consider isopropyl *p*-bromobenzenesulphonate to react by mixed kinetics in aqueous alcohol, but their evidence that the actual mechanism is a kind of hybrid of the typical $S_N2$-$S_N1$ mechanisms is not conclusive.

The first order rate constant for isopropyl benzenesulphonate in 50/50 v./v. methanol–water shows no acceleration on the addition of the strong base, $OH^-$(5), and but a small acceleration of rate was observed in the solvolysis of ethyl para-nitrobenzenesulphonate in a 30/70 alcohol–water mixture on the addition of a small amount of a strong base (7). From such evidence as this, we were led to expect that the study of a series of alkyl benzenesulphonates would yield data quite comparable to those of the corresponding halides and nitrates, and that the same tests for a change of mechanism would apply. These points of correspondence are extended prior to a discussion of the changes in the relative substituent effects, as changes in the R group or in the solvent alter the conditions from those favoring an $S_N2$ mechanism to those favoring the $S_N1$ mechanism.

## RESULTS

The difference between the $S_N2$ mechanism and the $S_N1$ mechanism is based in part on (*a*) the effect on the rate of substituting a strong nucleophilic reagent for a weaker one, (*b*) the effect of an increase in the ionizing properties of the solvent, and (*c*) the effect of changes in the structure of R (Equation 1) on the rate; and it will be sufficient for our purpose to establish a correspondence between the halides, nitrates, and benzenesulphonates on these points to justify certain hypotheses with respect to mechanism and to examine the relative effect of para-substituents on the basis of such assumptions.

In the kinetic studies of the organic halides, the effect on the rate of adding a strong base to a solvolytic reaction was one of the first and still remains one of

TABLE I

RATE DATA* SHOWING THE EFFECTS OF ADDED BASE ON THE SOLVOLYSIS OF METHYL, ETHYL, AND ISOPROPYL BENZENESULPHONATE

| Constant | Solvent | Base | Temp., °C. | Methyl | Ethyl | Isopropyl |
|---|---|---|---|---|---|---|
| $k_1 \times 10^4$ sec.$^{-1}$ | EtOH | — | 70 | 0.705 | 0.306 | 1.02 |
| $k_2 \times 10^4$ mol.$^{-1}$ l.sec.$^{-1}$ | EtOH | 0.02 *M* | 70 | 10300 | 401 | 70*** |
| $k_1 \times 10^4$ sec.$^{-1}$ | EtOH/$H_2O$** 50% | — | 50 | 0.654 | 0.349 | 4.64 |
| | | — | 25 | — | — | 0.250 |
| $k_1 \times 10^4$ sec.$^{-1}$ | | 0.02 *M* | 50 | 2.65 | — | 4.85 |
| | | 0.04 *M* | 25 | — | — | 0.254 |

**Data for a typical solvolytic run are included among the Experimental Details.*

***EtOH/$H_2O$ 50% refers to a mixture of equal volumes of alcohol and water. 80% EtOH/$H_2O$ refers to a mixture of 80 volumes of alcohol and 20 volumes of water.*

****Corrected for solvolysis.*

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the critical tests for detecting whether or not the rate-controlling step involves an ionizing mechanism (14, 16). In Table I are recorded the first order rate constants for methyl, ethyl, and isopropyl benzenesulphonates in dry ethanol and in mixed solvents of greater ionizing power with and without the addition of a strong base. A comparison of the trends evident in Table I with those discussed by Hughes, Ingold, and Shapiro (17) for the corresponding halides, particularly isopropyl bromide, shows that there is the same minimum in the solvolytic rates at ethyl, the order being Me > Et < IsoPro, while the increasing hindrance to the approach of a charged ion as a result of $\alpha$-methylation gives a bimolecular rate order of Me > Et > IsoPro. In ethanol the relative values for the reaction with $EtO^-$ for the benzenesulphonic esters are 1: 0.036: 0.0067. These are comparable to the values for the corresponding bromides of 1: 0.08: 0.002, but contrast with the much smaller differences in aqueous ethanol found by Baker and Easty (2) for the corresponding nitrates 1: 0.106: 0.134. Since the same bond is being broken for both the benzenesulphonates and the nitrates, the suggestion of these authors that dipole repulsion is a rate-controlling factor is open to question.*

In dry ethanol, the reaction of isopropyl benzenesulphonate is probably bimolecular, but in 50% alcohol–water the change in the first order constant from $2.50 \times 10^{-5}$ to $2.54 \times 10^{-5}$ on the addition of 0.04 molar $OH^-$ is of the order of a salt effect, and the second order rate "constant" was found to increase with time. In contrast, methyl benzenesulphonate does not give a "first order rate constant" in the presence of base but follows a bimolecular law as would be expected.

The effect of adding water to ethanol is to increase the ionizing ability of the solvent and thereby to accelerate the solvolytic reaction which depends on the stabilization of partial charges in the transition state; for the same reason the reaction involving the charged base is seen to be retarded because of the stabilization of the initial state, and the substitution of the highly solvated $OH^-$ for $EtO^-$. These qualitative results, first established for the halides, are all evident in the results reported in Table I for the benzenesulphonates.

*Effect of Solvent*

The effect of changing from a fair ionizing solvent to a good ionizing solvent, while of less diagnostic value for the purpose of establishing evidence for a change of mechanism (15), is very important for the purpose of this paper, since by this means we are able to change more gradually the factors which favor the $S_N1$ mechanism over those favoring the $S_N2$ mechanism. Data for the solvolysis of a series of para-substituted methyl, ethyl, and isopropyl benzenesulphonates in ethanol, methanol, ethanol–water, and in dioxane–water are reported in Tables II, III, IV, and V.

The benzenesulphonate esters reach comparable rates of solvolysis at lower temperatures than do the bromides (34) and the nitrates (2) and this may be attributed to the more ionic character of the C–O bond in the benzenesulphonic esters, particularly for the isopropyl esters. The result of this is evident in the

**Prof. P. L. Laughton has pointed out that since the sulphonate group possesses a comparable dipole, we would expect the same argument to apply to the reactions of these esters, and this is not so.*

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TABLE II

KINETIC DATA FOR SOLVOLYSIS OF A SERIES OF SULPHONIC ESTERS IN DRY ETHANOL

| Ester | Temp., °C. | $k_1 \times 10^5$,** sec.$^{-1}$ | $k_X/k_H$ | $E_A$ | log $B$, | $n$† | Range‡ |
|---|---|---|---|---|---|---|---|
| Me–*p*MeO* | 70 | 3.16 | 0.45 | 21,080 | 8.9272 | 3 | 70 –90 |
| Me–*p*Me | | 4.51 | 0.64 | 21,360 | 9.2628 | 2 | 62.5–80 |
| Me–*p*H | | 7.04 | 1.00 | 20,730 | 9.0551 | 3 | 70 –90 |
| Me–*p*Br | | (15.5) | 2.20 | 20,800 | 9.441 | 2 | 50 –62.5 |
| Me–*p*$NO_2$ | | 65.3 | 9.27 | — | — | — | — |
| Me–*m*$NO_2$ | | 77.6 | 11.1 | 20,690 | 10.062 | 4 | 45 –70 |
| E–*p*MeO | | 1.43 | 0.47 | 21,720 | 8.949 | 3 | 70 –90 |
| Et–*p*Me | | 1.93 | 0.63 | 21,980 | 9.208 | 5 | 45 –90 |
| Et–*p*H | | 3.06 | 1.00 | 21,450 | 9.1475 | 3 | 70 –90 |
| Et–*p*Br | | (4.72) | 1.92 | 21,300 | 9.233 | 3 | 40 –80 |
| Et–*p*$NO_2$ | | 27.8 | 9.08 | 21,680 | 10.247 | 4 | 40 –70 |
| Et–*m*$NO_2$ | | 32.8 | — | — | — | 3 | 45 –70 |
| IsoPro–*p*MeO | | 3.73 | 0.37 | 23,300 | 10.416 | 2 | 60 –70 |
| IsoPro–*p*Me | | 6.46 | 0.63 | 22,900 | 10.400 | 3 | 60 –80 |
| IsoPro–*p*H | 70 | 10.2 | 1.00 | 22,817 | 10.5327 | 3 | 50 –70 |
| | 50 | 1.26 | 1.00 | | | | |
| IsoPro–*p*Br | 70 | 26.6 | 2.61 | 22,330 | 10.6522 | 4 | 50 –80 |
| IsoPro–*p*$NO_2$ | 70 | 133.0 | 13.0 | 22,880 | 11.661 | 3 | 50 –70 |
| | 50 | 16.8 | 13.3 | | | | |
| IsoPro–*m*$NO_2$ | 50 | 21.9 | 17.4 | 22,100 | 10.535 | 3 | 50 –70 |

* *The method of notation will be obvious from this abbreviation of methyl para-methoxybenzenesulphonate.*

** *Initial concentration of ester was 0.013–0.010 molar.*

† *n is the number of temperatures for which rates were determined.*

‡ *In this column are recorded the minimum and maximum temperature for which rates were determined.*

TABLE III

KINETIC DATA FOR THE SOLVOLYSIS OF A SERIES OF METHYL, ETHYL, AND ISOPROPYL BENZENESULPHONIC ESTERS IN DRY METHANOL AT 50°C.

| Ester | $k_1 \times 10^5$, sec.$^{-1}$ | $k_X/k_H$ | $E_A$, cal. | log $B$, sec.$^{-1}$ | $n$ | Temp. range |
|---|---|---|---|---|---|---|
| Me–*p*Me* | (1.06)*** | 0.65 | 21,390 | 9.4938 | 5 | 30–80 |
| Me–*p*H | 1.63 | 1.00 | 20,880 | 9.334 | | |
| Me–*p*Br | 3.45 | 2.20 | 21,150 | 9.863 | 5 | 33–70 |
| Me–*p*$NO_2$ | 14.0 | 8.60 | — | — | | |
| Me–*m*$NO_2$ | 14.9 | 9.17 | — | — | | |
| Et–*p*Me | 0.493 | 0.62 | 22,800 | 9.9247 | 6 | 50–90 |
| Et–*p*H | 0.790** | 1.00 | 22,180 | 9.819 | 5 | 50–90 |
| Et–*p*$NO_2$ | 7.10 | 9.00 | 19,750 | 9.149 | | |
| IsoPro–*p*H | 3.91 | 1.00 | | | | |
| IsoPro–*p*Br | (9.23)*** | 2.36 | 23,200 | 11.522 | 5 | 28–62.5 |
| IsoPro–*p*$NO_2$ | 41.7 | 10.65 | 22,360 | 11.739 | 5 | 25–50 |
| IsoPro–*m*$NO_2$ | 44.2 | 11.28 | | | | |

* *See Note 1, Table II.*

** *Tomilla and Lindholm (33) report 0.800; $E_A$ 22,090; log A 9.84.*

*** *Interpolated.*

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TABLE IV

SOLVOLYTIC RATE CONSTANTS FOR A SERIES OF ALKYL BENZENESULPHONATES IN WATER–ETHANOL

| Ester | Temp. | 80/20 v./v. ethanol–water | | 50/50 v./v. ethanol–water | |
|---|---|---|---|---|---|
| | | $k_1 \times 10^5$, sec.$^{-1}$ | $k_X/k_H$ | $k_1 \times 10^5$, sec.$^{-1}$ | $k_X/k_H$ |
| Me–*p*Me | 50 | 2.22 | 0.665 | 4.41 | 0.67 |
| Me–*p*H | 50 | 3.34 | 1.00 | 6.60 | 1.00 |
| Me–*p*$NO_2$ | 50 | 35.3 | 10.6 | 61.7 | 9.35 |
| Me–*m*$NO_2$ | 50 | 36.1 | 10.8 | 56.7 | 8.59 |
| Et–*p*Me* | 50 | 0.952 | 0.64 | 2.17 | 0.62 |
| Et–*p*H | 50 | 1.49 | 1.00 | 3.49 | 1.60 |
| Et–*p*$NO_2$ | 50 | 16.5 | 11.7 | — | — |
| IsoPro–*p*Me | 25 | — | — | 1.47 | 0.59 |
| | 50 | 5.45 | 0.60 | 29.2 | 0.63 |
| IsoPro–*p*H | 25 | — | — | 2.50 | 1.00 |
| | 50 | 9.04 | 1.00 | 46.0 | 1.00 |
| IsoPro–*p*Br | 25 | — | — | 7.30 | 2.92 |
| IsoPro–*p*$NO_2$ | 25 | 8.60 | — | 44.4 | 17.7 |
| | 50 | 136 | 15.2 | — | — |
| IsoPro–*m*$NO_2$ | 25 | — | — | 34.2 | 13.7 |

**Ref. 34 gives 0.923 and 2.18 for corresponding solvents.*

TABLE V

KINETIC DATA FOR THE HYDROLYSIS OF A SERIES OF METHYL, ETHYL, AND ISOPROPYL BENZENESULPHONIC ESTERS IN 50/50 W./W. DIOXANE–WATER AT 50°C.

| Ester | Temp. | $k_1 \times 10^5$, sec.$^{-1}$ | $k_X/k_H$ | $E_A$, cal. | log $B$, sec.$^{-1}$ | $n$ | Temp. range |
|---|---|---|---|---|---|---|---|
| Me–*p*Me | 50 | 2.29 | 0.63 | 21,100 | 9.6221 | 5 | 30–71.5 |
| Me–*p*H | 50 | 3.62 | 1.00 | — | — | | |
| Me–*p*Br | 50 | 10.5 | 2.90 | 20,380 | 9.623 | 5 | 30–70 |
| Me–*p*$NO_2$ | 50 | 32.3 | 8.92 | — | — | | |
| Et–*p*Me | 50 | 1.08 | 0.60 | 21,500 | 9.566 | 3 | 40–70 |
| Et–*p*H | 50 | 1.80 | 1.00 | | | | |
| Et–*p*$NO_2$ | 50 | 18.5 | 10.2 | | | | |
| IsoPro–*p*Me | 50 | 1.53 | 0.56 | | | | |
| IsoPro–*p*H | 50 | 27.1 | 1.00 | | | | |
| IsoPro–*p*H | 25 | 1.63 | 1.00 | | | | |
| IsoPro–*p*Br | 50 | (6.31)* | 2.32 | 21,500 | 11.309 | 3 | 20–40 |
| IsoPro–*p*$NO_2$ | 25 | 23.0 | 14.1 | | | | |
| IsoPro–*m*$NO_2$ | 25 | 18.0 | 11.5 | | | | |

**Extrapolated.*

comparison of the effect of increasing the ionizing ability of the solvents on the solvolysis of the two series of compounds (Table VI).

The methyl compounds will solvolyze by an $S_N2$ mechanism in these solvents and while increasing the ionizing power of the solvent will accelerate both mechanisms; Table VI shows that the acceleration of the isopropyl compounds is more strongly influenced by the increasing ionizing power of the solvent and this is reflected by the increase in the value of the ratio $k_{\text{isopropyl}}/k_{\text{methyl}}$. While the larger values observed for the benzenesulphonate series and the inversion

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TABLE VI

A COMPARISON OF RELATIVE SOLVOLYTIC RATES* FOR THE SERIES METHYL, ETHYL, AND ISOPROPYL BENZENESULPHONATES WITH THE CORRESPONDING BROMIDES** IN A SERIES OF SOLVENTS AT 50°C.

| Ester | Solvent | Methyl | Ethyl | Isopropyl |
|---|---|---|---|---|
| Benzenesulphonate | Ethanol | 1 | 0.43 | 1.45 |
| Bromide | Ethanol | 1 | 0.37 | 0.28 |
| Benzenesulphonate | Methanol*** | 1 | 0.49 | 2.40 |
| Benzenesulphonate | 80/20 v./v. ethanol–water | 1 | 0.45 | 2.71 |
| Bromide | 80/20 v./v. ethanol–water | 1 | 0.39 | 0.54 |
| Benzenesulphonate | 50/50 v./v. ethanol–water | 1 | 0.53 | 6.97 |
| Bromide | 50/50 v./v. ethanol–water | 1 | 0.76 | 1.49 |
| Benzenesulphonate | Water | 1 | 0.95 | — |
| Bromide | Water | 1 | 1.08 | 11.0 |

*These are the over-all solvolytic rates.*
**Data from Ref. (34).*
***There are no corresponding data for the bromides available.*

of the ratio observed for the bromides in pure ethanol may both be attributed to a difference in the relative strength of the bond being broken, an influence which is also supported by the greater nucleophilic activity of the bromide ion (20), it is equally probable that because the C–O bond in the benzenesulphonate is more ionic in the initial state, this same characteristic facilitates solvolysis.

In establishing a trend toward a change in mechanism, it is important to note that the ratio of the solvolytic rate between the isopropyl and the methyl esters increased on changing from 50/50 ethanol–water to 50/50 dioxane–water while the actual rates decreased by one-half (Tables III and IV). These results may be attributed to the decrease in the nucleophilic activity of the solvent on replacing ethanol by dioxane, and this will have a disproportionate effect on the methyl benzenesulphonate. The ratio of $k_{\text{isopropyl}}/k_{\text{methyl}}$ for the corresponding nitrates in 90% alcohol–water at 60°C. is 0.95 and in 60% alcohol–water is 2.5. It will be noted that these results lie between those of the benzenesulphonates and the bromides although the order for the rates of solvolysis is benzenesulphonate > bromide > nitrate.

*Salt Effect*

The differential effect of added noncommon ions and common ions on the rate of solvolysis has proved an important approach to distinguishing between the $S_N1$ and $S_N2$ mechanism (6). Preliminary tests of the effect of added salt in 80/20 ethanol–water with isopropyl *p*-nitrobenzenesulphonate (Table IV) show the salt effect to be small for the noted concentration and the effect of the common and noncommon ion to be of the same order and sign. The lack of sensitivity of the solvolyzing benzenesulphonic esters to salt effects was also noted by Hammett and McCleary for the solvolysis of ethyl *p*-toluenesulphonate in dioxane–water (20), and more recently by Kochi and Hammond, who found that a 20-fold increase in ionic strength gave no more than a 10% change in rate for para-substituted benzyl toluenesulphonates which apparently react by an $S_N1$ mechanism (19).

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These data are sufficient to establish the correspondence between displacement reactions of the bromides, nitrates, and the sulphonates, and to show that for the latter series the solvent is to a greater degree than the former involved in a different way in the transition state where R (Equation 1) is methyl and where R is isopropyl. This distinction forms the basis of the classification under discussion.

*Effect of Substituents*

The effect of this apparent change in mechanism on the relative substituent effects is readily seen by reference to the column $k_X/k_H$ in Tables II, III, IV, and V. While the magnitude of the relative effect of a para-substituent on the rate of reaction is modified by the intervention of two saturated atoms between the aromatic ring and the seat of the reaction, the systematic changes which do occur conform to the reasonable expectation that electrostatic interaction between the substituent and partial charges in the transition state will increase as charge separation increases, tending toward a maximum in those cases where other evidence suggests a shift in mechanism from $S_N2$ to $S_N1$. As Swain has already observed in the case of the halides, these data for the benzenesulphonates show no large change in the relative effect of substituents with such a change in mechanism. This fact is well illustrated by the isopropyl benzenesulphonates when we compare the relative substituent effects in ethanol (Table II) where the reaction shows typical bimolecular characteristics to those observed in 50% aqueous ethanol (Table IV) where the conventional test of the effect of added base shows no increase in the first order rate constant (Table I) and so leads to the conclusion that the reaction approximates to the $S_N1$ mechanism.*

A change in the relative substituent effect is observed in the direction which would be expected if charge separation in the transition state were increased in the series Me–Et–IsoPro or when the ionizing property of the solvent is increased. The prediction that a change in mechanism would result in a large change (1) in the relative effect of the substituent is not confirmed for the case of the solvolysis of the benzenesulphonic esters. Since it is difficult to estimate by independent means the magnitude to be expected for the relative difference in substituent effects between an $S_N2$ and an $S_N1$ mechanism, we have concluded that the observed difference is evidence of a change of mechanism, rather than the opposite view held by Swain and Langsdorf based on evidence from the reactions of the organic halides.

In ethanol, where it may be assumed that the reaction follows an $S_N2$ mechanism, the effect of the para-methyl is the same for the three esters and this relative value of about 0.60 is maintained in the other solvents examined with the exception of an increase to 0.73 in pure water. The relative values of the para MeO and Br are about the same for the methyl and ethyl ester but show an increase for the isopropyl ester, and this difference increases still further

**Winstein, Grunwald, and Jones (34), on the basis of a comparison of relative rates of solvolysis in solvents of varying properties, consider the nucleophilic activity of the solvent to be still rate controlling for isopropyl p-bromobenzenesulphonate in aqueous alcohol. Our conclusion differs from this only in so far as we emphasize the increased importance of solvation in the transition state.*

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(from 2.61 to 2.96 for *p*-Br) in 50/50 ethanol–water. These changes in the relative effect of the substituent are in agreement with the above reasonable hypothesis that the electrostatic interaction of the substituent will increase when change in structure or solvent becomes more favorable to the stabilization of charges. It follows that, even in ethanol, which is not a good ionizing solvent, there is an apparently greater charge separation with the isopropyl ester than with the methyl or the ethyl esters, and this difference increases as the ionizing power of the solvent increases. These conclusions are most evident for the para- and meta-nitro substituents. Thus the ratio of $k_{NO_2}/k_H$ for the para-nitro substituted esters have for the methyl, ethyl, and isopropyl ester the values of 9.27, 9.08, and 13.0 in dry ethanol and have the values in methanol of 8.60, 9.67, and 10.65, respectively. In ethanol–water (80% ethanol) the higher values of 10.6, 11.7, and 15.2 are found and in 50% ethanol the values of the ratio for the methyl ester are 9.35 and for the isopropyl ester, 18.8. From these data we may obtain not only the general order of the relative change in the substituent effect for this reaction as we change from reaction conditions which favor a bimolecular solvolysis to one more favorable to rate-controlling ionization, but also further insight into the effect of $\alpha$-methylation on the charge separation in the transition state.

It was supposed that part of the effect of the para-nitro group might be attributed to the ability of this group to lower the energy of the forming ion by some type of resonance stabilization. To test this hypothesis, the corresponding methyl and isopropyl meta-nitro substituted esters were solvolyzed in the same solvents. The results are recorded beside those of the corresponding para-nitro compounds and it will be seen at once that in ethanol the meta-nitro group has a larger relative effect than the para-nitro group and this difference is larger for the isopropyl ester than for the methyl ester. The difference, though it still exists, is smaller in methanol while in 50% ethanol the para-substituent has a larger effect than the meta-nitro and this difference is larger for the isopropyl ester than for the methyl ester.

The greater effect of the meta-nitro group over the para-substituent may be taken as evidence that inductive effects are most important in the bimolecular reactions (25). The increase in the value of the $k_{pNO_2}/k_{mNO_2}$ ratio where conditions are altered to favor the $S_N1$ mechanism indicates the possibility of some resonance stabilization of the transition state and supports the hypothesis that ionization is of increasing importance in the rate-controlling step for the solvolysis of isopropyl benzenesulphonates in 50% ethanol–water. For those reactions which show mixed characteristics, the changes in the relative substituent effect provide no means of determining whether they arise as a result of an averaging process of two different mechanisms occurring simultaneously or whether the results indicate the increasing contribution of charge separation in the transition state as the ionizing properties of the solvent and the structure of R makes this course energetically more favorable. The data do support, however, the view that there is no sharp break between the two mechanisms, as can be seen by a comparison of the relative substituent effects in ethanol (Table II) with those in the better ionizing ethanol–water mixtures (Table IV).

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*Arrhenius Constants*

While the temperature dependence of these reactions has not been determined over a sufficiently wide range of temperature, nor with an accuracy greater than ± 250 cal., it is clear from Tables II, III, and V that the relatively small changes in the free energy of activation produced by the para-substituents reflect slight and apparently random changes in the Arrhenius parameters. At the present time there is no theory which provides a basis for relating the observed small increments to structural changes. In Table II, it will be noted that there is a decrease in rate between the methyl and the ethyl ester, and an increase of about 600 cal. in the activation energy. There is a further increase in the activation energy between the ethyl and the isopropyl esters, but this is more than compensated by an increase in the nonexponential term, $B$. Since there is independent evidence to suggest that the solvolysis of the isopropyl esters involves a larger ordering of the solvent in the transition state, the latter changes of the Arrhenius parameters are not to be expected (8, 26) and an alternate explanation is being explored.

Perhaps the most striking anomaly is the curious fact that the activation energy for the attack of the strong base $EtO^-$ in dry ethanol* and of the relatively weak base EtOH should both be about 21,000 cal., the difference in the relative rates of $10^3$ being accounted for by a change in the nonexponential factor.

*Experimental Details*

Ethanol: Commercial absolute ethanol was distilled from calcium oxide through a 2-ft. Stedman column and subsequently distilled prior to use from ethyl biphthalate and sodium (21).

Methanol: Anhydrous methanol from Brickman Limited was dried by dissolving 5 gm. magnesium per liter, and distilling.

Dioxane: Was purified by refluxing with hydrochloric acid, and after distillation and preliminary drying, distillation over sodium. B.p. 101–101.2°C.

Ethanol–water mixtures were made up by volume. The dioxane–water mixture was made up by weight.

Sulphonic esters: Methyl and ethyl benzene and toluene sulphonates were obtained from Eastman Kodak and were recrystallized. The remainder were synthesized either by the addition of the alkoxide to an ether solution of the corresponding sulphonyl chloride (22) or by the modified Tipson method (32). Isopropyl *p*-Me and *p*-MeO benzenesulphonate decomposed under normal distillation conditions and were distilled on a Distillation Products Spinning Molecular Still and subsequently purified by fractional freezing. Isopropyl *p*-bromobenzenesulphonate was recrystallized from petroleum (60–70°) ether and from the melt. The crude isopropyl *p*-nitrobenzenesulphonate was washed repeatedly with cold petroleum ether and subsequently recrystallized from ether and petroleum ether.

It was found expedient to treat the crude chloroform solution of meta-nitrobenzenesulphonate (Method 1) with a few drops of 30% hydrogen peroxide

*Unpublished results.

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in order to facilitate subsequent purification by recrystallization from ether and cyclohexane.

Where known, the physical constants were compared with the literature and in all cases the neutral equivalent obtained in 80% ethanol–water was closer than 1% to theoretical. These data are summarized in Table IV.

*Kinetic Studies*

All the data reported here were obtained with Monax Test Tubes; Pyrex Tubes, Kimble glass tubes, Corning alkali resistant glass proving less satisfactory in various degrees.

The bath temperatures were controlled by a Gouy modified thermoregulator (11) to better than 0.02°C. Temperatures were determined with a set of thermometers calibrated in the Meteorological Section of the National Research Laboratories. Time was determined by a clock driven by a current from the Standard Frequency Laboratory.

*Titration*

The greatest source of error in such work normally arises from errors of analysis. We materially reduced error from this source by the use of a differential titrimeter based on the circuit of Nichols and Kindt (24) but modified by (1) return to the "in-line" assembly of an earlier design, thus eliminating the Lumitron fan assembly, (2) the use of a 110 v. Mazda Projection lamp. The intensity was controlled by a Variac rather than the diaphragm, (3) the use of an $N_2$ (free of $CO_2$) mixed titration cell.

With such an aid the end point could be duplicated on successive titrations with an accuracy greater than it was possible to read a 5 ml. microburette

TABLE VIIA

SOLVOLYSIS OF METHYL *p*-METHYLBENZENESULPHONATE IN DRY METHANOL AT 70°C.

Sample—4.86 ml.
Normality of base–0.00971.
Initial concentration of ester—0.0150 molar.

| Time, min. | Titer, ml. | $a-x$ | $k_1 \times 10^5$, sec.$^{-1}$ |
|---|---|---|---|
| 0 | 0.696 | 7.531 | |
| 0 | 0.696 | | |
| 15 | 1.170 | 7.057 | (7.23) |
| 35 | 1.770 | 6.457 | 7.33 |
| 55 | 2.315 | 5.912 | 7.33 |
| 75 | 2.830 | 5.397 | 7.40 |
| 95 | 3.280 | 4.947 | 7.37 |
| 115 | 3.733 | 4.494 | 7.48 |
| 135 | 4.096 | 4.131 | 7.41 |
| 167 | 4.652 | 3.575 | 7.44 |
| 180 | 4.820 | 3.407 | 7.34 |
| 195 | 5.049 | 3.178 | 7.37 |
| | 8.229 | | |
| ∞ | 8.225 | | |

Average $k_1 = 7.36 \times 10^{-5}$ sec.$^{-1}$
Average % deviation from the mean—0.68%.

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TABLE VIIB

TEMPERATURE DEPENDENCE OF THE RATE OF SOLVOLYSIS OF METHYL *p*-METHYLBENZENESULPHONATE IN DRY METHANOL

| Temp., °C. | $k_1 \times 10^6$ abs. | $k_1 \times 10^6$ calc.* |
|---|---|---|
| 30.0 | 1.197 | 1.17 |
| 40.0 | 3.63 | 3.63 |
| 62.5 | 36.6 | 3.64 |
| 70 | 73.7 | 73.5 |
| | 73.4 | |
| 80 | 176.7 | 178.8 |

*The above data yield Arrhenius parameters of $E_A$ = 21,390 and log B = 9.4938.*
**Calculated from the Arrhenius constants.*

graduated to 0.01 ml. (E/MIL — Gold Line). Just as important as the gain in accuracy was the repetitive sensitivity from run to run and during the course of any one run. Where the titrimeter could not be used, we titrated in cold acetone using lacmoid as an indicator. Data in Table VIIA-VIIB for the solvolysis of methyl *p*-methylbenzenesulphonate in dry methanol are typical of the work reported here.

The data for ethyl *p*-toluene sulphonate in water were determined by a conductance method essentially as described by Gold (10).

*Accuracy of Data*

Rate constants were considered sufficiently accurate for the purpose of this comparison if the average percentage deviation from the mean was of the order of 1% or less for first order solvolytic rate constants and 2% for bimolecular rate constants.

TABLE VIII

PHYSICAL CONSTANTS OF SULPHONIC ESTERS

| Ester | $n_D^{20}$ | M.p. |
|---|---|---|
| Me–*p*MeO | 1.5290 | 30 |
| Me–*p*Me | 1.5169 | 28 |
| Me–*p*H | 1.5151 | |
| Me–*p*Br | — | 60.5 |
| Me–*p*$NO_2$ | | |
| Et–*p*MeO | 1.5238 | |
| Et–*p*Me | — | 32–33 |
| Et–*p*H | 1.5081 | — |
| Et–*p*Br | — | 39.0–39.4 |
| Et–*p*$NO_2$ | — | 92 –92.5 |
| IsoPro–*p*MeO | 1.5150 | — |
| IsoPro–*p*Me | 1.5028 | — |
| IsoPro–*p*H | 1.5003 | — |
| IsoPro–*p*Br | — | 32 |
| IsoPro–*p*$NO_2$ | — | 50 –51 |
| IsoPro–*m*$NO_2$ | — | 53 –54 |

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# STUDIES OF RDX AND RELATED COMPOUNDS
## XI. THE CONVERSION OF PHX TO AcAn[1]

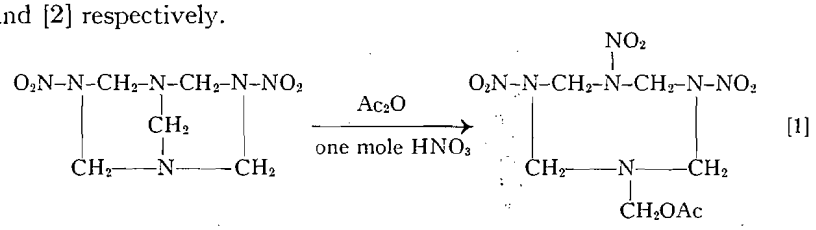
By R. A. Marcus[2] and C. A. Winkler

ABSTRACT

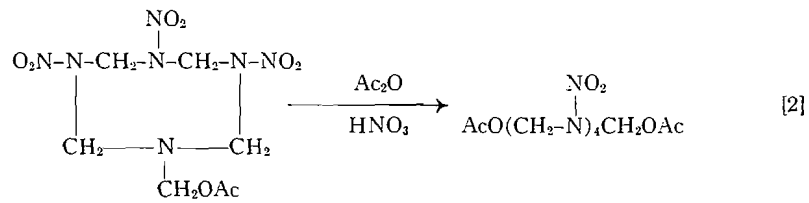
The formation of AcAn from PHX, nitric acid, and acetic anhydride has been investigated at various temperatures. The effects of added acetic acid and added salts have been determined. While the reaction is first order with respect to PHX, it is of an order 2.6 with respect to nitric acid. The reaction rate is significantly decreased by small concentrations of sodium nitrate. The reaction is also characterized by a secondary salt effect and a low apparent activation energy of about 2 kcal. mole$^{-1}$. A mechanism has been suggested in qualitative, and to some extent quantitative, agreement with the experimental data. It is postulated that the conversion of PHX involves a rate-controlling ionic reaction between PHX and nitric acid, and that this is followed by a rapid acetylation of the acidic intermediate to AcAn.

### INTRODUCTION

In the present paper of this series an attempt has been made to study in some detail a reaction of frequent occurrence in the chemistry of RDX and related compounds, namely the rupture of a methylene carbon–nitrogen bond. A search of the literature for a simple example of such a reaction, that is, where only one bond in the organic molecule was broken, revealed only two cases: (1) the formation of 2-acetoxymethyl-4,6,8-trinitrocyclotetramethylene tetramine (PHX) from 1,5-*endo*methylene-3,7-dinitrocyclo-2,4,6,8-tetramethylene-1,3,5,7-tetramine (DPT) and (2) the formation of 1,9-diacetoxypentamethylene-2,4,6,8-tetranitramine (AcAn) from PHX. These reactions are given in equations [1] and [2] respectively.




DPT PHX [1]




PHX AcAn [2]

Although the former is too rapid for kinetic investigation the latter presents

[1] *Manuscript received December 12, 1952.*
*Contribution from the Physical Chemistry laboratory, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.*
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no such objection, and its study constitutes the bulk of the present work.

## EXPERIMENTAL AND RESULTS

### *Materials*

Nitric acid of approximately 99% concentration was prepared by vacuum distillation of a solution of 480 gm. ammonium nitrate in 600 ml. concentrated sulphuric acid at a pressure of 1 mm. and temperature 40°-65°C. The acid so obtained was either colorless or very pale yellow. Any nitrogen dioxide present was removed by bubbling dried air through the liquid. The acid was stored in the dark at 0°C. The acetic anhydride, approximately 95% pure (5% acetic acid), was obtained from Mallinckrodt (A.R.) or Merck (C.P.). It was used directly without further purification and no appreciable difference was observed with the use of either sample.

The PHX was prepared from DPT which, in turn, was made from hexamine according to Bachmann's procedure (1). Solutions of 1.5 moles hexamine in 5.5 moles of acetic acid and of 3 moles of 99% nitric acid in 3.5 moles acetic anhydride were added continuously and in equivalent amounts to one mole acetic acid over a 60 min. period, at 27° to 30°C. The solution was cooled and stirred vigorously while the addition was made, and the stirring was continued for 30 min. after it was completed. Dilution with 800 ml. water at 65°C. yielded a precipitate of DPT which was filtered off, washed thoroughly with water, and recrystallized from acetone. To 5 gm. of DPT suspended in 23 ml. acetic anhydride was added 1 ml. of 99% nitric acid. PHX precipitated before all the DPT went into solution. The precipitate was filtered immediately and washed with a few milliliters of acetone. It melted at 152-3°C.

Although PHX has never been recrystallized from any solvent, different batches of PHX gave exactly similar AcAn yield–time data. The PHX obtained was therefore considered to be sufficiently pure for use in the present investigation. An impurity was isolated, however, and found to be present to the extent of 4% by weight. The results were indirectly corrected for the presence of this contaminant in a manner described later.

### *Experimental Procedure*

Solutions of "acetyl nitrate" were prepared (*a*) by pipetting the appropriate volume of nitric acid (at 0°C.) into an exact volume of acetic anhydride in a flask, (previously cooled in an ice bath) for each sample, or alternatively (*b*) by preparation of a fresh stock solution of nitric acid in acetic anhydride and withdrawal of aliquots for each experiment. Because of the large quantities of heat evolved, the acetic anhydride was, in the latter case, cooled to −78°C. before, and during, the addition of nitric acid. Aliquots were diluted with water to a standard volume and titrated for nitric acid with standard base, to a given pH as determined by a blank, according to the method of Betts, Stuart, and Winkler (3). Again the solutions, if not colorless, were rendered so by the same procedure as for nitric acid, described earlier. With the precaution of storing them in the dark at 0°C. they did not change titer over a period of at least eight hours. The presence of nitrogen dioxide had to be avoided since it was found to lower the yield of AcAn significantly.

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Stoppered flasks containing the acetyl nitrate were placed in a thermostat, equipped with a mechanical shaker, and controlled to ±0.1°C. After an interval of 10 min., during which the solution attained thermal equilibrium, the PHX was added. The solid dissolved almost completely in 30 sec. After appropriate reaction times the samples were diluted with distilled water to a standard volume, the mixtures allowed to stand for three days to ensure complete precipitation of AcAn, and then filtered through tared sintered glass crucibles and dried at 110°C. for several days. The data have been corrected for solubility losses which amounted to 10% of the weight of product on the average.

Variation of PHX concentration was limited by its small solubility in the reaction medium (e.g. at 35°C. the solubility in 20 ml. of solution was 0.5 gm. while at 15°C. it was 0.15 gm.).

In the experiments with added salts a weighed amount of salt was dissolved in 99% nitric acid and the solution diluted with the acid to a standard volume at 0°C. Aliquots of this solution were then pipetted into given volumes of acetic anhydride. This procedure avoided the difficulties associated with the very small rate of solution of these salts in acetic anhydride–nitric acid media.

The effect of added acetic acid on the reaction rate was also investigated. Standard solutions of glacial acetic acid in 95% acetic anhydride were prepared and aliquots withdrawn for each sample. Variation of the acetic acid concentration was limited by the small solubility of PHX in the solutions.

*Calculation of Rate Constants*

The curves obtained with acid concentrations greater than one molar, while first order for a large part of the reaction, are characterized by a slow secondary reaction to give AcAn or other water insoluble material. Fortunately, this slow secondary reaction can be readily differentiated from the main reaction to give AcAn, and the true final yield of AcAn was obtained by an obvious extrapolation, as in Fig. 1. The yields of AcAn are in general not 100%, because of a side

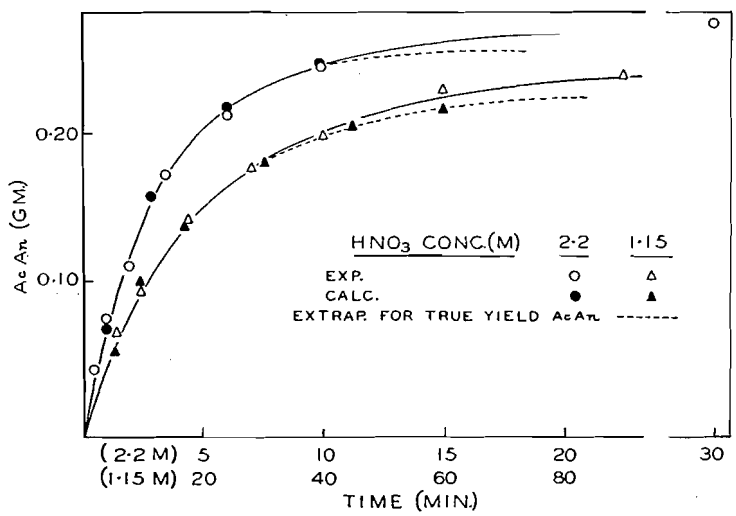



FIG. 1. Rate of AcAn formation at 15.1°C. with 0.0155 *M* PHX (0.20 gm.).

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reaction. These competitive reactions were determined to be of the same order with respect to PHX.

It can readily be shown that the kinetic equations obeyed by two competitive first order reactions are given by

$$(k_m + k_s)t = 2.3 \log_{10} m/(m - x_m) \quad [3]$$

and

$$k_m/(k_m + k_s) = m/a \quad [4]$$

where $a$ denotes the initial weight of PHX, $m$ the true final yield of AcAn, while $x_m$ and $x_s$ represent the yields of AcAn and by-product obtained in time $t$, and $k_m$ and $k_s$ are the corresponding rate constants.

The constant $k_m + k_s$ was determined by substituting in equation [3] the value of $m$, a value of $x_m$ and the corresponding value of $t$. As an added precaution, the AcAn yield–time curve was calculated from equation [3] with this value of $k_m + k_s$. Unless there was close agreement between calculated and experimental data, a small adjustment in $m$ was made and the procedure repeated.

At low values of $t$ the calculated results are in general slightly lower than the experimental data, because of the presence of the impurity mentioned earlier; the decomposition of this contaminant to give water-soluble products is complete at small reaction times. Consequently, for calculation of rate constants, the value of $t$ chosen for insertion in equation [3] was about $t_{1/2}$. In addition, if the amount of impurity be taken into account, there is good agree-

TABLE I

EFFECT OF NITRIC ACID CONCENTRATION ON $k_m$

| $HNO_3$ conc. | $10^2 k_m$ (min.$^{-1}$) at PHX concentrations of: | | | | | |
|---|---|---|---|---|---|---|
| | 0.0155 *M* at 15.1°C. | | 0.0232 *M* at 25.1°C. | | 0.0387 *M* at 25.1°C. | |
| 2.2 *M* | 31 | | 39, 36 | | 31, 32 | |
| 2.00 | 22 | | | | 25 | |
| 1.60 | 12 | | | | 13 | |
| 1.15 | 4.7 | | | | 7 | |
| 1.00 | 3.8 | | | | | |
| 0.60 | 1.0 | | 1 | | 1 | |
| | 0.0155 *M* | 0.0232 *M* | 0.0310 *M* | 0.0387 *M* | 0.0516 *M* | 0.0619 *M* |
| | at 35.1°C. | | | | | |
| 2.2 *M* | | 36 | 31,32 | 31 | | 31 |
| 2.0 | | | | | | 18 |
| 1.6 | | | | | 15(2) | |
| 1.15 | 6.1 | 6.1 | 6.0, 5.9 | 5.4 | | 4.8 |
| | | 9.2 | 5.7, 9.2 | | | |
| 0.60 | | 1 | | 0.8 | | |
| | 0.0179 *M* | | 0.0238 *M* | 0.0298 *M* | 0.0476 *M* | |
| 0.93 | 5.1 | | 5.1 | 4.6 | 3.7 | |

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ment, even at small values of $t$, between the experimental and calculated curves. There is also fairly good agreement between the relative $k_m$'s and the corresponding initial rates. The constants $k_m$ so obtained are accurate to better than ten per cent. The constants $k_s$, which are not determined as directly, are good only to about thirty per cent, and for this reason have not been given.

While the rate curves obtained with nitric acid concentrations greater than one molar were first order, this is not true for the lower acid concentrations. In the latter case the curves are characterized by a relatively rapid initial formation of AcAn followed by a slow secondary reaction. Because of this behavior, rate constants here were calculated by comparison of initial rates with data for 1.15 $M$ acid, using the relative yield of AcAn in four minutes as a good approximation of the initial rates with these low acid concentrations. In this procedure the data were first corrected for the presence of the water insoluble PHX impurity, using results obtained on its rate of decomposition to water-soluble product, in the reaction medium.

*Rate of Formation of AcAn*

The experimental data on the effect of nitric acid, of added salts and of added acetic acid are summarized in Tables I, II, and III, respectively.

TABLE II

EFFECT OF ADDED SALTS ON $k_m$ AT 35.1°C.

| $HNO_3$ conc.<br>PHX conc. | 2.2 $M$<br>0.0282 $M$ | | 1.15 $M$<br>0.0295 $M$ | | 1.15 $M$<br>0.0295 $M$ | |
|---|---|---|---|---|---|---|
| | $NaNO_3$, $M$ | $10^2k_m$ (min.$^{-1}$) | $NaNO_3$, $M$ | $10^2k_m$ (min.$^{-1}$) | $KClO_4$, $M$ | $10^2k_m$ (min.$^{-1}$) |
| | 0 | 3.2 | 0 | 6.0 | 0 | 6.0 |
| | 0.000145 | 3.2 | 0.000076 | 5.3 | 0.00034 | 6.5 |
| | 0.00113 | 1.9 | 0.000101 | 5.2 | 0.00177 | 8.7 |
| | 0.00255 | 1.4 | 0.00059 | 2.9 | 0.00455 | 13.5 |
| | 0.00524 | 1.1 | 0.00119 | 2.1 | 0.00966 | 16.8 |
| | 0.0102 | 0.83 | 0.00534 | 1.0 | | |
| | 0.0181 | 0.83 | 0.00960 | 1.0 | | |

TABLE III

EFFECT OF ADDED ACETIC ACID ON $k_m$

| $HNO_3$ conc. ($M$)<br>Temperature<br>PHX conc. ($M$) | 2.2<br>25.1°C.<br>0.0352 | 0.0211 | 1.15<br>35.1°C.<br>0.0352 | 0.0221 | 0.93<br>35.1°C.<br>0.0179 |
|---|---|---|---|---|---|
| Added HOAc conc. (Vol. %) | | | | | |
| 0 | 0.31 | 0.39 | 0.092 | 0.092 | 0.052 |
| 4 | 0.32 | | | | |
| 10 | 0.32 | | | | |
| 26 | 0.31 | 0.39 | 0.098 | 0.11 | 0.072 |

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From the data obtained at 15.1°C., a plot of log $k_m$ vs. log ($HNO_3$) shows that the reaction order with respect to nitric acid is 2.6. The small temperature coefficient of AcAn formation corresponds to an apparent activation energy of 2 kcal. mole$^{-1}$. In contrast, the corresponding value for the side reaction is of the order of 15 kcal. mole$^{-1}$.

*Disappearance of Nitric Acid and of PHX*

Using an electrometric method (3) for the estimation of nitric acid in aqueous acetic acid, it was observed that nitric acid reacted quantitatively, mole for mole, with PHX (though not with AcAn) in such media. This behavior necessitated the use of an analytical method for nitric acid applicable in the undiluted reaction medium. A suitable method, depending on the limited solubility of inorganic salts in these media was evolved; the details are given in an earlier paper (13).

These two analytical procedures determine the amount of nitric acid present in the diluted and undiluted reaction media, respectively. Since their values differ by an amount equivalent to the PHX present, a combination of these two methods provides a method for the estimation of PHX. However, this assumes that the products of the side reaction do not react with nitric acid on dilution of the reaction mixture. Since the amounts of nitric acid estimated by both methods were the same when reaction was complete, in spite of the by-products present, the above assumption is probably valid.

TABLE IV

RATE OF DISAPPEARANCE OF NITRIC ACID AND PHX AND RATE OF AcAn FORMATION WITH 1.17 *M* NITRIC ACID AT 35.1°C.

Reagents: 23.4 millimoles pale yellow nitric acid
6.20 millimoles PHX
20.0 ml. acetic anhydride

| Time, min. | − ΔPHX, mM. | − $\Delta HNO_3$, mM. | ΔAcAn, mM. | ΔPHX/ΔAcAn |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | |
| 20 | 1.55 | 2.85 | 0.75 | 2.1 |
| 60 | 3.0 | 4.1 | 1.35 | 2.2 |
| 120 | 3.6 | 5.2 | 1.95 | 1.85 |
| 240 | 5.75 | 7.6 | 2.8 | 2.05 |
| 360 | 5.85, 5.5 | 8.05, 8.3 | 3.3 | 1.8, 1.7 |

Because there is a large experimental error in the application of this analysis by difference to reaction conditions of high molar ratios of nitric acid to PHX, the determinations were made using low ratios of approximately four to one. However, the extent of the slow secondary reaction increased with decreasing acid concentration, thus placing, for theoretical purposes, a lower limit on the initial acid concentration which could be used. This necessitated the use of amounts of PHX which exceeded the solubility limit of the latter in the medium. It is therefore emphasized that the data given in Table IV were obtained under heterogeneous reaction conditions; this, however, does not detract from the conclusion drawn.

Some measurements of the rate of disappearance of nitric acid in homo-

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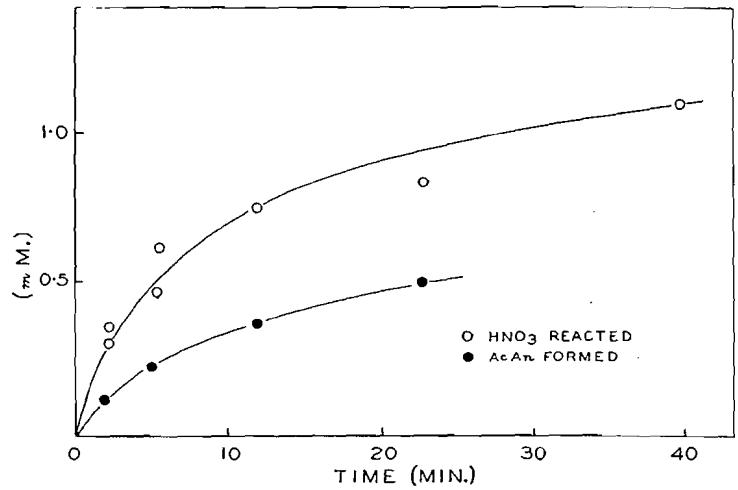



FIG. 2. Rate of AcAn formation and nitric acid disappearance with 1.15 *M* nitric acid and 0.0619 *M* PHX at 35.1°C.

geneous media were also made. Typical results are given in Fig. 2. The data show that the ratio of the rate of disappearance of nitric acid to the rate of formation of AcAn is approximately independent of the reaction time. The nitric acid reacted is greater than the AcAn formed although blank experiments without PHX showed no disappearance of nitric acid. Since the final yield of AcAn in these experiments was only about 50%, the difference is therefore due to a competitive reaction. Since the data obey Wegscheider's Test (20), this side reaction must be of the same order with respect to PHX as the main reaction, within experimental error.

A similar conclusion may be drawn from the data given in Table IV. However, in this case the acid concentration decreased from 1.2 *M* to 0.8 *M* during the course of reaction. Consequently, this conclusion is valid only if the ratio of rate constants for AcAn formation and side reaction is independent of acid concentration in this range. A direct measure of this ratio is the final yield of AcAn, as obtained by the extrapolation described earlier. Since this yield was found to be approximately constant over this range of acid concentration, the conclusion stands.

The data in Table IV also suggest that the nitric acid decomposition is greater than that of PHX. This fact may not be theoretically significant since in this case the acid was pale yellow and the excess consumed may have been due to autoreduction in the presence of nitrogen dioxide.

## DISCUSSION

Summarizing the experimental data:

(*a*) The rate of formation of AcAn is proportional to $(HNO_3)^{2\cdot6}(PHX)$. However, the rate constant, $k_m$, falls off slightly with increasing PHX concentration.

(*b*) $k_m$ is markedly decreased by added $NaNO_3$ but increased by $KClO_4$.

(*c*) The reaction rate is markedly affected by concentrations of these added salts

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which are much less than the stoichiometric concentrations of PHX and of $HNO_3$.

(*d*) The formation of AcAn parallels the disappearance of nitric acid and of PHX.

(*e*) $k_m$ is increased by added acetic acid.

(*f*) Some conductivity measurements, not reported in the previous section, showed that the addition of PHX to an acetic anhydride – nitric acid medium resulted in a marked, rapid increase of conductivity. This behavior suggests that PHX is somewhat basic and that the formation of its conjugate acid, $PHXH^+$, is rapid. Presumably, the hydrogen ion in $PHXH^+$ is attached to the lone, non-nitramine nitrogen atom in PHX.

Consistent with these experimental results are the following alternative mechanisms:

(I)
$$2HNO_3 \rightleftharpoons NO_2OH_2^+ + NO_3^- \quad [5]$$

$$PHX + NO_2OH_2^+ \longrightarrow H_2^+O\text{-}(CH_2\text{-}N)_4\text{-}CH_2OAc \quad [6]$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

$$Ac_2O + H_2^+O\text{-}(CH_2\text{-}N)_4\text{-}CH_2OAc \longrightarrow AcO\text{-}(CH_2\text{-}N)_4\text{-}CH_2OAc + AcOH \quad [7]$$
$$\qquad\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad NO_2\qquad\qquad\qquad\qquad\qquad NO_2$$

(II)
$$PHX + HNO_3 \rightleftharpoons PHXH^+ + NO_3^- \quad [8]$$

$$PHXH^+ + RONO_2 \longrightarrow RO\text{-}(CH_2\text{-}N)_4\text{-}OAc + H^+ \quad [9]$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2$$

While the R group of the product of reaction [9], X, may be H, Ac, or $NO_2$ the latter is rather improbable since the formation of AcAn would then involve the acetylation of the nitric ester, X. Such a reaction has not yet been observed for analogous nitric esters in $HNO_3$–$Ac_2O$ media. If R is H, then the product of (9) may also be $XH^+$, and AcAn would result from the acetylation of X or of $XH^+$. A reaction between $PHXH^+$ and $NO_2OH_2^+$ has not been suggested in mechanism II because of the large electrostatic repulsion involved.

Clearly there can be only one rate controlling step, which is seen from the data to be reaction [6] or [9]. Reaction [7] would be expected to be rapid since acetylations are generally acid catalyzed.

There is considerable evidence that nitracidium ion, $NO_2OH_2^+$ or $NO_2^+$, exists in media of similar type to that studied here (2, 8, 9), while other studies (17, 19) have shown it to be the probable nitrating agent in a variety of reactions somewhat analogous to the present one. While the present data alone do not appear to eliminate either mechanism I or II, the validity of the former may be assumed for purposes of discussing the quantitative aspects of the data, namely the salt effects and order of the reaction with respect to nitric acid. This does not, of course, reject the possibility that AcAn formation may proceed by the other mechanism.

*Salt Effects*

Numerous investigators (6, 7, 8, 10, 14, 15) have shown that perchloric acid is a much stronger acid than nitric acid in divers solvents. It may be assumed,

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therefore, that the $ClO_4$ group arising from $KClO_4$ exists largely as $ClO_4^-$ rather than as unionized $HClO_4$ in $HNO_3$–$Ac_2O$ media.

Three possible effects of added salts are: repression of ionization by a common ion, primary and secondary salt effects. The second of these may be neglected in the first approximation since the activated complex of (6) is also a monovalent ion and therefore the ratio of activity coefficients in the theoretical expression for the rate constant is essentially independent of the ionic strength, $\mu$.

It will be assumed that the concentration of the nitrate ion is appreciably greater than the more basic acetate ion in $HNO_3$–$Ac_2O$–AcOH media so that $\mu = (NO_3^-)$ in the absence of $KClO_4$. In addition to [5] the following equilibria probably occur in such media:

$$HNO_3 + S \rightleftharpoons SH^+ + NO_3^- \qquad [10]$$

$$HNO_3 + PHX \rightleftharpoons PHXH^+ + NO_3^- \qquad [11]$$

where S represents a solvent molecule and $SH^+$, the conjugate acid. Another possible source of nitrate ions is the ionization of nitrogen pentoxide, which in turn might arise from the dehydration of nitric acid by acetic anhydride. However, *as a source of nitrate ion* these reactions are thermodynamically equivalent to reaction [5] if the nitracidium ion postulated there exists in the dehydrated form, $NO_2^+$. The subsequent discussion of the salt effect is independent of the postulated form of nitracidium ion.

All ion activity coefficients, $f$, will be assumed to be given by the simple Debye-Hückel expression, $-\log f = A\sqrt{\mu}$, where $A$ depends only on the absolute charge of the ion for a given medium. In this approximation, the activity coefficients of neutral molecules are essentially independent of $\mu$. It also follows from datum (*c*) that the concentrations of PHX and of $HNO_3$ may be taken as essentially independent of added salt.

According to these assumptions there is no primary salt effect so that $k_m$ is directly proportional to $(NO_2OH_2^+)$, while the latter is given by the equilibrium expression,

$$f^2(NO_2OH_2^+)\ (NO_3^-) = \text{const.} \qquad [12]$$

From these relations and the previous expression for $\log f$ it follows immediately that

$$\log_{10} k_m(NO_3^-) = 2A\sqrt{\mu} + \text{const.} \qquad [13]$$

Furthermore, addition of the expressions for the equilibrium constants of [5], [10], and [11] leads to

$$f^2(NO_2OH_2^+ + SH^+ + PHXH^+)\ (NO_3^-) = \text{const.} \qquad [14]$$

In the absence of added nitrate the sum of the concentrations of these cations equals $(NO_3^-)$. From [13] and [14] it may then be concluded that

$$\log_{10} k_m = A\sqrt{\mu} + \text{const.} \qquad [15]$$

To compare [13] and [15] with the data, an estimate of $\mu$ is necessary. The value of $\mu$ in the absence of added salt may be determined as follows. Denoting the concentrations of nitrate ion and of added sodium nitrate by $y$ and $x$ respectively, equation [14] may be written as

$$f^2(y - x)y = \text{const.} \qquad [14']$$

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Also, from equation [12] and the proportionality between $k_m$ and $(NO_2OH_2^+)$,

$$k_m y f^2 = \text{const.} \qquad [16]$$

Differentiating [14′] and [16] with respect to $x$, eliminating $dy/dx$ between these equations, taking the limit of the resultant equation at $x = 0$ and neglecting a very small term involving $df/dx$ (which is justified at $x = 0$)

$$\left[\frac{dk_m}{dx} + \frac{k_m}{y}\right]_{x=0} = 0. \qquad [17]$$

Using this equation, the concentration of nitrate ion, $y$, at $x = 0$ was estimated from the limiting slope of a plot $k_m$ vs. $x$ (cf. Table II) to be $2.6 \times 10^{-4}$ $M$ and ca. $8 \times 10^{-4}$ $M$ when the nitric acid concentration was 1.15 $M$ and 2.2 $M$, respectively, the PHX concentration 0.0295 $M$, and the temperature, 35.1°C.

In the presence of added nitrate, $\mu = y = (y - x) + x$. Elimination of $yf^2$ between [14′] and [16] leads to

$$(y - x) = \text{const. } k_m. \qquad [18]$$

The proportionality constant may be determined from the previously estimated value of $y$ at $x = 0$ and the corresponding value of $k_m$. The more accurate data at 1.15 $M$ nitric acid were used for this purpose. The magnitude of $(y - x)$ may then be estimated from [18] for any value of $x$ for which $k_m$ has been determined. Since $x$ is also known, $\mu$ may then be calculated.

With $\mu$ so estimated, equation [13] can be compared with the data on effect of added nitrate. In this equation $(NO_3^-) = \mu$. Using the data given in Table II, (1.15 $M$ $HNO_3$, added $NaNO_3$), $\log_{10} k_m(NO_3^-)$ was plotted vs. $\sqrt{\mu}$ in Fig. 3 and from the slope, $A = 5$.

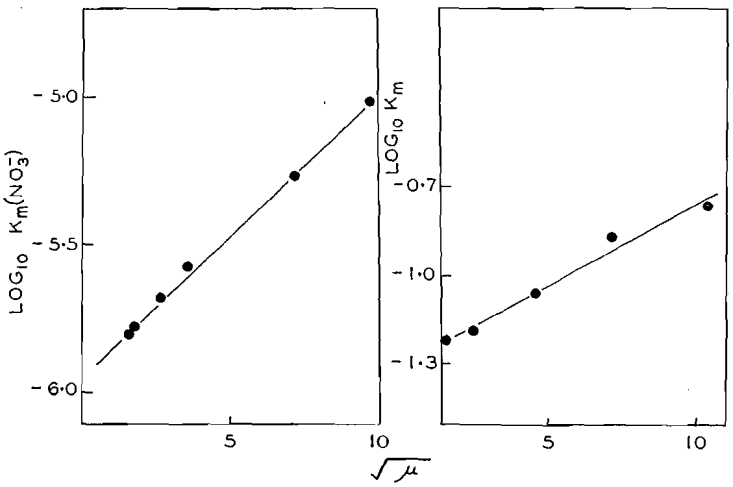



FIG. 3. Effect of ionic strength on rate of formation of AcAn.

In the presence of $KClO_4$ of concentration $z$, $\mu = (y + z)$ and $y$ is given by [18] where $x$ is now equal to zero. With $\mu$ thus determined, equation [15] was compared with the data on the effect of added $KClO_4$ given in Table II. The plot of $\log_{10} k_m$ vs. $\sqrt{\mu}$, given in Fig. 3, has slope, $A = 5$.

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These experimental values of $A$ may be compared with the theoretical value given by

$$A = \frac{z^2e^3\sqrt{2\pi N/1000}}{2.3(DkT)^{3/2}}$$

where $N$ is Avogadro's number, $D$ the dielectric constant of the medium, and the remaining symbols have their usual significance. At 35°C. the theoretical value of $A$ is approximately equal to 4, assuming $D \cong 20$, the value for pure anhydride. The dielectric constant of acetic anhydride–nitric acid media has not yet been determined.

*Order of Reaction with Respect to Nitric Acid*

In the following, it will be assumed that nitric acid exists largely in the form of acetyl nitrate because of equilibrium (20), and that the nitrate ion arises mainly from [10] and [11] rather than from [5] owing to the presumed relative basicities and assumed low concentration of nitric acid. With these assumptions it is possible to derive an expression for the dependence of $k_m$ on the acid concentration in good agreement with the data.

$$HNO_3 + Ac_2O \rightleftharpoons AcONO_2 + AcOH \qquad [20]$$

According to the second assumption the constant in equation [14] is directly proportional to $(HNO_3)$ so that [14] becomes

$$f^2(NO_3^-)^2 = \text{const. } (HNO_3). \qquad [21]$$

On the other hand the constant in equation [12] is proportional to $(HNO_3)^2$, while $(NO_2OH_2^+)$ is proportional to $k_m$, so that elimination of $(NO_3^-)$ between [12] and [21] leads to

$$k_{corr.} = \text{const. } (HNO_3)^{3/2} \qquad [22]$$

where $k_{corr.} = f\,k_m$.

$k_{corr.}$ is therefore given by [23] where $A = 5$

$$\log_{10}k_{corr.} = \log_{10}k_m - A\sqrt{\mu}. \qquad [23]$$

If $b$ denotes the stoichiometric concentration of $HNO_3$ and $c$ the concentration of acetic acid originally present in the 95% acetic anhydride ($c = 0.8\ M$), then $(AcONO_2) \simeq b$ and $(AcOH) \simeq (b + c)$, according to the first assumption. Elimination of $(HNO_3)$ between [22] and the expression for the equilibrium constant of [20] then leads to

$$\text{const. } k_{corr.}^{2/3} = bc + b^2. \qquad [24]$$

Finally, since $\mu = (NO_3^-)$, it follows from [21] and the expression for the equilibrium constant of [20] that, to a good approximation,

$$\mu = \text{const.}\sqrt{bc + b^2}. \qquad [25]$$

The proportionality constant in equation [25] was estimated from the data $\mu = 2.6 \times 10^{-4}M$ when $b = 1.15\ M$ and $c = 0.8\ M$. With $\mu$ thus determined for any value of $b$, $k_{corr.}$ was calculated from [23] and is given in Table V.

The proportionality constant in [24] was estimated from the value of $k_{corr.}$ at $b = 1.6\ M$, namely, $k_{corr.} = 0.097$ min.$^{-1}$. Equation [24] and the data are compared in Table V.

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TABLE V

COMPARISON OF EXPERIMENTAL AND THEORETICAL "$k$'S"

| $HNO_3$, $M$ "b" | $k_m$ (min.$^{-1}$) | $k_{corr.}$ (min.$^{-1}$) | |
|---|---|---|---|
| | Expt. | Expt. | Calc. |
| 2.2 | 0.31 | 0.24 | 0.22 |
| 2.0 | 0.22 | 0.17 | 0.17 |
| 1.6 | 0.12 | 0.097 | 0.097 |
| 1.15 | 0.047 | 0.039 | 0.043 |
| 1.00 | 0.038 | 0.032 | 0.031 |
| 0.60 | 0.01 | 0.009 | 0.01 |

Considering the good agreement between the experimental and calculated values of $k_{corr.}$, a closer examination of the two assumptions made at the beginning of this section appears desirable. The very large heat of mixing of $HNO_3$–$Ac_2O$ mixtures is quite noteworthy. This heat of reaction is almost certainly not to be attributed to ionization, which was seen in an earlier section to occur to a very minor extent. Furthermore, its magnitude is appreciably greater than would be expected from the changes in van der Waals or hydrogen bonding forces on mixing. Consequently, it appears that some chemical reaction such as the formation of acetyl nitrate or of nitrogen pentoxide via [20] or [26], respectively, occurs to an appreciable extent.

$$2\,HNO_3 + Ac_2O \rightleftharpoons N_2O_5 + 2\,AcOH \qquad [26]$$

Some evidence concerning these equilibria has become available since the completion of the present work. An analysis (18) of the vapor of $HNO_3$–$Ac_2O$ mixtures suggests that at 50% nitric acid the solution is mainly acetyl nitrate, while nitrogen pentoxide is an important constituent at higher acid concentrations and acetyl nitrate at lower ones.

From a comparison (9) of the near ultraviolet absorption spectra of these mixtures with that of nitrogen pentoxide solutions, Jones and Thorn inferred that nitric acid existed largely as nitrogen pentoxide in these media, both at high and low stoichiometric concentrations of nitric acid. However, no comparison with acetyl nitrate solutions was given and a more detailed study of the spectra is necessary. From an examination of the structures of nitrogen pentoxide and of acetyl nitrate, and of the spectra (9) of nitrogen pentoxide and of ethyl nitrate, it seems possible that these results may also be consistent with the presence of large concentrations of acetyl nitrate in these media. While it has been suggested that acetyl nitrate is either not present in this medium or is formed very slowly (5, 11), the published data are not inconsistent with the assumptions of the present paper.

It is also of interest to observe that acetyl nitrate can be prepared by a vacuum distillation of mixtures of nitrogen pentoxide with acetic anhydride (4, 16). Finally, postulation of equilibrium [26] rather than of [20] does not appear to lead to quantitative agreement with the observed effect of nitric acid on $k_m$.

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However, it seems clear that the composition of nitric acid – acetic anhydride media is not yet definitely established.

The effect of added acetic acid is qualitatively consistent with the present assumptions but is smaller than would be expected from equation [24]. This equation neglects the extent of dimerization of acetic acid (12) and the possible greater basicity of acetic acid as compared with acetic anhydride, both of which become increasingly important effects at higher concentration of acetic acid. The latter effect would increase the nitrate ion concentration and thereby tend to repress the formation of nitracidium ion. It can be shown that both effects provide a qualitative explanation of the discrepancy between the calculated and observed effects of added acetic acid.

The slight decrease of $k_m$ with increased PHX concentration can be attributed to the corresponding increase of nitrate ion and the resultant decrease of nitracidium ion concentration by the common ion effect.

According to the mechanism presented, the apparent activation energy of 2 kcal. per mole represents the activation energy of the rate determining step (reaction 6) together with the temperature coefficient of the concentration of nitracidium ion.

Finally, it is of interest to observe that the nitration of PHX in nitric acid – acetic anhydride media is rather similar to the nitration of benzene in the same media. It was found (5) that the latter reaction was first-order with respect to benzene, approximately third-order with respect to nitric acid, and was accelerated by added acetic acid. However, its apparent activation energy, 12 kcal. mole$^{-1}$, is appreciably higher than that found for the nitration of PHX. The analogous behavior of the nitration of PHX and benzene in this solvent and the interpretation of the nitration of substituted benzenes in the same solvent by a nitracidium ion mechanism are consistent with the mechanism outlined in the present paper.

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# SOME METHYL-SUBSTITUTED PYRIDYL AND QUINOLYLPHENYL CARBINOLS

By R. F. Knott, J. Ciric, and J. G. Breckenridge

In the course of work being carried out in these laboratories, we investigated the preparation and reactivity of Grignard reagents prepared from 3-, 4-, and 6-methylpyridine and 4-methylquinoline with bromine in the 2-position in each case. As has been shown by Wibaut and co-workers (2) for 2-bromopyridine, Grignard reagents of this type are not readily formed in good yield and are relatively unreactive toward other reagents, and although we tried a wide variety of solvents and reaction conditions, we were unable to do more than isolate in small yield the reaction products of the Grignard reagents with benzaldehyde, i.e. the methyl-substituted pyridyl- (and quinolyl-) phenyl carbinols.

## EXPERIMENTAL

The methylbromopyridines were prepared from the corresponding amino compounds, and 2-bromo-4-methylquinoline from 4-methylcarbostyril. Tetrahydrofuran was found to be the most satisfactory solvent for the pyridine compounds, and after addition of benzaldehyde to the solution of the Grignard reagent, followed by extraction, distillation *in vacuo* gave the carbinols in low yield. With the quinoline derivative, the best results were obtained using the "entrainment" method of Grignard (1), but again the yield of the carbinol was low; a small amount of the corresponding ketone was also isolated from the reaction mixture. The compounds produced are shown in the following table:

| | Compound | Yield, % | M.p., °C. | Analyses | |
|---|---|---|---|---|---|
| | | | | Calc. | Found |
| I | 2-(3-Methyl)pyridylphenyl carbinol | 5 | 57–58° | C, 78.35%<br>H, 6.58%<br>N, 7.03% | C, 78.40%<br>H, 6.55%<br>N, 6.88% |
| II | 2-(4-Methyl)pyridylphenyl carbinol | 14 | 89–90° | " | C, 78.23%<br>H, 6.71%<br>N, 7.05% |
| III | 2-(6-Methyl)pyridylphenyl carbinol | 19 | 86° | " | C, 78.45%<br>H, 6.50%<br>N, 7.56% |
| IV | Picrate of III | — | 130° | N, 13.08% | N, 12.52% |
| V | 2-(4-Methyl)quinolylphenyl carbinol | 10 | 132° | C, 81.90%<br>H, 6.06%<br>N, 5.62% | C, 81.93%<br>H, 6.18%<br>N, 5.98% |
| VI | 2-(4-Methyl)quinolylphenyl ketone | — | 109° | C, 82.56%<br>H, 5.30%<br>N, 5.66% | C, 82.53%<br>H, 5.30%<br>N, 6.08% |
| VII | Phenylhydrazone of VI | — | 136° | C, 81.90%<br>H, 5.63%<br>N, 12.45% | C, 82.20%<br>H, 5.67%<br>N, 12.26% |

all melting points are corrected; analyses done by Micro-Tech Laboratories.

ACKNOWLEDGMENT

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# CONDUCTANCES, DENSITIES, AND FLUIDITIES OF SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE AT 35°[1]

BY A. N. CAMPBELL, A. P. GRAY[2], AND E. M. KARTZMARK

ABSTRACT

The equivalent conductances of concentrated solutions of ammonium and silver nitrates have been determined up to saturation at 35.00°C. with a probable error of 0.1%. The equivalent conductances behave in a normal manner for strong electrolytes in aqueous solution, being approximately linear with the first power of the concentration, though slightly convex to the concentration axis. The viscosities and fluidities of these same solutions have been determined both at 25.00°C. and 35.00°C. with a probable error of 0.2%. Ammonium nitrate solutions exhibit the phenomenon of "negative viscosity" which tends to disappear at higher temperatures, the viscosity minimum or fluidity maximum shifting towards higher dilution. The silver nitrate fluidities decrease continuously with concentration, the curve showing less tendency to linearity at high concentrations than that for ammonium nitrate. The densities of the solutions at both temperatures have been determined with an apparent error of 0.02%. Apparent molal volumes have been calculated from these figures at 35.00 C. The concentrations of the saturated solutions of both salts at 25.00 C. and 35.00°C. have been determined by the conductance method and are in good agreement with the published data. The average temperature coefficients of fluidity and conductance for both salts have been evaluated between 25.00°C. and 35.00°C. and an approximate constancy of the ratio of fluidity coefficient to conductance coefficient has been observed beyond 2 molar. The ratios appear to have the mean value of 1.12 for both salts in spite of a considerable difference in the individual coefficients.

## THEORETICAL

This paper is a record of experimental work on the conductance, density, and viscosity of solutions of ammonium nitrate and of silver nitrate at 25° and 35°C. It is part of a general campaign of work on the conductance of strong solutions of salts (3).

### *Previous Work on the Present Problem*

#### *Ammonium Nitrate*

Although an enormous amount of conductance work of extremely high accuracy has been reported in the literature since 1930, it appears that ammonium nitrate has been largely neglected. No data could be found in the literature for ammonium nitrate conductance except those quoted in the International Critical Tables for 18.00°C. (8) and that of Scatchard and Prentiss for 10.0°C. (14). The conductance of this salt therefore is not known in dilute solution either at 25.00°C. or 35.00°C., although the limiting conductances may be obtained from the limiting ionic conductances and their temperature coefficients at infinite dilution.

The only data to be found in the literature for the viscosity of ammonium nitrate solutions are those obtained by Getman in 1908 (5).

[1] *Manuscript received January 8, 1953.*
*Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Manitoba.*

[2] *Holder of Cominco Research Fellowship, 1951-1952.*



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*Silver Nitrate*

The conductance of this salt has been very accurately determined by Shedlovsky in the region up to 0.1 $N$ (15), at 25.00°C. It has been pointed out by MacInnes, Shedlovsky, and Longsworth (12) that silver nitrate is somewhat "abnormal" in that it shows no deviation from the Onsager straight line slope up to a concentration of 0.002 $N$, whereas for the alkali halides agreement to 0.001 $N$ is exceptional. They also point out that the observed limiting slope of the transference number of silver nitrate is of opposite sign to that predicted on the basis of the theory. A complete investigation over the range of concentrated solutions at 25° and 95°C. has been made by us (3).

Some very accurate data for the viscosity of silver nitrate solutions at 25.00°C. and 0.00°C. have been obtained by Jones and Colvin (10) up to a concentration of 5 molar.

## EXPERIMENTAL

*Purification of Materials*

Conductance measurements in the dilute region are very greatly influenced by the presence of even minute amounts of impurities in the salts. In this work, however, the specific conductances are so high that the solvent correction is completely negligible. Further, since the over-all accuracy expected is no better than 0.1%, the purity of the salts is not nearly as critical in these concentrated solutions. Nevertheless, the best materials available were purified and dried according to the following methods:

(i) *Ammonium Nitrate*

This was part of a bulk lot obtained from the Consolidated Mining and Smelting Company during the last war. The salt was cycled through at least three crystallizations from water followed by a final recrystallization from water and ethanol. It was then placed in an oven at 80°C. for 24 hr., removed, finely ground in an agate mortar, and replaced in the oven for an additional 24 hr. The grinding was repeated several times to ensure the absence of any occluded mother liquor and the salt was finally stored over sulphuric acid until required.

(ii) *Silver Nitrate*

The silver nitrate was that supplied by the Johnson, Matthey and Mallory Company, and was adequately pure but for the presence of some water. It was felt that nothing would be gained by recrystallization and the salt was carefully fused in a platinum dish, ground in an agate mortar to a fine powder, and stored over sulphuric acid in a darkened space. The resulting salt was pure white in appearance, and showed no visible evidence of decomposition.

(iii) *Potassium Chloride*

A good reagent grade potassium chloride was recrystallized twice from water and fused in a platinum dish. The salt was then ground very finely and kept over sulphuric acid.

(iv) *Conductance Water*

The specific conductivity of this water was of the order of $1.5 \times 10^{-6}$ mhos

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which indicated a purity entirely adequate for the concentrated solutions and for the calibration of the viscometers.

*Preparation of the Solutions*

With the exception of the four saturated solutions, all were made up by weight. The weights were calibrated. The density of the air was calculated from a knowledge of the temperature, humidity, and atmospheric pressure, and corrections to vacuum were made in every case.

The concentrations of the saturated solutions were determined by dilution of a weighed amount of the solution to a convenient lower concentration by weight. The specific conductance of the dilute solution was then determined and from a graph of specific conductance versus weight per cent, at 25°C. the weight per cent of the diluted solution was found.

*Temperature Control*

All thermometers were calibrated against a platinum resistance standard. The 25°C. thermostat showed no variance in temperature detectable on a

TABLE I

DENSITIES AND SPECIFIC AND EQUIVALENT CONDUCTANCES OF AQUEOUS AMMONIUM NITRATE SOLUTIONS AT 35.00°C.

| Concentration | | $d_4^{35}$, | $K$, | $\Lambda$, |
|---|---|---|---|---|
| Wt. % | Molarity | gm./ml. | mho cm.$^{-1}$ | mho cm.$^2$ |
| 0.4324 | 0.0538 | 0.9958 | 0.00823 | 153.1 |
| 7.9779 | 1.0234 | 1.0269 | 0.1222 | 119.4 |
| 12.963 | 1.6940 | 1.0461 | 0.1881 | 111.0 |
| 14.533 | 1.9104 | 1.0523 | 0.2068 | 108.2 |
| 18.352 | 2.4504 | 1.0688 | 0.2528 | 103.2 |
| 28.572 | 3.9749 | 1.1136 | 0.3545 | 89.17 |
| 38.071 | 5.5065 | 1.1579 | 0.4210 | 76.46 |
| 47.424 | 7.1318 | 1.2038 | 0.4554 | 63.86 |
| 50.378 | 7.6705 | 1.2188 | 0.4590 | 59.84 |
| 59.457 | 9.4086 | 1.2667 | 0.4465 | 47.46 |
| 66.012 | 10.749 | 1.3035 | 0.4141 | 38.52 |

TABLE II

DENSITIES AND SPECIFIC AND EQUIVALENT CONDUCTANCES OF AQUEOUS SILVER NITRATE SOLUTIONS AT 35.00°C.

| Concentration | | $d_4^{35}$, | $K$, | $\Lambda$, |
|---|---|---|---|---|
| Wt. % | Molarity | gm./ml. | mho cm.$^{-1}$ | mho cm.$^2$ |
| 1.6612 | 0.0986 | 1.0082 | 0.01306 | 132.5 |
| 20.051 | 1.4023 | 1.1882 | 0.1197 | 85.37 |
| 24.350 | 1.7757 | 1.2389 | 0.1413 | 79.55 |
| 36.551 | 3.0322 | 1.4094 | 0.1983 | 65.41 |
| 42.849 | 3.8230 | 1.5158 | 0.2252 | 58.91 |
| 45.764 | 4.2306 | 1.5705 | 0.2372 | 56.06 |
| 51.422 | 5.1064 | 1.6874 | 0.2590 | 50.71 |
| 51.844 | 5.1784 | 1.6970 | 0.2606 | 50.32 |
| 57.194 | 6.1438 | 1.8250 | 0.2782 | 45.28 |
| 64.283 | 7.6633 | 2.0253 | 0.2954 | 38.55 |

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Beckmann thermometer. The 35°C. thermostat showed a variation of ± 0.02°C.

*Measurement of Equivalent Conductances*

This has been previously described (3). Our data for specific and equivalent conductances are given in Tables I and II.

*The Measurement of Relative Viscosity*

It was desirable to obtain a measure of accuracy for viscosity determinations comparable to that of the conductance data. The capillary viscometer is most commonly employed in research work of this nature and has the advantage of being simple in principle and operation, but the simple Ostwald equation commonly employed with an Ostwald viscometer cannot be used for accurate work unless care is taken to design the viscometer in such a way that errors may either be accurately compensated for or made negligible. The latter alternative is much to be preferred and is the subject of a number of papers on viscometer design, most notable of which are by Willihnganz, McCluer, Fenske, and McGrew (19), and by Jones (9). It was decided that a suitable viscometer was that designed by Cannon and Fenske for nonviscous liquids (4), and two were obtained from the H. S. Martin Glass Co.

The drainage and kinetic energy corrections to the measurements were considered to be negligible by virtue of the rather narrow capillary diameter which gave an efflux time in excess of 200 sec., for all of the measurements. The surface tension correction was not allowed for in such a viscometer because the change in surface tension between the calibrating liquid, water, and an aqueous salt solution does not cause a large effect. The working volume correction was rendered negligible by the rather unique and quite sensitive method of filling the pipettes. The viscometer is inverted and the capillary arm is placed in the liquid. Suction is then applied to the wide-bore arm and the liquid is drawn to the capillary mark. This method of loading was found to be very convenient and gave quite reproducible results. Two stop watches were used which were periodically checked against station WWV, Washington, and found to be reliable for periods well in excess of the efflux times. The measurement was repeated until at least three consecutive readings were in agreement to 0.2 sec. which was the practical limit of the stop watches. The first viscometer was then transferred from one bath to the other and vice versa. It was found experimentally that the efflux time suffered no change, when a solution was heated from 25° to 35° without refilling, from the result when the filling was done at 35° as well as 25°. Each was again allowed to come to equilibrium and the procedure was repeated. The viscometer constants were checked frequently with conductance water and showed no variation over the period of this work.

All the pertinent viscosity data are tabulated for the two salts at 25.00° and 35.00° in Tables III, IV, V, and VI. The fluidities are plotted in Figs. 5 and 6 together with our previous results at 25.00°C.

*The Determination of the Density*

In this determination a simple Weld pycnometer was employed. Although

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TABLE III

DENSITY AND VISCOSITY DATA FOR AMMONIUM NITRATE AT 25.00°C.

| Molarity | Density, gm. ml.$^{-1}$ | | Viscosity, centipoise | Fluidity, rhes |
|---|---|---|---|---|
| | Exptl. | Calc. | | |
| 0.0000 | 0.99707 | 0.99707 | 0.8937 | 111.9 |
| 0.0540 | 0.99883 | 0.99883 | 0.8924 | 112.0 |
| 1.0261 | 1.02957 | 1.02957 | 0.8635 | 115.8 |
| 1.7009 | 1.05028 | 1.05029 | 0.8564 | 116.7 |
| 1.9184 | 1.0567 | 1.0569 | 0.8561 | 116.8 |
| 2.4611 | 1.0735 | 1.0734 | 0.8604 | 116.2 |
| 3.9940 | 1.1190 | 1.1187 | 0.9005 | 111.1 |
| 5.5346 | 1.1637 | 1.1636 | 0.9846 | 101.6 |
| 7.1685 | 1.2100 | 1.2101 | 1.1324 | 88.30 |
| 7.7100 | 1.2251 | 1.2252 | 1.1200 | 83.35 |
| 9.4584 | 1.2734 | 1.2734 | 1.5047 | 66.46 |
| 10.8027 | 1.3100 | 1.3098 | 1.8820 | 53.13 |

TABLE IV

DENSITY AND VISCOSITY DATA FOR SILVER NITRATE AT 25.00°C.

| Molarity | Density, gm. ml.$^{-1}$ | | Viscosity, centipoise | Fluidity, rhes |
|---|---|---|---|---|
| | Exptl. | Calc. | | |
| 0.0000 | 0.99707 | 0.99707 | 0.8937 | 111.9 |
| 0.0989 | 1.0112 | 1.0110 | 0.9005 | 111.0 |
| 1.4077 | 1.1928 | 1.1926 | 0.9871 | 101.3 |
| 1.7830 | 1.2440 | 1.2440 | 1.0208 | 97.96 |
| 3.0458 | 1.4157 | 1.4156 | 1.1630 | 86.00 |
| 3.8399 | 1.5225 | 1.5225 | 1.2770 | 78.30 |
| 4.2526 | — | 1.5779 | 1.3427 | 74.48 |
| 5.1313 | 1.6953 | 1.6952 | 1.5031 | 66.52 |
| 5.2027 | 1.7049 | 1.7047 | 1.5198 | 65.80 |
| 6.1730 | 1.8336 | — | 1.7342 | 57.65 |
| 7.6996 | 2.0349 | — | 2.1693 | 46.10 |

TABLE V

DENSITY AND VISCOSITY DATA FOR AMMONIUM NITRATE AT 35.00°C.

| Molarity | Density, gm. ml.$^{-1}$ | Viscosity, centipoise | Fluidity, rhes |
|---|---|---|---|
| 0.000 | 0.99406 | 0.7225 | 138.4 |
| 0.0538 | 0.99575 | 0.7222 | 138.5 |
| 1.0234 | 1.0269 | 0.7119 | 140.5 |
| 1.6940 | 1.0461 | 0.7114 | 140.5 |
| 1.9104 | 1.0523 | 0.7132 | 140.2 |
| 2.4505 | 1.0688 | 0.7211 | 138.7 |
| 3.9749 | 1.1136 | 0.7639 | 131.0 |
| 5.5065 | 1.1579 | 0.8427 | 118.7 |
| 7.1318 | 1.2038 | 0.9748 | 102.6 |
| 7.6705 | 1.2188 | 1.0325 | 96.85 |
| 9.4086 | 1.2667 | 1.2951 | 77.21 |
| 10.749 | 1.3035 | 1.6139 | 61.96 |

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TABLE VI

DENSITY AND VISCOSITY DATA FOR SILVER NITRATE AT 35.00°C.

| Molarity | Density, gm. ml.$^{-1}$ | Viscosity, centipoise | Fluidity, rhes |
|---|---|---|---|
| 0.0000 | 0.99406 | 0.7225 | 138.4 |
| 0.0986 | 1.0082 | 0.7289 | 137.2 |
| 1.4023 | 1.1882 | 0.8100 | 123.5 |
| 1.7757 | 1.2389 | 0.8385 | 119.3 |
| 3.0322 | 1.4094 | 0.9584 | 104.3 |
| 3.8230 | 1.5158 | 1.0557 | 94.72 |
| 4.2306 | 1.5705 | 1.1074 | 90.30 |
| 5.1064 | 1.6874 | 1.2401 | 80.64 |
| 5.1784 | 1.6970 | 1.2533 | 79.78 |
| 6.1438 | 1.8250 | 1.4281 | 70.02 |
| 7.6633 | 2.0253 | 1.7786 | 56.24 |

this instrument is not capable of the highest accuracy, it has many practical advantages over the more elaborate and time consuming methods which are commonly employed for high precision measurements (11, 18). The pycnometer had a capacity of approximately 25 ml. No advantage would have been gained by the use of a larger bottle since uncertainties due to adsorption of moisture on large surfaces become considerable beyond 30 ml. The technique employed in the use of this pycnometer was exactly that of Weissberger (17). The appropriate buoyancy corrections were made from a knowledge of the temperature, pressure, and humidity.

The empirical equation of Gucker (6) for the densities of ammonium nitrate solutions at 25.00°C. up to saturation is: $d_4^{25} = 0.997077 + 0.032628c - 9.63 \times 10^{-4}c^{3/2} - 4.73 \times 10^{-5}c^2$. This equation represents the experimental data of Adams and Gibson (1) to two parts in the fifth decimal place. The experimental densities for six ammonium nitrate solutions determined in a single day are presented in Table VII, together with values calculated from this equation.

TABLE VII

| Weight % $NH_4NO_3$ | Normality | $d_4^{25}$ | |
|---|---|---|---|
| | | Experimental | Calculated |
| 1.4812 | 0.1856 | 1.00305 | 1.00305 |
| 1.7248 | 0.2163 | 1.00403 | 1.00404 |
| 6.2710 | 0.8010 | 1.02251 | 1.02249 |
| 10.048 | 1.3031 | 1.03803 | 1.03809 |
| 15.537 | 2.0599 | 1.06124 | 1.06124 |
| 24.759 | 3.4075 | 1.10167 | 1.10165 |

The density data for the determinations at 25.00°C. and 35.00°C. are contained in Tables III, IV, V, and VI. For comparative purposes Table III also contains the values calculated from Gucker's equation (6). Calculated values

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for silver nitrate at 25.00°C. for concentrations up to 5 molar were also obtained from the equation of Jones and Colvin (10):

$$d_4^{25} = 0.997074 + 0.141956c - 0.002603c^{3/2}$$

These values are included in Table IV.

*Apparent Molal Volume*

The apparent molal volumes of ammonium nitrate solutions at 25.00°C. have been very accurately determined by Adams and Gibson (1) and by Gucker (6). The apparent molal volumes of silver nitrate at 25.00°C. have been determined by Bauer (2). The agreement of his values with ours is dependent on the agreement of the density figures. Our density data differ from their accurate results by as much as two units in the fourth decimal place and consequently the molal volume data presented in Table VIII for

TABLE VIII

THE APPARENT MOLAL VOLUMES OF $NH_4NO_3$ AND $AgNO_3$ SOLUTIONS AT 35.00°C.

| Ammonium nitrate | | | | Silver nitrate | | | |
|---|---|---|---|---|---|---|---|
| $c$ | $\sqrt{c}$ | $d_4^{35}$ | $\Phi$ | $c$ | $\sqrt{c}$ | $d_4^{35}$ | $\Phi$ |
| 1.0234 | 1.011 | 1.0269[0] | 48.2 ± .2 | 1.4023 | 1.184 | 1.1881[9] | 31.6 ± .1 |
| 1.6940 | 1.301 | 1.0460[7] | 49.6 ± .1 | 1.7757 | 1.332 | 1.2388[8] | 32.2 ± .1 |
| 1.9104 | 1.382 | 1.0523[0] | 49.9 ± .1 | 3.0322 | 1.741 | 1.4093[8] | 33.22 ± .06 |
| 2.4504 | 1.565 | 1.0687[9] | 49.9 ± .1 | 3.8230 | 1.955 | 1.5157[6] | 33.73 ± .05 |
| 3.9749 | 1.994 | 1.1136[2] | 50.27 ± .05 | 4.2306 | 2.057 | 1.5705[4] | 33.93 ± .04 |
| 5.5065 | 2.347 | 1.1578[6] | 50.60 ± .04 | 5.1064 | 2.259 | 1.6873[7] | 34.32 ± .03 |
| 7.1318 | 2.671 | 1.2037[6] | 50.95 ± .03 | 5.1784 | 2.276 | 1.6969[5] | 34.36 ± .03 |
| 7.6705 | 2.770 | 1.2188[1] | 51.05 ± .03 | 6.1438 | 2.479 | 1.8249[7] | 34.85 ± .03 |
| 9.4086 | 3.067 | 1.2667[0] | 51.38 ± .02 | 7.6633 | 2.768 | 2.0253[2] | 35.53 ± .03 |
| 10.749 | 3.278 | 1.3034[9] | 51.57 ± .02 | | | | |

35.00°C. are quoted to only as many figures as this error justifies. The probable errors in the apparent molal volume, determined on the assumption that the 35.00°C. density figures were of comparable accuracy to those at 25.00°, were calculated and included in the table.

*The Temperature Coefficients*

It is commonly stated that the variation of conductance with temperature may be expressed by means of an equation, usually of the form

$$\Lambda_{t°}/\Lambda_{25°} = 1 + a(t - 25) + b(t - 25)^2 + \ldots$$

where $a$ and $b$ are constants to be determined.

There is no generally applicable formula for the temperature dependence of viscosity or fluidity, but it is agreed, both on empirical and theoretical grounds, that it should contain an exponential expression of the form, $e^{E/RT}$.

The proper evaluation of the coefficients of the above equation and the determination of the temperature dependence of the fluidity must be left until further data are obtained in the range between 35.00°C. and 95.0°C. The procedure followed by us (3) in the determination of "coefficients" between 25.00° and 95.0°C. was adopted. The variation of both the equivalent conductance and the fluidity between 25.00°C. and 35.00°C. was assumed to be

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linear and average temperature coefficients were evaluated. No appreciable error was introduced by evaluating graphically the coefficients at concentrations somewhat removed from the experimental points. The results are presented in Table IX. The ratio of the temperature coefficient of fluidity to the

TABLE IX

TEMPERATURE COEFFICIENTS OF CONDUCTANCE AND FLUIDITY BETWEEN 25.00° AND 35.00°C.

| Molarity | Ammonium nitrate | | | Silver nitrate | | |
|---|---|---|---|---|---|---|
| | Coefficient of: | | $\gamma/\beta$ | Coefficient of: | | $\gamma/\beta$ |
| | Fluidity, $\gamma$ | Conductance, $\beta$ | | Fluidity, $\gamma$ | Conductance, $\beta$ | |
| 0.00 | $2.37 \times 10^{-2}$ | $1.86 \times 10^{-2}$ | 1.27 | $2.37 \times 10^{-2}$ | $1.88 \times 10^{-2}$ | 1.26 |
| 1.00 | 2.14 | 1.85 | 1.16 | 2.20 | — | — |
| 2.00 | 2.00 | 1.69 | 1.18 | 2.15 | 1.90 | 1.13 |
| 3.00 | 1.86 | 1.65 | 1.13 | 2.13 | 1.90 | 1.12 |
| 4.00 | 1.77 | 1.56 | 1.13 | 2.07 | 1.88 | 1.10 |
| 5.00 | 1.69 | 1.50 | 1.13 | 2.03 | 1.85 | 1.10 |
| 6.00 | 1.62 | 1.44 | 1.13 | 2.08 | 1.92 | 1.08 |
| 7.00 | 1.58 | 1.43 | 1.10 | 2.12 | 1.95 | 1.09 |
| 8.00 | 1.53 | 1.39 | 1.10 | 2.14 | 1.92 | 1.11 |
| 9.00 | 1.50 | 1.38 | 1.09 | — | 1.93 | — |
| 10.00 | 1.53 | 1.30 | 1.18 | — | — | — |

temperature coefficient of equivalent conductance is of interest and this ratio is also included.

*The Saturated Solutions*

These results are of special interest from the point of view of solubilities, and since they are probably not of comparable accuracy, they are not included in tables with the other solutions but are presented separately in Table X.

TABLE X

CONCENTRATION, DENSITY, CONDUCTANCE, AND FLUIDITY OF SATURATED SOLUTIONS AT 25.00° AND 35.00°C.

| Salt | $t$,°C. | Wt. % | Lit. solubility, wt. % | $d$ | Lit. $d$ | Molarity | $K$ | $\Lambda$ | $\phi$ |
|---|---|---|---|---|---|---|---|---|---|
| $NH_4NO_3$ | 25.00 | 67.3 | 67.6 | 1.3174 | 1.3197 | 11.08 | 0.3519 | 31.76 | 50.05 |
| | 35.00 | 71.5 | 71.6 | 1.3384 | 1.3394 | 11.95 | 0.3702 | 30.98 | 48.06 |
| $AgNO_3$ | 25.00 | 71.0 | 71.0 | 2.3019 | 2.3021 | 9.62 | 0.2509 | 26.10 | 33.25 |
| | 35.00 | 75.4 | 75.4 | 2.4530 | — | 10.90 | 0.2943 | 27.00 | 33.09 |

## DISCUSSION OF RESULTS

*Conductance*

The variation of equivalent conductance with concentration at 35.00°C. is seen (Figs. 1 and 2) to be similar to that (3) at 25.00°C. The approximately linear variation at high concentrations persists although a noticeable curvature

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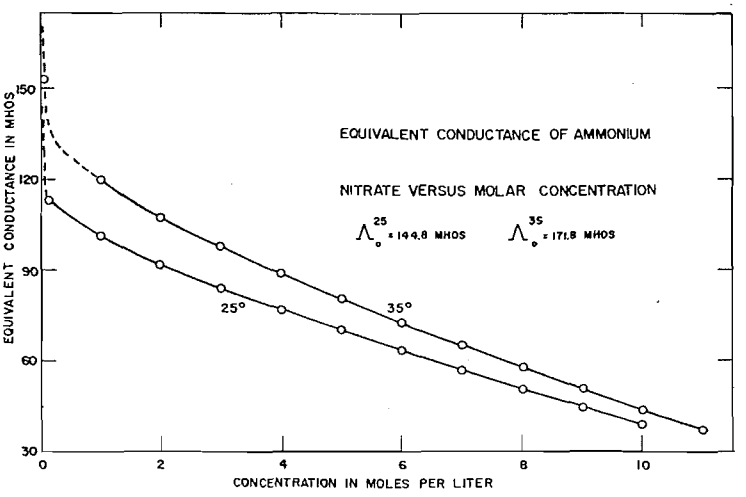



FIG. 1

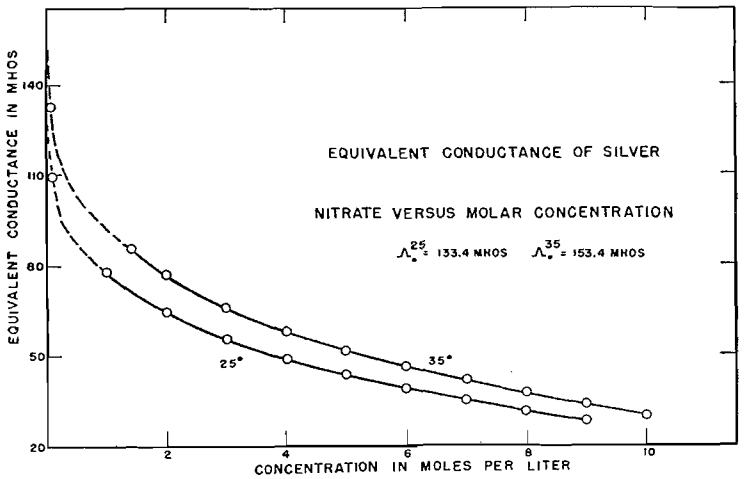



FIG. 2

may be detected on a large scale plot. The trend to increasing curvature with rising temperature is evident from the data at 95.00°C. (3) where the deviations from linearity are quite pronounced. The equivalent conductances of ammonium nitrate are numerically greater than those of silver nitrate and tend to linearity at a lower concentration. The values at infinite dilution were obtained from the published ionic conductances and their temperature coefficients and are included in Figs. 1 and 2 to demonstrate the great variation in the dilute solution range.

Figs. 3 and 4 illustrate the behavior of the specific conductance with increase of concentration. At 95.00°C. the specific conductance of a 12 molar solution is approximately the same as that of a 4 molar solution in spite of a

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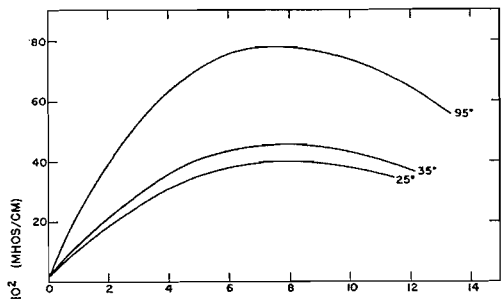



FIG. 3 $NH_4NO_3$ SPECIFIC CONDUCTANCE VERSUS MOLARITY

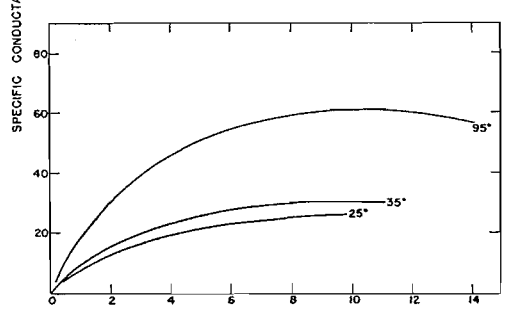



FIG. 4 $AgNO_3$ SPECIFIC CONDUCTANCE VERSUS MOLARITY

FIGS. 3 & 4

threefold increase in electrolyte concentration. This phenomenon was often noted in the early literature (16) and interpreted as the "interplay of ionization and concentration". It has only been observed infrequently in the modern literature (13) because of the lack of conductance work in the concentrated region. It seems probable that the existence of a maximum indicates the association of ions in some manner or other. In view of the present ideas on the structure of concentrated electrolytic solutions, the maximum might be explained by a more ordered lattice-like structure of the ions. In this connection it is interesting that the maxima occur at substantially the same concentration with rise in temperature, but, if anything, appear to move toward higher dilution. This behavior is not contradictory to the view that dissociation normally increases with rising temperature, since the decrease in dielectric constant, and variations in ion-solvent effects might well compensate for the increase in thermal energy. In fact it was the conclusion of early workers on independent evidence that electrolytic dissociation decreased at higher temperatures (16). Some authors would undoubtedly attribute the decrease in specific conductance to the increase in viscosity, but this does not constitute an explanation at all, especially since the variation of viscosity in no way parallels that of the conductance.

When the equivalent conductance is plotted against temperature a linear curve is obtained. This has been done for solutions of silver nitrate and of ammonium nitrate of various concentrations in Figs. 5 and 6. In order to

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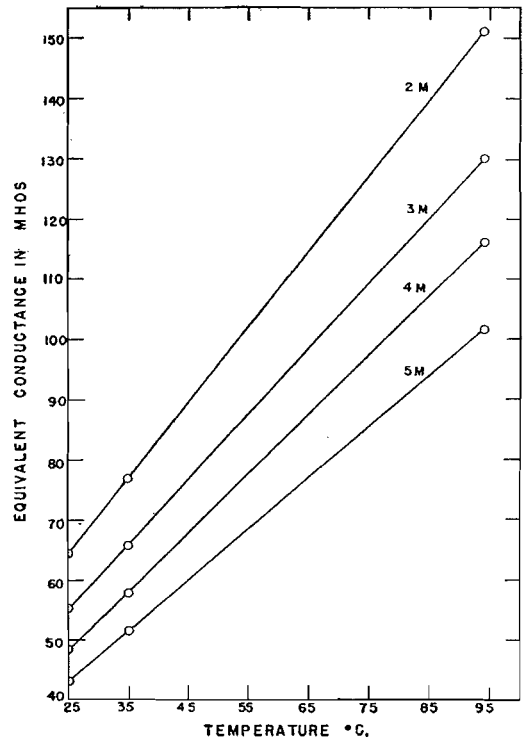



FIG. 5

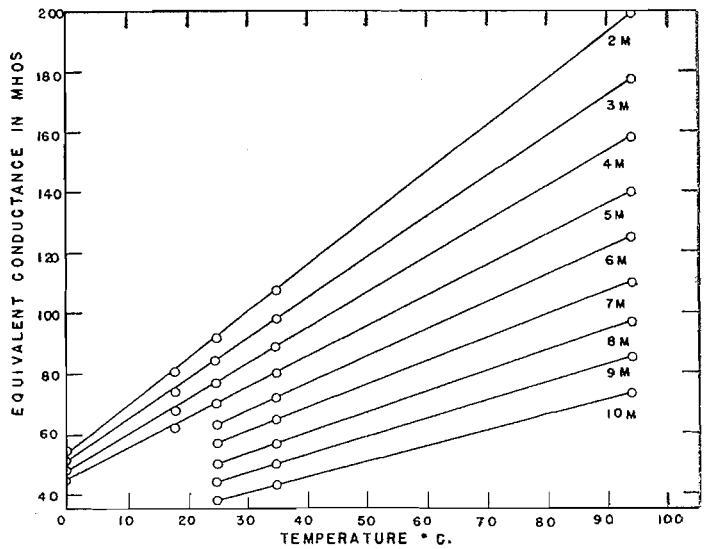



FIG. 6

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construct Figs. 5 and 6 we have utilized the data of the Critical Tables taken from various sources as well as our own data. We have no explanation to offer of this linearity; that it is a coincidence is hardly likely. It certainly is not behavior that would be expected from the supposed complexity of the structure of concentrated solutions of strong electrolytes.

The fluidity data for ammonium nitrate lie very well along a smooth curve at both temperatures (Fig. 7), exhibiting a maximum between 1.7 and 2.0

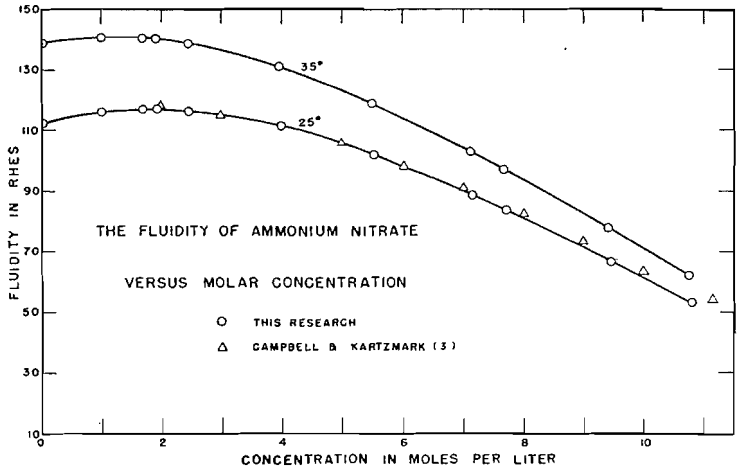



FIG. 7

molar at 25.00°C. and between 1.2 and 1.5 molar at 35.00°C. The fluidities approach linearity at the higher concentrations, the 35.00°C. curve being the more nearly linear. Our earlier data (3) for 25.00°C. are included.

The fluidity-concentration dependence of silver nitrate (Fig. 8) differs considerably from that of ammonium nitrate. The curves are S-shaped and show

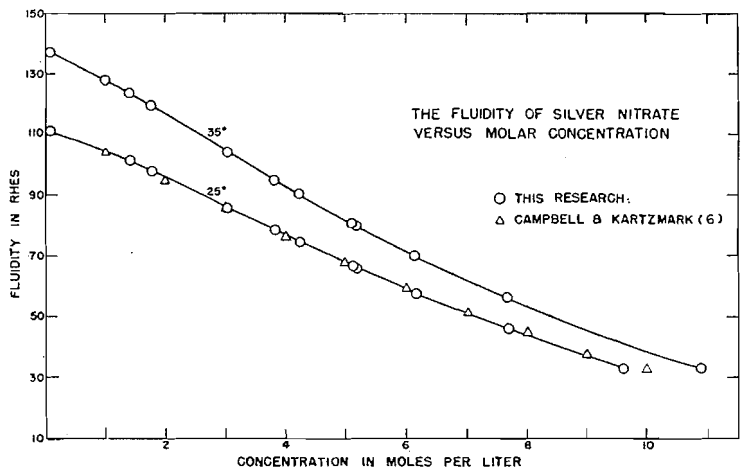



FIG. 8

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a tendency to flatten out at high concentrations. Our earlier data (3) are again included.

The average coefficients of fluidity evaluated between 25.00°C. and 35.00° C. and tabulated in Table IX show a behavior roughly parallel to that of the conductance coefficients as shown by the approximate constancy of their ratios. The ratios, $\gamma/\beta$, are surprisingly constant considering the probable error of from 4 to 8% in both coefficients. The fluidity coefficients are markedly different from those evaluated by us for the 25-95° range, illustrating the nonlinear dependence of fluidity on temperature. The assumption of linearity between 25.00°C. and 35.00°C. is perhaps not serious and some comparison may be made.

The apparent constancy of the ratio with concentration was pointed out by us previously (3), but an observation of perhaps greater significance is that the ratio is the same for both silver nitrate and ammonium nitrate, indicating a proportionality between the two coefficients, at least for these two salts. This shows that above 2 molar the factors which cause an increase of conductance with temperature have a proportional effect on the fluidity. The differences between the values for conductance and for fluidity are to be expected since each phenomenon proceeds by a different mechanism. Nevertheless the close relationship is clearly demonstrated, and it is probable that a mathematical treatment of the theory would contain an identical term for both conductance and fluidity.

Although the density data are quite accurate enough for use in evaluating the viscosities and the molar concentrations, they are not sufficiently so to allow the ultimate calculation of the partial molal volumes. The apparent molal volumes of ammonium and silver nitrate solutions at 35.00°C. are presented in Table VIII. Estimated errors are included on the assumption that the probable error in the densities is two parts in the fourth decimal place.

## CONCLUSION

The most notable observations in this work, apart from the accumulation of experimental data, are that the plot of $\Lambda$ vs. temperature is in every case a straight line, and that in the region of high concentration the (isothermal) plot of $\Lambda$ vs. concentration approaches a straight line. For the former observations we have no explanation to offer. The latter observation is not new. Indeed, Hasted, Ritson, and Collie (7) point out that any equation purporting to represent the conductance behavior over the complete range of concentration would have to reduce at low concentrations to a form in which $\Lambda$ is proportional to $\sqrt{c}$ and for high concentrations to a form for which $\Lambda$ is proportional to $c$. This is mathematically possible, but there is not much point in it, unless the equation can be deduced from an acceptable model.

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# PHOTOLYSIS OF MERCURY DIMETHYL[1]

By Richard E. Rebbert[2] and E. W. R. Steacie

ABSTRACT

The photolysis of mercury dimethyl was investigated over the temperature range from 125° to 250°C. The results indicate that methane is formed only by an abstraction reaction and ethane is formed only by recombination, at least under the conditions used in these experiments. It is concluded that the activation energy of the reaction

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + CH_2HgCH_3$$

is 10.8 ± 0.3 kcal./mole.

## INTRODUCTION

An extensive investigation was recently conducted in this laboratory to determine the activation energies of a number of reactions of the type (8)

$$CH_3 + RH \rightarrow CH_4 + R.$$

The source of the methyl radicals in all this work was the photolysis of acetone. In order to establish these results with more certainty, it was thought profitable to repeat some of these experiments using another source of methyl radicals. For this purpose, mercury dimethyl was chosen. However, before it could be used as a source of methyl radicals, some aspects of its own photolysis had to be more fully investigated. In particular it was necessary to establish that the ethane came only from the recombination of methyl radicals and not from a reaction such as

$$CH_3 + Hg(CH_3)_2 \rightarrow C_2H_6 + Hg + CH_3.$$

Although mercury dimethyl is an excellent source of methyl radicals, it is not quite as useful as acetone for two reasons. First, it begins to decompose thermally around 250°C. which limits the temperature range over which it can be used. Secondly, its vapor pressure is only 6 cm. at room temperature which limits the range over which the pressure may be varied conveniently. However, outside of these inconveniences, a very good parallelism can be drawn between the photolysis of mercury dimethyl and acetone. Both give a very good Arrhenius plot for $k_1/k_2^{\frac{1}{2}}$ from 125°C. to over 250°C., where $k_1$ is the rate constant for the abstraction reaction and $k_2$ is the rate constant for the recombination of methyl radicals. However, for both acetone and mercury dimethyl there seems to be curvature in the Arrhenius plot below 125°C. In both cases, the ratio $k_1/k_2^{\frac{1}{2}}$ is essentially independent of the light intensity over more than a twentyfold variation, and both ratios are only very slightly pressure dependent. There is a small increase of $k_1/k_2^{\frac{1}{2}}$ with a decrease of pressure. This may be due to a partial third body restriction for the recombination of methyl radicals. Further work is being done in this laboratory in the case of acetone to check this point.

[1] *Manuscript received March 19, 1953.*
*Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2999.*
[2] *National Research Council of Canada Postdoctorate Fellow, 1951-1953.*



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## EXPERIMENTAL

### *Apparatus*

The light source was an Hanovia S-500 medium pressure arc. It was turned on about one hour before each run in order for it to reach constant intensity. A nearly parallel beam of light was produced by a system of two quartz lenses and two stops. This beam almost filled the reaction cell.

The quartz reaction cell was 10 cm. long and 5 cm. in diameter with a volume of 179.5 cc. This was the volume used in all calculations. The cell was placed in an aluminum block furnace which was twice the length of the cell. The over-all temperature was manually controlled to better than $\pm$ 1.0°C. during each run. The temperature was measured by means of three copper-constantan thermocouples placed in the middle and at either end of the cell.

At various times a chlorine gas filter and a Corning 7-54 or 986 filter were used. Also relative intensities could be determined by means of a R.C.A. 935 photoelectric vacuum cell in conjunction with a battery of 250 volts and a galvanometer.

The remaining apparatus consisted of storage vessels, a mercury manometer, McLeod gauge, and analytical system. The cell and mercury dimethyl storage vessel were separated from the rest of the apparatus by means of mercury cutoffs. The analytical system consisted of a LeRoy (4) still and a combination Toepler pump and gas burette. Later, another LeRoy still and a small mercury diffusion pump were added to facilitate the separation of the gases.

### *Material*

The mercury dimethyl was obtained from the Delta Chemical Works. However, since it contained appreciable quantities of ether, it was necessary to fractionate it. Before fractionation, the vapor pressure at 0°C. was about 20 mm. Afterwards it was 17.7 mm. at 0°C. and 0.015 mm. at $-$ 78°C. (acetone–dry ice mixture). The value reported in the literature is 17.4 mm. at 0°C. and 0.0145 mm. at $-$ 80°C. (7). Its purity was then checked on the mass spectrometer and it was found to contain 0.11% ether.

## RESULTS

In Tables I, II, and III are given the results of the runs performed to determine the activation energy of the reaction of methyl radicals with mercury dimethyl, the effect of variation of light intensity, and the effect of variation of concentration. Table IV gives the amount of photochemical decomposition of mercury dimethyl calculated for the same amount of absorbed light and corrected at the higher temperatures for any thermal reaction. It is seen to be approximately constant over the temperature range from 26°C. to 239°C., i.e. the quantum yield does not vary appreciably over this range of temperature.

We also found that approximately 38% of the incident light (between 2300-3000 Å) was absorbed by mercury dimethyl at a pressure of 40 mm. (at 125°C.) in a reaction cell 10 cm. long. However, this increased to better than 60% at a pressure of 52 mm. (at 240°C.). A chlorine gas filter and a Corning

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7-54 or 986 filter were used to isolate the region between 2300-3000 Å.

In addition to methane and ethane, small quantities of ethylene, propane, and propylene were reported in some of the runs in which analyses were made with a mass spectrometer. However, correcting for all these gases did not change the $k_1/k_2^{\frac{1}{2}}$ ratio by more than the experimental error in the gas analysis.

TABLE I

THE PHOTOLYSIS OF MERCURY DIMETHYL

| Temp. (°K.) | Pressure of $Hg(CH_3)_2$ (mm.) | Time (sec.) | Products (micromoles) | | $k_1/k_2^{\frac{1}{2}} \times 10^{13}$ |
|---|---|---|---|---|---|
| | | | $CH_4$ | $C_2H_6$ | |
| *Low intensity runs*† | | | | | |
| 373 | 37.7 | 16,200 | 0.20 | 5.12 | 0.42 |
| 398 | 39.9 | 13,500 | 0.40 | 4.96 | 0.93 |
| 398 | 39.2 | 18,000 | 0.56 | 5.37 | 1.1 |
| 413 | 40.8 | 10,800 | 0.55 | 4.21 | 1.5 |
| 422 | 42.3 | 10,800 | 0.79 | 4.49 | 2.1 |
| 423 | 42.2 | 14,400 | 1.00 | 4.73 | 2.3 |
| 439 | 44.5 | 9,000 | 1.38 | 6.06 | 3.5 |
| 448 | 45.0 | 9,060 | 1.43 | 4.26 | 4.3 |
| 462 | 46.3 | 14,400 | 3.99 | 8.94 | 6.6 |
| 463 | 46.4 | 7,200 | 1.73 | 3.42 | 6.6 |
| 473 | 47.6 | 7,200 | 2.50 | 3.97 | 8.9 |
| 481 | 48.8 | 7,200 | 3.59 | 5.95 | 10.3 |
| 493 | 49.7 | 7,200 | 4.18 | 4.29 | 14.2 |
| 513 | 51.8 | 5,400 | 5.07 | 3.49 | 21.9 |
| *High intensity runs*†† | | | | | |
| 443 | 44.0 | 1,800 | 0.89 | 9.92 | 4.0 |
| 449 | 44.7 | 1,800 | 1.00 | 9.78 | 4.6 |
| 472 | 47.8 | 1,200 | 1.31 | 7.24 | 8.3 |
| 473 | 47.5 | 1,800 | 2.01 | 10.71 | 8.7 |
| 498 | 50.5 | 1,200 | 2.36 | 7.42 | 14.8 |
| 504 | 51.0 | 1,800 | 4.31 | 11.30 | 19.5 |
| 525 | 52.7 | 900 | 3.42 | 5.85 | 28.1 |

†*The low intensity runs were performed with a chlorine gas filter and a Corning 7-54 filter.*
††*The high intensity runs were performed without any filters.*

TABLE II

THE EFFECT OF VARIATION OF LIGHT INTENSITY IN THE PHOTOLYSIS OF MERCURY DIMETHYL
All runs performed at 439°K.

| $Hg(CH_3)_2$ pressure (mm.) | Time (sec.) | Products (micromoles) | | Relative* intensity | $k_1/k_2^{\frac{1}{2}} \times 10^{13}$ |
|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_6$ | | |
| 44.0 | 1,800 | 0.87 | 13.03 | 21.3 | 3.4 |
| 45.3 | 900 | 0.44 | 6.33 | 20.8 | 3.4 |
| 47.3 | 3,600 | 0.90 | 5.73 | 4.90 | 3.5 |
| 44.5 | 9,000 | 1.38 | 6.06 | 2.14 | 3.5 |
| 43.9 | 16,200 | 1.67 | 4.86 | 1.00 | 3.5 |

**The relative light intensity was calculated on the amount of products formed in unit time.*

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TABLE III

THE EFFECT OF VARIATION OF CONCENTRATION IN THE PHOTOLYSIS OF MERCURY DIMETHYL
All runs performed at 439°K.

| $Hg(CH_3)_2$ pressure (mm.) | Time (sec.) | Products (micromoles) | | $k_1/k_2^{\frac{1}{2}} \times 10^{13}$ |
|---|---|---|---|---|
| | | $CH_4$ | $C_2H_6$ | |
| 47.3 | 3,600 | 0.90 | 5.73 | 3.5 |
| 44.5 | 9,000 | 1.38 | 6.06 | 3.5 |
| 24.5 | 3,600 | 0.43 | 3.82 | 3.9 |
| 12.9 | 10,800 | 0.44 | 3.59 | 4.6 |
| 6.4 | 12,600 | 0.18 | 2.23 | 4.5 |

TABLE IV

RELATIVE QUANTUM YIELDS

| Pressure of $Hg(CH_3)_2$ (mm.) | Temp. (°C.) | $Hg(CH_3)_2$ decomposed ($\frac{1}{2}$ $CH_4$ + $C_2H_6$) (micromoles/hr.) | Light absorption (%) | $Hg(CH_3)_2$ decomposed at constant absorbed intensity (29.5%) | Relative Q.Y. (± 0.1) |
|---|---|---|---|---|---|
| 29.2 | 26 | 1.44 | 17.8 | 2.39 | 0.92 |
| 36.7 | 99 | 2.60 | 29.5 | 2.60 | 1.00 |
| 41.8 | 141 | 3.28 | 40.2 | 2.41 | 0.93 |
| 47.3 | 198 | 4.95 | 52.5 | 2.78 | 1.07 |
| 51.3 | 239 | 6.77 | 64.5 | 3.10 | 1.20 |

In the subsequent calculations, therefore, the figures used are the ones obtained by the gas analysis since only a few analyses were made with the mass spectrometer.

Finally, it may be noted that in the few runs checked with the photoelectric cell, there was an increase of absorption as more mercury dimethyl was decomposed. This effect occurred only at the high temperatures where an appreciable amount of methane was formed. This increase of absorption must be due to the formation of some product which absorbs even more strongly than the mercury dimethyl in the region 2300-3000 Å. The most probable products are $C_2H_5HgCH_3$ and $(CH_3HgCH_2)_2$.

## DISCUSSION

In the temperature range from 125°C. to 250°C., the main steps in the photolysis of mercury dimethyl may be described by the following equations:

$$Hg(CH_3)_2 + h\nu \rightarrow Hg + 2CH_3 \quad [0]$$

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + CH_2HgCH_3 \quad [1]$$

$$2CH_3 \rightarrow C_2H_6 \quad [2]$$

$$CH_3 + CH_2HgCH_3 \rightarrow C_2H_5HgCH_3 \quad [3]$$

$$2CH_2HgCH_3 \rightarrow (CH_3HgCH_2)_2 \quad [4]$$

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We exclude a reaction as

$$CH_2HgCH_3 \rightarrow CH_2 + Hg + CH_3 \quad [5]$$

since such a reaction would yield chains which would increase the amount of mercury dimethyl decomposed as the temperature is increased, and as seen from Table IV this is not the case.

Moreover, Polanyi (6) has postulated that the $CH_2HgCH_3$ radical is very stable even at temperatures over 500°C. This conclusion is based on the thermal decomposition of mercury dimethyl in a flow system in the presence of various other gases. The rate constant, which was determined by measuring the amount of mercury and also the amount of methane and ethane formed, is found to be the same in the presence or absence of toluene. With the addition of toluene, methane is also formed from the following reaction:

$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2 \quad [6]$$

in addition to reactions [1] and [2]. Since this lowers the steady state concentration of methyl radicals, less methane is formed from reaction [1] in the presence of toluene and consequently less $CH_2HgCH_3$ radicals are formed with toluene than without it. Now if the $CH_2HgCH_3$ radicals decomposed, a higher rate constant would be obtained without toluene than with it. However, this is contrary to what was found, and hence he concluded that the $CH_2HgCH_3$ radical is stable.

We also exclude the reaction

$$CH_3 + CH_3HgCH_3 \rightarrow C_2H_6 + Hg + CH_3 \quad [7]$$

since this also would lead to a chain reaction. Reaction [7] was suggested in previous work to account for the slight increase of ethane with an increase of temperature. However, this effect can easily be accounted for by the increasing amount of light absorption with temperature. The light absorption doubles from 100°C. to 250°C. In agreement with this, Professor Noyes (5) has told us that in some recent work at his laboratory the quantum yield of mercury dimethyl was approximately 1.0 at 25°C. and also at 200°C. These results certainly indicate that reaction [7] cannot be occurring to any extent under our conditions. Reaction [7] has also been excluded in the pyrolysis of mercury dimethyl by Polanyi (6) and also by Ingold and Lossing (3) who have followed the production of radicals in the reaction by means of a mass spectrometer. Gomer and Noyes (2) included a reaction of the type of reaction [7] proceeding through an intermediate complex. The evidence for this reaction was a falling off in the slope of the plot of $R_{C_2H_6}/R_{CH_4}$ versus $R_{CH_4}$ at very high intensities, where $R_{C_2H_6}$ and $R_{CH_4}$ are the rates of formation of ethane and methane respectively. It may be that at such high intensities reaction [7] does occur to some extent, but it is certainly not important under our conditions.

Reactions [3] and [4] are included to remove the $CH_3HgCH_2$ radicals formed in reaction [1]. No attempt was made to isolate these products. The only supporting evidence is the increase of absorption with time.

From the above mechanism, we have

$$R_{CH_4} = k_1 [CH_3] [Hg(CH_3)_2] \quad \text{and}$$
$$R_{C_2H_6} = k_2 [CH_3]^2.$$

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Hence,

$$\frac{k_1}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}} [Hg(CH_3)_2]$$

$$= \frac{P_1 Z_1}{P_2^{\frac{1}{2}} Z_2^{\frac{1}{2}}} e^{-(E_1 - \frac{1}{2}E_2)/RT},$$

where $E_1$ and $E_2$ are the activation energies of reaction [1] and [2]; $Z_1$ and $Z_2$, the number of collisions occurring between methyl radicals with mercury dimethyl and methyl radicals with each other at unit concentration in unit time; and $P_1$ and $P_2$ are the steric factors for the two reactions.

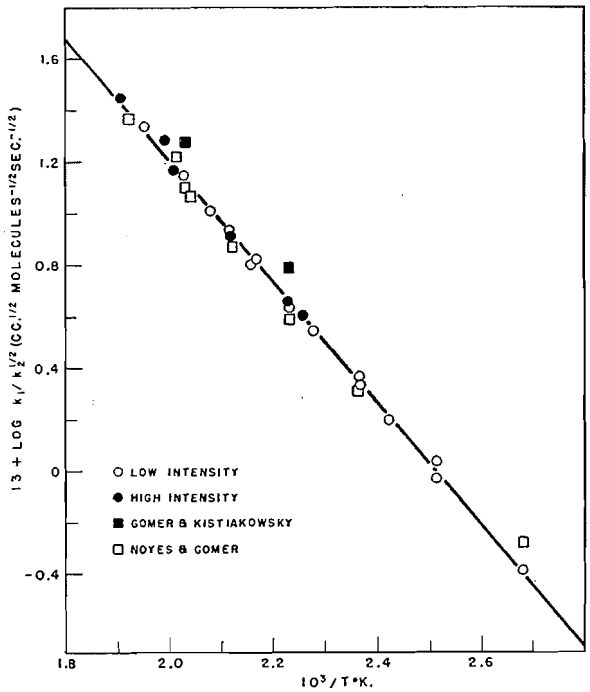



FIG. 1

In Fig. 1 the logarithm of $k_1/k_2^{\frac{1}{2}}$ is plotted against the reciprocal of the absolute temperature. All rate constants are in molecules, cc., and sec. The best line through all points has been found by the method of least squares to be

$$\log (k_1/k_2^{\frac{1}{2}}) = -7.07 - (2360/T).$$

The slope of this line gives a value of 10.8 kcal. per mole for $E_1 - \frac{1}{2}E_2$. Also in Fig. 1 are plotted the values of $k_1/k_2^{\frac{1}{2}}$ determined by Gomer and Noyes (2) and by Gomer and Kistiakowsky (1), but recalculated according to the above method. The results of Gomer and Noyes are in excellent agreement with our own, even though they were performed at 20.0 mm. pressure (at 300°K.),

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while ours were done at 30.0 mm. pressure (at 300°K.). The results of Gomer and Kistiakowsky are also seen to be in fair agreement.

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# THE STABILITY OF SOME COMPLEXES OF TRIVALENT COPPER[1]

By M. W. Lister

ABSTRACT

New methods are given for the preparation of sodium copper (111) tellurate, $Na_9Cu(TeO_6)_2.16H_2O$, and sodium copper (111) periodate, $Na_7Cu(IO_6)_2.20H_2O$, previously reported by Malatesta. Additional analytical evidence is presented that these are really compounds of trivalent copper. The dissociation of the ions in alkaline aqueous solution was examined through the ability of the uncomplexed copper to catalyze the decomposition of sodium hypochlorite. Evidence is presented that the uncomplexed copper ion is $Cu(OH)_4^-$, and this gives both a 1-1 and a 1-2 complex with both tellurate and periodate. The 1-2 complexes appear to be $Cu(HTeO_6)_2^{-7}$ and $Cu(IO_6)_2^{-7}$ respectively; the 1-1 complexes are less stable. The equilibrium constants for the reversible dissociation of these ions into their simpler constituents in aqueous solution at 40°C. are as follows: tellurate, 1-1 complex $K_1 = 1.8 \times 10^{-6}$; 1-2 complex $K_2 = 1.1 \times 10^{-11}$; periodate, 1-1 complex $K_1 = 3.4 \times 10^{-5}$; 1-2 complex $K_2 = 8.0 \times 10^{-11}$. The smaller the constant the more stable the complex ion. In the case of the tellurate complex $K_2$ is proportional to the square of the hydroxide ion concentration and these values are for 0.400 $M$ sodium hydroxide; with periodate $K_2$ is independent of the hydroxide concentration. Experiments at various temperatures give 20 kcal. as the heat of the reaction forming the 1-2 tellurate complex from the simple ions, and 7½ kcal. for the 1-2 periodate complex. The stannate, stibnate, and selenate ions showed no signs of forming analogous compounds.

Reports of trivalent copper compounds have appeared at various times for at least a hundred years (e.g. References 2, 4, 6, and 9), but the instability of the substances obtained often made it impossible to prepare samples of reproducible composition, or to purify an impure sample. Hence there was always some doubt about the valency of the copper, and it was not really proved that the oxidizing power of the substances could not be ascribed to some other chemical grouping, such as peroxide. However Malatesta (7) prepared a number of crystallizable compounds by complexing the copper with telluric or periodic acids, and it was evident that these compounds were much more stable than those previously obtained. Their analyses agreed well with trivalent copper compounds, and they were diamagnetic which makes it certain that the copper is in an odd valency state. To oxidize the copper Malatesta used persulphate or electrolytic oxidation, which admittedly might give rise to peroxides, but the diamagnetism would seem to dispose of this possibility.

The present work describes the preparation of what are substantially the same compounds by oxidation with sodium hypochlorite. This is a further argument against supposing peroxide to be present, because this is rapidly decomposed by hypochlorite. It was also found that this method of preparation allowed information to be obtained about the stability of the complex ions in solution, as well as giving evidence for their formulae. This is based on the fact, reported by Chirnoaga (3) and checked in the present work, that copper catalyzes the decomposition of hypochlorite, and that the rate of decomposition is directly proportional to the amount of copper present. This observation

[1] *Manuscript received January 19, 1953.*
*Contribution from the Department of Chemistry, University of Toronto, Toronto, Ont.*



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suggested the idea that it might be possible to measure the amount of uncomplexed copper present by measuring the rate of catalytic decomposition of hypochlorite. The results obtained were consistent with this supposition; and, accepting this, it then became possible to determine the formulae of the complex ions in solution, and to measure the equilibrium constants for their formation from their constituent ions; by operating at several temperatures the heats of these reactions were obtained. A number of somewhat similar anions were also examined for complexing properties with copper, but no stable complex was found.

## EXPERIMENTAL

### *1. Preparation of Sodium Copper (III) Periodate*

Various methods of preparing this compound were tried; of these the following is probably the most satisfactory.

The hypochlorite solution was made by passing chlorine into sodium hydroxide solution in the usual way: it was about 1.5 *M* in sodium hypochlorite and 0.4 *M* in sodium hydroxide. Twelve grams of sodium hydroxide was added to 160 ml. of this solution, and after this had dissolved a solution of 2.55 gm. of copper (II) chloride dihydrate dissolved in 80 ml. of water was added. This gives an immediate precipitate of the blue $Cu(OH)_2$ which turns black in a few seconds to give what is presumably either $Cu_2O_3$ or $Cu(OH)_3$. This is appreciably soluble in sodium hydroxide solution. To this mixture 8.8 gm. of sodium periodate, $Na_2H_3IO_6$, was added dissolved in 60 ml. of 0.6 *M* sulphuric acid. Most of the copper dissolved and the solution was rapidly filtered. On standing a brown powder separated. This was filtered on sintered glass, washed with cold dilute sodium hydroxide solution, and dried over calcium chloride. This brown product analyzed as $Na_7Cu(IO_6)_2.16H_2O$; as the following results show.

$Na_7Cu(IO_6)_2.16H_2O$ calc.: Na 16.8%, Cu 6.6%, $IO_6$ 46.5%, $H_2O$ 30.0%;
obs.: Na 16.8%, Cu 7.4%, $IO_6$ 46.8%, $H_2O$ 30.3%.

The analysis was carried out as follows. For sodium, a weighed sample was reduced with sulphur dioxide, copper (I) iodide was filtered off, and the filtrate was evaporated with added sulphuric acid and finally ignited with ammonium carbonate, and the resulting sodium sulphate weighed. The copper was determined on another sample by weighing as copper (I) iodide. The periodate was determined by dissolving a weighed sample in dilute sulphuric acid, adding potassium iodide, and titrating the iodine formed with thiosulphate. The water was found by the loss of weight at 105°C.

The valency of the copper was checked by finding the oxidation equivalent weight of the substance (i) by adding a weighed sample to acidified potassium iodide solution; and (ii) by adding a weighed sample to dilute sulphuric acid (when oxygen is evolved and $Cu^{++}$ formed), then adding potassium iodide. In both cases the iodine liberated was titrated with thiosulphate. In the first case the equivalent weight is the molecular weight divided by 18; in the second case by 17. The results were:

(i) Equivalent weight, calc.: 958.6/18 = 53.26;
obs.: 53.42;

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(ii) Equivalent weight, calc.: 958.6/17 = 56.39;
obs.: 56.08.

This was checked by making up a solution of this compound in dilute alkali and determining its oxidizing normality in the two ways given above, with the results:

(i) 0.0828 *N* Ratio 1.056; calc. 18/17 = 1.059;
(ii) 0.0784 *N*.

This compound is thus very similar to the $Na_7Cu(IO_6)_2.12H_2O$ reported by Malatesta (7).

*2. Preparation of Sodium Copper (111) Tellurate*

One gram of copper (11) chloride dihydrate was dissolved in 30 ml. of water and added to 60 ml. of warm (50°C.) sodium hypochlorite solution containing an additional 5 gm. of sodium hydroxide. After stirring, 3.4 gm. of sodium tellurate, $Na_2H_4TeO_6$, was added, dissolved in a minimum amount of 0.4 *M* sulphuric acid. The solution was well stirred and warmed to 75°C., and rapidly filtered from any undissolved copper oxide. On cooling the filtrate, brown crystals separated. These were filtered, washed with dilute sodium hydroxide, and dried. They analyzed as follows:

$Na_9Cu(TeO_6)_2.20H_2O$; calc.: Na 19.2%, Cu 5.9%, Te 23.7%, $H_2O$ 33.4%;
obs.: Na 19.0%, Cu 6.0%, Te 23.0%, $H_2O$ 33.9%.

The sodium was estimated by removing the tellurium from a weighed sample by saturating with sulphur dioxide and filtering, then the copper (after sulphur dioxide was boiled off) by saturating with hydrogen sulphide and filtering, and evaporation of the filtrate with sulphuric acid, as before: the resulting sodium sulphate was weighed. The copper was determined by adding a little potassium iodide to a sample dissolved in dilute sulphuric acid; the iodine formed was removed by titration with thiosulphate; then the copper (1) iodide was filtered and weighed. The tellurium was precipitated by sulphur dioxide and weighed. The water loss appeared to go in two stages: on drying at 95°C. between 15 and 16 $H_2O$ were lost; on heating to 150°C. the loss was as reported above.

The oxidation equivalent weight was found, as before, either by (i) adding the salt to acidified potassium iodide solution, or (ii) adding the salt to dilute sulphuric acid, and later adding potassium iodide. The results were:

(i) Equivalent weight: calc.: 1078/2 = 539;
obs.: 535;
(ii) Equivalent weight: calc.: 1078;
obs.: 1080.

In the first case Cu(111) goes to Cu(1); in the second Cu(11) goes to Cu(1).

Both of these compounds lose oxygen on acidification, giving the ordinary blue copper ion. It was noticed that when dilute sulphuric or nitric acid (2-3 *M*) was added to either of the solid salts, a scarlet color was briefly visible near the surface of the salt. It seems possible that this is the color of the $Cu^{+++}$ ion; this color rapidly disappeared, and the half life of this ion in acid solution at room temperature can only be a few seconds.

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Another preparation of the complex periodate, crystallized at a higher temperature gave analytical results agreeing with the compound $Na_7Cu(IO_6)_2.12H_2O$, reported by Malatesta. This gave 7.0% copper (calc. 7.2%); and equivalent weights (i) on adding to potassium iodide solution: 49.3 (calc. 49.2); and (ii) on adding to acid followed later by potassium iodide: 51.4 (calc. 52.1).

*3. Measurements in Solution*

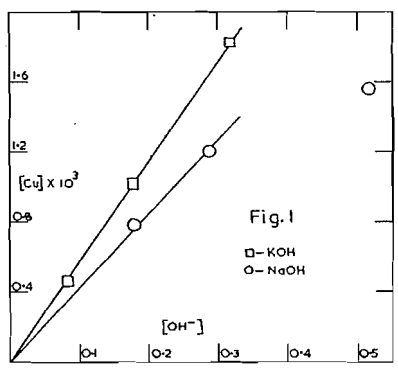
The solubility of copper in alkaline hypochlorite solutions was measured with a view to obtaining information on the ion present before addition of periodate or tellurate. Dilute aqueous copper chloride was added to the sodium hypochlorite solution until a permanent precipitate was obtained, the solution was filtered, and the copper concentration measured. This was done either by (i) measurement of the rate of oxygen evolution; or (ii) by gravimetric analysis: hydrogen peroxide decomposes hypochlorite, and precipitates any copper present (probably as CuO); this was filtered, washed, and dissolved in dilute sulphuric acid; the copper was converted to cuprous iodide and weighed as such on a porous glass filter. The estimation of copper from the rate of oxygen evolution is explained later. The results were:

(i) Solution in 1.022 *M* sodium hypochlorite. This solution also contained sodium chloride and some sodium chlorate, and the ionic strength before the addition of the copper was 3.7. The alkali concentrations were altered by adding concentrated hydrochloric acid from a burette with the tip dipping well into the stirred solution (before addition of copper).

| [NaOH]: | 0.179 | 0.286 | 0.518 *M* |
|---|---|---|---|
| [Cu]: | 0.79 | 1.20 | $1.56 \times 10^{-3} M$ |

(ii) Solution in 0.61 *M* potassium hypochlorite; ionic strength 1.5.

| [KOH]: | 0.082 | 0.177 | 0.319 *M* |
|---|---|---|---|
| [Cu]: | 0.46 | 1.03 | $1.83 \times 10^{-3} M$ |




The results are plotted in Fig. 1. At the lower concentrations there is a rough proportionality between the copper and hydroxide concentrations, this suggests that the copper ion in these solutions is $Cu(OH)_4^-$, formed by

$$Cu(OH)_3 \text{ (solid)} + OH^- \longrightarrow Cu(OH)_4^-.$$

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This would be similar to the zincate ion $Zn(OH)_4^{--}$. However it is surprising that copper, with a lower charge on the ion, is less soluble in hydroxide solutions than zinc. These experiments do not altogether exclude the possibility that copper trihydroxide is present as a colloidal dispersion peptized by hydroxide ions. In support of this we have the somewhat erratic point at higher concentration. It was also observed that if barium chloride was added to the hypochlorite, and any barium carbonate formed was filtered off, then copper chloride added to the solution in small amounts gave no precipitate; but on now adding a little sodium carbonate there was formed a red or pink precipitate which contained virtually all the copper. This again could be a case of coprecipitation of barium cuprate(III)—Krüger (6) describes a red precipitate $BaCu_2O_4$, or perhaps $Ba(Cu(OH)_4)_2$—on barium carbonate, but it is a surprisingly complete precipitation. On the whole it seems fair to conclude that at low concentrations, and we shall be dealing with very low concentrations of uncomplexed copper in the periodate or tellurate solutions, the copper is present as $Cu(OH)_4^-$, but that this is not certain at high concentrations.

*4. Apparatus and Reagents for the Measurement of Equilibrium Constants*

The general method used in these experiments was to add a known amount of copper chloride to a known volume of sodium hypochlorite solution, and then to measure the rate of oxygen evolution at a definite temperature. Known amounts of sodium periodate or tellurate were now added, and the rate again measured after time was allowed for it to come to a steady value.

*Apparatus*

The solution was contained in a 1 liter flask fitted with a mercury sealed stirrer and connected through a capillary to a water jacketed gas burette. The flask had a side arm for addition of reagents or removal of samples for analysis. It was immersed in a thermostat regulated to $\pm$ 0.05°C.

*Reagents*

*Sodium hypochlorite.*—This was prepared by passing chlorine into sodium hydroxide solution, so sodium chloride was also present. The initial composition of this stock solution was 1.69 *M* sodium hypochlorite, 1.93 *M* sodium chloride, 0.022 *M* sodium chlorite, 0.029 *M* sodium chlorate, 0.400 *M* sodium hydroxide, and 0.030 *M* sodium carbonate: the ionic strength was therefore 4.19. During a run, and also slowly on storage, some of the hypochlorite was converted to chloride and chlorate, but this does not change the ionic strength. It is difficult to be certain that such a solution does not itself contain traces of copper which might affect the later results. However its rate of oxygen evolution was only that which could have been produced by $1.0 \times 10^{-6} M$ copper, so this is an upper limit to the amount of copper which could be present as an impurity. Furthermore this rate of evolution persisted in the presence of considerable amounts of periodate, which makes it very probable that this rate is due to the uncatalyzed decomposition of sodium hypochlorite. The observed rates were corrected for this uncatalyzed decomposition, when they were used to calculate the amount of uncomplexed copper present.

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*Copper chloride.*—This was a reagent grade, recrystallized from water. Its solutions were made up by direct weighing, though this was always checked by titrating the copper in the solution iodometrically.

*Sodium periodate.*—This was made by heating potassium iodide with excess alkaline sodium hypochlorite. On cooling, sodium periodate crystallizes out. The crystals were washed and dried, and analyzed as $Na_2H_3IO_6$. Potassium periodate was also used, and was a reagent grade product analyzing as $KIO_4$.

*Tellurium dioxide.*—A reagent grade of tellurium dioxide was used, dissolved in dilute potassium hydroxide solution. The tellurium content was checked by precipitation as tellurium (by sulphur dioxide), and weighing. It will be noticed that the tellurium was added as tellurite, not tellurate, but it is oxidized by the hypochlorite. This reaction was used to prepare sodium tellurate, when making sodium copper (III) tellurate.

*5. Rate of Reaction Catalyzed by Copper*

It was first necessary to establish the kinetics of the decomposition by copper in order to be able later to deduce the concentration of the uncomplexed copper from the observed rates of reaction. Chirnoaga (3) measured the rate of this decomposition and found it to be the first order with respect to copper and hypochlorite. However his solutions differed considerably from the present ones, being more dilute in hypochlorite and much more concentrated in copper; in fact much of his copper must have been present as a suspension of copper hydroxide.

In the following runs known amounts of copper chloride were added to the stock hypochlorite, and the mixture maintained at a constant temperature; at intervals samples were analyzed for hypochlorite and the rate of oxygen evolution was measured. It was necessary to allow a considerable time to elapse between adding copper chloride and measuring the rate of gas evolution, as the concentration of gas in solution changes with its rate of evolution, thus leading to an apparent induction period. The following results show the rate to be the first order with respect to copper. In that case the actual rate of gas evolution will be proportional to the weight of copper regardless of the total volume of solution. Accordingly in column 5 of Table I the rate of oxygen evolution (in ml./min.) divided by the number of gram molecules of copper present is given. All the runs in Table I were at 50°C.

In Fig. 2 the column, rate/Cu, is plotted against the hypochlorite concentration. It is seen that by doing this these runs are superimposed, proving that the reaction is first order with respect to copper. However the dependence on hypochlorite is less simple, since the points lie on a line that does not extrapolate to the origin; in fact we can write:

$$\text{Rate} = [\text{Cu}].\{a + b\,[\text{ClO}^-]\}$$

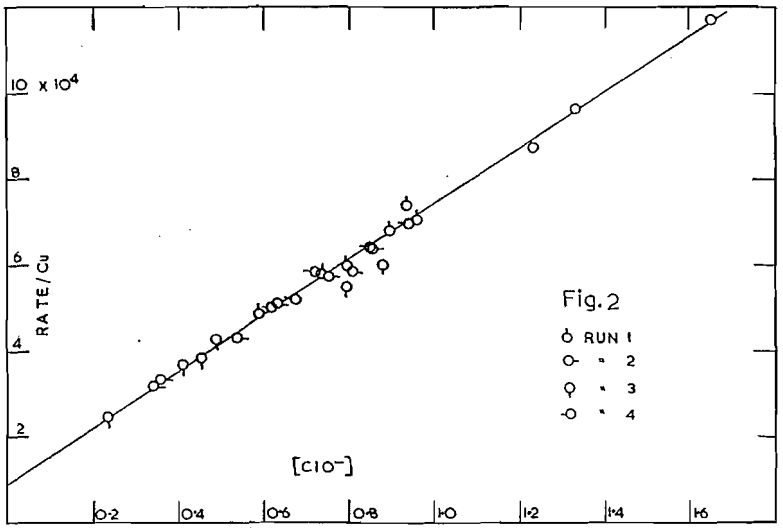
where $a$ and $b$ are constants. This would indicate that two reactions are present: (i) a preponderant reaction similar to that found by Chirnoaga which is first order with respect to copper and hypochlorite; and (ii) a less important reaction independent of the hypochlorite, which is presumably a spontaneous decomposition of the oxidized copper. The values of the constants at 50°C. are

$$\text{Rate} = [\text{Cu}].\{0.9 + 6.5\,[\text{ClO}^-]\} \times 10^4$$

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TABLE I

| Run | Copper added | Gas rate, ml. NTP/min. | Mean [ClO⁻] | Rate/Cu |
|---|---|---|---|---|
| 1 | 0.5 ml. of 0.0300 *M* $CuCl_2$ | 1.059 | 0.956 *M* | $7.06 \times 10^4$ |
| | | 1.110 | 0.935 | 7.40 |
| | | 1.016 | 0.895 | 6.77 |
| | Total vol. 799 ml. | 0.899 | 0.794 | 5.99 |
| | | 0.872 | 0.738 | 5.81 |
| | | 0.727 | 0.589 | 4.85 |
| 2 | 4 ml. of 0.00295 *M* | 0.754 | 0.854 | 6.39 |
| | 6 ml. of 0.00295 *M* | 1.040 | 0.811 | 5.87 |
| | 8 ml. of 0.00295 *M* | 1.362 | 0.754 | 5.77 |
| | 10 ml. of 0.00295 *M* | 1.507 | 0.635 | 5.11 |
| | 12 ml. of 0.00295 *M* | 1.533 | 0.539 | 4.33 |
| | 14 ml. of 0.00295 *M* | 1.390 | 0.370 | 3.37 |
| | 16 ml. of 0.00295 *M* | 1.538 | 0.344 | 3.26 |
| | Total vol. 850 ml. | | | |
| 3 | 2 ml. of 0.0300 *M* | 3.593 | 0.887 | 5.99 |
| | | 3.300 | 0.797 | 5.50 |
| | Total vol. 810 ml. | 2.597 | 0.489 | 4.33 |
| | | 2.305 | 0.459 | 3.84 |
| | | 2.221 | 0.414 | 3.70 |
| | | 1.545 | 0.231 | 2.58 |
| 4 | 2 ml. of 0.00279 *M* | 0.388 | 0.940 | 6.95 |
| | 6 ml. of 0.00279 *M* | 1.068 | 0.855 | 6.38 |
| | 10 ml. of 0.00279 *M* | 1.636 | 0.729 | 5.86 |
| | 14 ml. of 0.00279 *M* | 2.039 | 0.675 | 5.22 |
| | 18 ml. of 0.00279 *M* | 2.526 | 0.625 | 5.03 |
| | Total vol. 800 ml. | | | |
| 5 | 2 ml. of 0.0277 *M* | 6.51 | 1.65 | 11.78 |
| | Total vol. 512 ml. | | | |
| 6 | 1 ml. of 0.0277 *M* | 2.43 | 1.23 | 8.77 |
| | Total vol. 509 ml. | | | |
| 7 | 1 ml. of 0.0277 *M* | 2.68 | 1.33 | 9.67 |
| | Total vol. 538 ml. | | | |




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where the rate is expressed in gm-atoms of oxygen liberated per minute per liter of solution. The uncatalyzed rate only makes a very small contribution to these total rates, being between 0.02 and 0.04 ml./min. There is also a slow conversion of hypochlorite to chlorate which is independent of the oxygen production. Another quantity that was varied in the runs described below was the concentration of sodium hydroxide; accordingly its effect on the catalyzed rate was determined with the result:

| [NaOH] | [ClO⁻] | Gas rate |
|---|---|---|
| 0.170 *M* | 0.935 *M* | 1.405 ml./min. |
| 0.622 | 0.910 | 1.361 |

The amount of copper was constant. The change in rate is very close to that to be expected from the fall in the sodium hypochlorite concentration. Hence sodium hydroxide does not affect the rate. The temperature dependence of the rate was of course important, and similar measurements were made at 30 and 40°C. These gave an over-all energy of activation of 15.5 kcal./gm-mol. for the gas evolution.

*6. Runs with Complexing Anions*

The general procedure was to add known amounts of copper chloride to sodium hypochlorite solution, followed later by known amounts of sodium tellurate or periodate, or the sodium salt of any other anion being investigated. The rates of oxygen evolution under the various conditions were then measured; as always it was necessary to allow some time to elapse after any change for the gas rate to reach a steady value. The results are given in Table II.

TABLE II

| Run | Temp., °C. | Vol. of solution, ml. | [ClO⁻] (mean) | [Cu] (total) | [Anion] (total) | Gas rate, ml. NTP/ min. | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 40° | 581.5 | 0.98*M* | $4.76 \times 10^{-5}M$ | $2.69 \times 10^{-3}M$ | 0.0157 | Tellurate added |
| 2 | 50° | 800 | 0.90 | $1.73 \times 10^{-5}$ | 0 | 0.943 | |
| | | | 0.81 | $1.73 \times 10^{-5}$ | $2.73 \times 10^{-3}$ | 0.048 | Periodate added |
| 3 | 40° | 511.5 | 1.65 | $1.082 \times 10^{-4}$ | 0 | 2.96 | |
| | | | 1.55 | " | $4.56 \times 10^{-5}$ | 2.10 | Periodate |
| | | | 1.47 | " | 13.68 | 1.00 | added |
| | | | 1.41 | " | 22.8 | 0.194 | |
| | | | 1.38 | " | 31.9 | 0.021 | |
| 4 | 40° | 555 | 0.885 | $1.074 \times 10^{-4}$ | 0 | 1.57 | |
| | | | 0.85 | " | $3.65 \times 10^{-5}$ | 1.195 | Periodate |
| | | | 0.825 | " | 7.3 | 0.945 | added |
| | | | 0.80 | " | 10.95 | 0.695 | |
| | | | 0.77 | " | 14.6 | 0.47 | |
| | | | 0.745 | " | 18.25 | 0.25 | |
| | | | 0.725 | " | 21.9 | 0.115 | |
| 5 | 40° | 573 | 1.65 | 0 | 0 | 0.0170 | Effect of NaOH on equilibrium with periodate |

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TABLE II (*concluded*)

| Run | Temp., °C. | Vol. of solution, ml. | $[ClO^-]$ (mean) | [Cu] (total) | [Anion] (total) | Gas rate, ml. NTP/ min. | Remarks |
|---|---|---|---|---|---|---|---|
| 5 | 40° | 573 | 1.55*M* | 0 | $20.4 \times 10^{-5}$ | 0.0160 | NaOH $Na_2CO_3$ |
| | | | 1.52 | $9.67 \times 10^{-5}$ | " | 0.687 | 0.382 0.029*M* |
| | | | 1.48 | " | " | 0.637 | 0.695 0.036 |
| | | | 1.45 | " | " | 0.631 | 0.942 0.045 |
| 6 | 40° | 543.5 | 1.58 | $1.008 \times 10^{-4}$ | 0 | 2.78 | |
| | | | 1.50 | " | $21.4 \times 10^{-5}$ | 0.216 | Periodate added |
| 7 | 40° | 538 | 1.33 | $5.15 \times 10^{-5}$ | 0 | 1.218 | |
| | | | 1.30 | " | $10.52 \times 10^{-5}$ | 0.196 | Periodate added |
| 8 | 30° | 573.5 | 1.355 | $8.41 \times 10^{-5}$ | $16.8 \times 10^{-5}$ | 0.087 | Periodate |
| | 40 | | 1.34 | " | " | 0.235 | added |
| | 50 | | 1.315 | " | " | 0.568 | |
| | 50 | | 1.29 | " | $3.96 \times 10^{-3}$ | 0.053 | |
| 9 | 40° | 587 | 1.30 | $16.34 \times 10^{-5}$ | 0 | 4.28 | 0.400 *M* NaOH |
| | | | 1.25 | " | $13.15 \times 10^{-5}$ | 1.65 | Tellurate added |
| | | | 1.23 | " | 26.3 | 0.187 | |
| | | | 1.20 | " | 32.9 | 0.069 | |
| 10 | 50° | 587 | 1.18 | $16.34 \times 10^{-5}$ | $32.9 \times 10^{-5}$ | 0.208 | Tellurate added 0.400 *M* NaOH |
| 11 | 60° | 587 | 1.15 | $16.34 \times 10^{-5}$ | $32.9 \times 10^{-5}$ | 0.610 | Tellurate added 0.400 *M* NaOH |
| 12 | 40° | 557.5 | 1.25 | $1.72 \times 10^{-4}$ | 0 | 3.81 | 0.400 *M* NaOH |
| | | | 1.18 | " | $0.673 \times 10^{-4}$ | 2.42 | Tellurate added |
| | | | 1.12 | " | 2.02 | 0.605 | |
| | | | 1.10 | " | 4.035 | 0.0255 | |
| 13 | 40° | 576 | 1.28 | $1.663 \times 10^{-4}$ | $33.55 \times 10^{-5}$ | 0.037 | 0.162 *M* NaOH |
| | 50 | | 1.22 | " | " | 0.1165 | 0.162 *M* NaOH |
| | 50 | | 1.18 | " | " | 0.217 | 0.471 *M* NaOH |
| 14 | 50° | 576 | 1.13 | $1.663 \times 10^{-4}$ | $5.80 \times 10^{-3}$ | 0.043 | Tellurate added |
| 15 | 50° | 586 | 1.17 | $1.634 \times 10^{-4}$ | $33.0 \times 10^{-5}$ | 0.1085 | 2.27 *M* NaCl |
| | | | 1.15 | " | " | 1.102 | 2.57 *M* NaCl |
| | | | 1.13 | " | " | 0.104 | 2.87 *M* NaCl |
| 16 | 40° | 564 | 1.25 | $1.70 \times 10^{-4}$ | 0 | 3.84 | Stannate added |
| | | | 1.23 | " | $1.40 \times 10^{-4}$ | 4.59 | |
| | | | 1.21 | " | 4.89 | 4.76 | |
| 17 | 40° | 594 | 1.25 | $1.62 \times 10^{-4}$ | $3.29 \times 10^{-4}$ | 4.75 | Stibnate added |
| | | 619 | 1.18 | 1.55 | 19.7 | 4.60 | |
| 18 | 40° | 620 | 1.15 | $1.55 \times 10^{-4}$ | $3.65 \times 10^{-3}$ | 4.38 | Selenate added |

## DISCUSSION OF RESULTS

The general assumption that we shall make in interpreting these results is that the rate before and after the addition of the complexing agent gives the fraction of the copper that is not complexed and still present as $Cu(OH)_4^-$. The rates are first to be corrected for the uncatalyzed evolution of oxygen,

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and allowance has to be made for the fall in hypochlorite concentration. With this assumption we have enough data for the determination of the equilibrium constant for the decomposition of the complex ion into simple ions. There is some justification of this general assumption from the results in Table II. Firstly, as will be seen in more detail later, there is the internal consistency of the results; and, secondly, there is the fact that a large excess of periodate or tellurate reduces the rate to the uncatalyzed rate, since now virtually all the copper is complexed. The uncatalyzed rates calculated for the conditions in runs 1, 2, 8 (last part), and 14 are

| RUN | OBS. RATE | CALC. RATE |
|---|---|---|
| 1 | 0.0157 | 0.0145 ml./min. |
| 2 | 0.048 | 0.049 |
| 14 | 0.043 | 0.049 |
| 8 | 0.053 | 0.056 |

In runs 1 and 14 excess tellurate was present; in runs 2 and 8 excess periodate.

Another point that must be considered is whether an appreciable fraction of the copper present is divalent. It seems reasonable to suppose that when a trivalent copper atom catalyzes the decomposition of a hypochlorite ion, it is reduced to divalent copper, which is subsequently oxidized back by more hypochlorite. This oxidation can be observed qualitatively by means of the color change when copper chloride is added to sodium hypochlorite: small amounts of copper at room temperature (20°C.) are oxidized very rapidly, the color change appearing complete virtually as soon as the solutions are mixed and certainly within a second or two. At the same temperature 1 ml. of 0.0277 *M* copper chloride added to hypochlorite gave an oxygen evolution of 0.25 ml./min. This corresponds to $2.77 \times 10^{-5}$ gm-atoms of copper liberating $2.2 \times 10^{-5}$ gm-atoms of oxygen every minute, or one atom of oxygen per copper atom every 76 sec. Thus at the most perhaps 2% of the copper could be divalent; this is an upper limit since each reduction of trivalent copper might give more than one oxygen atom. We cannot suppose that more than one copper atom is involved per oxygen atom, or the reaction would not be first order in copper.

Since the ionic strengths of the solutions are quite large, the calculated equilibrium constants will not be the true thermodynamic equilibrium constants, since we have ignored, or rather failed to evaluate, the activity coefficients. The uncomplexed copper concentration, although found from a rate of reaction, is really a concentration and not an activity. If $c_1$ is the total copper concentration before complexing, when the reaction goes at a rate $r_1$; and if $c_2$ is the concentration of uncomplexed copper after periodate is added, etc., when the rate of reaction is $r_2$, then

$$\frac{r_2}{r_1} = \frac{a_2}{a_1} = \frac{c_2 f_2}{c_1 f_1}$$

where $a$ and $f$ are the corresponding activities and activity coefficients. The calculated value of $c_2$ is taken to be

$$c_2(\text{calc.}) = c_1 \cdot \frac{r_2}{r_1} = c_2 \cdot \frac{f_2}{f_1}.$$

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In practice, since the ionic strength remains virtually constant throughout a run, $f_2$ will be very nearly equal to $f_1$, so that $c_2$(calc.) = $c_2$. Hence the equilibrium constants reported below are ratios of concentration, not activity. It is impractical to use this experimental method at low ionic strength, since we need a considerable concentration of hypochlorite to ensure a rapid oxidation of any divalent copper.

The calculation of equilibrium constants was done by the following equations. As we shall see in a moment the results support the view that only 1-1 complexes of formula Cu(anion), or 1-2 complexes of formula Cu(anion)$_2$, are formed. Let $K_1$ be the equilibrium constant for the reaction;

$$\text{Cu(111)} + \text{anion} \longrightarrow \text{1-1 complex}$$

so $K_1 = \dfrac{[\text{Cu}].[\text{anion}]}{[\text{1-1 complex}]}$.

Let $K_2$ similarly be the constant for:

$$\text{Cu(111)} + 2\ \text{anion} \longrightarrow \text{1-2 complex}$$

so $K_2 = \dfrac{[\text{Cu}].[\text{anion}]^2}{[\text{1-2 complex}]}$.

Let $a$ = total concentration of copper;
let $ay$ = total concentration of the complexing anion, and
let $p$ = fraction of the gas rate that remains after the complexing anion is added. Then our assumption means that

$$[\text{Cu}] = ap.$$

There are also equations for the mass balance of the copper:

$$a = [\text{Cu}] + [\text{1-1 complex}] + [\text{1-2 complex}]$$

and of the anion:

$$ay = [\text{anion}] + [\text{1-1 complex}] + 2[\text{1-2 complex}].$$

Eliminating the unknown concentrations of the anion and the complexes, these equations lead to

$$\text{[i]} \qquad K_2(K_1 - ap)\left\{\frac{(1-p)}{p}K_1 - a(y - 1 + p)\right\} = a^2K_1^2(y - 2 + 2p)^2.$$

This equation enables us to evaluate $K_1$ and $K_2$ if we find the gas rate for two values of $y$, which is the ratio of the total anion to total copper present. It leads in two particular cases to simpler equations which are of interest. Firstly, if only the 1-1 complex is formed, $K_2$ is infinite, and equation [i] reduces to

$$\text{[ii]} \qquad K_1 = \frac{ap}{1-p}(y - 1 + p).$$

Secondly, if only the 1-2 complex is formed, $K_1$ is infinite, and equation [i] reduces to

$$\text{[iii]} \qquad K_2 = \frac{a^2p}{1-p}(y - 2 + 2p)^2.$$

These simpler equations are of use in obtaining approximate values of the constants.

Equations [ii] and [iii] also show that, in a plot of $y$ against $p$, if only a stable 1-1 complex is formed, so that $K_1$ is small and $K_2$ large, then the points will

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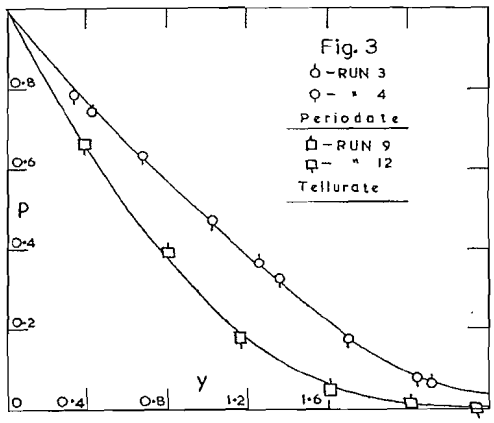
TABLE III

| Run | Temp., °C. | $R_0$ (calc.) | Rate (corr.) | $y$ | $p$ | |
|---|---|---|---|---|---|---|
| 3 | 40° | 2.79 | 2.08 | 0.422 | 0.745 | |
| | | 2.66 | 0.98 | 1.265 | 0.368 | |
| | | 2.56 | 0.176 | 2.108 | 0.0688 | |
| | | 2.53 | 0.003 | 2.951 | 0.0012 | |
| 4 | 40 | 1.51 | 1.185 | 0.340 | 0.787 | |
| | | 1.47 | 0.935 | 0.680 | 0.636 | |
| | | 1.43 | 0.685 | 1.021 | 0.478 | |
| | | 1.39 | 0.46 | 1.361 | 0.330 | |
| | | 1.35 | 0.24 | 1.702 | 0.178 | |
| | | 1.32 | 0.105 | 2.042 | 0.0795 | |
| 6 | 40 | 2.68 | 0.194 | 2.098 | 0.0724 | |
| 7 | 40 | 1.18 | 0.178 | 2.042 | 0.151 | |
| 8 | 30 | 0.91 | 0.081 | 1.999 | 0.089 | |
| | 40 | 2.08 | 0.216 | 1.999 | 0.104 | |
| | 50 | 4.50 | 0.511 | 1.999 | 0.114 | |
| 9 | 40 | 4.13 | 1.63 | 0.805 | 0.395 | |
| | | 4.07 | 0.168 | 1.610 | 0.0413 | |
| | | 3.98 | 0.051 | 2.012 | 0.0128 | |
| 10 | 50 | 8.65 | 0.156 | 2.012 | 0.0180 | |
| 11 | 60 | 17.1 | 0.464 | 2.012 | 0.0272 | |
| 12 | 40 | 3.60 | 2.40 | 0.391 | 0.667 | |
| | | 3.44 | 0.59 | 1.173 | 0.172 | |
| | | | | 2.346 | 0.003 | |
| 13 | 40 | 3.96 | 0.0185 | 2.018 | 0.00465 | (0.162 *M* NaOH) |
| | 50 | 8.36 | 0.0632 | 2.018 | 0.00755 | (0.162 *M* NaOH) |
| | 50 | 8.12 | 0.166 | 2.018 | 0.0205 | (0.471 *M* NaOH) |
| 15 | 50 | 8.06 | 0.0725 | 2.018 | 0.0090 | (2.27 *M* NaCl) |
| | | 7.94 | 0.0665 | 2.018 | 0.0084 | (2.57 *M* NaCl) |
| | | 7.82 | 0.069 | 2.018 | 0.0088 | (2.87 *M* NaCl) |

fall near the line $y + p = 1$. Similarly if only a stable 1-2 complex is formed, so that $K_1$ is large and $K_2$ small, then the points fall near the line $y + 2p = 2$. Table III gives the values of $y$ and $p$ calculated from the results of Table II, and some of these are plotted in Fig. 3.

In Table III the column headed $R_0$(calc.) gives the calculated value of what the rate would be if no periodate or tellurate had been added. In the next column is the observed rate corrected for the uncatalyzed rate, and $p$ is the ratio of these two quantities. From Fig. 3 it is evident that in the copper periodate system the most stable complex is the 1-2 complex, with evidence of a much less stable 1-1 complex. The same is true of the copper tellurate system, except that the 1-1 complex is considerably more stable. To evaluate the constants the values of $p$ at $y = 1$ and $y = 2$ were interpolated on the best line through the experimental points, and these values were substituted

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in equation [i]. The constants so found for 40°C. are:

| | TELLURATE | PERIODATE |
|---|---|---|
| $K_1$ | $1.8 \times 10^{-6}$ | $3.4 \times 10^{-5}$ |
| $K_2$ | $1.1 \times 10^{-11}$ | $8.0 \times 10^{-11}$ |

The fit given by these constants is shown in Fig. 3, where the solid line through the experimental points is obtained by substituting these values of $K_1$ and $K_2$ in equation [i] and plotting the resulting curve. The fit seems adequate, though on account of experimental error the accuracy is not high. The points used are from runs 3 and 4 for periodate, and runs 9 and 12 for tellurate; there are small differences in the copper concentrations between these runs so a mean value was used in the calculations. Both $K_1$ and $K_2$ are sensitive to errors in $p$, as can be seen by putting $y = 2$ in equation [iii] which then becomes approximately $K_2 = 4a^2p^3$. It cannot be claimed that the possible error in the constants is less than perhaps 20%. Runs 6, 7, and 8 agree with the constants so evaluated. By substituting $K_1$ and $K_2$ at the appropriate values of $a$ and $y$ in equation [i] values of $p$ can be calculated to compare with the experimental ones, with the result:

| RUN | $p$(OBS.) | $p$(CALC.) | $a$ |
|---|---|---|---|
| 6 | 0.072 | 0.072 | $10.1 \times 10^{-5}$ |
| 7 | 0.145 | 0.140 | 5.15 |
| 8 | 0.104 | 0.107 | 8.4 |

As these values of $p$ agree over a range of copper concentrations, this shows that (as assumed above) there is one copper atom in the complex. The point may also be made here that it is impossible to obtain a curve anywhere near all the experimental points by assuming only a 1-1 or only a 1-2 complex. A 1-2 complex alone cannot give points below the line $y + 2p = 2$. A 1-1 complex alone gives a curve which, if it fits the experimental points at $y = 1$, is much too high at $y = 2$: for periodate the value of $p$ at $y = 2$ would be 0.265 (obs. 0.09); for tellurate the value would be 0.085 (obs. 0.013).

Run 5 shows that varying the concentration of sodium hydroxide has little effect on the oxygen rate in copper periodate, at least when roughly two periodates are present per copper atom. The equation for the formation of the complex is therefore presumably one which does not involve $OH^-$ ions. Rae (8) found periodic acid to be effectively dibasic with dissociation con-

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stants about $2.3 \times 10^{-2}$ and $10^{-6}$. Hill's results (5) show that the solid phase in contact with a saturated solution containing 0.11 $M$ or more sodium hydroxide is $Na_3H_2IO_6$. Thus presumably the third dissociation constant is greater than $10^{-13}$. As the concentration of sodium hydroxide in the present work was 0.38 $M$ or greater, the free periodate ions would be mostly $H_2IO_6^{-3}$, and this would make the reversible reaction whose constant is $K_2$

$$Cu(OH)_4^- + 2\ H_2IO_6^{-3} \rightleftharpoons Cu(IO_6)_2^{-7} + 4\ H_2O. \qquad [a]$$

This is admittedly a very large charge on an ion, but it is a large ion, and its formula is supported by the solid $Na_7Cu(IO_6)_2.16H_2O$ which separates from more concentrated solutions.

Run 8, in combination to a lesser extent with other runs, gives information about the variation with temperature of the equilibrium constant for the copper periodate system from results in the neighborhood of $y = 2$, when the 1-2 complex is the chief one formed. These results were therefore treated as follows. $K_2$ was calculated by the approximate formula, equation [iii], and from its variation a heat of reaction for the reaction [$a$] given above was deduced. The results of run 8 give:

Temperature: 30° 40° 50°C.

$K_2$(approx.): 2.2 3.4 $4.7 \times 10^{-11}$.

This makes the reaction giving the complex ion exothermic by $7\frac{1}{2}$ kcal. (perhaps $\pm$ 1 kcal.). These approximate values of $K_2$ differ by a factor of about 2 from the more accurate ones owing to the presence of the 1-1 complex; but they probably give a fair estimate of the temperature variation of $K_2$, and hence of the heat of reaction.

Similarly for the copper tellurate complex the effect of sodium hydroxide is found from runs 9, 10, and 13. This effect can be seen in Table IV, where values of the approximate $K_2$ (from equation [iii]) are given.

TABLE IV

| Run | Temp., °C. | [NaOH] | $K_2$ (approx.) | $K_2$/[NaOH] | $K_2$/[NaOH]$^2$ |
|---|---|---|---|---|---|
| 13 | 40° | 0.162 $M$ | $0.91 \times 10^{-13}$ | $5.6 \times 10^{-13}$ | $35 \times 10^{-13}$ |
| 9 | 40° | 0.400 | 4.9 | 12.2 | 31 |
| 13 | 50° | 0.162 | 2.3 | 14 | 87 |
| 10 | 50° | 0.400 | 11.3 | 28 | 71 |
| 13 | 50° | 0.471 | 20.1 | 43 | 91 |

It is evident that $K_2$ is roughly proportional to [NaOH]$^2$. Run 15 was made to check that sodium chloride did not cause a comparable effect, either through some unknown reaction of the chloride ion or through changes in ionic strength; as can be seen from Table II sodium chloride had a negligible effect. The exact reaction with tellurate is less certain than with periodate. Blanc (1) found telluric acid to be dibasic, with dissociation constants $7 \times 10^{-7}$ and $4 \times 10^{-11}$. However salts up to $M_4H_2TeO_6$ are known (the compound $Ag_6TeO_6$

may well be covalent). If we have $H_2TeO_6^{-4}$ ions in alkaline solution (pH above 13) the reversible reaction would be:

$$Cu(OH)_4^- + 2\ H_2TeO_6^{-4} \rightleftharpoons Cu(HTeO_6)_2^{-7} + 2\ OH^- + 2\ H_2O.$$

$H_4TeO_6^{-2}$ ions would require the complex to be $Cu(H_3TeO_6)_2^{-3}$. Runs 9, 10, and 11 give results at different temperatures, and treating them as for the copper periodate complex, the results give:

| Temperature: | 40° | 50° | 60°C. |
|---|---|---|---|
| $K_2$(approx.): | 4.9 | 11.3 | $33 \times 10^{-13}$. |

This makes the heat of reaction close to 20 kcal.

Finally in runs 16, 17, and 18 the chemically somewhat similar ions, stannate, stibnate, and selenate, were examined. No sign of a reduction in the rate of oxygen evolution was observed; presumably therefore no analogous complex ions are formed. In fact with stannate there was some enhancement of the rate, the reason for this being at present unknown. It should be added, to complete the picture with periodate and tellurate, that it was found that these ions, when no copper was present, had no effect on the rate.

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# COMPARISON OF BARLEY GUMS ISOLATED BY VARIOUS PROCEDURES[1]

By W. O. S. Meredith, T. A. Watts, and J. A. Anderson

ABSTRACT

A barley gum that is believed to be the undegraded, water-soluble, nonstarch polysaccharide of the grain has been isolated. Aqueous solutions of this gum are extremely viscous and are stable. Enzymes that degrade gum during simple aqueous extraction were inactivated first by refluxing barley grist in boiling 85% alcohol followed by extraction of the dried grist with a 1% solution of papain. Gums of lower degree of polymerization, as judged by viscosity measurements, were obtained by aqueous extraction and acid treatments. Two enzyme systems that degrade gums are thought to be present in barley. One (which is inactivated by alcohol) degrades the initially soluble gum and brings an initially insoluble form into solution. The second system (which is inactivated by papain) accompanies and degrades the initially soluble gum during aqueous extraction or in aqueous solutions of the preparation. The purest gum contains only 0.1% nitrogen, and this may be part of the molecular complex. Mild, cold, alkali treatment of this gum reduces molecular size considerably as measured by viscosity of solutions. "X"-enzyme isolated from a bacterial source cleaves the gum into two oligosaccharides of glucose and a component containing D-glucose, L-arabinose, D-xylose, and D-galactose. No free sugars are produced.

Changes in endosperm structure during malting of barley are assumed to be brought about by dissolution of the hemicellulose material of cell walls by cytases, and cell constituents are thus exposed to attack by amylolytic and proteolytic enzymes. Little is known about either the cereal hemicelluloses or the cytases, but the cell wall materials are now considered to be complex polysaccharides that resemble the plant gums in composition and properties (12, 14). Isolation of these in native form clears the way for the study of their properties and composition and for studies of the enzymes that degrade them. An additional key to understanding the malting process may thus be obtained.

Barley and malt gums—water-soluble, nonstarch polysaccharides containing D-glucose, L-arabinose, and D-xylose—and enzymes that degrade them are being studied intensively in several laboratories (2, 3, 4, 10, 14, 16, 17), and there is general agreement that these gums and their degradation products contribute markedly to wort and beer viscosity and perhaps to other beer properties (9, 13). Degradation of the gums by enzymes, presumably cytases or hemicellulases, is accompanied by decrease in solution viscosity (14, 16, 17); indeed change in viscosity of solution is the best measure of enzymatic activity (2, 17). There are some differences in composition and properties of gums recovered in the same way from barley and malt (10, 15, 16), and these differences may well reflect the changes that take place in the kernel when barley "modifies" to become malt. The barley gum is changed during malting, but it is not clear yet whether it disappears and is replaced by other nonstarch polysaccharides that were insoluble in the barley or whether much of the barley

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gum is still recoverable as malt gum (10, 14, 15, 16). This problem can only be resolved by preparation of pure isolates from raw barley, growing barley, and from malt, that can be directly compared for composition and properties. Such isolates would also be ideal substrates for detection and measurement of enzymatic activity. Preparation of such isolates is fraught with many difficulties, chiefly arising from enzymatic degradation of material during extraction. Gums produced in earlier studies in this laboratory (10) were unstable in solution, presumably because of contamination with enzymes. A method has now been devised, and is here described, for isolation of barley gum that appears to be degraded to a minimum extent. This isolation method will later be applied to germinating barley and to malt.

Preece, Ashworth, and Hunter (15) refluxed barley grist in boiling alcohol in order to inactivate enzymes present in barley, and recovered and dried the grist before extracting the water-soluble gums. A similar procedure was included in the studies reported in this paper, but additional treatment with a proteolytic enzyme was required before a barley gum that was stable in aqueous solution was obtained. The final product produced extremely viscous, stable, aqueous solutions. It contains the same sugars found previously—D-glucose, L-arabinose, and D-xylose, and a trace of D-galactose—and may well be the naturally occurring material. Nitrogen content of gum was finally reduced to less than 0.1%. Various acid, precipitation, and enzymatic treatments were used to reduce the nitrogen content of gum; the results thus provide information on the role of nitrogen in the gum and its influence on some properties.

## MATERIALS AND METHODS

### *Barley*

Further aliquots of the barley that was used in previous studies (10), namely Montcalm barley grown at the University of Manitoba in 1949, were used. Barley grist was prepared by grinding 500-gm. lots in a Wiley mill with a 1 mm. sieve.

### *Alcohol Treatment of Barley Grist*

Grist was boiled under reflux for 30 min. with five parts of 85% ethyl alcohol (specific gravity 0.85). The cooled mixture was centrifuged and the extracted grist was air-dried. Specific gravity of the alcohol must be adjusted carefully as variations in strength of alcohol produce variations in gum properties. This treatment is similar to that used by Preece *et al.* (15), except that a single rather than a double alcohol treatment is used.

### *Preparation of Gum*

The basic procedure was extraction of barley grist, raw or alcohol treated, with eight parts of water at room temperature for two hours with continuous stirring (10). The spent grains were removed by centrifuging and the gum was precipitated by adding the liquor to three volumes of ethyl alcohol. The product was recovered by centrifuging and solvent exchange using ethyl alcohol, acetone, and ether (10).

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Additional treatments of mash or liquor were also studied. These were the addition of trichloroacetic acid, hydrochloric acid, or papain, to the liquor or to the mash. Addition of such agents to the liquor is termed "precipitation method" in this report, and addition to the mash is called "extraction method". Details of the various procedures are given below.

*Precipitation Method*

The three precipitants were allowed to remain with the liquor for 15 min. before proceeding to the next stage of the procedure. Trichloroacetic acid was added to the liquor to produce a 6% concentration; any precipitate was removed before the liquor was added to alcohol. Sufficient hydrochloric acid was added to the liquor to bring the pH to that produced by 6% trichloroacetic acid; this value was pH 1.0. Powdered papain was ground into solution with distilled water and undissolved material was removed by centrifuging. Sufficient solution was added to the liquor to bring the concentration of papain to 1%. The papain was precipitated by making the solution to 6% concentration of trichloroacetic acid, and the precipitate was removed by centrifuging.

*Extraction Method*

Barley grist was extracted by 6% trichloroacetic acid, hydrochloric acid of pH 1.0, or 1% papain solution for two hours at room temperature as in the regular procedure. Papain was removed by the trichloroacetic acid treatment described above for the precipitation method.

*Gum Characteristics*

*Viscosity and Concentration*

One per cent solutions were prepared by mixing gum and distilled water and stirring the mixture till the gum was dispersed. Dispersion was assisted by heating the solution to about 90°C. for 10 min. Insoluble material was removed by centrifuging. Viscosity measurements were made in an Ostwald viscosimeter at 30°C. within about an hour after preparation of solution and again after 24 hr. Concentration of gum was determined by drying an aliquot of solution at 105°C. overnight.

*Nitrogen Determination*

A modified micromethod similar to that used by Levi and Anderson (7), but using sodium sulphate and mercuric sulphate instead of selenium, was employed. The experimental error was less than 4% of the amount of nitrogen determined.

*Sugar Components*

Small samples of gum (about 30 mgm.) were hydrolyzed with 1 ml. of normal sulphuric acid in sealed tubes for 16 hr. The hydrolyzate was neutralized by passage through Duolite A-7 resin and the percolate dried by distillation under reduced pressure.

Chromatographic examination of the mixed sugars in the residues was made using the same solvents and procedures described previously (10). The aniline

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phosphate spray of Bryson and Mitchell (5) was used for locating the sugar spots.

*Amino Acid Components*

Gums were hydrolyzed in the same way as for sugar identification, but with normal hydrochloric acid. Salts were removed by repeated distillation under reduced pressure.

Resolution of the amino acids in the residues was obtained by means of the solvents butanol/acetic acid/water in ratios 4:1:5 (8, 11) and butanol/benzene/pyridine/water in ratios 4:2:2:5 (8). The paper was Whatman No. 1 and the colors were developed by spraying with 0.1% ninhydrin in butanol and drying at 90°C. for 10 min. Proline was identified by isatin in acid butanol (1).

## RESULTS AND DISCUSSION

The investigation developed into a factorial study of raw and alcohol-treated barley treated with each of two acids, trichloroacetic acid and hydrochloric acid, and one enzyme, papain. These acids and papain treatments were applied to the aqueous extracts of the barley and also as extracting solutions. The resulting data may be presented in many ways, but for convenience they are given in Table I in a standard form for a factorial experiment. This permits

TABLE I

DATA FOR BARLEY GUMS OBTAINED BY DIFFERENT PROCEDURES

| Property | Precipitation method | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Raw barley extract | | | | Alcohol-treated barley extract | | | |
| | (1) Water | (2) T.C.A.* | (3) HCl | (4) Papain | (5) Water | (6) T.C.A.* | (7) HCl | (8) Papain |
| Yield, % | 3.4 | 2.1 | 2.7 | 1.8 | 1.1 | 1.1 | 1.1 | 0.9 |
| Nitrogen, % | 3.00 | 0.50 | 2.14 | 0.12 | 0.46 | 0.50 | 0.30 | 0.07 |
| Viscosity of aqueous solution, cp. | 2.34 | 3.55 | 2.77 | 4.07 | 48.2 | 64.1 | 33.3 | 75.8 |
| Viscosity reduction after 24 hr., % | 50 | 1.7 | 1.1 | 1.0 | 62 | 61 | 3.0 | 1.0 |
| | Extraction method | | | | | | | |
| | Raw barley | | | | Alcohol-treated barley | | | |
| | (1) Water | (2) T.C.A.* | (3) HCl | (4) Papain | (5) Water | (6) T.C.A.* | (7) HCl | (8) Papain |
| Yield, % | 3.4 | 2.3 | 2.8 | 1.7 | 1.1 | 1.5 | 1.8 | 1.3 |
| Nitrogen, % | 3.00 | 0.73 | 1.97 | 0.12 | 0.46 | 0.50 | 0.82 | 0.08 |
| Viscosity of aqueous solution, cp. | 2.34 | 12.8 | 11.8 | 3.66 | 48.2 | 32.1 | 44.8 | 752.0 |
| Viscosity reduction after 24 hr., % | 50 | 21 | 10 | 1.0 | 62 | 18 | 13 | 2.9 |

*Trichloroacetic acid.

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ready comparison of all sets of data. Each of the four sections contains the comparable data for water, trichloroacetic acid, hydrochloric acid, and papain procedures. These are related in that hydrochloric acid was used as a means of separating the effect of acidity of trichloroacetic acid from its precipitating effect, and trichloroacetic acid was used to remove papain from its solution before gum was precipitated.

The comparison between simple aqueous extraction of raw and alcohol-treated barley is discussed in the following subsection, and this is followed by discussion of acid treatment of the aqueous extracts. The methods of extraction are compared with each other and with the "precipitation" procedures in the third subsection. The use of papain as a precipitant and as an extracting agent is discussed in the fourth subsection and compared with the other treatments in the fifth subsection. The next subsection deals with certain properties of the gum obtained by papain extraction of alcohol-treated barley, or "papain" gum. This is followed by a general discussion of the results in relation to other studies.

*Effect of Alcohol Treatment of Barley*

The simple effect of refluxing the barley grist in boiling 85% alcohol prior to extraction of gum is demonstrated by comparison of columns 1 and 5 in the upper half of Table I. The gum from alcohol-treated barley is lower in yield and nitrogen content than that from raw barley. These changes are accompanied by a marked increase in solution viscosity, but stability of gum solution (measured by viscosity reduction after 24 hr.) is not improved.

The characteristics of the gum from raw barley are practically identical with those reported previously (10), and the same sugars, D-glucose, L-arabinose, and D-xylose, were found in the gum. Although the properties of the gum from alcohol-treated barley were different from those of the gum from raw barley, there was no change in sugar composition as judged by appearance of chromatograms of acid-hydrolyzed gums.

The differences between the two gums in yield and solution viscosity are in accord with the suggestion of Preece and Ashworth (14) that barley contains two types of nonstarch polysaccharides of similar composition that are attacked by an enzyme system present in barley. One type is the true water-soluble gum, and this is reduced in molecular complexity by the enzyme system during extraction. The other type is initially less soluble, but its solubility is increased by action of the enzyme system. Our results suggest that this enzyme system was inactivated by the boiling alcohol extraction, so that the product from treated barley is likely to be the true initially soluble polysaccharide.

The instability of solutions of the gum from alcohol-treated barley was somewhat surprising in view of the marked increase in solution viscosity. The latter condition is an indication that the gum was in a more highly polymerized state than that from the raw barley. Refluxing the gum in boiling alcohol failed to improve stability, but boiling of aqueous solutions of gum improved stability of the recovered product (2). Other methods were therefore attempted.

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A suggestion had been made previously that nitrogen complexes may play some role in determining the viscosity and stability of gum solution (9, 10). The data in Table I support this view, as the gum from alcohol-treated barley is considerably lower than the raw-barley gum in nitrogen content, and certain amino acids—leucine, isoleucine, valine, and proline—present in the latter, were not detected in the former. Alcohol treatment of barley grist therefore has lowered nitrogen content of gum, and removed certain types of nitrogen complexes, but an "instability factor", probably an enzyme system, survives this treatment.

*Effect of Acid Treatments of Barley Extracts*

Columns 2 and 3 of the upper half of Table I contain data on the effect of acid treatment of the aqueous extracts of raw barley on the gum properties. Columns 6 and 7 give information on comparable gums obtained from alcohol-treated barley.

Trichloroacetic acid treatment reduced yield and nitrogen content of gum from raw barley and increased solution viscosity and stability. Hydrochloric acid had much the same effect but yield and nitrogen content reductions were not as great.

Yield and nitrogen content of gums produced from alcohol-treated barley by the acid treatments were not affected. The trichloroacetic acid treatment increased solution viscosity but there was no improvement in stability. The hydrochloric acid treatment decreased solution viscosity but improved stability. The net result is that the acid treatments of extraction liquor from alcohol-treated barley produced no improvement in gum properties.

All gums contained D-glucose, L-arabinose, and D-xylose, with D-glucose predominating as judged by area and density of the spots on chromatograms. The amino acid compositions of all gums from raw barley were similar. The composition of gums obtained by acid treatments of alcohol-treated barley differed from that obtained without acid treatment and resembled those from water extracts of raw barley in that leucine, isoleucine, and valine were detected.

The effect of acid treatment of extracts provides further evidence of the mixed character of gum extracted from raw barley. Yields of gum from acid-treated extracts of raw barley are invariably higher than those obtained from similar treatment of alcohol-treated barley, which suggests solution of other material during extraction. But both types of gum are degraded as shown by low solution viscosity. The instability of raw barley gums may be attributed to further degradation of the material that becomes soluble during extraction. This degradation appears to be inhibited by both trichloroacetic acid and hydrochloric acid. Trichloroacetic acid does not appear to inhibit the degradation of the initially soluble gum by factors carried with it.

*Effect of Acid Extraction of Barleys*

The lower half of Table I contains data for the properties of gums obtained by extraction of barley with acid solutions. The two acids had similar results when applied to raw barley. The increases in viscosity of gum solutions were

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relatively great, and although the solutions were more stable than those of the water-extracted gum they were not completely stable. Extraction of alcohol-treated barley with acid solutions increased yield, but solution viscosities were reduced and this may be attributed to impurities in the gum. Stability of solutions was improved, but the net result was no improvement in gum quality. Amino acid and carbohydrate compositions of all gums were similar to those obtained by treatment of the aqueous extracts of raw barley with acid.

Acid extraction of raw barley as compared with acidification of extracts produced gum solutions of higher viscosities. Some control of gum degradation is therefore achieved by acidification of the mash, but the effect is not as great as that obtained by alcohol treatment of the barley. The actions of trichloroacetic acid and alcohol treatments appear to be somewhat similar, but they are not identical and there is an indication that the effects are additive. This suggests that at least two enzyme systems are involved in the degradation of gum during preparation, and that the different treatments inhibit different enzymes.

No acid treatment produced satisfactory gum, but the results indicated that trichloroacetic acid could be safely used as a protein precipitant without seriously altering gum properties. This was important as the next part of the investigation required that papain be removed from solution by some precipitant.

*The Effect of Papain as a Precipitant and an Extractant*

The failure of acid treatment to improve the quality of gum obtained from alcohol-treated barley suggested that nitrogenous material, possibly associated with contaminants of gum or with instability factors, may be held in fairly close combination with the polysaccharide. Such combinations might be physical or chemical, but they appear to protect the nitrogenous material from denaturation by acid. The possibility of protein elimination by proteolytic enzymes was therefore investigated.

Columns 4 and 8 of the upper section of Table I contain data on gums prepared after addition of papain to water extracts of barley and of alcohol-treated barley. Corresponding data for gums after extraction of both original materials with papain solution are given in the lower section of the table.

The outstanding properties of the gums obtained after papain treatment are low nitrogen contents, and high viscosity and stability of solutions. The instability factor has been eliminated from all four types of gum, but treatments prior to addition of the papain are still reflected in the differences in viscosity of solutions. Although treatment with papain of extracts from raw barley eliminated protein material, the product, as would be expected, produced solutions of low viscosity. Papain treatment of extracts from alcohol-treated barley reduced yield slightly, and the resultant gum was highest of the series in viscosity of solution. This increase in viscosity may be attributed primarily to the stabilization of the solution.

Extraction of barley with papain solution was even more efficient in pro-

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duction from alcohol-treated barley of a stable gum with high viscosity of solution; this procedure also stabilized the gum from raw barley. The differences between the gums from raw and alcohol-treated barley were even more striking than previously. Papain treatment produced similar gums from raw barley when used as a precipitant or as an extractant. The results for alcohol-treated barley show the additive effect of alcohol and papain treatments, as the extraction procedure produced gum with highest viscosity of solution (752 cp.) and presumably with the highest degree of polymerization. This "papain" gum appears to be the undegraded, initially water-soluble, nonstarch polysaccharide of barley. Other gums are presumed to be degraded forms of this polysaccharide and some preparations may contain degraded forms of the initially insoluble polysaccharide.

All gums prepared by papain treatment were similar in composition. The principal sugar was D-glucose, but L-arabinose and D-xylose were present, and for the first time in this study D-galactose was identified as a constituent of the gums. Nitrogen content of all gums was low, and only aspartic acid, lysine, serine, glycine, and alanine were identified as amino acid components.

*Comparison of Papain with Other Treatments*

Although the most striking differences between papain treatment and acid treatments are the stability of all gums obtained by the former treatment and the high viscosity of solution of gum from alcohol-treated barley, there are other interesting differences. Papain reduced nitrogen content of gum to very low levels, and the number of amino acids detected was reduced. Only lysine and serine, and possibly alanine, aspartic acid, and glycine, were common to all gums. Leucine, isoleucine, and valine were present in all gums from raw barley, and in gum obtained by acid treatment of alcohol-treated barley. The removal of protein, and of specific amino acids, by papain indicates that much of the nitrogenous material in the other gums was carried with them as a contaminant. Part may be carried merely because of similar solubility, and part may be bound to the gum in some manner; some of this bound material might be enzymes.

The occurrence of D-galactose in all the gums obtained by papain treatment is also of interest, as this sugar was not detected in hydrolyzates of the other gums in this study. This sugar had been detected in gums prepared previously (10), and its presence might be related to degree of polymerization of gum.

*Properties of Gum Obtained by Papain Extraction of Alcohol-treated Barley*

As the gum obtained by papain extraction of barley grist that had been refluxed in boiling 85% alcohol is highly viscous in solution and stable, it is believed to most nearly represent the undegraded, initially soluble, nonstarch polysaccharide present in the barley. This seems to be the most desirable material for study of composition and structure, and for use as a substrate for study of enzymes; additional tests were therefore made on this gum to determine its suitability for our purposes. These tests are discussed briefly in the following paragraphs.

*Susceptibility to Enzyme Attack*

The susceptibility of the "papain" gum to enzymatic degradation was

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tested in two ways, the first of which was a check on the presence of active enzymes in the gums obtained when alcohol or papain were not used in the isolation processes.

Aliquots of solutions of other gums were added to portions of a solution of "papain" gum. Addition of 1 ml. of a 1% solution of raw barley gum to 7 ml. of the substrate caused a reduction in viscosity from 69 cp. to 59 cp. in 30 min. Similar results were obtained by addition of a solution of gum obtained directly from alcohol-treated barley; viscosity dropped from 140 cp. to 123 cp. in two hours and to 4 cp. in 24 hr. The presence of enzymes in the crude gums is thus confirmed. The "X"-enzyme described by Bass, Meredith, and Anderson (2) was also tested on the "papain" gum. The concentration of the "X"-enzyme was not known, but a 0.01 ml. aliquot added to 7 ml. of "papain" gum solution reduced viscosity from 375 cp. to 4.5 cp. in three hours. The "papain" gum is therefore a suitable substrate for studies of "X"-enzyme.

*Components of Gum*

The main component of the gum is D-glucose, but there are appreciable amounts of L-arabinose and D-xylose, and traces of D-galactose; no quantitative measurements of these have been made as yet. In order to study the products of enzymatic hydrolysis, the "papain" gum solution (mentioned above) that was reduced to a viscosity of 4 cp. by "X"-enzyme was dried under reduced pressure and chromatographed. No free sugars were detected, but three spots of low $R_g$ were observed. Larger amounts were then chromatographed, and the three slow moving products were stripped from the paper and hydrolyzed by acid. The slowest moving material produced mainly L-arabinose and D-xylose with some D-glucose and D-galactose. The other two materials produced only D-glucose. These three fractions could not be obtained unless the gum had been degraded by the enzyme system. This suggests the possibility that the gum is composed of several polysaccharides that are either attacked at different rates by the enzyme system, or are released from combination.

The amino acid composition of all gums prepared by use of papain is strikingly similar to that of gum obtained from alcohol-treated barley by simple aqueous extraction. The small amount of nitrogenous material that remains in or with the gums is reasonably constant. This suggests that some protein material that is very difficult to remove from the gums may be part of the molecular complex, or an enzyme-substrate complex, the enzyme moiety of which is inactivated by papain.

*Effect of Alkali*

Attempts to eliminate nitrogen from the "papain" gum by redispersion in water and addition of trichloroacetic acid failed to remove any nitrogen. The product that was recovered by addition of alcohol was identical with the original in properties. As alkali had been used in previous studies to eliminate nitrogen, it seemed worth while to use alkali treatment on the gum produced by papain treatment.

A number of gums from alcohol-treated barley were tested and all dissolved

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readily in normal sodium hydroxide to give 1.0% solutions. Viscosity determinations were made on these solutions, and the results were considerably lower than corresponding values for aqueous solutions. When these gums were recovered from alkaline solution by alcoholic precipitation, etc., and dissolved in water, the viscosities of solutions were around 4 cp. This indicates that they are extremely labile in alkaline solution and suggests that considerable structural changes are brought about in the gum by alkali. Nitrogen content of these gums was not altered by alkali treatment, and no fractions were obtained when solutions were chromatographed in the same way as for enzymatically degraded gum.

As alkali solutions are standard solvents in preparing polysaccharides for studies on structure by means of methylation, and for freeing polysaccharides from protein without change in polysaccharide structure, the results of mild alkali treatment on these barley gums are somewhat curious. Alkali does seem to cause considerable change in molecular complexity of the gums as judged by viscosity of solutions.

Sensitivity of a carbohydrate towards alkali is not common, but our results are not unique, as Wolfrom, Sutherland, and Schlamowitz (18) have recently described a galactogen from beef lung that is degraded by boiling in 30% potassium hydroxide. The sensitivity of barley gum to cold normal alkali does indicate need for cautious interpretation of structural analysis.

## GENERAL DISCUSSION

The main object of the investigation was to obtain a barley gum that is highly viscous and stable in solution, and would thus represent as closely as possible the naturally occurring polysaccharide, which is presumably cell wall material. This material and also material closely related to it, but differing in initial water solubility, is degraded during malting and mashing, and the degradation products are important factors influencing the viscosity and perhaps other properties of wort and beer.

A barley gum corresponding closely, it is believed, to the naturally occurring polysaccharide was isolated. It was obtained by inactivating enzymes in the barley by treatment of barley grist with boiling alcohol, extraction of the grain with aqueous papain solution, removal of papain with trichloroacetic acid, and precipitation of gum by alcohol. This product provides a useful reference compound for detailed study of the changes in cell wall material that are brought about by malting and mashing. The gum also appears to merit studies of its structure and to be useful as a substrate for studies of the cytase-like enzyme systems of barley and malt.

Experiences with the various instability factors encountered during the investigation provides information of value in studying the changes in gum characteristics during malting and in elucidating gum structure.

Gum extracted directly with water from raw barley appears to contain material derived from two types of gum—initially soluble gum and another that is initially insoluble but is made soluble during extraction. This is in accord with the concept of Preece and Ashworth (14).

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Evidently there are two main enzyme systems that degrade the nonstarch polysaccharides. One of the systems is inactivated by alcohol treatment and the other by papain. Both enzyme systems must be inactivated in order to obtain initially soluble gum in uncontaminated and undegraded form. Papain extraction produced more gum from raw barley than from alcohol-treated barley, so that the former product may be assumed to contain a mixture similar to that in preparations obtained by aqueous extraction of raw barley. All the material is degraded to some extent, but the product is stable in solution. One may then postulate that the enzyme system inactivated by alcohol can reduce both types of gum—soluble and initially insoluble—to a fairly low degree of polymerization even in the presence of papain. When this system is inactivated by alcohol treatment the bringing into solution of the initially insoluble material is prevented and the initially soluble material is degraded at a slow rate, or in a different way, by the other enzyme system that is finally inhibited by papain. This papain-sensitive system may be more specific in its action than the other system. These two enzyme systems are probably extremely important in the malting process and will be studied in later investigations.

All gums contain mainly D-glucose, but L-arabinose and D-xylose are also present. But there are two distinctions between the "papain" gum and the other gums worth mentioning. The first is the presence of D-galactose in the "papain" gum, and this might be related to molecular complexity. The second is the considerably reduced nitrogen content. A high precentage of the nitrogen in the crude gums is extraneous material precipitated with the polysaccharides, but the purest gum still contains around 0.1% nitrogen. This could be within the error of measurement, but hydrolysis of the "papain" gum produced free amino acids that were detected by chromatography. This small amount of nitrogenous material may then be an integral part of the whole gum—a cement that holds the polysaccharide together. Convincing evidence of a protein-carbohydrate linkage is lacking, and will be difficult to provide. The reaction of gum with relatively mild alkali provides some information on this point.

The "papain" gum is sensitive to a normal solution of sodium hydroxide. Viscosity of the alkaline solution is much lower than that of water solutions. Solution viscosity of recovered material is around 4 cp. as compared with the original value of around 750 cp. If polysaccharide structure is not affected by alkali, then the alkali must have acted on the small amount of residual nitrogenous material in the gum, and thereby reduced molecular size. This mechanism seems possible if the protein is acting as a binding agent that holds some polysaccharide mixture together. However, no fractions were obtained when the alkali treated gum was chromatographed in the same way as gum that had been hydrolyzed by enzymes. The alternative is to assume that cold alkali treatment which is relatively mild in terms of alkaline treatments commonly used in carbohydrate chemistry depolymerizes the polysaccharides to an appreciable extent. The resolution of these alternatives must await detailed study of gum components and structure.

Since the above phases of our work have been completed, Preece and Mackenzie (16) have published a description of fractionation of barley gum. They

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obtained a pure laevorotatory polyglucosan by treatment of extract liquor of barley with graded amounts of ammonium sulphate. A preliminary study of their procedure indicates that a pure laevorotatory polyglucosan can also be obtained from a papain extract of our alcohol-treated barley grist, and less readily from a solution of "papain" gum. This polyglucosan is quite viscous in solution, and is thus a useful addition to available substrates for testing cytolytic activity. Its properties and relation to the original gum will be studied. However, it seems advisable to recall that ammonium sulphate is recognized as a peptizing agent for proteins.

Structural studies have been commenced at the University of Minnesota, and Gilles, Meredith, and Smith (6) have reported on a preliminary investigation made with the gum isolated by aqueous extraction from alcohol-treated barley. Methylation of the gum either directly or through its acetate provided a methylated product that was fractionated into three components. These were: (*a*) a methylated araboxylan ($[\alpha]_D$ — 160° in acetone), (*b*) a methylated poly-$\alpha$-glucosan ($[\alpha]_D$ + 158° in acetone), and (*c*) methylated poly-$\beta$-glucosan ($[\alpha]_D$ — 9° in acetone). Results of chemical fractionation of the gum obtained by papain treatment of alcohol-treated barley are not yet available, but the enzymatic hydrolysis of this gum by "X"-enzyme produced three fractions—a pentosan and two oligoglucosides—which are strikingly similar to those obtained by Gilles *et al.*

Concurrent studies of chemical and enzymatic hydrolysis of gum, or gum fractions, are thus proving useful and complementary in elucidating the molecular architecture of the nonstarch polysaccharides of barley.

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# THE ELECTRODE BEHAVIOR OF PLATINUM[1]

By A. K. Wiebe and C. A. Winkler

ABSTRACT

A potential of $-0.305 \pm 0.005$ volt (relative to a saturated calomel electrode) was obtained at a freshly prepared platinum surface within 30 sec. of immersion in oxygen-free $N/5$ sulphuric acid saturated with hydrogen. In electrolytes saturated with nitrogen or oxygen potentials of $+0.05 \pm 0.01$ volt and $+0.745 \pm 0.005$ volt respectively were more slowly attained. The times required for the electrode to reach maximum potentials, $t_{max}$, when it was made a cathode, and corresponding values of $t_{max}$ when it was rendered anodic, were determined over a range of currents. The values of $t_{max}$ appear to provide a method of determining the surface areas of platinum electrodes.

## INTRODUCTION

Recent studies in this laboratory (11) with mercury cathodes immersed in $N/5$ sulphuric acid indicated that during electrolysis hydrogen was adsorbed on the mercury cathode such that each surface atom of mercury accommodated one atom of hydrogen. Furthermore, this hydrogen appeared to be retained by the mercury for some time after electrolysis was stopped. Evidence was also obtained which tended to throw some doubt on the validity of the Bowden–Rideal method (2) of area measurement.

Similar experiments with platinum electrodes yielded the results recorded in the present paper.

## EXPERIMENTAL AND RESULTS

The cathode ray oscillograph unit and Leeds and Northrup type K potentiometer arrangement were identical with those described in previous papers (7, 8, 10, 11) except that a reversing switch was installed to facilitate reversing the current between the limits of hydrogen and oxygen evolution. The electrolytic cell and experimental methods were also the same in all essential respects. An auxiliary platinum electrode was incorporated into the cell so that the solution could be pre-electrolyzed without affecting the operating electrode.

The platinum electrodes were prepared by fitting machined lucite plugs to both ends of a re-entrant male ground joint. A $\frac{1}{8}$ in. brass rod threaded into the lucite plug at the solution end passed through a similar plug at the back of the electrode so that the complete assembly could be drawn together with a nut. A platinum disk of appropriate size, punched from a sheet of pure metal and roughened for good adhesion, was pressed to the face of the lucite plug which had been previously softened with a few drops of chloroform. Contact between the platinum and the brass rod was established with a small copper spring. The lucite plug at the solution end was cemented into place with lucite–chloroform solution to prevent electrolyte from leaking in. An apparent area of the platinum face of 0.80 cm.$^2$ was the smallest that the design would conveniently permit.

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All electrode surfaces were prepared by grinding with # 225 optical compound (American Optical Co.) and water on a glass surface.

A steady state potential of $-0.305 \pm 0.005$ volt (relative to the saturated calomel electrode) was obtained at a freshly prepared platinum surface within 30 sec. of immersion in oxygen-free $N/5$ sulphuric acid saturated with hydrogen (curve I, Fig. 1, top). The initial potential change, which occurred from

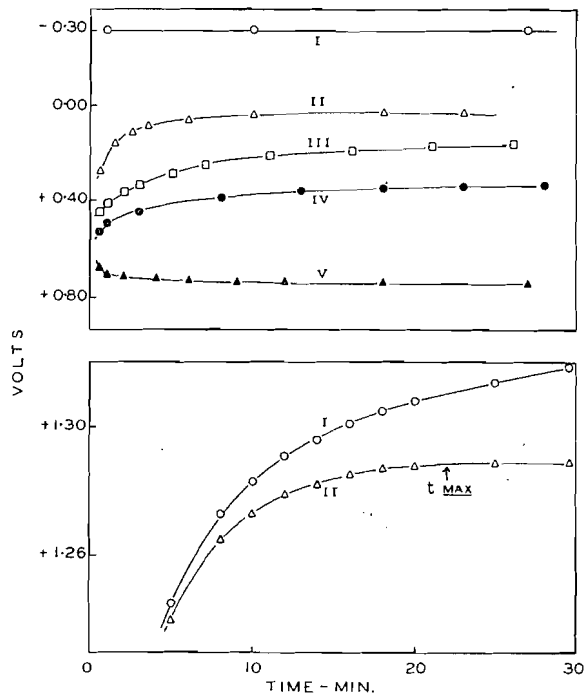



FIG. 1. Top:
Potentials of a platinum electrode in unstirred $N/5$ sulphuric acid electrolyte.
Curve I: Oxygen-free electrolyte, saturated with hydrogen.
II: Oxygen-free electrolyte, saturated with nitrogen.
III: Oxygen concentration approximately $7 \times 10^{-5}$ molar in nitrogen-saturated electrolyte.
IV: Oxygen concentration approximately $3 \times 10^{-4}$ molar in nitrogen-saturated electrolyte.
V: Oxygen-saturated electrolyte.
Bottom:
Uncorrected and corrected potential–time curves for a platinum electrode in $N/5$ sulphuric acid electrolyte. Current $1.10 \times 10^{-4}$ amp.
Curve I: Uncorrected.
II: Corrected.

potentials more positive than $-0.30$ volt, was much too rapid to follow in detail. When an electrode was immersed in electrolyte saturated with nitrogen, a similar but much less rapid potential change was observed, which reached a value of $+0.05 \pm 0.01$ volt in about 15 min. (curve II, Fig. 1, top) while in oxygen-saturated electrolyte a potential of $+0.745 \pm 0.005$ volt was approached from more negative values (curve V, Fig. 1, top). The potential changed to more positive values when oxygen was introduced into nitrogen-

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saturated electrolyte (by electrolysis at an auxiliary platinum electrode) but considerable quantities of oxygen were required to bring about an observable change in the potential curves (curves III and IV, Fig. 1, top). Furthermore, there was no evidence of any definite potential corresponding to some minimum quantity of oxygen as was observed with mercury (II). The platinum electrode potentials in nitrogen-saturated electrolyte containing oxygen were not reproducible and corresponded perhaps to conditions of the electrode surface which depended upon the relative concentrations of oxygen and nitrogen in solution.

The potential difference between a platinum electrode immersed in hydrogen-saturated electrolyte (−0.30 volt) and one immersed in electrolyte saturated with oxygen (+0.75 volt) was approximately one volt. These large variations of potential, brought about by changing only the gas dissolved in the electrolyte, would seem to indicate that the observed potentials were the result of some state of the electrode surface involving these gases. The very rapid initial change to a stable and reproducible potential observed when a platinum electrode was immersed in electrolyte saturated with hydrogen would seem to indicate the occurrence of a surface reaction involving very strong forces. This reaction may be the chemisorption of hydrogen. On the other hand, the much slower potential changes observed in solutions containing nitrogen and oxygen indicate surface changes involving much weaker forces. The reactions in these cases may be the strong physical adsorption of molecular oxygen and nitrogen, with oxygen probably the more strongly adsorbed.

When potential build-up curves were established on a mercury cathode (11) in oxygen-free electrolyte saturated with hydrogen (i.e. from initial potentials of about −0.61 volt) two distinct curves were obtained. The initial build-up curve, obtained by passing a small current for the first time across the face of a freshly prepared surface, was nonlinear while the subsequent curve, obtained by allowing the potential to decay on open circuit and again closing the circuit, was linear and reached the steady state potential in a much shorter period of time. In contrast, the initial and subsequent curves on a platinum cathode immersed in hydrogen-saturated solution were identical unless the current was switched on immediately after the electrode was introduced into the electrolyte. However, when the electrolyte was saturated with nitrogen, two distinct build-up curves were obtained as with mercury. The initial curve was now independent of the time of immersion of the electrode prior to switching on the current, provided there was no hydrogen present. In marked contrast with mercury, the initial potential build-up curves on a platinum electrode did not appear to be measurably affected by traces of oxygen.

The time required for the potential to reach a maximum when current was made to flow for the first time across the face of a freshly prepared platinum electrode immersed in $N/5$ sulphuric acid saturated with nitrogen (i.e. $t_{max}$) was determined for the electrode acting as a cathode and as an anode. With the electrode acting as a cathode, the potential increased smoothly to a maximum after which a slow, almost linear, potential change to more positive values occurred. When the electrode was made anodic, no maximum potential

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was observed. After an initial nonlinear curve the potential continued to change to more positive values at a linear rate which was in most cases exactly equal to that following the maximum potential at the cathode. The slow linear potential changes varied between 0.2 and 2 mv./min. depending on the current used, and since they were in the same direction for both anode and cathode, they appeared to be the result of some secondary process for which corrections must be made.

A plot of uncorrected and corrected values for a typical potential build-up curve obtained at a platinum anode is shown in Fig. 1, bottom. The correction, determined from the final approximately linear portion of the curve, is 1 mv./min. Corrections were applied to both anodic and cathodic potential build-up curves and since the final portions of the resultant curves were in all cases very smooth, the values of $t_{max}$ were taken directly from the corrected curves.

The values of $t_{max}$ shown in Table I were obtained by first making the

TABLE I

TYPICAL VALUES OF $t_{max}$ IN $N/5$ SULPHURIC ACID SATURATED WITH NITROGEN

| | Zero to anodic | | Anodic to cathodic |
|---|---|---|---|
| Current, amp. $\times 10^4$ | $t_{max}$, min. | $t_{max}/2$, min. | $t_{max}$, min. |
| 4.9 | 9.2 | 4.6 | 3.8 |
| 4.6 | 10.6 | 5.3 | 4.8 |
| 4.0 | 9.4 | 4.7 | 4.2 |
| 3.0 | 11.6 | 5.8 | 6.6 |
| 1.9 | 19.4 | 9.7 | 9.0 |
| 1.1 | 12.6 | 11.3 | 12.8 |
| 0.65 | 44 | 22 | 18 |
| 0.53 | 50 | 25 | 24 |
| 0.41 | 64 | 32 | 29 |
| 0.30 | 90 | 45 | 37 |

electrode an anode and after $t_{max}$ (anodic) reversing the current so that it became a cathode. For a current range ($4.9 \times 10^{-4} - 0.30 \times 10^{-4}$ amp.) $t_{max}$ for the anode was twice the corresponding value of $t_{max}$ for the cathode. When a freshly prepared electrode was made cathodic and the current was reversed after $t_{max}$, the value of $t_{max}$ for the anode was approximately three times that for the cathode (Table II). On again reversing the current, $t_{max}$ for the cathode was approximately equal to that observed when the electrode was first made cathodic and was one third of $t_{max}$ observed when the current was reversed after first making the electrode cathodic.

If the quantity of current passed at the cathode in the interval $t_{max}$ is designated one equivalent, then three equivalents are required to establish $t_{max}$ when the current is reversed to make the electrode anodic. Upon again making the electrode cathodic by reversing the current, one equivalent is required to establish $t_{max}$. A freshly prepared platinum anode requires two equivalents to establish $t_{max}$ (anodic) while as before, $t_{max}$ (cathodic) is established with one equivalent after the current has been reversed.

To explain the foregoing results, it is suggested that:

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TABLE II

TYPICAL VALUES OF $t_{max}$ IN $N/5$ SULPHURIC ACID SATURATED WITH NITROGEN

| Zero to cathodic | Cathodic to anodic | | Anodic to cathodic |
|---|---|---|---|
| $t_{max}$, min. | $t_{max}$, min. | $t_{max}/3$, min. | $t_{max}$, min. |
| 3.9 | 15.0 | 5.0 | 5.6 |
| 4.5 | 15.5 | 5.2 | 5.6 |
| 3.6 | 15.6 | 5.2 | 5.7 |
| 3.3 | 14.7 | 4.7 | 5.2 |
| 4.0 | 15.4 | 5.1 | 5.3 |
| 3.2 | 14.5 | 4.8 | 5.2 |
| 3.9 | 16.5 | 5.5 | 4.8 |
| 3.9 | 15.2 | 5.1 | 5.2 |
| Average 3.8 | | 5.1 | 5.3 |
| Current $2.53 \times 10^{-4}$ amp. | | $2.49 \times 10^{-4}$ amp. | $2.53 \times 10^{-4}$ amp. |
| Area 230 cm.$^2$ | | 310 cm.$^2$ | 320 cm.$^2$ |

*Apparent area of electrodes = 0.80 cm.$^2$*

1. When a freshly prepared platinum electrode is made cathodic, hydrogen ions are discharged and the atoms adsorbed on the cathode surface in the ratio of one atom of hydrogen to one of platinum until the surface is saturated at the point corresponding to $t_{max}$.

2. Upon then making the electrode anodic by reversing the current, one equivalent of current is required to remove the film of adsorbed hydrogen and a further two equivalents are required to establish a monatomic film of oxygen in which one atom of oxygen is accommodated by each surface atom of platinum.

3. When a platinum electrode with a freshly prepared surface is made anodic, two equivalents of current are required to deposit a monatomic film of oxygen on the platinum surface in the ratio of one atom of oxygen to one of platinum.

4. Upon now making the electrode cathodic by reversing the current, only one equivalent of current is passed in the interval from $t_{max}$ anodic to $t_{max}$ cathodic. This would seem to indicate that the film of oxygen is displaced from the surface through the reaction $O + O \rightarrow O_2$ (solution), while the hydrogen atoms go directly to the platinum surface.

The values of $t_{max}$ provide a method of calculating the true surface areas of platinum electrodes by the application of Faraday's laws to the quantities of current involved if it is accepted that at $t_{max}$ each surface atom of platinum accommodates one atom of hydrogen at the cathode or one atom of oxygen at the anode. The area occupied by each atom of hydrogen or of oxygen at the surface would then be identical with the effective area of a surface platinum atom. The value of 6.3 Å$^2$, calculated from bulk density on the assumption that the atoms in solid platinum are close packed, would seem to be a reasonable approximation for the effective area of a platinum atom at the surface.

The areas of platinum electrodes were calculated as above from values of $t_{max}$ representing the average for the eight experiments shown in Table II.

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The area calculated from $t_{max}$ (zero to cathodic) was about 27% less than the area calculated from $t_{max}$ (cathodic to anodic) or $t_{max}$ (anodic to cathodic). Thus, when hydrogen is removed from the electrode surface by electrolysis, an actual increase of area appears to take place. Additional evidence for this view would seem to be derived from those experiments which show that a platinum electrode on which the direction of a small current has been reversed between the limits of hydrogen and oxygen evolution becomes very active catalytically (1). An increase of catalytic activity indicates a surface change to some less stable configuration. Such a change could quite conceivably be accompanied by an increase in the true surface area.

Opinions differ concerning the possible existence of a film of hydrogen on an electrode surface when studies are made in which the polarizing current is reversed between the limits of oxygen and hydrogen evolution. Other workers (1, 3–6) have considered only the linear sections of the various potential build-up curves whereas the entire curves have been considered in the present study. The general shapes of the potential build-up curves observed in this study for platinum electrodes are similar to those described by Bowden (1).

The apparent capacitance at cathodes and at anodes of platinum was determined by the method first used successfully by Bowden and Rideal (2). This method involves determination of the rate of potential change with a C.R.O. in the linear portions of the subsequent potential build-up curves. The subsequent curves are obtained after allowing the potential to decay from the initial potential build-up on a freshly prepared electrode.

The apparent capacitance per unit area at the cathode was obtained by dividing the total apparent capacitance, measured in nitrogen-saturated solutions, by the areas calculated from values of $t_{max}$ obtained from both cathodic and anodic initial potential build-up curves (Table III). The apparent

TABLE III

THE APPARENT CAPACITANCE AT A PLATINUM CATHODE IN $N/5$ SULPHURIC ACID SATURATED WITH NITROGEN

| Current, amp. $\times 10^4$ | $A_0$, cm.$^2$ | $A_h$, cm.$^2$ | Apparent capacitance, microcoulombs/volt | |
|---|---|---|---|---|
| | | | Total | Per cm.$^2$ |
| 4.9 | 480 | 440 | 43,000 | 90 |
| 4.6 | 570 | 530 | 76,000 | 140 |
| 4.0 | 410 | 400 | 44,000 | 110 |
| 3.0 | 410 | 470 | 42,000 | 100 |
| 1.9 | 430 | 410 | 53,000 | 130 |
| 1.1 | 290 | 320 | 52,000 | 170 |
| 0.65 | 330 | 380 | 38,000 | 120 |
| 0.53 | 300 | 300 | 45,000 | 150 |
| 0.41 | 300 | 280 | 60,000 | 210 |
| Average | | | | 140 |

*Apparent area of cathode = 0.80 cm.$^2$*

*$A_0$ = areas calculated by the application of Faraday's laws to values of $t_{max}$ derived from anodic potential build-up curves.*

*$A_h$ = areas similarly calculated from initial potential build-up curves at the cathode.*

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TABLE IV

THE APPARENT CAPACITANCE AT A PLATINUM ANODE IN $N/5$ SULPHURIC ACID SATURATED WITH OXYGEN

| Current, amp. $\times 10^4$ | $A_0$, cm.$^2$ | Apparent capacitance, microcoulombs/volt | |
|---|---|---|---|
| | | Total | Per cm.$^2$ |
| 2.39 | 430 | 2500 | 5.8 |
| 1.19 | 310 | 1630 | 5.3 |
| 1.21 | 340 | 1800 | 5.3 |
| 1.20 | 280 | 1790 | 6.4 |
| 1.19 | 370 | 1960 | 5.3 |
| 1.63 | 380 | 2010 | 5.3 |
| 1.26 | 330 | 1970 | 6.0 |
| Average | | | 5.6 |

capacitance per cm.$^2$ at the anode was obtained by dividing the total apparent capacitance, measured in oxygen-saturated electrolyte, by the areas calculated from values of $t_{max}$ derived from initial potential build-up curves at the anode (Table IV). The apparent capacitance determined in this way was 140 microcoulombs per volt cm.$^2$ at the cathode (average of 10 measurements) and 5.6 microcoulombs per volt cm.$^2$ at the anode (average of seven experiments).

The large difference in the apparent capacitance at the cathode and anode would seem to eliminate the possibility that the linear portions of the subsequent build-up curves result from the charging of a Helmholtz double layer of ions in the electrolyte near the electrode surface. A true capacitance from this cause should be approximately equal at both the cathode and anode since the electrolyte was essentially the same in both cases. Although a double layer of ions at the cathode might be expected to differ somewhat from a similar double layer at the anode, it is difficult to rationalize the very large difference of apparent capacitance (which differed by a factor of about 25) on the basis of such a mechanism. It should, perhaps, be borne in mind that the measurement of an apparent capacitance involves the passage of a small current for a period of about one second or less. To establish an appreciable concentration gradient of ions, a similar current would have to be passed for several minutes (9).

Although the electrode behavior of mercury and platinum showed quite substantial differences, these differences appear to be more of degree than of kind. Both metals seem to be capable of accommodating a monatomic film of hydrogen. With mercury this film must be deposited by electrolysis and does not appear to be very stable whereas with platinum a similar film is formed directly from molecular hydrogen in solution and is so adherent that its removal brings about a substantial change in the surface characteristics of the metal. Similarly, both metals appear to be capable of accommodating a monatomic film of oxygen. In this case it is on mercury that such a film is formed from molecular oxygen in solution while on platinum a similar film must be de-

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posited by electrolysis. Where conditions are so arranged that these films of hydrogen or of oxygen are formed by electrolysis without appreciable side reactions, they appear to provide a convenient and accurate method of arriving at the true surface area of an electrode.

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# CONTRIBUTION TO THE STUDY OF PYRAZOLONES[1]

By Paul E. Gagnon, Jean L. Boivin,[2] and Méüde Tremblay[3]

ABSTRACT

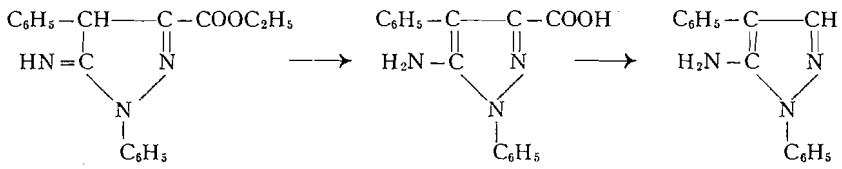
1,4-Diphenyl-3-carbethoxy-5-aminopyrazole yielded 1,4-diphenyl-5-aminopyrazole by hydrolysis and decarboxylation. The phenylhydrazone of ethyl phenyloxalacetate gave a pyrazolone which was transformed into 1,4-diphenyl-3-amino-5-pyrazolone. The 2,4-diphenyl-3-amino-5-pyrazolone was obtained from ethyl phenylcyanoacetate and phenylhydrazine by heating in acetic acid. 4-Alkyl-3-hydroxy- and 3-amino-5-pyrazolones and 4,4-dialkyl-3-oxo- and 3-imino-5-pyrazolones, substituted in position 2 by carbanilino or $\alpha$- or $\beta$-naphthyl groups, were prepared from ethyl mono- or disubstituted malonates and cyanoacetates, 4-phenylsemicarbazide, and $\alpha$- and $\beta$-naphthylhydrazines. Ultraviolet absorption spectra were determined in neutral and acid solutions.

## INTRODUCTION

Pyrazolones have been studied extensively for the last few years. For instance, ethyl mono- and disubstituted cyanoacetates with hydrazine and its derivatives gave rise to 5-pyrazolones having amino or imino groups in position 3 (3, 5, 6, 7, 9). Similarly, mono- and disubstituted malonates yielded 5-pyrazolones with hydroxy or oxo groups in position 3 (1, 4).

One of the objects of the present work was to synthesize 1,4- and 2,4-diphenyl-3-amino-5-pyrazolones and determine their structures. Another object was the preparation of 4-alkyl-3-hydroxy and 3-amino-5-pyrazolones and 4,4-dialkyl-3-oxo and 3-imino-5-pyrazolones substituted in position 2 and the determination of their ultraviolet absorption spectra.

1,4-Diphenyl-3-carbethoxy-5-iminopyrazolone (I) (2) was hydrolyzed in order to transform the imino group into an oxo group but the product of the reaction was 1,4-diphenyl-3-carboxy-5-aminopyrazole (II) which yielded 1,4-diphenyl-5-aminopyrazole (III).

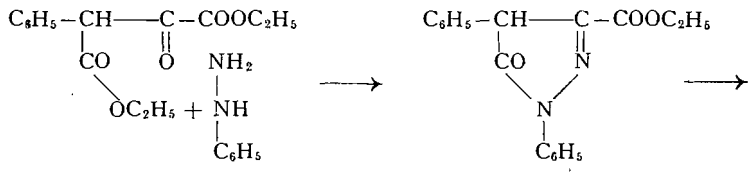


I II III

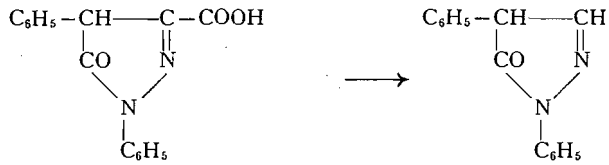
However, by heating together ethyl phenyloxalacetate and phenylhydrazine, 1,4-diphenyl-3-carbethoxy-5-pyrazolone (IV) (10) was obtained. The carbethoxy group in position 3 was hydrolyzed and by decarboxylation a known

[1] *Manuscript received March 19, 1953.*
*Contribution from the Department of Chemistry, Laval University, Quebec. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.*
[2] *Defence Research Board, C.A.R.D.E., Valcartier, Que.*
[3] *Graduate student, holder of a Bursary of the Scientific Research Bureau of the Province of Quebec in 1950–1951 and later recipient of financial assistance from the Defence Research Board of Canada.*

product, 1,4-diphenyl-5-pyrazolone (VI) (12, 13), was formed. This result leaves no doubt as to the constitution of the starting material 1,4-diphenyl-3-carbethoxy-5-pyrazolone (IV).

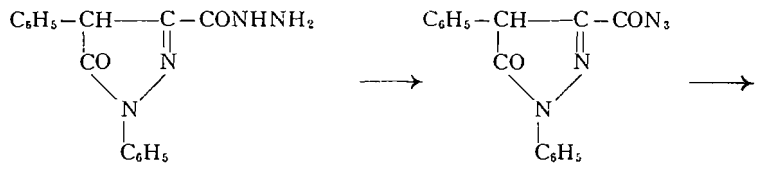


IV

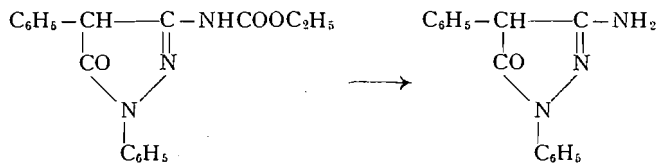


V VI

From 1,4-diphenyl-3-carbethoxy-5-pyrazolone the synthesis of 1,4-diphenyl-3-amino-5-pyrazolone was effected. A Curtius degradation on the 3-carbethoxy group was made through the hydrazide (VII), azide (VIII), and urethane (IX). The alkaline hydrolysis of the urethane yielded 1,4-diphenyl-3-amino-5-pyrazolone (X).

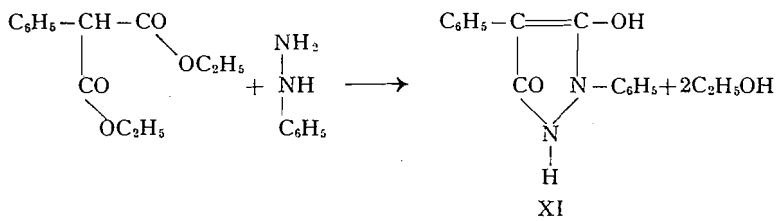


VII VIII



IX X

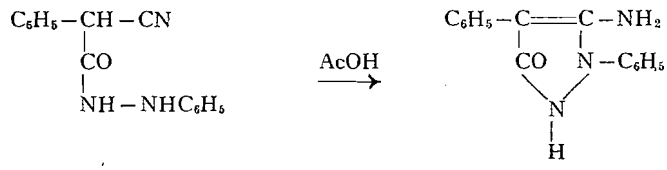
In order to obtain the 2,4-diphenyl-3-amino-5-pyrazolone, ethyl phenylmalonate was condensed with phenylhydrazine in the presence of sodium ethylate and 2,4-diphenyl-3-hydroxy-5-pyrazolone (XI) was formed.



XI

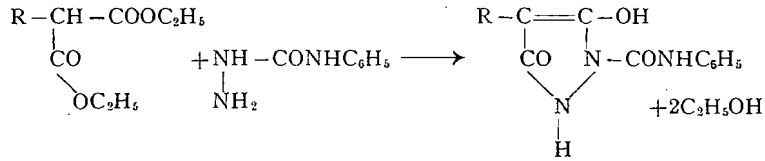
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It was intended to use this compound (XI) as starting material and transform the hydroxy group in position 3 into an amino group, but at that time it was found that 2,4-diphenyl-3-amino-5-pyrazolone (XII) could be obtained more easily by heating with acetic acid during many hours the phenylhydrazide of ethyl phenylcyanoacetate (11). All attempts which had previously been made when using sodium ethylate or sodium hydroxide instead of acetic acid had been unsuccessful.



XII

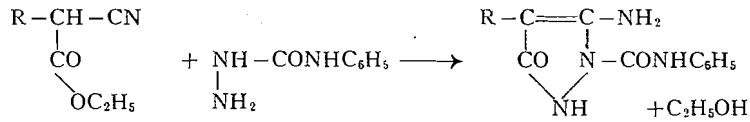
4-Alkyl-3-hydroxy-2-carbanilino-5-pyrazolones (XIII) were prepared according to the method used by Conrad and Zart (1). Ethyl malonates monosubstituted with hexyl, heptyl, or octyl groups were condensed in the presence of sodium ethylate with 4-phenylsemicarbazide.



XIII

With $\alpha$- or $\beta$-naphthylhydrazine hydrochloride under similar conditions, ethyl malonates $\alpha$-substituted with butyl, amyl, hexyl, heptyl, octyl, or benzyl groups yielded 4-alkyl-3-hydroxy-2-($\alpha$ or $\beta$)-naphthyl-5-pyrazolones (XIV).

4-Monosubstituted-3-amino-2-carbanilino-5-pyrazolones (XV) were obtained from ethyl cyanoacetates $\alpha$-substituted with butyl, amyl, hexyl, heptyl, octyl, and benzyl groups also in the presence of sodium ethylate.



XV

4,4-Dialkyl-3-oxo-2-carbanilino-5-pyrazolones (XVI) were prepared from ethyl malonates disubstituted with butyl, hexyl, heptyl, octyl, and benzyl groups and 4-phenylsemicarbazide.

Ethyl dibenzylmalonate and $\beta$-naphthylhydrazine hydrochloride gave 4,4-dibenzyl-3-oxo-2-$\beta$-naphthyl-5-pyrazolone (XVII) under the same experimental conditions.

Ethyl cyanoacetates disubstituted with butyl, amyl, hexyl, and octyl groups were heated under reflux with sodium ethylate and 4-phenylsemicarbazide to yield 4,4-dialkyl-3-imino-2-carbanilino-5-pyrazolones (XVIII).

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TABLE I

4-PHENYL-5-PYRAZOLONES

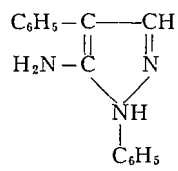
| Substituents | | | Formula | M.p., °C. | Analysis | | Ultraviolet absorption maxima | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Nitrogen, % | | Neutral | | Acid | |
| 3 | 2 | 1 | | | Calc. | Found | Å | Log $E_m$ | Å | Log $E_m$ |
| $COOC_2H_5$ | | $C_6H_5$ | $C_{18}H_{16}O_3N_2$ | 142–143 | 9.09 | 8.77 | 2410 | 4.32 | 2450 | 4.27 |
| COOH | | $C_6H_5$ | $C_{16}H_{12}O_3N_2$ | 192–193 | 10.00 | 9.53 | 2440 | 4.40 | 2450 | 4.34 |
| | | $C_6H_5$ | $C_{15}H_{12}ON_2$ | 196–197 | 11.75 | 11.4 | 2550<br>2830 | 4.34<br>4.18 | 2440 | 4.16 |
| $CONHNH_2$ | | $C_6H_5$ | $C_{16}H_{14}O_2N_4$ | 203–204 | 19.04 | 18.9 | 2400 | 4.50 | 2420 | 4.52 |
| $NHCOOC_2H_5$ | | $C_6H_5$ | $C_{18}H_{17}O_3N_3$ | 193–194 | 13.00 | 13.0 | 2520<br>3050 | 4.31<br>3.50 | 2510<br>2980 | 4.38<br>3.49 |
| $NH_2$ | | $C_6H_5$ | $C_{15}H_{13}ON_3$ | 153–156d | 16.73 | 15.9 | 2560 | 4.26 | 2540 | 4.20 |
| OH | $C_6H_5$ | | $C_{15}H_{12}O_2N_2$ | 172–173 | 11.11 | 11.6 | 2350<br>2820 | 4.18<br>3.30 | 2340<br>2800 | 4.16<br>3.31 |
| $NH_2$ | $C_6H_5$ | | $C_{15}H_{13}ON_3$ | 234–236 | 16.73 | 16.0 | 2800 | 4.26 | 2500 | 4.18 |

The properties and analysis of the pyrazolones are given in Tables I, II, III, and IV.

*Ultraviolet Absorption Spectra*

The ultraviolet absorption spectra were determined in neutral and acid solution by a method already described (7).

1,4-Diphenyl-5-aminopyrazole (Fig. 1) has a single ultraviolet absorption maximum of high intensity, log $E_m = 4.31$, at short wave length, 2490 Å in neutral medium. On acidification, the maximum is shifted to shorter wave length. It has been shown that pyrazolones with a low absorption maximum at high wave length have a 2:3 double bond or an imino group, and that those with a high maximum at short wave length have a double bond between two carbon atoms (3, 6, 7). Moreover, the hypsochromic shift was attributed to the formation of a salt by an amino group (11). From these results one may be justified to conclude that structure XIX is the only one present.



XIX

1,4-Diphenyl-3-amino-5-pyrazolone (Fig. 2) has only one ultraviolet absorption maximum of high intensity at short wave length either in neutral or

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TABLE II

3-HYDROXY-5-PYRAZOLONES

| Substituents | | Formula | M.p., °C. | Analysis | | Ultraviolet absorption maxima | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Nitrogen, % | | Neutral | | Acid | |
| 4 | 2 | | | Calc. | Found | Å | Log $E_m$ | Å | Log $E_m$ |
| $C_6H_{13}$ | $CONHC_6H_5$ | $C_{16}H_{21}O_2N_3$ | 170–171 dec. | 13.86 | 13.7 | 2380 | 4.05 | 2370 | 3.99 |
| $C_7H_{15}$ | $CONHC_6H_5$ | $C_{17}H_{23}O_2N_3$ | 160–162 dec. | 13.28 | 13.6 | 2380 | 4.20 | 2380 | 4.10 |
| $C_8H_{17}$ | $CONHC_6H_5$ | $C_{18}H_{25}O_2N_3$ | 150–151 | 12.69 | 13.5 | 2540 | 4.37 | 2540 | 4.38 |
| $C_8H_{17}$ | $\alpha$-$C_{10}H_7$ | $C_{21}H_{26}O_2N_2$ | 184–185 | 8.28 | 7.97 | 2400<br>3140 | 4.32<br>3.74 | 2380<br>3050 | 4.29<br>3.74 |
| $C_6H_5CH_2$ | $\alpha$-$C_{10}H_7$ | $C_{20}H_{16}O_2N_2$ | 169–170 | 8.86 | 8.54 | 2230<br>2770 | 4.76<br>3.88 | 2235<br>2810 | 4.71<br>3.94 |
| $C_4H_9$ | $\beta$-$C_{10}H_7$ | $C_{17}H_{18}O_2N_2$ | 172–173 | 9.93 | 10.0 | 2440<br>2975 | 4.45<br>4.28 | 2320<br>3010 | 4.67<br>3.90 |
| $C_6H_{11}$ | $\beta$-$C_{10}H_7$ | $C_{18}H_{20}O_2N_2$ | 157–158 | 9.46 | 9.32 | 2440<br>2980 | 4.47<br>4.01 | 2330<br>2940 | 4.61<br>3.92 |
| $C_6H_{13}$ | $\beta$-$C_{10}H_7$ | $C_{19}H_{22}O_2N_2$ | 155–156 | 9.03 | 8.67 | 2270<br>2890 | 4.54<br>3.92 | 2310<br>3000 | 4.61<br>3.90 |
| $C_7H_{15}$ | $\beta$-$C_{10}H_7$ | $C_{20}H_{24}O_2N_2$ | 152–153 | 8.64 | 8.79 | 2450<br>3000 | 4.45<br>4.00 | 2320<br>2990 | 4.52<br>3.88 |
| $C_8H_{17}$ | $\beta$-$C_{10}H_7$ | $C_{21}H_{26}O_2N_2$ | 147–148 | 8.28 | 8.02 | <br>3000 | <br>3.97 | 2340<br>3000 | 4.61<br>3.89 |
| $C_6H_5CH_2$ | $\beta$-$C_{10}H_7$ | $C_{20}H_{16}O_2N_2$ | 189–190 | 8.86 | 8.80 | 2350<br>3000 | 4.53<br>3.75 | <br>3000 | <br>3.79 |

TABLE III

3-AMINO-2-CARBANILINO-5-PYRAZOLONES

| Substituents | Formula | M.p., °C. | Analysis | | Ultraviolet absorption maxima | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Nitrogen, % | | Neutral | | Acid | |
| 4 | | | Calc. | Found | Å | Log $E_m$ | Å | Log $E_m$ |
| $C_4H_9$ | $C_{14}H_{18}O_2N_2$ | 117–118 | 20.43 | 20.3 | 2380 | 4.22 | 2420 | 4.30 |
| $C_5H_{11}$ | $C_{15}H_{20}O_2N_4$ | 115–116 | 19.44 | 19.4 | 2480 | 4.34 | 2380 | 4.24 |
| $C_6H_{13}$ | $C_{16}H_{22}O_2N_4$ | 113–114 | 18.54 | 17.9 | 2420 | 4.50 | 2370 | 4.22 |
| $C_7H_{15}$ | $C_{17}H_{24}O_2N_4$ | 110–111 | 17.72 | 17.8 | 2450 | 4.33 | 2400 | 4.28 |
| $C_8H_{17}$ | $C_{18}H_{26}O_2N_4$ | 264–265 | 16.97 | 16.8 | 2460<br>2920 | 4.18<br>3.68 | 2430<br>2840 | 4.30<br>3.77 |
| $C_6H_5CH_2$ | $C_{17}H_{16}O_2N_4$ | 240–245 | 18.18 | 17.5 | 2880 | 3.79 | 2790 | 3.73 |

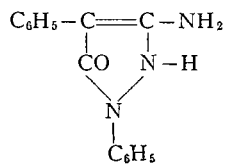
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TABLE IV

4,4-DIALKYL-5-PYRAZOLONES

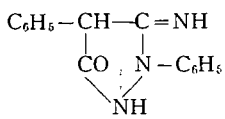
| Substituents | | | Formula | M.p., °C. | Analysis | | Ultraviolet absorption maxima | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Nitrogen, % | | Neutral | | Acid | |
| 4 | 3 | 2 | | | Calc. | Found | Å | log $E_m$ | Å | log $E_m$ |
| $(C_4H_9)_2$ | O | $CONHC_6H_5$ | $C_{18}H_{25}O_3N_3$ | 217–218 | 12.68 | 12.9 | 2550 | 3.74 | 2520 | 3.81 |
| $(C_6H_{13})_2$ | O | $CONHC_6H_5$ | $C_{22}H_{33}O_3N_3$ | 198–199 | 10.85 | 10.8 | 2530 | 3.74 | 2510 | 3.77 |
| $(C_7H_{15})_2$ | O | $CONHC_6H_5$ | $C_{24}H_{37}O_3N_3$ | 199–200 | 10.12 | 10.3 | 2510 | 3.72 | 2450 | 3.83 |
| $(C_8H_{17})$ | O | $CONHC_6H_5$ | $C_{26}H_{41}O_3N_3$ | 194–195 | 9.48 | 9.50 | 2530 | 3.69 | 2520 | 3.75 |
| $(C_6H_5CH_2)_2$ | O | $CONHC_6H_5$ | $C_{24}H_{21}O_3N_3$ | 243–245 | 10.52 | 10.6 | 2400 | 3.39 | 2400 | 4.41 |
| $(C_6H_5CH_2)_2$ | O | $\beta$-$C_{10}H_7$ | $C_{24}H_{22}O_2N_2$ | 243–244 | 6.89 | 6.42 | 2990 | 3.89 | 2970 | 3.89 |
| $(C_4H_9)_2$ | NH | $CONHC_6H_5$ | $C_{18}H_{26}O_2N_4$ | 234–236 | 16.97 | 17.3 | | | | |
| $(C_5H_{11})_2$ | NH | $CONHC_6H_5$ | $C_{20}H_{30}O_2N_4$ | 95–97 | 15.64 | 15.9 | 2460 | 4.48 | 2400 | 4.25 |
| $(C_6H_{13})_2$ | NH | $CONHC_6H_5$ | $C_{22}H_{34}O_2N_4$ | 100–102 | 14.51 | 14.9 | 2450 | 4.54 | 2380 | 4.15 |
| $(C_8H_{17})_2$ | NH | $CONHC_6H_5$ | $C_{26}H_{42}O_2N_4$ | 167–168 | 12.67 | 13.4 | 2700 | 3.82 | 2660 | 3.89 |

acid solution, which is indicative of the presence of a 3:4 ethylenic double bond as shown by formula XX.

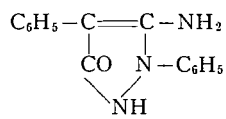


XX

2,4-Diphenyl-3-amino-5-pyrazolone (Fig. 2) has an absorption maximum at long wave length in neutral medium and this suggests that form XXI is present. But in acid solution a comparison of the curve of the 2,4 with that of the 1,4-diphenyl-3-amino-5-pyrazolone reveals that form XXII then exists.



XXI



XXII

4-Monosubstituted-3-hydroxy-2-carbanilino-5-pyrazolones (R = $C_6H_{13}$, $C_7H_{15}$, or $C_8H_{17}$) exhibit only one absorption band in neutral or acid solution at short wave length (Fig. 3) which is indicative of an ethylenic bond (4). They may have the structures XXIII or XXIV.

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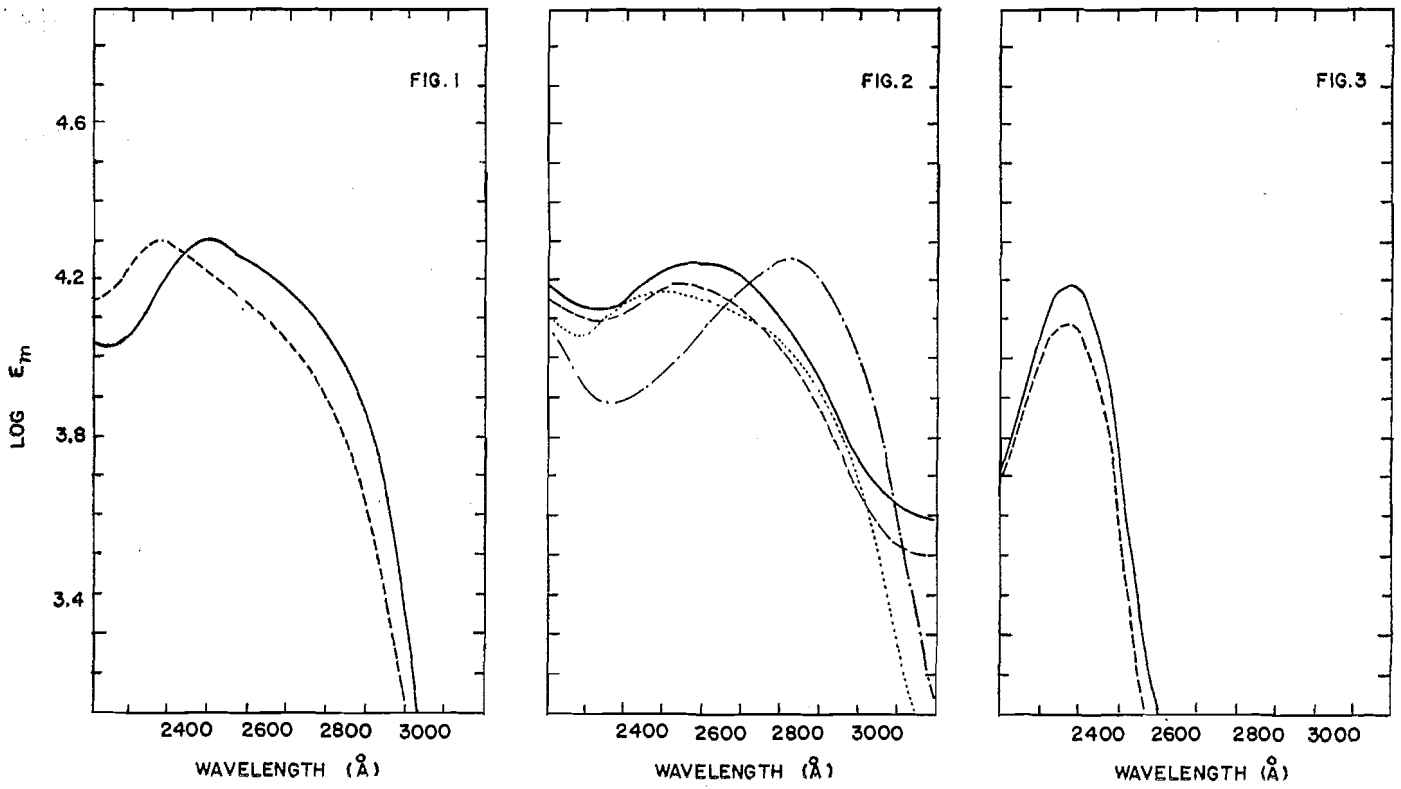



FIG. 1. Ultraviolet absorption spectrum of 1,4-diphenyl-5-aminopyrazole: ———— in neutral solution, – – – – – in acid solution.
FIG. 2. Ultraviolet absorption spectrum of 1,4-diphenyl-3-amino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 2,4-diphenyl-3-amino-5-pyrazolone: – · – · – · – in neutral solution, . . . . . in acid solution.
FIG. 3. Ultraviolet absorption spectrum of 4-heptyl-3-hydroxy-2-carbanilino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution.

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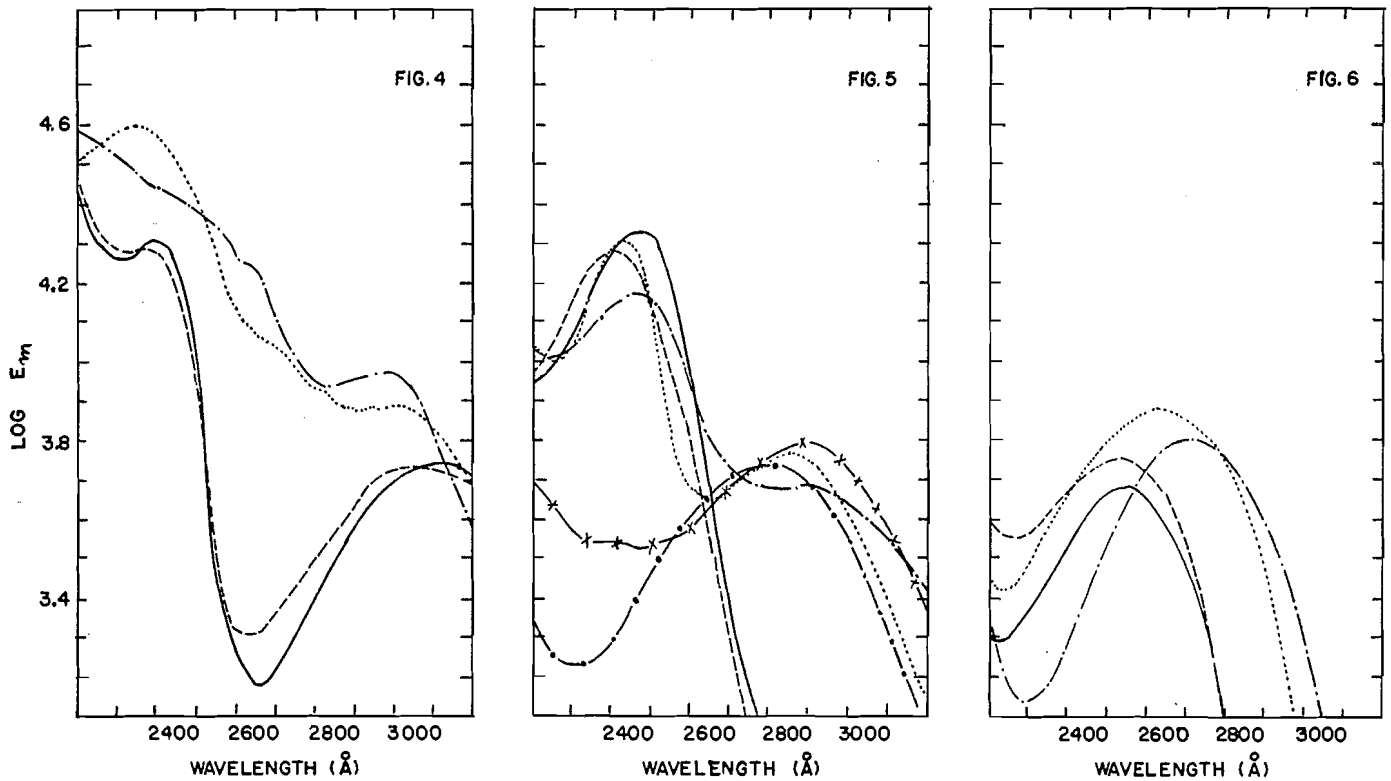
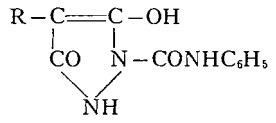


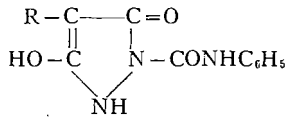

FIG. 4. Ultraviolet absorption spectrum of 4-octyl-3-hydroxy-2-α-naphthyl-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 4-octyl-3-hydroxy-2-β-naphthyl-5-pyrazolone: – · – · – · – in neutral solution, . . . . . in acid solution.

FIG. 5. Ultraviolet absorption spectrum of 4-heptyl-3-amino-2-carbanilino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; of 4-octyl-3-amino-2-carbanilino-5-pyrazolone: – · – · – · – in neutral solution, . . . . . in acid solution; and of 4-benzyl-3-amino-2-carbanilino-5-pyrazolone: – x – x – x – in neutral solution, – • – • – • – • – in acid solution.

FIG. 6. Ultraviolet absorption spectrum of 4,4-dioctyl-3-oxo-2-carbanilino-5-pyrazolone: ———— in neutral solution, – – – – – in acid solution; and of 4,4-dioctyl-3-imino-2-carbanilino-5-pyrazolone: – · – · – · – in neutral solution, . . . . . in acid solution.



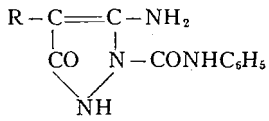
XXIII



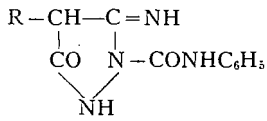
XXIV

The spectra of 4-monosubstituted-3-hydroxy-2-$\alpha$-naphthyl-5-pyrazolones (R = $C_8H_{17}$ or $C_6H_5CH_2$) and 4-monosubstituted-3-hydroxy-2-$\beta$-naphthyl-5-pyrazolones (R = $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$, $C_7H_{15}$, $C_8H_{17}$, or $C_6H_5CH_2$) (Fig. 4) are greatly influenced by the absorption of the naphthalene chromophore (3, 8). However, these pyrazolones probably have structures similar to the previous ones XXIII or XXIV.

The absorption curves of most of the 4-alkyl-3-amino-2-carbanilino-5-pyrazolones (R = $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$, or $C_7H_{15}$) (Fig. 5) exhibit in neutral and acid solution only one maximum of high intensity at short wave length. This fact together with the slight shift on acidification indicates the presence of an amino group as in structure XXV.



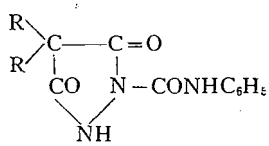
XXV



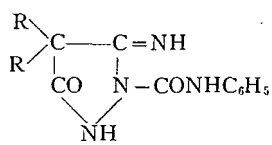
XXVI

On the other hand 4-octyl-3-amino-2-carbanilino-5-pyrazolones (Fig. 5) have two ultraviolet absorption maxima in neutral and acid solution, one at short wave length and one at long wave length. One must conclude that two forms, one with an amino group in position 3, structure XXV, and another with an imino group XXVI, are present. 4-Benzyl-3-amino-2-carbanilino-5-pyrazolone (Fig. 5) has only one maximum at long wave length and consequently has structure XXVI.

4,4-Dialkyl-3-oxo-2-carbanilino-5-pyrazolones (R = $C_4H_9$, $C_6H_{13}$, $C_7H_{15}$, $C_8H_{17}$, or $C_6H_5CH_2$) and 4,4-dialkyl-3-imino-2-carbanilino-5-pyrazolones (R = $C_4H_9$, $C_5H_{11}$, $C_6H_{13}$, or $C_8H_{17}$) (Fig. 6) certainly have structures XXVII and XXVIII in neutral and acid solution since they are the only ones possible.



XXVII



XXVIII

## EXPERIMENTAL*

*1,4-Diphenyl-3-carboxy-5-aminopyrazole* (II)

To 1,4-diphenyl-3-carbethoxy-5-aminopyrazole (2) (1.0 gm., 0.003 mole) was added sodium hydroxide (10%, 50 ml.) in absolute alcohol (25 ml.). The mixture was heated under reflux for three hours and the solution was poured into ice water. On neutralization with dilute acetic acid the starting material

* *All melting points are uncorrected.*

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was obtained and removed by filtration. By acidification to pH 3 with hydrochloric acid, a white solid precipitated. This compound was recrystallized from alcohol: m.p. 109–110° C. Yield, 0.5 gm. (60%). Calc. for $C_{16}H_{13}O_2N_3$: N, 15.05%. Found: N, 14.7%.

*1,4-Diphenyl-5-aminopyrazole* (III)

1,4-Diphenyl-3-carboxy-5-aminopyrazole (1.1 gm., 0.004 mole) was heated at 200° C. for 45 min., until all the carbon dioxide had been expelled. The cold solid residue was recrystallized from ethanol: m.p. 136–137° C. Yield, 0.3 gm. (32%). Calc. for $C_{15}H_{13}N_3$: N, 17.87%. Found: N, 17.3%.

*1,4-Diphenyl-3-carbethoxy-5-pyrazolone* (IV)

Ethyl phenyloxalacetate (33.5 gm., 0.127 mole) was mixed with phenylhydrazine (10.8 gm., 0.1 mole) and the mixture was heated on a steam bath for an hour and in an oil bath at 210° C. for two hours. The material was dissolved in alcohol and the solution poured into dilute alkali. The alkaline solution was filtered and the filtrate was acidified with acetic acid. The product (10) was recrystallized from dilute alcohol: m.p. 142–143° C. Yield, 18 gm. (50%). Calc. for $C_{18}H_{16}O_3N_2$: N, 9.09%. Found: N, 8.77%.

*1,4-Diphenyl-3-carboxy-5-pyrazolone* (V)

1,4-Diphenyl-3-carbethoxy-5-pyrazolone (4.0 gm., 0.013 mole) was heated on a steam bath with alcoholic potash for one hour. The product was poured into ice water and the solution treated with an excess of hydrochloric acid (50%). The white precipitate that separated was recrystallized from chloroform: m.p. 192–193° C. Calc. for $C_{16}H_{12}O_3N_2$: N, 10.00%. Found: N, 9.53%.

*1,4-Diphenyl-5-pyrazolone* (VI)

1,4-Diphenyl-3-carboxy-5-pyrazolone was heated in a metal bath at 200° C. for 30 min. The solid residue (12, 13) was recrystallized from ethanol: m.p. 196–197° C. Calc. for $C_{15}H_{12}ON_2$: N, 11.75%. Found: N, 11.4%.

*1,4-Diphenyl-3-carboxyhydrazido-5-pyrazolone* (VII)

1,4-Diphenyl-3-carbethoxy-5-pyrazolone (7.7 gm., 0.025 mole) was added to boiling hydrazine hydrate (100%, 10 ml.). The mixture was refluxed for six hours and evaporated to dryness. The residue was dissolved in cold hydrochloric acid and poured into ice water. On neutralization with sodium hydroxide, a solid separated and was recrystallized from alcohol: m.p. 203–204° C. Calc. for $C_{16}H_{14}O_2N_4$: N, 19.04%. Found: N, 18.9%.

*1,4-Diphenyl-3-carbethoxyamino-5-pyrazolone* (IX)

A solution of 1,4-diphenyl-3-carboxyhydrazido-5-pyrazolone in hydrochloric acid was cooled to 0° C. and covered with ether. Sodium nitrite dissolved in water was added dropwise to the mechanically stirred mixture until the diazotization was complete, as shown by the starch–iodide test paper. The ethereal layer was decanted and the aqueous solution extracted several times with ether. The extracts were washed with sodium bicarbonate (10%), dried over anhydrous sodium sulphate, and evaporated to dryness under reduced pressure.

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The solid product, the azide melting at about 160° C. (with deflagration), was dissolved in absolute ethanol and the solution was refluxed for 20 hr. A white solid material separated: m.p. 193–194° C. The urethane was sublimed at 180° C. (1 mm.). Calc. for $C_{18}H_{17}O_3N_3$: N, 13.00%. Found: N, 13.0%.

*1,4-Diphenyl-3-amino-5-pyrazolone* (X)

1,4-Diphenyl-3-carbethoxyamino-5-pyrazolone (0.6 gm.) was treated with dilute (10%) sodium hydroxide and the mixture was refluxed for three hours, cooled, filtered, and acidified with dilute (50%) acetic acid. The brown precipitate formed was dissolved in absolute ether. The ethereal solution was dried over anhydrous sodium sulphate, evaporated to dryness, and the solid residue was recrystallized from benzene: m.p. 153–156° C. (with decomposition). The product decomposed at 140° C. (1 mm.) in an attempt to sublime it. Calc. for $C_{15}H_{13}ON_3$: N, 16.73%. Found: 15.9%.

*2,4-Diphenyl-3-hydroxy-5-pyrazolone* (XI)

Ethyl phenylmalonate (11.8 gm., 0.05 mole) and phenylhydrazine (5.4 gm., 0.05 mole) were added to a cold solution of sodium (2.4 gm., 0.1 mole) in absolute ethanol (75 ml.). The solution was refluxed for 18 hr., the alcohol was evaporated under reduced pressure, and the residue dissolved in water. The water insoluble material was recrystallized from alcohol: m.p. 172–173° C. Yield, 9 gm. (70%). Calc. for $C_{15}H_{12}O_2N_2$: N, 11.11%. Found: 11.6%.

*2,4-Diphenyl-3-amino-5-pyrazolone* (XII)

The phenylhydrazine derivative of ethyl phenylcyanoacetate (4.2 gm., 0.017 mole) (11) was dissolved in boiling glacial acetic acid (50 ml.) and the solution refluxed for 72 hr. On cooling, a solid crystallized and was dissolved in a cold sodium hydroxide solution (5%, 400 ml.). The alkaline solution was filtered, some insoluble materials were thus removed, and the filtrate was acidified with acetic acid. The white precipitate was recrystallized from ethanol: m.p. 234–236° C. Yield, 2.0 gm. (47%). Calc. for $C_{15}H_{13}ON_3$: N, 16.73%. Found: N, 16.0%.

*4-Monosubstituted-3-hydroxy-5-pyrazolone* (XIII and XIV)

Mixtures of ethyl monosubstituted malonates (0.033 mole) and hydrazine derivatives, 4-phenylsemicarbazide or $\alpha$- or $\beta$-naphthylhydrazine hydrochloride (0.033 mole) were added to cold solutions of sodium (0.10 mole) in absolute ethanol (75 ml.). After the solutions were refluxed for 18 hr., the alcohol was evaporated under reduced pressure and the residues dissolved in water. The solutions were extracted with ether, filtered to remove the insoluble material, and the aqueous layers were acidified with acetic acid (50%). Solids separated and were recrystallized with ethanol. Some of them were sublimed under reduced pressure (1 mm.) at 10° C. below their melting points.

The 4-monosubstituted-3-hydroxy-5-pyrazolones obtained are listed together with their melting points, analyses, and ultraviolet spectrophotometric data in Table II.

*4-Monosubstituted-3-amino-2-carbanilino-5-pyrazolones* (XV)

The 4-monosubstituted-3-amino-2-carbanilino-5-pyrazolones were prepared

in the same way as above, except that the ethyl monosubstituted malonates used were replaced by ethyl monosubstituted cyanoacetates.

They are listed together with their melting points, analyses, and ultraviolet spectrophotomeric data in Table III.

*4,4-Disubstituted-3-oxo-5-pyrazolones* (XVI and XVII)

Using the same procedure as outlined for 4-monosubstituted-3-hydroxy-5-pyrazolones, 4,4-disubstituted-3-oxo-5-pyrazolones were obtained from ethyl disubstituted malonates and 4-phenylsemicarbazide or β-naphthylhydrazine hydrochloride and their melting points, analyses, and ultraviolet spectrophotometric data are listed in Table IV.

*4,4-Disubstituted-3-imino-2-carbanilino-5-pyrazolones* (XVIII)

Ethyl dialkyl cyanoacetates were treated with 4-phenylsemicarbazide just as indicated for 4-alkyl-3-hydroxy-5-pyrazolones to yield 4,4-dialkyl-3-imino-2-carbanilino-5-pyrazolones.

Their properties are summarized in Table IV.

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# CHARACTERIZATION OF DINITROALKYL PHENOLS[1]

By G. G. S. Dutton, T. I. Briggs,[2] B. R. Brown,[3] and M. E. D. Hillman

ABSTRACT

Amine salts of dinitroalkyl phenols have been suggested as herbicides and insecticides. A selection of such amine salts was examined as to their suitability for characterizing dinitroalkyl phenols. The following new salts are described: the piperidine, morpholine, and cyclohexylamine salts of each of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, 2,6-dinitro-4-methylphenol, 4,6-dinitro-2-isopropylphenol, 2,6-dinitro-4-isopropylphenol, 4,6-dinitro-2-(*sec*-butyl)-phenol, 2,6-dinitro-4-(*tert*-butyl)-phenol, and 2,6-dinitro-4-(*tert*-amyl)-phenol. In addition, the preparation of 4,6-dinitro-2-isopropylphenol and 2,6-dinitro-4-isopropylphenol does not appear to have been previously described. The use of these salts, and similar ones with other amines, is recommended for the preparation of crystalline derivatives of dinitrophenols.

## INTRODUCTION

Dinitroalkyl phenols have been shown to be effective as insecticides (2, 3) and selective weed killers (6). In connection with a study of such compounds as herbicides a selection of dinitroalkyl phenols has been prepared. The amine salts of these dinitroalkyl phenols were prepared and were found to be excellent derivatives for the characterization of these compounds.

The reported method of preparing such amine salts (4) (sodium salt of phenol + amine hydrochloride) has given in our hands crystalline mixtures of the phenol and the desired salt. The discrepancies between the reported melting points of some of these salts (4) and those described here are attributed to this cause. Bell's melting point (1) of 171° C. for piperidinium 2,4-dinitrophenoxide agrees well with our figure of 172° C.

## EXPERIMENTAL

The phenols selected for nitration were 2-and 4-methylphenol, 2- and 4-isopropylphenol, 4-(*tert*-butyl)-phenol, and 4-(*tert*-amyl)-phenol. The latter two were prepared by the method of Putnam (5) and the remainder, together with 2,4-dinitrophenol and 2,4-dinitro-2-(*sec*-butyl)-phenol, were obtained as commercial products.

### *4,6-Dinitro-2-isopropylphenol*

2-Isopropylphenol (25 gm.) was dissolved in glacial acetic acid (60 cc.) and this solution was added dropwise, with constant stirring, to a solution of nitric acid (40 cc., $d = 1.5$) and glacial acetic acid (75 cc.) which had been cooled to −15° C. in a stainless steel beaker. The addition took about three quarters of an hour, after which time the mixture was allowed to come slowly to room temperature over a period of one and a half hours. The solution was kept at room temperature for one half hour and then poured onto cracked ice.

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The yellow precipitate which resulted was filtered off, dissolved in chloroform, and carefully washed to remove all trace of acid. The chloroform solution was then dried over magnesium sulphate and after removal of the solvent, the residual oil was distilled under high vacuum to give the 4,6-dinitro-2-isopropylphenol as a clear yellow oil boiling at 132° C. (0.15 mm.). The oil solidified on cooling and on recrystallization from ethanol gave a yellow solid, m.p. 54° C., yield, 65%.

In a similar manner all the other dinitrophenols were prepared and the results shown in Table I.

TABLE I

DINITROALKYL PHENOLS

| Phenol | M.p., °C. | Yield, % |
|---|---|---|
| 2,4-Dinitro | 114 | * |
| 4,6-Dinitro-2-methyl | 86 | 67 |
| 2,6-Dinitro-4-methyl | 82 | 60 |
| 4,6-Dinitro-2-isopropyl | 54 | 66 |
| 2,6-Dinitro-4-isopropyl | 68 | 65 |
| 4,6-Dinitro-2-(*sec*-butyl) | 42 | * |
| 2,6-Dinitro-4-(*tert*-butyl) | 95 | 80 |
| 2,6-Dinitro-4-(*tert*-amyl) | 66 | 50 |

**Commercial sample.*

*Piperidine Salt of 4,6-Dinitro-2-methylphenol*

4,6-Dinitro-2-methylphenol (0.5 gm.) was placed in an Erlenmeyer flask and a small excess of piperidine (0.75 gm.) was added. Benzene (10 cc.) was then added and the mixture gently warmed for five minutes. Petroleum ether (25 cc., 30–60° C.) was then added when the salt crystallized as colored flakes. The precipitate was filtered off, washed with petroleum ether, and recrystallized from a mixture of benzene (five parts), ethanol (one part), and petroleum ether (two parts).

In a similar way the piperidine, morpholine, and cyclohexylamine salts of all the dinitrophenols were prepared and these are listed in Tables II, III, and IV.

TABLE II

PIPERIDINE SALTS OF DINITROALKYL PHENOLS

| Phenol | Formula | M.p., °C. | Nitrogen, % | | Description |
|---|---|---|---|---|---|
| | | | Calc. | Found | |
| 2,4-Dinitro | $C_{11}H_{15}N_3O_5$ | 172* | 15.61 | 15.54 | Orange needles |
| 4,6-Dinitro-2-methyl | $C_{12}H_{17}N_3O_5$ | 157 | 14.83 | 14.93 | Yellow needles |
| 2,6-Dinitro-4-methyl | $C_{12}H_{17}N_3O_5$ | 195 | 14.83 | 14.86 | Orange needles |
| 4,6-Dinitro-2-isopropyl | $C_{14}H_{21}N_3O_5$ | 204 | 13.50 | 13.52 | Yellow needles |
| 2,6-Dinitro-4-isopropyl | $C_{14}H_{21}N_3O_5$ | 218 | 13.50 | 13.44 | Orange plates |
| 4,6-Dinitro-2-(*sec*-butyl) | $C_{15}H_{23}N_3O_5$ | 154 | 12.92 | 12.93 | Yellow needles |
| 2,6-Dinitro-4-(*tert*-butyl) | $C_{15}H_{23}N_3O_5$ | 232 | 12.92 | 12.92 | Orange needles |
| 2,6-Dinitro-4-(*tert*-amyl) | $C_{16}H_{25}N_3O_5$ | 198 | 12.39 | 12.54 | Orange plates |

* *Ref.(1).*

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TABLE III

MORPHOLINE SALTS OF DINITROALKYL PHENOLS

| Phenol | Formula | M.p., °C. | Nitrogen, % | | Description |
|---|---|---|---|---|---|
| | | | Calc. | Found | |
| 2,4-Dinitro | $C_{10}H_{13}N_3O_6$ | 169 | 15.49 | 15.36 | Yellow needles |
| 4,6-Dinitro-2-methyl | $C_{11}H_{15}N_3O_6$ | 189 | 14.74 | 14.76 | Red plates |
| 2,6-Dinitro-4-methyl | $C_{11}H_{15}N_3O_6$ | 217 | 14.74 | 14.73 | Orange plates |
| 4,6-Dinitro-2-isopropyl | $C_{13}H_{19}N_3O_6$ | 204 | 13.42 | 13.54 | Orange needles |
| 2,6-Dinitro-4-isopropyl | $C_{13}H_{19}N_3O_6$ | 216 | 13.42 | 13.55 | Yellow flakes |
| 4,6-Dinitro-2-(*sec*-butyl) | $C_{14}H_{21}N_3O_6$ | 147 | 12.84 | 12.89 | Red needles |
| 2,6-Dinitro-4-(*tert*-butyl) | $C_{14}H_{21}N_3O_6$ | 232 | 12.84 | 12.92 | Orange needles |
| 2,6-Dinitro-4-(*tert*-amyl) | $C_{15}H_{23}N_3O_6$ | 174 | 12.32 | 12.22 | Yellow plates |

TABLE IV

CYCLOHEXYLAMINE SALTS OF DINITROALKYL PHENOLS

| Phenol | Formula | M.p., °C. | Nitrogen, % | | Description |
|---|---|---|---|---|---|
| | | | Calc. | Found | |
| 2,4-Dinitro | $C_{12}H_{17}N_3O_5$ | 158 | 14.83 | 14.85 | Yellow needles |
| 4,6-Dinitro-2-methyl | $C_{13}H_{19}N_3O_5$ | 171 | 14.13 | 14.23 | Yellow needles |
| 2,6-Dinitro-4-methyl | $C_{13}H_{19}N_3O_5$ | 193 | 14.13 | 14.16 | Orange needles |
| 4,6-Dinitro-2-isopropyl | $C_{15}H_{23}N_3O_5$ | 207 | 12.92 | 12.95 | Yellow needles |
| 2,6-Dinitro-4-isopropyl | $C_{15}H_{23}N_3O_5$ | 213 | 12.92 | 12.99 | Orange needles |
| 4,6-Dinitro-2-(*sec*-butyl) | $C_{16}H_{25}N_3O_5$ | 210 | 12.38 | 12.44 | Yellow needles |
| 2,6-Dinitro-4-(*tert*-butyl) | $C_{16}H_{25}N_3O_5$ | 230 | 12.38 | 12.39 | Orange needles |
| 2,6-Dinitro-4-(*tert*-amyl) | $C_{17}H_{27}N_3O_5$ | 219 | 11.90 | 11.93 | Yellow needles |

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# STEROIDS

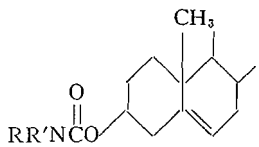
## II. REACTION OF AMINES WITH CHOLESTERYL CHLOROFORMATE AND PYROLYSIS OF N-BENZYL CHOLESTERYL CARBAMATE[1]

By A. F. McKay and G. R. Vavasour

ABSTRACT

Cholesteryl chloroformate can be used to isolate small amounts of amines from aqueous solutions as N-substituted cholesteryl carbamates. These derivatives are easily isolated and identified. Their possible use for the identification of amines obtained in degradative studies is discussed. The thermal decomposition of N-benzyl cholesteryl carbamate gives carbon dioxide, cholesterol, cholest-3,5-diene, and *sym*-dibenzylurea. A mechanism of formation of these products is discussed.

During the course of a previous investigation (5) of the preparation of N-substituted-3-aminocholest-5-enes it was noted that Bergmann and Haskelberg (1) had reported the formation of 3-anilinocholest-5-ene by heating cholesteryl chloroformate with methylaniline. If this latter reaction had occurred it would have offered a simple method of preparation of N-substituted-3-aminocholest-5-enes. However, all attempts to repeat this work were unsuccessful. On the other hand, it was found that cholesteryl chloroformate combines with primary and secondary amines to give practically quantitative yields of N-substituted cholesteryl carbamates (I). In this manner Verdino and Schadendorff (6) and Kucherov and Kocheshkov (2) have prepared a




I

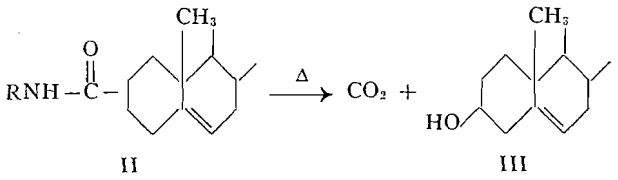
number of N-aryl cholesteryl carbamates. This method has been changed to recover amines [as the N-substituted cholesteryl carbamates (cf. Table I)] from their dilute aqueous solutions. Since these derivatives are formed rapidly and with ease this procedure provides an excellent method for the identification of biologically important amines often obtained in dilute solution during degradation studies. Also the large increase in molecular weight in transforming methyl-, dimethyl-, ethylamines, etc., into the corresponding N-substituted cholesteryl carbamates is a decided advantage. Thus it is considered that these derivatives will be a distinct asset in assisting in the identification of amines from biological sources.

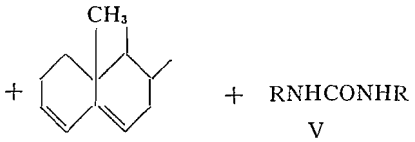
Wieland, Honold, and Vila (7) first reported the preparation of cholesteryl chloroformate and its thermal transformation to 3-$\beta$-chlorocholest-5-ene. The melting point of their product was below the accepted melting point of pure 3-$\beta$-chlorocholest-5-ene so this work was repeated. It was found that

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*Contribution from Defence Research Chemical Laboratories, Ottawa, Ontario. Issued as D.R.C.L. Report No. 111.*

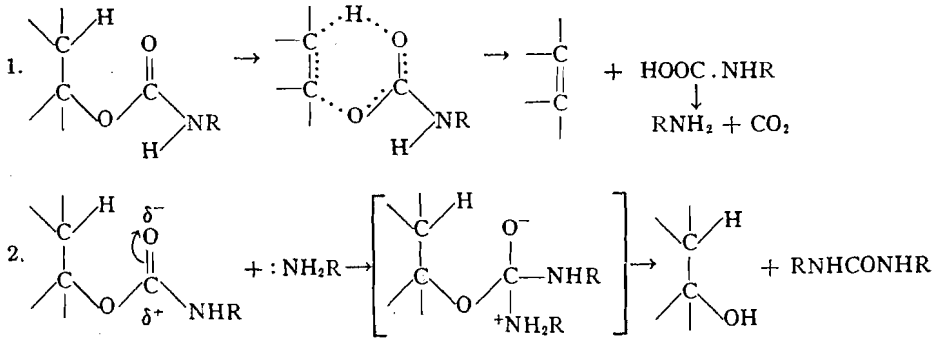
pyrolysis of cholesteryl chloroformate at 150° C. gives a quantitative yield of carbon dioxide and about 20% hydrogen chloride along with cholesteryl chloride contaminated with unsaturated hydrocarbon. Pure cholesteryl chloride (m.p. 95–96° C.) could only be obtained by chromatographing on alumina. The unsaturated hydrocarbon fractions were not identified. In the pyrolysis of N-benzyl cholesteryl carbamate, cholest-3,5-diene (IV) was identified in the unsaturated hydrocarbon fraction (*vide infra*).

In order to be certain that no rearrangement of N-substituted cholesteryl carbamates to 3-aminocholest-5-enes occurs under any conditions of heating, the thermal decomposition of N-benzyl cholesteryl carbamate (II) was studied in detail. No 3- or 6-benzylaminocholest-5-enes were present in the degradation products of any of the several runs. Instead the products were identified as carbon dioxide, 3-$\beta$-hydroxycholest-5-ene (cholesterol) III, cholest-3,5-diene (IV), and *sym*-dibenzylurea. Generally a small quantity (1–10%) of the N-benzyl cholesteryl carbamate (II) was recovered unchanged.




If the thermal decomposition of N-benzyl cholesteryl carbamate occurred by the same mechanism as the Chugaev reaction (the thermal decomposition of xanthate esters to produce olefins) then one would expect a good yield of cholest-3,5-diene and no cholesterol [cf. the thermal decomposition of cholesteryl methyl xanthate (3)]. The formation of cholesterol and cholest-3,5-diene together in the pyrolysis of N-benzyl cholesteryl carbamate suggests that two reactions are occurring as follows.




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The first reaction, which is pictured with the cyclic transition state similar to that used for the thermal decomposition of cholesteryl methyl xanthate by O'Connor and Nace (3), would produce cholest-3,5-diene, carbon dioxide, and benzylamine, while reaction by the second path would give cholesterol and *sym*-dibenzylurea. If it is considered (without support other than that carbon dioxide is produced in 50% yield and its measurement is quantitative) that both these reactions occur to approximately the same extent, then the products have been obtained from the thermal decomposition of N-benzyl cholesteryl carbamate in the following yields; carbon dioxide (102%), cholesterol (86%), *sym*-dibenzylurea (77%), cholest-3,5-diene (20–40%). The low yields of *sym*-dibenzylurea may be due to partial volatilization of the benzylamine before complete reaction occurred. This is partly corroborated by the slight difference in weight between the weights of starting material and the weights of carbon dioxide plus nonvolatile products. The hydrocarbon, cholest-3,5-diene, was the most difficult product to account for quantitatively. This could be caused by treatment of the ether solution with hydrogen chloride to substantiate the absence of 3- or 6-benzylaminocholest-5-enes.

## EXPERIMENTAL[2]

### *Cholesteryl Chloroformate*

Fifty grams of cholesterol was converted into cholesteryl chloroformate (m.p. 119.5–121° C., $[\alpha]_D^{24}$ −26.7) in 86% yield using essentially the method of Wieland *et al.* (7). The acetone mother liquor from the crystallized cholesteryl chloroformate gave a second crop which melted 117.5–119° C. The total yield was 92%.

### *N-Methyl-N-phenyl Cholesteryl Carbamate*

Cholesteryl chloroformate (2.0 gm., 0.004 mole) and methylaniline in 25 cc. of dry acetone were refluxed for two hours. After the solution was cooled and partially evaporated two crops of crystals (m.p. 127.5–131° C.) were obtained, yield 2.35 gm. (100%). One crystallization from acetone raised the melting point to 131–133° C., $[\alpha]_D^{24}$ −6.8. Calc. for $C_{35}H_{53}NO_2$: C, 80.90; H, 10.28; N, 2.69%. Found: C, 80.86; H, 10.36; N, 2.78%.

### *Treatment of Cholesteryl Chloroformate with Methylaniline*

Two grams (0.004 mole) of cholesteryl chloroformate and 1.3 gm. (0.012 mole) of methylaniline on mixing together evolved much heat and crystals were deposited. This mixture was refluxed for three hours under nitrogen. The reaction mixture became homogeneous after 90 min. of heating. The cooled solution was poured into 100 cc. of 10% hydrochloric acid solution after which a very tacky gum separated. This gum was dissolved in hot *n*-butanol as described by Bergmann and Haskelberg (1) for the isolation of cholesteryl aniline. However, although several runs were made, no cholesteryl

[2] *All melting points were determined on a Kofler block. Chloroform was used as a solvent for the optical rotation determinations. Microanalyses were performed by C. W. Beazley, Skokie, Illinois.*

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aniline could be obtained from the gum. In some cases a few milligrams of dark solid, which melted at 75–105° C. were obtained.

*N-Benzyl Cholesteryl Carbamate*

N-Benzyl cholesteryl carbamate (m.p. 148.5–149.5° C., $[\alpha]_D^{24.6}$ −18.7°) was prepared in 89% yield by the method described above for the preparation of N-methyl-N-phenyl cholesteryl carbamate. The melting point reported in the literature (6) for N-benzyl cholesteryl carbamate is 148° C.

*N-Alkyl Cholesteryl Carbamates*

*Method A.*—Two mole equivalents of an alkylamine were added to cholesteryl chloroformate dissolved in ether. The heat of reaction was sufficient to reflux the ether. At the end of one hour the lumps of amine hydrochloride were broken up and removed by filtration and washed with ether. The ethereal filtrate and washings on evaporation to dryness gave practically quantitative yields of the N-alkyl cholesteryl carbamates. Generally one crystallization from alcohol was sufficient for purification.

*Method B.*—Cholesteryl chloroformate (1.0 gm., 0.002 mole) was dissolved in 100 cc. of ether and shaken with 1% aqueous amine (two mole equivalents) solution. The carbamates were isolated by evaporation of the water-washed ether solutions (N-methyl cholesteryl carbamate, which was insoluble in ether, was filtered off, and washed with ether). The crude products were purified by one crystallization from either acetone or 95% ethanol. The N-alkyl cholesteryl carbamates prepared by methods *A* and *B* are listed in Table I.

TABLE I

N-SUBSTITUTED CHOLESTERYL CARBAMATES

| Substituents | Method | Yield, % | M.p., °C. | $[\alpha]_D^{24}$ | Formula | Carbon | | Hydrogen | | Nitrogen | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calc'd. | Found | Calc'd. | Found | Calc'd. | Found |
| Methyl | B | 95 | 204–205 | −33.0 | $C_{29}H_{49}NO_2$ | 78.50 | 78.76 | 11.13 | 11.20 | 3.16 | 2.95 |
| Dimethyl | B | 95 | 112–113 | −27.1 | $C_{30}H_{51}NO_2$ | 78.71 | 78.85 | 11.24 | 11.44 | 3.06 | 2.77 |
| Ethyl | B | 94 | 161.5–162 | −29.0 | $C_{30}H_{51}NO_2$ | 78.71 | 78.70 | 11.24 | 11.38 | 3.06 | 2.63 |
| *n*-Propyl | B | 95 | 141–142 | −26.2 | $C_{31}H_{53}NO_2$ | 78.93 | 78.85 | 11.33 | 11.34 | 2.97 | 2.74 |
| Isopropyl | B | 95 | 147.5–148.5 | −26.8 | $C_{31}H_{53}NO_2$ | 78.93 | 78.87 | 11.33 | 11.36 | 2.97 | 2.82 |
| Allyl | B | 91 | 142–143 | −23.5 | $C_{31}H_{51}NO_2$ | 79.25 | 79.05 | 10.94 | 11.26 | 2.98 | 2.58 |
| *n*-Butyl | A | 99 | 128–129 | −27.6 | $C_{32}H_{55}NO_2$ | 79.11 | 79.21 | 11.41 | 11.32 | 2.88 | 3.20 |
| Isoamyl | B | 100 | 128–130 | −23.7 | $C_{33}H_{57}NO_2$ | 79.29 | 79.13 | 11.49 | 11.42 | 2.80 | 2.70 |

*Pyrolysis of Cholesteryl Chloroformate*

Four grams (0.009 mole) of cholesteryl chloroformate were intimately mixed with a 10-fold quantity of finely ground Pyrex glass and placed in a flask. After all the air had been displaced from the apparatus with nitrogen, the outlet was connected to a gas absorption train containing a silver nitrate–dilute nitric acid solution in a wash-tower, a U-tube of Drierite, and a weighed U-tube charged with Ascarite and magnesium chlorate. The flask containing the cholesteryl chloroformate was placed in an oil bath preheated to 160° C. and the temperature was maintained at 150 ± 5° C. for two hours. A slow stream of nitrogen was introduced into the apparatus during the reaction

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period. At the end of this time 0.375 gm. (96%) of carbon dioxide had been evolved and 0.248 gm. (equivalent to 20% of the chlorine of cholesteryl chloroformate being evolved as hydrogen chloride) of silver chloride was precipitated.

The residual mixture of glass and pyrolysis product was refluxed with acetone (50 cc.), filtered while hot, and the glass washed with ether. Evaporation of the solvents gave 3.5 gm. of solid (m.p. 73–79° C.). A portion (0.505 gm.) of this product was chromatographed on 20 gm. of alumina in a 24 mm. tube using 50 ml. portions of *n*-pentane as the eluant. It was found necessary to run a second chromatogram on this material. This procedure gave 212.2 mgm. (40.7%) of crude 3-β-chlorocholest-5-ene (m.p. 91–95° C.). One crystallization from acetone raised the melting point to 94.5–95.5° C., yield 90 mgm. This product did not depress the melting point of an authentic sample of 3-β-chlorocholest-5-ene. The remaining fractions from the chromatograms were oils or oily solids.

*Thermal Decomposition of N-Benzyl Cholesteryl Carbamate*

This was carried out in the same way as the decomposition of cholesteryl chloroformate. Forty grams of finely powdered Pyrex (to pass 28 mesh) and 4.0 gm. (0.0077 mole) of N-benzyl cholesteryl carbamate were intimately mixed and heated together for one hour at 290 ± 10° C. by immersion in a potassium nitrate – sodium nitrite bath. During the heating 0.174 gm. (51%) of carbon dioxide was evolved. After cooling, the organic material was extracted from the glass with hot chloroform and alcohol in turn. These solutions were combined, taken to dryness under nitrogen, and finally dried in a vacuum desiccator. The tan solid (3.8 gm.) was triturated with 50 cc. of absolute ether and the insoluble material recovered, yield 0.68 gm. (74%). This solid melted at 170–171° C. alone and on admixture with an authentic sample of *sym*-dibenzylurea. The ethereal filtrate was shaken with 10% hydrochloric acid and washed with 10% sodium bicarbonate solution and water. The organic layer was evaporated under nitrogen and dried *in vacuo*. This residue on treatment with 50 cc. *n*-pentane gave a white solid, yield 0.85 gm. (m.p. 124–141° C.). Treatment of this solid in the usual manner with digitonin gave a digitonide from which 0.54 gm. of cholesterol (m.p. 144.5–146.5° C.) was recovered. One recrystallization from 95% alcohol raised its melting point to 147.5–148.5° C. which was not depressed by mixture melting point with authentic cholesterol. The filtrate from the digitonide was treated to remove excess digitonin and then taken to dryness. Trituration of the residue with petroleum ether (30–60° C.) yielded a further 0.02 gm. (2.1%) of *sym*-dibenzylurea (m.p. 170.5–171.5° C.) and 0.03 gm. of unchanged N-benzyl cholesteryl carbamate (m.p. 147.5–148.5° C.) which was identified by mixed melting point.

The pentane solution was taken to dryness leaving a residue of 2.1 gm. This was redissolved in 50 cc. pentane and an aliquot containing 1.0 gm. chromatographed on 30 gm. of alumina (Alcoa, F-20, neutralized and reactivated). This column was washed with 100 cc. portions of solvent (cf. Table II).

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TABLE II

LIQUID CHROMATOGRAM

| Fraction No. | Solvent* | Residue (mgm.) | M.p. (°C.) |
|---|---|---|---|
| 1 | P | 193.7 (557.9)** | 70–74 (70.5–75.5)** |
| 2 | P | 61.8 (26.9)** | Oil (67.5–70.0)** |
| 3–11 | P, P.E. to B | 35.0 | Oils |
| 12–17 | B | 153.2 | Semisolids |
| 18–21 | B–E (9: 1) | 195.7 | From 115° to 137° |
| 22 | B–E (9: 1) | 38.6 | 133–140° |
| 23–29 | B–E (9: 1 to 1: 1) | 163.5 | 125–135° |
| 30–39 | E, E–C, C–A (9: 1 to 1: 1) | 207.9 | Dark oils |

* *P = pentane, P.E. = pet. ether (65–68°), B = benzene, E = ether, C = chloroform, A = acetone.*

** *The values in parentheses refer to another run made essentially to obtain a better value on the yield of cholest-3,5-diene.*

Fraction 1 on crystallization from 5.3 cc. of ethyl acetate – methanol (3: 1) yielded 390 mgm. of crystals (m.p. 78.5–80.0° C., $[\alpha]_D^{23}$ −112°). Another recrystallization gave material melting at 78.5–79.5° C., $[\alpha]_D^{23}$ −116 and $\lambda_{max}^{alc.}$ 235 mμ. Anal. calc. for $C_{27}H_{44}$: C, 87.97; H, 12.03%. Found: C, 87.83; H, 12.44%. The constants reported for cholest-3,5-diene are m.p. 80–81° C., $[\alpha]_D^{20}$ −129.6 (4), $\lambda_{max}$ 235 mμ (8).

Fraction 2 recrystallized in the same manner gave 9 mgm. of solid which melted at 73–78° C.

Fractions 3–11 and 30–39 resisted all attempts at purification.

Fractions 12–17 were recrystallized from acetone to give 32 mgm. of N-benzyl cholesteryl carbamate (m.p. 145–147° C.) identified by mixture melting point.

Fractions 18–29 were also recrystallized from acetone to yield 123.4 mgm. of cholesterol (m.p. 147.5–149.0° C.) which was identified by a mixture melting point with authentic cholesterol.

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## NOTE

### A NEW SYNTHESIS OF URANIUM TRIFLUORIDE*

By O. J. C. Runnalls

The compound uranium trifluoride is difficult to prepare. The attempts to synthesize uranium trifluoride have been summarized recently by Katz and Rabinowitch (3). They describe two successful methods.

(*a*) Uranium tetrafluoride is reduced at 1000°C. with rigorously-purified hydrogen (6). The reaction proceeds according to

$$2UF_4 + H_2 \longrightarrow 2UF_3 + 2HF. \quad [1]$$

Traces of moisture and oxygen must be removed from the apparatus before use by thorough degassing, to prevent the contamination of the product by uranium dioxide.

(*b*) Uranium tetrafluoride is reduced at 1050°C. with finely-divided uranium (2, 7) prepared from the decomposition of uranium hydride.

$$3UF_4 + U \longrightarrow 4UF_3. \quad [2]$$

The reaction is complete after two hours in an argon atmosphere.

According to the available thermodynamic data, it should be possible to prepare uranium trifluoride by the aluminum reduction of uranium tetrafluoride at a high temperature by the reaction

$$3UF_4 + Al \longrightarrow 3UF_3 + AlF_3. \quad [3]$$

Aluminum trifluoride could be removed by sublimation in vacuum to obtain an aluminum-free product. However, uranium trifluoride begins to disproportionate at 1000°C.

$$4UF_3 \longrightarrow 3UF_4 + U. \quad [4]$$

This reaction is accelerated by the sublimation from the system of volatile uranium tetrafluoride. Obviously, the uranium trifluoride would be contaminated with finely-divided uranium which would ignite on exposure to air, forming uranium dioxide.

Klemm and Voss reported (4) that the monofluoride of aluminum volatilized from a mixture of aluminum and its trifluoride when heated above 700°C. in vacuum. Their X-ray results indicated that aluminum monofluoride was stable only in the gaseous state and disproportionated on condensation.

$$3AlF \longrightarrow AlF_3 + 2Al. \quad [5]$$

If aluminum monofluoride were more volatile than aluminum trifluoride, as has been predicted by Brewer (1), the synthesis of uranium trifluoride free of aluminum should proceed at a temperature where uranium trifluoride is stable and uranium tetrafluoride relatively nonvolatile.

$$UF_4 + Al \longrightarrow UF_3 + AlF. \quad [6]$$

Experimental reductions have been carried out using the stoichiometric amounts of uranium tetrafluoride and aluminum satisfying the above equation.

*Issued as A.E.C.L. No. 50.

The uranium tetrafluoride was prepared by the hydrofluorination of uranium dioxide at 650°C. "Super-pure" aluminum filings ( − 28 to + 60 mesh) were intimately mixed with 3-4 gm. of uranium tetrafluoride. The mixture was heated in a graphite crucible by a tungsten coil surrounded with molybdenum radiation shields, in vacuum. At a crucible temperature of 800°C. a black condensate slowly appeared on the surface of the pyrex flask containing the furnace assembly. At 900°C., the evolution of gas was rapid and ceased after 1.5 hr. After the product had cooled in vacuum it was easily removed from the crucible as one sintered, black mass. The weight loss of the original charge indicated that the gas evolved during the reaction was, in fact, aluminum monofluoride (see Table I). Further, a chemical analysis of the sublimate yielded an Al:F ratio of 1.09:1.

TABLE I

WEIGHT LOST ON HEATING URANIUM TETRAFLUORIDE AND ALUMINUM TO 900°C.

| Experiment | Charge | | Reduction time | Theoretical weight loss, gm. | | Experimental weight loss, gm. |
|---|---|---|---|---|---|---|
| | $UF_4$,gm. | Al, gm. | | Calculated as AlF | Calculated as $AlF_3$ | |
| 1 | 3.8646 | 0.3318 | 1.5 hr. | 0.5655 | 1.0330 | 0.5671 |
| 2 | 3:6162 | 0.3105 | 1.5 | 0.5292 | 0.9667 | 0.5463 |
| 3 | 4.0285 | 0.3459 | 1.5 | 0.5896 | 1.0769 | 0.6035 |
| 4 | 3.5172 | 0.3020 | 1.5 | 0.5148 | 0.9403 | 0.5320 |
| 5 | 4.7552 | 0.4083 | 2.0 | 0.6959 | 1.2712 | 0.7403 |

The theoretical weight percentage of uranium in uranium trifluoride is 80.7. Samples from experiments 3 and 4 were analyzed at 80.2% and 80.7% uranium respectively. The major contaminant of uranium trifluoride prepared in the above manner is likely to be uranium dioxide. X-ray powder diffraction patterns of samples 3 and 4 revealed only uranium trifluoride lines, thus limiting any contamination by uranium dioxide to less than 2%. Further evidence supporting a high chemical yield in the process resulted from a chemical analysis for uranium trifluoride using a recently published method by Manning, Miller, and Rowan (5). The method is based on a determination of the total reducing power of the sample. The latter prepared several uranium trifluoride samples by reaction 2, the purest analyzing at about 91% uranium trifluoride. By comparison, our samples 3 and 4 were analyzed at 89.2% and 90.7% uranium trifluoride respectively. It is reasonable to assume that this analytical method may indicate a total uranium fluoride content lower than the absolute percentage present.

ACKNOWLEDGMENT

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# THE PROTEOLYTIC ENZYMES OF MICROORGANISMS

## V. EXTRACELLULAR PEPTIDASES PRODUCED BY FUNGI GROWN IN SUBMERGED CULTURE[1]

BY W. B. MCCONNELL,[2] E. Y. SPENCER,[3] AND J. A. TREW[4]

ABSTRACT

The culture media from selected fungi grown in submerged culture have been shown to contain enzymes capable of hydrolyzing some synthetic dipeptides and their derivatives. Readily measurable amounts of aminopeptidase, carboxypeptidase, and dipeptidase activity were found, and differences between the systems elaborated by different organisms were observed. The most rapid hydrolysis of N-cbzo-α-L-glutamyl-L-glutamic acid (I) and of N-cbzo-α-L-glutamyl-DL-alanine (II) by *Gliocladium roseum* PRL 86 occurred at pH 4.8 to 4.9. I was hydrolyzed most rapidly by *Alternaria tenuis* PRL 369 at pH 4.7. The activation energies for the hydrolysis of I by PRL 369 and of II by PRL 86 were found to be 11,000 and 15,000 calories per mole, respectively. The activation energy for the hydrolysis of I by PRL 86 was estimated as being between 10,000 and 13,000 calories per mole.

## INTRODUCTION

Although the proteolytic systems elaborated by molds and actinomycetes have been known and studied for a number of years, there is little information available regarding the number and nature of the individual proteases present in the crude enzyme preparations. The work of Berger, Johnson, and Peterson (2) suggests that these are fairly complex mixtures. In 1936 they made a study of 30 common molds and reported that extracts of the mycelium contained a proteinase and at least five peptidases; a carboxypolypeptidase, an aminopolypeptidase, a dipeptidase, and two enzymes that hydrolyze diglycine and triglycine. Investigations of proteases excreted into the culture medium have been particularly limited. Crewther (12) reported the isolation of crystals containing proteinase from a medium in which *Aspergillus niger* had grown in still culture. Dion (13) studied the optimum conditions for production of extracellular proteases by a number of molds and actinomycetes grown in submerged culture. McConnell (19) found that crude preparations from these culture media were capable of hydrolyzing a number of proteins at a pH near 8, and that in general a considerable amount of free amino acid was liberated. It seems probable that

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the extracellular proteases, like those obtained from mycelium (3), contain a number of different proteolytic constituents.

It appeared of interest to further characterize these crude mold enzymes by using synthetic substrates. The results indicate that the crude extracellular protease systems may be considered as complex systems. Some of the characteristics of the carboxypeptidase components are discussed.

## EXPERIMENTAL

### *Preparation of Enzymes*

Crude fungal proteases were produced by growing the organisms in submerged culture using a Klim–glucose medium containing either calcium or magnesium carbonate. They were supplied by Dr. W. M. Dion who has described their preparation in detail (13). At the end of the growth period the medium was freed of mycelium by filtration, lyophilized, and stored dry until required for hydrolysis studies. The organisms used were *Mortierella renispora* PRL 26, *Gliocladium roseum* PRL 79, *Gliocladium roseum* PRL 86, *Trichoderma viride* PRL 92, *Fusarium* sp. PRL 232, *Chaetomium* sp. PRL 319, *Alternaria tenuis* PRL 369, and *Streptomyces* sp. PRL 376. Throughout the remainder of this paper the enzymes are referred to by the identification number of the organisms from which they were produced.

### *Preparation of Substrates*

A list of the substances used together with some comments on their preparation follows.

N-Cbzo-glyclglycine,* m.p. 178°C. (reported m.p. 178°C. (5)), was prepared according to the method of Hanson and Smith (16). Hydrogenolysis in acetic acid with platinum oxide catalyst yielded glycylglycine, decomposed 215–220°C. (reported m.p. 215–220°C. with decomposition (14)). The mixture of diastereoisomers, N-cbzo-α-L-glutamyl-DL-alanine ethyl ester, was prepared according to the procedure of Bergmann, Zervas, and Fruton (6,17) and the substance was hydrolyzed to N-cbzo-α-L-glutamyl-DL-alanine which was recrystallized from ethyl acetate to a composition melting at 153°C. The same method was used to prepare N-cbzo-α-L-glutamylglycine with a melting point of 141.5°C. (reported m.p. 143°C. (15)). N-Cbzo-α-L-glutamyl-L-glutamic acid diethyl ester, prepared as described by Bergmann (5,11), was saponified with *N* sodium hydroxide for 45 min. The mixture was acidified with hydrochloric acid and N-cbzo-α-L-glutamyl-L-glutamic acid was recovered as a precipitate. It sintered at 140–145°C., m.p. 174°C. (reported to sinter at 145°C., m.p. 176°C. (5)). Hydrogenolysis of 2.8 gm. of N-cbzo-α-L-glutamyl-L-glutamic acid diethyl ester in 25 ml. of absolute ethanol, 2 ml. of glacial acetic acid, and 0.1 gm. of platinum oxide yielded α-L-glutamyl-L-glutamic acid diethyl ester. The catalyst was removed by filtration and the solvent evaporated *in vacuo*. After recrystallization from ethanol it melted at 136–137°C. (reported m.p. 137°C. (5)). α-L-Glutamyl-L-glutamic acid was prepared by hydrogenolysis of N-cbzo-α-L-glutamyl-L-glutamic acid in glacial acetic acid. The residue was taken up in a minimum

* *The term "carbobenzoxy" is abbreviated as "cbzo" throughout this report.*

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volume of water, two or three volumes of ethanol were added, and after it had stood for two days in the cold the precipitate was collected. M.p. 190°C. (reported m.p. 205°C. (5), 184–185°C. (9)).

*Methods for Hydrolysis Study*

Estimation of peptidase activity was done by observing the rate of liberation of free amino acids from buffered solutions of the synthetic substrates under controlled conditions of temperature. Digestion mixtures contained 1.0 ml. of substrate solution (0.125 *M*), 0.50 ml. of buffer solution (1 *M*), and 0.75 ml. of enzyme solution (dried culture medium diluted to one-half original volume). Cobalt chloride (0.01 *M*, 0.25 ml.) was also added to give a total volume of 2.5 ml. The mixture was incubated in a water bath controlled at 37°C. ± 0.05°C. Aliquots of 0.20 ml. were removed immediately after mixing and at convenient time intervals thereafter. These were analyzed for free amino acids according to a ninhydrin procedure described by McConnell (20). Two drops of dilute sulphuric acid were added to the sample of digestion mixture in the microdiffusion cells to help lower the pH of the heavily buffered solutions to the required value. The increase in free amino acids during the digestion was expressed in terms of percentage hydrolysis of the peptide bond in the substrate taken. The increase in free amino acid during the digestion was assumed to arise from the hydrolysis of peptide bonds. Hydrolysis of a peptide bond in a dipeptide would yield two free amino acid molecules whereas hydrolysis of a monosubstituted dipeptide would yield only one amino acid.

## EXPERIMENTAL RESULTS AND DISCUSSION

*Demonstration of Peptidase Activity*

Eight organisms previously shown to produce appreciable amounts of proteo-

TABLE I

DEMONSTRATION OF PEPTIDASE ACTIVITY IN EXTRACELLULAR FUNGAL PROTEASES

| | | PERCENT HYDROLYSIS | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | ENZYME | | | | | | | |
| SUBSTRATE | APPROX. pH | PRL 26 | PRL 79 | PRL 86 | PRL 92 | PRL 316 | PRL 319 | PRL 369 | PRL 376 |
| α-L-glutamyl-L-glutamic Acid | 3.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| N-cbzo-α-L-glutamyl-L-glutamic Acid | 5.5 | 9.6 | 76 | 97 | 45 | 3.0 | 40 | 51 | 1.0 |
| N-cbzo-α-L-glutamyl-DL-alanine | 7.5 | 16 | 23 | 40 | 9.6 | 18 | 0 | 0 | 7.6 |
| α-L-glutamyl-L-glutamic Acid diethyl Ester | 10.5 | 32 | 7.8 | 21 | 10 | 19 | 7.1 | 25 | 6.7 |
| N-cbzo-α-L-glutamyl-glycine | 11.0 | 33 | 18 | 2.1 | 10 | 28 | 28 | 24 | 10 |

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lytic activity (13) were tested for their ability to hydrolyze a number of peptides and their derivatives. Activity toward the synthetic materials was fairly general. The observations are illustrated in Table I and are a selection of results obtained after digestion periods of 24 hr.

The data in Table I may be supplemented by noting that in 20 hr. a preparation of PRL 79 in phosphate buffer at pH 7.6 was found to hydrolyze 30% of the N-cbzo-glycylglycine and 4.3% of the glycylglycine. Low pH (3.5) probably accounts, in part, for the observed absence of activity toward α-L-glutamyl-L-glutamic acid. At least some of the preparations digested the latter slowly above pH 4, and PRL 26, PRL 86, and PRL 369 in faintly alkaline solution (pH 7.2–7.4) caused 5.6, 9.5, and 6.5% hydrolysis respectively in 24 hr. at 37°C.

Table I shows that each enzyme used was capable of digesting one or more of the substrates to the extent of at least 10% in 24 hr. Since the survey does not constitute a study of the many variable conditions, it is probable, that with the use of optimum conditions, much greater activity would be observed. The activity toward all of the substrates of the type N-cbzo-α-L-glutamyl-L-glutamic acid, α-L-glutamyl-L-glutamic acid diethyl ester, and α-L-glutamyl-L-glutamic acid indicates the presence of carboxypeptidase, aminopeptidase, and dipeptidase (3). Berger, Johnson, and Peterson (2) had observed similar peptidases in mycelium extracts, and it is therefore not surprising that they also occur as extracellular proteases.

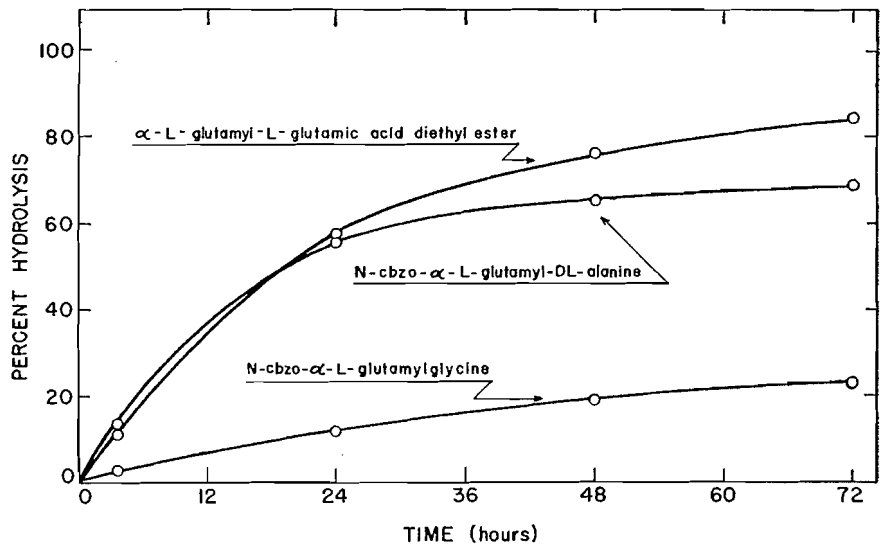



FIG. 1. The effect of time on the hydrolysis of some synthetic substrates by PRL 86.

Fig. 1 is typical of results obtained when the progress of the digestion was followed for several days. The hydrolyses were done at 37°C. in phosphate buffer pH 6. The N-cbzo-α-L-glutamylglycine was hydrolyzed very slowly at this pH; only about 23.8% of it being consumed during a 72 hr. period. In the early stages of digestion the rates of degradation of N-cbzo-α-L-glutamyl-DL-alanine and of α-L-glutamyl-L-glutamic acid diethyl ester were practically the same. After 50 to 60% of these materials had been hydrolyzed it became

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apparent that the rate of liberation of amino acids from the alanine-containing peptides was decreasing rapidly. At the end of 72 hr. only 69.5% of N-cbzo-α-L-glutamyl-DL-alanine had reacted, whereas over 85% of the α-L-glutamyl-L-glutamic acid diethyl ester had been hydrolyzed. Although a number of alternative explanations are possible it is interesting to note that the rapid decrease in hydrolysis rate of the diastereoisomeric mixture is in harmony with previous observations that optical isomers react at different rates in the presence of enzyme catalysts (6, 7). The observed hydrolysis of 69.5% for the peptide derivative of DL-alanine nevertheless shows that at least some of both isomers was being hydrolyzed.

*Studies with N-Substituted Dipeptides*

The experiments recorded so far have suggested that the extracellular peptidase systems of the molds used are of considerable complexity. It is evident that to understand the effects of variables such as pH and temperature, separate consideration of each enzyme–substrate system is required. Attention was therefore directed toward a somewhat more detailed study of the action of PRL 86 and PRL 369 on some N-substituted dipeptides.

The results of measurement of the effect of pH on three such enzyme–substrate combinations are given in Fig. 2. The digestions were carried out for

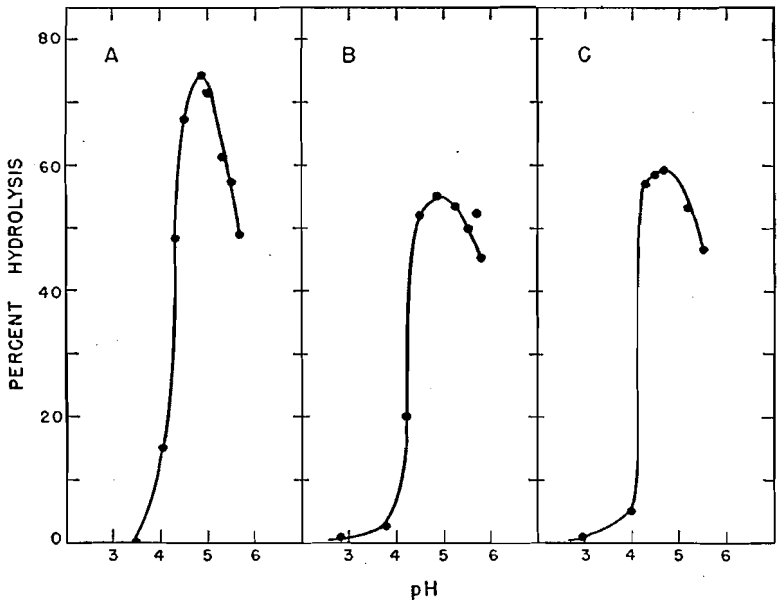



FIG. 2. The effect of pH on the activity of fungal peptidase.
A. N-Cbzo-α-L-glutamyl-L-glutamic acid digested with PRL 86.
B. N-Cbzo-α-L-glutamyl-DL-alanine digested with PRL 86.
C. N-Cbzo-α-L-glutamyl-DL-alanine digested with PRL 369.

24 hr. in phthalate buffer using methods outlined. The evidence of a fairly sharp optimum pH at pH 4.8 to 4.9 is of particular interest. Previous reports of peptidase activity would suggest maximum activity nearer neutrality (18, 21, 4). It is also of interest to note that the proteases were previously reported to have maximum activity above pH 7 (19, 23). The observed low activity at neutral or

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slightly alkaline pH would appear to be characteristic of the carboxypeptidase component and of the particular substrates used rather than being a general property of the fungal protease systems.

Some experiments on pH effect with a phosphate buffer showed that the nature of the buffer itself had an influence on activity. The per cent hydrolysis in 24 hr. obtained with PRL 86 acting on N-cbzo-α-L-glutamyl-L-glutamic acid and on N-cbzo-α-L-glutamyl-DL-alanine was only about three quarters as much with the phthalate buffer as when a phosphate buffer was used at the same pH. As only a very narrow pH range was common to both these buffers, good quantitative comparison was difficult. The shape of the curve with phosphate buffers at different pH values was, so far as could be observed, the same as with the phthalate buffer and suggests maximum digestion rates near or below pH 5.

The hydrolysis rates of some enzyme–substrate combinations were followed for about 14 hr. at three different temperatures. Fig. 3 contains the results for N-cbzo-α-L-glutamyl-DL-alanine when hydrolyzed with PRL 86. Since the lines are approximately linear during the first four or five hours, the slopes were used to characterize the digestion rates at each temperature. The slopes of the lines at 36.5°C., 25°C., and 14.5°C. were estimated from the curves of Fig. 3 as being 4.35, 2.20, and 1.1% hydrolysis per hour.

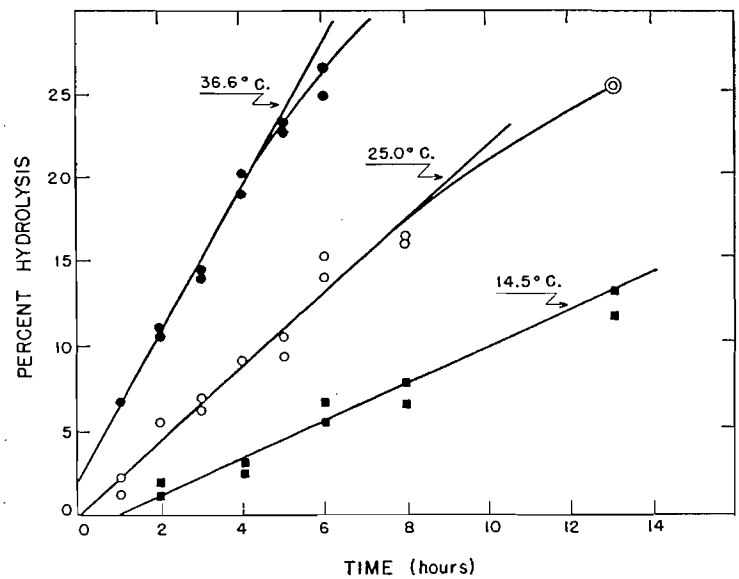



FIG. 3. The effect of temperature on the action of PRL 86 on N-cbzo-α-L-glutamyl-DL-alanine.

A linear relation was observed between the reciprocal of the absolute temperature and the logarithm of the slopes. The activation energy as estimated from these results by conventional methods would be about 11,000 calories per mole. Similar curves were obtained using PRL 369 to digest N-cbzo-α-L-glutamyl-L-glutamic acid, at the three temperatures. An activation energy near 15,000 cal. was found. Results with PRL 86 and N-cbzo-α-L-glutamyl-L-glutamic acid were more erratic and by the slopes of the lines an Arrhenius plot with some deviation

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from linearity was noted. It was estimated however that the activation energy for the temperature range used was somewhere between 10,000 cal. and 13,000 cal. per mole. The activation energies obtained in this work are of the same order as other values previously reported for the enzymatic hydrolysis of proteins and synthetic protease substrates. Casein at pH 8.1 and benzoyl-L-arginine amide at pH 7.8 when hydrolyzed with trypsin have been reported to give activation energies of 15,400 (22) and 14,900 (10) respectively. Similarly chymotrypsin hydrolysis of casein at pH 7.7 and of benzoyltyrosylglycyl amide at pH 7.7 gave activation energies of 12,000 (1) and 10,500 (10) respectively.

Attempts were made to compare the crude mold proteases with pancreatin (Takamine Laboratory, Clinton, N.S.) and with pepsin (Nutritional Biochemicals, Cleveland, Ohio) with regard to rate of hydrolysis of the synthetic substrates. Although the mold enzymes were found to attack the synthetic substrates, no digestion by pepsin of N-cbzo-α-L-glutamyl-L-glutamic acid, α-L-glutamyl-L-glutamic acid diethyl ester, or N-cbzo-α-L-glutamyl-DL-alanine was observed either at pH 2.5 or 4.6. The pepsin solution used for addition to the digestion mixture contained 20 mgm. per ml. Results with the same concentration of pancreatin were not reproducible, probably because considerable amounts of free amino acids were found to be liberated from the pancreatin preparation itself. Although quantitative data are not reported for pancreatin, it appeared to have no greater activity toward these substrates than the mold enzyme preparations. The following observations obtained with the substrate poly-γ-methyl-L-glutamate* are of interest. PRL 369 at pH 5.7 liberated about 7.8% of the glutamic acid from a 0.57% dispersion of the polymer in 20 hr. PRL 86 at pH 5.7 and pepsin at pH 3 liberated no measurable amount of glutamic acid and little or no hydrolysis occurred with pancreatin at pH 8.5. This is in agreement with the results of Blakley *et al.* (8) who found in addition slight hydrolysis of a copolymer of polylysine and glutamic acid and greater hydrolysis with the more complex copolymer of polylysine – glutamic acid.

No evidence was obtained to indicate that cobalt was necessary as an activator for the mold peptidases. Its use in all the digestion mixtures was only justified as a precaution to help ensure that maximum activity was obtained. Ions such as $Zn^{++}$, $Mn^{++}$, and $Mg^{++}$ which are also known to take part in the action of metal peptidase were not added. The Klim-containing medium in which the enzymes were produced should supply requirements for these ions.

Much additional work is required to develop a more complete picture of the nature of the extracellular proteolytic systems produced by the molds. The present work suggests that they are complex mixtures of enzymes. The experiments on the effect of pH, although suggesting a rather unique and characteristic pH optimum toward the substrates available, fail to distinguish between the carboxypeptidases from the different molds and should be repeated on a variety of different proteases. Similarly the results from the study on temperature effects tend to suggest a similarity rather than differences between the extra-

* *Supplied by Mr. L. Wiseblatt, University of Saskatchewan. Average chain length: about eight glutamic acid residues.*

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cellular carboxypeptidases of the molds used. The information obtained through this work should also prove useful in attempts to fractionate different types of proteolytic activity in the crude preparations. It is probable that further work would be most profitable if done with preparations which had been at least partially purified.

ACKNOWLEDGMENT

One of us (J. A. T.) wishes to acknowledge financial assistance provided by the National Research Council of Canada.

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# THE POTENTIOMETRIC TITRATION OF CARBONATE SOLUTIONS CONTAINING URANIUM[1]

By J. Halpern

ABSTRACT

Potentiometric titrations with hydrochloric acid were carried out on standard sodium carbonate solutions containing varying amounts of uranyl nitrate. The results confirmed the fact that uranium is present in such solutions as the complex ion $UO_2(CO_3)_3^{\equiv}$. It was found that only the free $CO_3^{--}$ is titrated with $H^+$ up to the first end point at pH = 8.2. The complex ion is very stable and is decomposed only on further addition of acid when the complexed $CO_3^{--}$ along with the $HCO_3^-$ in the solution is converted to carbonic acid before the second end point. The pH at which the second end point occurs is lowered from its normal value of 4.0 in the presence of uranium. This effect is attributed to hydrolysis of the $UO_2^{++}$ ion. The necessary corrections for determining carbonate and bicarbonate in the presence of uranium are given.

## INTRODUCTION

Carbonate solutions are commonly used to extract uranium from its ores (2, 3). The determination of the $CO_3^{--}$ and $HCO_3^-$ concentrations in the leach solutions containing uranium, by the normal procedure (5) of titrating with standard hydrochloric acid to consecutive end points at pH values of 8.2 and 4.0, is complicated by the formation of a complex ion (6) between $UO_2^{++}$ and $CO_3^{--}$ as follows:

$$UO_2^{++} + 3\ CO_3^{--} \rightarrow UO_2\ (CO_3)_3^{\equiv}. \qquad [1]$$

The interpretation of the titration results depends on whether the $CO_3^{--}$ tied up in this complex is converted to $HCO_3^-$, along with the free $CO_3^{--}$, before the first end point, or whether the complex is sufficiently stable to prevent this reaction from occurring until a lower pH is reached.

To obtain quantitative information on this point, a study was made in which titration curves were obtained for a series of solutions containing known amounts of $UO_2^{++}$ and $CO_3^{--}$.

## EXPERIMENTAL

### *Materials*

Solutions were prepared by dissolving weighed amounts of reagent grade $UO_2(NO_3)_2.6H_2O$ and sodium carbonate in distilled water.

### *Titration Procedure*

Aliquots of solutions of known composition were titrated with standard hydrochloric acid and the pH change followed with a Beckman Model H2 pH meter. Titration curves were plotted and end points corresponding to maxima in the slopes of these curves were determined in the usual manner (4). All titrations were carried out at room temperature (20°C.).

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## RESULTS

A series of five solutions containing $4.71 \times 10^{-2}$ M./l. sodium carbonate and amounts of $UO_2(NO_3)_2$ ranging from zero to $7.13 \times 10^{-3}$ M./l. were titrated with 0.0984 *N* hydrochloric acid. The titration curves are shown in Fig. 1. The volumes of hydrochloric acid corresponding to the first and second end points, for each solution, are given in Table I along with the pH values at which these end points occurred.

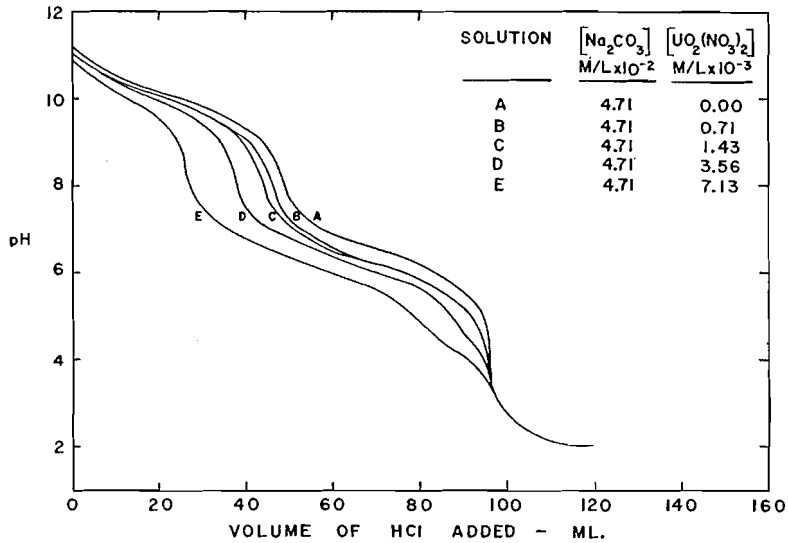



FIG. 1. Titration curves for sodium carbonate solutions containing varying amounts of $UO_2(NO_3)_2$. One hundred milliliter samples titrated with 0.0984 *N* hydrochloric acid.

TABLE I

TITRATION OF VARIOUS SOLUTIONS OF $Na_2CO_3$ AND $UO_2(NO_3)_2$ WITH 0.0984 *N* HCl
VOLUME OF EACH SOLUTION TITRATED (*V*)—100 ML.

| Solution | Total concentrations (M./l.) | | | First end point | | | Second end point | | |
|---|---|---|---|---|---|---|---|---|---|
| | $[CO_3^{--}]_T$ | $[HCO_3^-]$ | $[UO_2^{++}]$ | Vol. HCl($V_1$), ml. | $\Delta V_1$, ml. | pH | Vol. HCl($V_2$), ml. | $\Delta V_2$, ml. | pH |
| A | $4.71 \times 10^{-2}$ | 0.0 | 0.0 | 48.0 | 0 | 8.25 | 96.0 | 0 | 4.0 |
| B | " | " | $7.13 \times 10^{-4}$ | 46.0 | −2.0 | 8.1 | 96.0 | 0 | 3.8 |
| C | " | " | $1.43 \times 10^{-3}$ | 43.5 | −4.5 | 8.2 | 96.0 | 0 | 3.8 |
| D | " | " | $3.56 \times 10^{-3}$ | 37.5 | −10.5 | 8.2 | 97.0 | 1.0 | 3.4 |
| E | " | " | $7.13 \times 10^{-3}$ | 26.5 | −21.5 | 8.25 | 97.0 | 1.0 | 3.2 |

As the concentration of $UO_2^{++}$ in the solution is progressively increased from zero to $7.13 \times 10^{-3}$ M./l. the following effects are noted.

1. The volume of hydrochloric acid corresponding to the first end point (at pH = 8.2) is reduced from 48.0 ml. to 26.5 ml.

2. The total amount of hydrochloric acid corresponding to the second end point remains substantially unchanged at 96.5 ± 0.5 ml.

3. While the pH at which the first end point occurs remains substantially

unchanged at 8.2, the pH of the second end point is progressively lowered from 4.0 to 3.2.

## DISCUSSION

These results confirm the fact that the uranium is present quantitatively in the solutions examined as the complex ion, $UO_2(CO_3)_3^{\equiv}$. The complex appears to be very stable and is not decomposed at the equivalence point for the conversion of free $CO_3^{--}$ to $HCO_3^-$. For a solution containing a given total concentration of $CO_3^{--}$, the shift in the first end point, $\Delta V_1$, which marks this equivalence point, is thus related to the concentration of uranium, $[UO_2^{++}]$, as follows:

$$-\Delta V_1 = 3V[UO_2^{++}]/N \qquad [2]$$

where $V$ is the volume (ml.) of the sample being titrated, and $N$ is the normality of the hydrochloric acid.

This is confirmed in Fig. 2 where the experimental points for $-\Delta V_1$, taken from Table I, are seen to fall within experimental accuracy on a plot of $3V[UO_2^{++}]/N$.

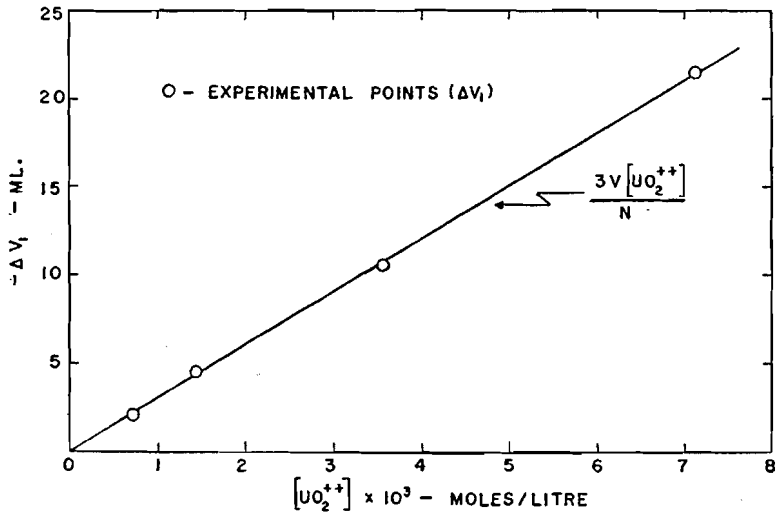



FIG. 2. Effect of $UO_2^{++}$ concentration on the first end point.

The first end point in the titration, at pH 8.2, thus corresponds to the equivalence point of the reaction,

$$(CO_3^{--})_F + H^+ \rightarrow HCO_3^-. \qquad [3]$$

The titration results also demonstrate that the $UO_2(CO_3)_3^{\equiv}$ ion does break down before the second end point at pH 4 is reached and the $CO_3^{--}$ liberated is converted to carbonic acid. The second end point thus corresponds to the equivalence points of the following reactions:

$$HCO_3^- + H^+ \rightarrow H_2CO_3, \qquad [4]$$

$$UO_2(CO_3)_3^{\equiv} + 6H^+ \rightarrow UO_2^{++} + 3\,H_2CO_3. \qquad [5]$$

Thus the total amount of hydrochloric acid required to give the second end point is independent of the $UO_2^{++}$ concentration. This is also confirmed by the results in Table I.

The concentrations of $CO_3^{--}$ and $HCO_3^-$ in a solution containing uranium

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are thus related to the first and second titration end points, $V_1$ and $V_2$, by the following equations:

$$[CO_3^{--}]_F = (V_1/V) \times N, \quad [6]$$

$$[CO_3^{--}]_T = (V_1/V) \times N + 3\,[UO_2^{++}], \quad [7]$$

$$[HCO_3^-] = [(V_2 - 2V_1)/V] \times N - 6\,[UO_2^{++}], \quad [8]$$

where $[CO_3^{--}]_F$ and $[CO_3^{--}]_T$ are the concentrations of free and total $CO_3^{--}$ respectively.

The corrected values of $[CO_3^{--}]_F$, $[CO_3^{--}]_T$, and $[HCO_3^-]$, calculated from the titration results using these relations, are given in Table II and are seen to agree within experimental accuracy with the known values.

TABLE II

CALCULATION OF $[CO_3^{--}]$ AND $[HCO_3^-]$ FROM TITRATION RESULTS

| Solution | $[UO_2^{++}]$, M./l. | True concentration (M./l.) | | | Apparent conc. (M./l.) | Corrected concentration (M./l.) | | |
|---|---|---|---|---|---|---|---|---|
| | | $[CO_3^{--}]_T$ | $[CO_3^{--}]_F$* | $[HCO_3^-]$ | $[HCO_3^-]$ | $[CO_3^{--}]_F$ | $[CO_3^{--}]_T$ | $[HCO_3^-]$ |
| A | 0.0 | $4.71 \times 10^{-2}$ | $4.71 \times 10^{-2}$ | 0.0 | 0.0 | $4.71 \times 10^{-2}$ | $4.71 \times 10^{-2}$ | 0 |
| B | $7.13 \times 10^{-4}$ | " | $4.50 \times 10^{-2}$ | " | $0.36 \times 10^{-2}$ | $4.52 \times 10^{-2}$ | $4.73 \times 10^{-2}$ | $-5 \times 10^{-4}$ |
| C | $1.43 \times 10^{-3}$ | " | $4.28 \times 10^{-2}$ | " | $0.88 \times 10^{-2}$ | $4.31 \times 10^{-2}$ | $4.74 \times 10^{-2}$ | $2 \times 10^{-4}$ |
| D | $3.56 \times 10^{-3}$ | " | $3.64 \times 10^{-2}$ | " | $2.17 \times 10^{-2}$ | $3.69 \times 10^{-2}$ | $4.75 \times 10^{-2}$ | $2 \times 10^{-4}$ |
| E | $7.13 \times 10^{-3}$ | " | $2.57 \times 10^{-2}$ | " | $4.37 \times 10^{-2}$ | $2.58 \times 10^{-2}$ | $4.71 \times 10^{-2}$ | $5 \times 10^{-4}$ |

* *Calculated from the equation* $[CO_3^{--}]_F = [CO_3^{--}]_T - 3\,[UO_2^{++}]$.

If the corrections for the formation of the $UO_2(CO_3)_3^{\equiv}$ complex are not applied, and the titration results are interpreted in the usual way, each complexed $CO_3^{--}$ ion is counted as two $HCO_3^-$ ions since it is titrated only at the second end point. As shown in Table II, this leads to an erroneously high apparent concentration of $HCO_3^-$.

*Effect of $UO_2^{++}$ on the pH of the End Points*

The progressive lowering of the pH of the second end point from 4.0 to 3.2 in the presence of uranium can be attributed to the hydrolysis of the uranyl ion (1), exemplified in the following equations:

$$UO_2^{++} + HOH \rightarrow UO_2(OH)^+ + H^+, \quad [9]$$

$$2UO_2^{++} + HOH \rightarrow (UO_2)_2OH^{+++} + H^+. \quad [10]$$

At the first end point, the uranium is still largely tied up in the form of carbonate complex ions, as shown earlier, and there is an insufficient concentration of free $UO_2^{++}$ to reduce the pH appreciably from the normal value of 8.2 through similar hydrolysis.

The lowering of the pH of the second end point constitutes a further possible source of error in the determination of $CO_3^{--}$ in the procedure commonly followed in routine determinations, i.e., that of titrating to predetermined constant end points (i.e. at pH of 8.2 and 4.0). The titration curves in Fig. 1 show that the second end point, estimated by this procedure, may be subject to considerable error when uranium is present.

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# AN EFFECT OF POLYMERIZATION TEMPERATURE ON THE HUGGINS CONSTANT $k'$ FOR A DIENE POLYMER[1]

By L. H. Cragg and G. R. H. Fern[2]

ABSTRACT

Samples of poly(butadiene-*co*-styrene) were polymerized in redox systems at 5° and −18° C., the recipes being such as to yield samples similar in composition, in percentage conversion, and in intrinsic vistex to those prepared at 50°, 40°, 30°, and 15° C. for an earlier study. The two samples were carefully fractionated and the viscosity functions $[\eta]$, $\beta$, and $k'$ were determined for each of the fractions. $k'$ was shown to be the same for all the fractions of a given sample—an indication that there is little or no branching at these low temperatures. Comparison with the earlier results reveals, however, that for unbranched species $k'$ increases as the temperature of polymerization decreases, from $0.32_7 \pm 0.008$ at 50° to $0.37_0 \pm 0.005$ at −18° C. This increase in $k'$ is attributed to an increase in the *trans*-1,4-content of the polymer.

## INTRODUCTION

In earlier papers, evidence was presented that the Huggins slope constant $k'$ (8) can be a useful measure of branching in high polymers (10, 5, 3, 4). When polymers containing branched species were carefully fractionated, the values of $k'$ obtained with the fractions decreased regularly with the intrinsic viscosity of the fractions, finally reaching, with the lower fractions, a constant value $\underline{k}'$ characteristic of linear species of the same polymer (5, 3, 4). When samples of poly(butadiene-*co*-styrene), prepared at several different temperatures but alike in other respects, were studied in this way, the extent of branching was found to decrease with decreasing polymerization temperature. In other words, as the temperature of polymerization was lowered, more of the fractions were found to have a $k'$ value equal to the base value $\underline{k}'$ common to unbranched species. In fact, when the polymerization temperature was 15°C., all of the fractions had the same $k'$. It was noted, however, that this constant value of $k'$ at 15°C. was a little higher than the base value at 30°C. The increase was slight but too definite to be ignored. Accordingly, the investigation has been extended to still lower temperatures. This paper reports evidence, so obtained, that the effect is real and significant.

## EXPERIMENTAL

The apparatus and procedure have already been described in detail (4). With the exception of the polymers, the materials (solvents, etc.) for this investigation were the same as those used earlier (4). The two *polymer* samples were prepared in much the same way as before, the only difference being the temperature of polymerization—5°C. and −18°C.—and the slight modifications (6) in the recipe that were required to make the intrinsic vistex, the percentage

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*Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ont. Financial assistance was received, in the form of a research grant, from the National Research Council of Canada, and, in the form of a scholarship, from the Research Council of Ontario.*

[2] *Present address: Imperial Oil Co. Ltd., Sarnia, Ont.*



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conversion, and the time of reaction nearly the same in these as in the earlier samples, namely, 1.9–2.0 dl./gm., 60–62%, and 17–18 hr., respectively.

## RESULTS AND DISCUSSION

From each of the samples eight fractions of about equal size—each approximately 1/15th of the whole sample—were obtained by careful fractionation. For each of these fractions, values of $[\eta]$, $\beta$ (the slope constant in the Fuoss equation $(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c$ (12)), and $k'$ were obtained as before.

TABLE I

DATA FOR FRACTIONS OF THE RUBBER POLYMERIZED AT 5° C. (RF 17)
$W$ = 5.048 gm., $C$ = 1.009 gm./100 ml., $W'$ = 4.64 gm.

| Fraction | $w$ (gm.) | $w_x$ ($\times 10^2$) | $[\eta]$ | $\beta$ | $k'$ |
|---|---|---|---|---|---|
| 1 | $0.270_4$ | 5.82 | $3.25_1$ | $0.13_3$ | $0.36_7$ |
| 2 | $0.316_4$ | 6.81 | $2.81_0$ | $0.12_7$ | $0.37_3$ |
| 3 | $0.357_7$ | 7.70 | $2.41_3$ | $0.13_2$ | $0.36_8$ |
| 4 | $0.301_9$ | 6.50 | $2.27_7$ | $0.13_4$ | $0.36_6$ |
| 5 | $0.411_5$ | 8.86 | $2.03_7$ | $0.13_5$ | $0.36_5$ |
| 6 | $0.366_3$ | 7.89 | $1.78_8$ | $0.12_8$ | $0.37_2$ |
| 7 | $0.265_2$ | 5.71 | $1.61_7$ | $0.13_7$ | $0.36_3$ |
| 8 | $0.361_2$ | 7.78 | $1.49_2$ | $0.13_4$ | $0.36_6$ |
| | | | | Average | $0.36_8$ |

TABLE II

DATA FOR FRACTIONS OF THE RUBBER POLYMERIZED AT −18° C. (RF 18)
$W$ = 4.949 gm., $C$ = 0.990 gm./100 ml., $W'$ = 4.55 gm.

| Fraction | $w$ (gm.) | $w_x$ ($\times 10^2$) | $[\eta]$ | $\beta$ | $k'$ |
|---|---|---|---|---|---|
| 1 | $0.256_5$ | 5.63 | $3.85_0$ | $0.12_9$ | $0.37_1$ |
| 2 | $0.283_1$ | 6.22 | $2.91_1$ | $0.12_8$ | $0.37_2$ |
| 3 | $0.324_3$ | 7.12 | $2.61_0$ | $0.13_2$ | $0.36_8$ |
| 4 | $0.334_4$ | 7.34 | $2.36_4$ | $0.13_0$ | $0.37_0$ |
| 5 | $0.283_3$ | 6.22 | $2.17_7$ | $0.12_7$ | $0.37_3$ |
| 6 | $0.247_7$ | 5.44 | $1.98_2$ | $0.12_9$ | $0.37_1$ |
| 7 | $0.257_1$ | 5.65 | $1.83_0$ | $0.13_4$ | $0.36_6$ |
| 8 | $0.317_2$ | 6.97 | $1.66_0$ | $0.13_2$ | $0.36_8$ |
| | | | | Average | $0.37_0$ |

The results are given in Tables I and II. In these tables $W$ is the total weight of the original rubber sample, $W'$ is the weight of rubber in $W$ (assuming 8% of the original sample to be materials extractable by the ethanol–toluene azeotrope), $C$ is the original concentration of the solution from which the fractions were separated, $w$ is the weight of a fraction, and $w_x$ is its weight fraction.

All the fractions of the polymer prepared at 5°C. have the same value of $k'$ within the limits of precision, namely, $0.36_8 \pm 0.005$. Similarly, for the fractions of the polymer prepared at −18°C. there is a characteristic value of $k'$, $0.37_0 \pm 0.005$. There is, therefore, no evidence of branching in these samples and hence

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the conclusion that there is little or no branching in cold rubber prepared at or below 15°C. receives additional support.

These two values of $k'$, $0.36_8$ and $0.37_0$, do not differ significantly from each other, but they do differ significantly from the corresponding values for the polymers prepared at the higher temperatures. For example, $k'$ for the 15°C. polymer is $0.34_3$ (the values obtained for the individual fractions being $0.34_2$, $0.35_2$, $0.34_4$, $0.34_3$, $0.33_9$, $0.34_0$). The difference is, therefore, much too great to attribute to experimental error. That this increase in $k'$ with decreasing temperature of polymerization is a real effect is more evident still when all the data available are considered, as in Fig. 1, where $k'$ is plotted against the polymeriza-

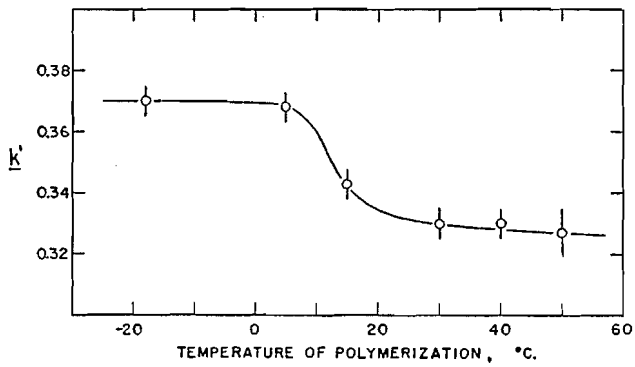



FIG. 1. Variation of $\underline{k}'$ with temperature of polymerization.

tion temperature. (For each of the higher temperatures at which branched species are formed, the value of $k'$ plotted is $\underline{k}'$, the "base value" characteristic of the unbranched species (4). In the figure the length of a vertical line indicates roughly the precision of the $\underline{k}'$ value.)

Since all viscosity measurements were made in the same solvent, benzene, and at the same temperature, 25.0°C., the observed differences in $k'$ must be due to differences in the polymer molecules themselves. They cannot be due to changes either in molecular weight or in molecular weight distribution, because the measurements of $k'$ were made on fractions, and in a given sample $k'$ was independent of molecular weight. They cannot be due to branching, for it has been shown that branching decreases with decreasing polymerization temperature, and an increase in $k'$ would indicate an increase in branching. Moreover, all the evidence shows that branching does not affect all fractions to the same degree (3, 4, 5).

They must, therefore, be due to changes in the structure of the molecular chain. But again we can eliminate most of the possibilities. Differences in composition of the molecules—i.e., in the ratio of butadiene to styrene units—cannot be responsible. Beatty and Zwicker (2) have shown that for such polymers as these the proportion of styrene is the same, within experimental error, for all the fractions of a polymer sample and differs only slightly for polymers prepared at different temperatures, averaging 21.7 at 50°C. and 22.8 at −18°C. Yet, the fractions of a sample prepared at 0°C. from a recipe in

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which the monomer ratio was 85:15 gave $k'$ values of $0.037_0$,* which is just what would be expected of a sample prepared at that temperature from a 72 : 28 recipe, and certainly this change in monomer ratio would cause a greater difference in the proportion of styrene in the molecules than would the change in polymerization temperature.

There remain three other possibilities, each related to a form of chain isomerism. In any vinyl polymer a type of isomerism analogous to rotational isomerism can occur (11). Species with different spatial arrangements of successive substituent groups on the polymethylene chain may have widely differing properties (13). Indeed, the decrease in $k'$ with increasing polymerization temperature that was observed in polystyrene by Alfrey, Bartovics, and Mark (1) was attributed by Huggins (9) to such differences in chain configuration. This cannot, however, be the cause of the changes in $k'$ that we have observed. In the polymer samples which we studied the proportion of bound styrene would be about 22% by weight (2, 7) so that successive styrene residues would, on the average, be separated from each other by six or seven butadiene residues. Hence, the arrangement of substituents in the styrene portions of the chain would have little or no effect on the properties of the polymer. In such polymers the types of isomerism found in diene polymers (like polybutadiene, for example) would, on the other hand, be quite significant. These are the structural isomerism resulting from the possibility of either 1,4 or 1,2 additions of the butadiene, and the geometrical (*cis–trans*) isomerism made possible by the double bond left in each 1,4 diene unit in the chain. Infrared analysis has shown that in polymers of the type we have studied the ratio of 1,4 to 1,2 units changes very slightly with the temperature of polymerization; according to Hart and Meyer the 1,2-content is 22% at 50°C. and 20% at −18°C. (7). By contrast, the ratio of *trans*-1,4 to *cis*-1,4 units increases significantly with decreasing polymerization temperature; Hart and Meyer found the *trans*-1,4-content to be 65% at 50°C. and 84% at −18°C. (7).

Of the variables known to be affected by a change in polymerization temperature, *cis–trans* isomerism, then, would seem to be the only possible source of the differences in $k'$ that we have observed. This, of course, does not prove that it is the source. But at least one would expect that any effect on $k'$ of an increase in the *trans*-1,4-content would be an increase in $k'$. More of the *trans* configuration would mean a stiffer and hence less compressible molecule. (For example, gutta percha, which is largely the *trans* isomer of polyisoprene, is much harder and less elastic than natural rubber, the *cis* form.) And of two polymer species in solution, the one whose molecules are less compressible should give the higher value of $k'$.

Summing up, then, we can say that a change in the temperature of polymerization of poly(butadiene-*co*-styrene) causes a parallel change in $k'$ and in *trans*-1,4-content of the polymer chains and, further, that it is reasonable to attribute the change in $k'$ to the isomeric change.

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# ON KHELLACTONE[1]

By E. Späth,[2] W. Gruber,[3] and O. Matzke[4]

ABSTRACT

A hitherto unknown minor constituent of the seeds of *Ammi visnaga* Lam. is converted under the influence of 5% alcoholic potassium hydroxide into a compound which seems to be a coumarin. Treatment with methyl-alcoholic alkali yields a substance $C_{15}H_{16}O_5$, whereas treatment with ethyl-alcoholic alkali gives a substance $C_{16}H_{18}O_5$. Dehydrating agents convert both optically active compounds into the same optically inactive dehydration product $C_{14}H_{12}O_4$ (Substance A). The further investigations carried out with Substance A were: oxidation, after methylation, which yielded α-hydroxyisobutyric acid; fusion with potassium hydroxide, which gave phloroglucinol. On treatment with diluted caustic alkalies two definite products, $C_{10}H_6O_5$, probably an acid, and $C_{11}H_8O_4$, a ketone, were obtained.

The main constituents of the umbelliferous plant *Ammi visnaga* Lam., khellin, visnagin, and chellol-glucoside, have been thoroughly investigated chemically as well as pharmacologically (3, 4, 5, 6) but only a few investigations of minor constituents have been published (3).

Recently Steinegger (7) extracted the seeds of *Ammi visnaga* Lam. cultivated in Switzerland. He separated 1,2- and 1,4-pyrones carefully and found a previously unknown coumarin $C_{17}H_{18}O_6$, m.p. 187–188°. Some time ago we worked up the ether extract of Egyptian Chellah seeds and isolated a new substance, which also seemed to be a coumarin. Owing to difficulties in getting the necessary raw material we could not elucidate the structure of this coumarin, khellactone, completely. However, since khellactone has a vasodilator action similar to that of khellin, the results are published in order to encourage further investigations.

The crude ether extract was washed with 0.5% aqueous potassium hydroxide to remove free acids and phenols and then evaporated. The residue underwent the so-called "lactone separation", in which lactones, esters, etc. are converted into salts of the corresponding acids by treatment with alcoholic potassium hydroxide after which the acids are again set free with hydrochloric acid. Hydroxy acids, originating from lactones, give ring closure when treated with hydrochloric acid and thus form neutral lactones which are easily separated from acids derived from esters, e.g. glycerides. The diluted and acidified saponification mixture was allowed to stand for several hours and then extracted with a large amount of ether. To avoid emulsification, the ethereal solution was percolated with 0.5% aqueous potassium hydroxide solution until an acidified sample of the percolate showed no more precipitation. The residue on evaporation of the ether was redissolved in ether, percolated a second time in the same way, and finally purified by vacuum distillation and recrystallization; yield 0.06%, white crystals, dimorphous, lower m.p. 137–138°C., higher m.p. 167–168°C.

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*Contribution from the Second Chemical Institute, University of Vienna, Austria; taken from the thesis presented by O. Matzke in partial fulfillment of the requirements for the Ph.D. degree.*
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Either form can be obtained from the melt by using the appropriate seed crystal. The analysis suggested a formula $C_{16}H_{18}O_5$; methoxyl determination (Zeisel's method) indicated one $OCH_3$-group. Determination of active hydrogen (Zerewitinoff's method) at room temperature showed about one-half hydrogen atom; but at 100°C. the result indicated one active hydrogen atom. Microhydrogenation (1) (in glacial acetic acid with palladium black) indicated one double bond; optical activity: $[\alpha]_D^{20^\circ} = -37.1$.

Since it was probable that the active hydrogen belonged to an alcoholic hydroxy-group we tried to introduce a second double bond into the molecule by dehydration. Dehydration could be effected with phosphorus pentoxide, and with still better yields using hydrobromic acid in glacial acetic acid. The resulting derivative (Substance A) was also dimorphous: lower m.p. 147°C., higher m.p. 157–158°C. It was not optically active. The presence of a second double bond in the molecule was proved by microhydrogenation (1). With *p*-nitrophenylhydrazine, A gave a derivative, m.p. 223–224°C., which we consider to be a *p*-nitrophenylhydrazone. Finally the results of the combustion suggested a gross formula $C_{14}H_{12}O_4$, obviously originating from the original compound $C_{16}H_{18}O_5$ by loss of $C_2H_6O$.

This ethyl group was probably introduced during the lactone separation, owing to the treatment with ethyl-alcoholic potassium hydroxide, and the effect of the dehydrating agent was to split it off again. In this case the alkoxyl group, found by Zeisel analysis, should be an ethoxyl instead of a methoxyl group. In order to identify it, the ester of 3,5-dinitrobenzoic acid was synthesized from the silver salt of the acid and the alkyl iodide formed in the Zeisel apparatus through cleavage of the khellactone, following the method of Furter (2). The resulting product was the ethyl ester of the 3,5-dinitrobenzoic acid.

A fresh batch was then worked up using methyl-alcoholic potassium hydroxide and gave another coumarin, m.p. 156–158°C., in 0.18% yield (based on the dry weight of seeds). The Furter method for identifying the alkoxyl group gave the methyl ester of 3,5-dinitrobenzoic acid. Methoxyl analysis (Zeisel-Vieböck method) and combustion gave values which agreed unequivocally with the gross formula $C_{15}H_{16}O_5$.

We propose for this compound the name of methyl khellactone and for the product of the first extraction the name of ethyl khellactone. These names for the two derivatives of the genuine substance are justified by the fact that both yielded Substance A when boiled with hydrobromic acid in glacial acetic acid. It is therefore clear that the alkoxyl groups were introduced during the isolation. We did not have enough "Chellah" seeds to carry out a new extraction so as to isolate the unaltered khellactone.

While the treatment with the alcoholic alkali and the dehydration with strong acids may have caused drastic changes in the khellactone molecule, nevertheless we have carried out a few experiments in the hope of getting some indications of the basic structure of the molecule.

After fusing ethyl khellactone with a mixture of sodium and potassium hydroxide, phloroglucinol was isolated, characterized as the triacetate and compared with an authentic sample.

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Again Substance A was methylated with dimethyl sulphate and potassium hydroxide and to the resulting oil in alkaline solution was added 1% potassium permanganate solution in small portions at a temperature of 30°C. until the red color was stable for some time. About 5.5 moles of oxygen was consumed. α-Hydroxyisobutyric acid was isolated and characterized as the phenylhydrazide.

Treatment of Substance A with alkali gave very interesting results. With 10% aqueous or alcoholic alkaline solutions the reaction was complex, but with 0.5–5.0% alkaline solutions in the cold two substances were formed (B and C).

Substance B, obtained by high vacuum distillation (0.005 mm. Hg, 170°C. air bath), consisted of compact prisms, m.p. 257–258°C.; easily soluble in dilute alkali bicarbonate solutions. These solutions showed strong blue fluorescence whereas the solutions in concentrated sulphuric acid showed a violet fluorescence. With ferric chloride, Substance B showed a color reaction similar to that of salicyclic acid. The combustion values agreed best with a formula $C_{10}H_6O_5$; no alkoxyl group. However, Substance B is not identical with umbelliferone-6-carboxylic acid or with umbelliferone-8-carboxylic acid, as shown by depression of the mixed melting points. It could not be decarboxylated with quinoline and copper powder (Naturkupfer "C", Kahlbaum).

Substance C was also isolated by high vacuum distillation (0.005 mm. Hg, 200° air bath), intense yellow prisms, m.p. 264°C. (dec.). It was soluble only in caustic alkali and the solutions did not show any fluorescence. With *p*-nitrophenylhydrazine in dilute acetic acid it yielded immediately a *p*-nitrophenylhydrazone. The combustion values were compatible with a gross formula $C_{11}H_8O_4$; no alkoxyl group present.

Compounds B and C are probably related in the same way as an *o*-hydroxyketone and the corresponding acid, formed in the alkaline cleavage of a γ-pyrone. Further investigations with these two cleavage products could not be carried out however, since the amounts on hand were too small.

## EXPERIMENTAL

Melting points were made on the Kofler block and are corrected.

### *Extraction and Isolation of Ethyl Khellactone*

Two thousand grams of finely ground seeds of *Ammi visnaga* Lam. were extracted with ether for 100 hr.; the ether was then decanted and made up to 2000 ml. with ether and percolated with 0.5% aqueous potassium hydroxide. The ethereal solution, now free from substances soluble in alkali, was evaporated to dryness and the lactone separation applied on the residue which was then treated with 450 ml. of 5.0% ethyl-alcoholic potassium hydroxide. The mixture was allowed to stand for two hours with occasional shaking, then diluted with 2.5 liters of water and extracted with ether. The aqueous layer was acidified to Congo red with hydrochloric acid and kept for one day after which it was exhaustively extracted with ether and again percolated with 0.5% aqueous potassium hydroxide. Evaporation of the ether left a yellowish oil with a sweet smell; the lactone separation was repeated on this oil, using only 150 ml. of 5.0% ethyl-alcoholic potassium hydroxide. The product was distilled *in vacuo* (0.03

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mm. Hg, 160–180°C. air bath) giving a crude yield of 1.268 gm. Purification by recrystallization from ether–petroleum ether under pressure gave long needles, m.p. 166–167°C. On cooling, the substance solidifies at 165°C., softens again at 150°C., and resolidifies at 138–137°C. On careful heating of the melting point apparatus both melting points, 137–138°C. and 166–167°C., can be observed. For $C_{16}H_{18}O_5$ calc.: C, 66.20, H, 6.23, $OC_2H_5$, 15.51%; found: C, 66.47, H, 6.28, $OC_2H_5$, 15.68%.

*Dehydration to Substance A*

(*a*) *With Phosphorus Pentoxide*

Ethyl khellactone (38.4 mgm.) was mixed with phosphorus pentoxide (40 mgm.) and distilled *in vacuo* (0.001 mm. Hg, 170°C. air bath). Yield: 8.4 mgm. of an oil which solidified immediately. Purification was by recrystallization from ether until a constant melting point of 157–158° was reached. This substance was dimorphous: lower m.p. 147°.

(*b*) *With Hydrobromic Acid and Glacial Acetic Acid*

Ethyl khellactone (30.0 mgm.) was refluxed for 35 min. with 0.06 ml. hydrobromic acid and 0.04 ml. glacial acetic acid at 130°, the mixture then diluted with 2 ml. water and extracted with ether. The ethereal layer was shaken with sodium bicarbonate solution and finally the ether was evaporated. The residue was sublimed *in vacuo*, 0.002 mm. Hg, 145–150°C. (air bath); yield: 7 mgm. After recrystallization from ether under pressure the melting point was 156–158°C.; the mixed melting point of this substance and the one prepared after the phosphorus pentoxide method showed no depression. For $C_{14}H_{12}O_4$ calc.: C, 68.84, H, 4.95%; found: C, 68.85, H, 5.08%.

*Identification of the Alkoxyl Group*

Ethyl khellactone (7.8 mgm.) was boiled with hydriodic acid ($d$ = 1.7) in a Zeisel apparatus, following the method of Furter. The alkyl iodide was carried over into a cooled ethereal suspension of the silver salt of 3,5-dinitrobenzoic acid. After sealing the receiver and heating for two hours in the water bath the ethereal solution was decanted from the silver halide and the solution washed with dilute aqueous potassium hydroxide, hydrochloric acid, and finally with water. After evaporation of the ether the residue was distilled in a high vacuum and had a melting point 91–92°C., not depressed by admixture with synthetic ethyl 3,5-dinitrobenzoate.

*Extraction and Isolation of Methyl Khellactone*

This was carried out as described above for the preparation of ethyl khellactone, except that for the lactone separation 5% methyl-alcoholic potassium hydroxide solution was used instead of 5% ethyl-alcoholic solution. After purification by recrystallization and sublimation *in vacuo* (0.005 mm. Hg) the melting point was 156–158°C. and the mixed melting point with ethyl khellactone showed depression. This method of isolation, using methanol instead of ethanol, gave much better yields: 200 gm. of the dry seeds gave 0.4 gm. methyl khellactone while 2000 gm. of the dry seeds gave only 1.268 gm. of ethyl khellactone.

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For $C_{15}H_{16}O_7$ calc.: C, 65.21, H, 5.84, $OCH_3$, 11.22%; found: C, 65.48, H, 5.93, $OCH_3$, 11.05, 11.33%.

*Identification of the Methoxyl Group*

This analysis was carried out according to Furter's method, as described above. The ester obtained had a melting point of 103–104°C., which was not depressed by admixture with an authentic sample of methyl 3,5-dinitrobenzoate. (The mixed melting point with the ethyl 3,5-dinitrobenzoate showed a heavy depression.)

*Cleavage of the Methyl Khellactone with Hydrobromic Acid and Glacial Acetic Acid*

Methyl khellactone (290 mgm.) was refluxed for 30 min. with 0.6 ml. of 48% hydrobromic acid and 0.6 ml. of glacial acetic acid. The reaction mixture was worked up as described for ethyl khellactone. The reaction product melted at 157–158°C. and showed no depression in a mixed melting point with Substance A derived from ethyl khellactone; yield 188 mgm., i.e. 67%. For $C_{14}H_{12}O_4$ calc.: C, 68.84, H, 4.95%; found: C, 68.80, H, 4.71%.

*p-Nitrophenylhydrazone of Substance A*

Substance A (10 mgm.) was dissolved in 1.5 ml. of 80% acetic acid and a solution of 9 mgm. of *p*-nitrophenylhydrazine in 1.5 ml. of dilute acetic acid added. The *p*-nitrophenylhydrazone separated immediately and was collected after two hours and purified by recrystallization from 5% acetic acid, m.p. 233–235°C. (decomp.).

*Microhydrogenation of Substance A*

Substance A (5.716 mgm.) was hydrogenated in 5 ml. of glacial acetic acid with 12.32 mgm. palladium black (735 mm., 19.7°C.). After four and one-half hours two molecules of hydrogen were absorbed (= 1160 $mm.^3$). The resulting tetrahydro-product was a colorless oil, which did not crystallize. The amount was too small for further investigations.

*Fusion of Ethyl Khellactone with Potassium Hydroxide*

To a homogeneous melt of 10 gm. potassium hydroxide and 10 gm. sodium hydroxide, 64 mgm. of khellactone was added and the mixture heated for 10 min. with stirring. After cooling, the reaction cake was dissolved in water, acidified with hydrochloric acid, and extracted with ether for 18 hr. After evaporation of the ether and distillation *in vacuo* (0.05 mm. Hg) the main product (130–170°C. air bath) was directly converted into the acetyl product by boiling with acetyl chloride. Purification of this product by distillation *in vacuo* (0.05 mm. Hg) gave the main product at 120–130° (air bath) consisting of white crystals, m.p. 96–98°, undepressed when mixed with a synthetic specimen of "phloroglucinol-triacetate".

*Oxidation of Substance A with Potassium Permanganate*

Substance A (97 mgm.) was dissolved in 4 ml. 5% aqueous potassium hydroxide and methylated with 1.0 ml. dimethyl sulphate and 5 ml. 10% aqueous potassium hydroxide in the usual way. Finally the reaction mixture was slightly acidified, extracted with ether, the ethereal solution exhaustively

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washed with 0.5% potassium hydroxide, the yellow alkaline solution acidified and extracted with ether. Evaporation of the ether and distillation *in vacuo* (0.05 mm. Hg) yielded 73 mgm. of a yellowish oil. This oil was dissolved in 15 ml. of 1% aqueous potassium hydroxide (the solution showed an intense yellow color), the volume brought to 50 ml., and at a temperature of 30°C. 1% aqueous potassium permanganate solution was added dropwise. After addition of 15.5 ml. of the permanganate solution (5.5 moles of oxygen) the violet color was stable for about 30 min. The oxidation mixture was worked up as usual and the resulting product finally fractionated *in vacuo* (0.05 mm. Hg): main product (4 mgm.) at a temperature of 70–85°, white, hygroscopic crystals, m.p. 73–75°C.; mixed m.p. with synthetic α-hydroxyisobutyric acid 73–75°C.

Since the melting point as well as the mixed melting point of the phenylhydrazides from the synthetic acid and our degradation product were identical, the degradation product was proved to be α-hydroxyisobutyric acid.

*Alkaline Cleavage of Substance A*

(*a*) *With 10% Alcoholic Potassium Hydroxide*

Substance A was completely decomposed, so that on acidification only resinous products were obtained.

(*b*) *With 5% Alcoholic Potassium Hydroxide*

Substance A (95 mgm.) was kept for two hours with 5% methyl-alcoholic potassium hydroxide (orange-yellow solution). The reaction mixture was then diluted with 250 ml. of water, acidified with hydrochloric acid (the color of the solution changed to yellow), kept overnight, and exhaustively extracted with ether. The ethereal solution was treated with 500 ml. of 0.5% potassium hydroxide. There was no residue on evaporation of the ether; therefore the yellow, alkaline solution was acidified to Congo red and extracted with ether. The residue was distilled *in vacuo* (0.005 mm. Hg). There were two distinct fractions; after a forerun (to 150°C.):

(1) Substance B: 160–180° (air bath), white crystals (30 mgm.); after recrystallization from ether under pressure, m.p. 256–258°. For $C_{10}H_6O_5$ calc.: C, 58.26, H, 2.93%; found: C, 58.56, H, 2.93%.

M.p. of umbelliferone-6-carboxylic acid 265–268°C.; mixed m.p. with the above substance 205–215°C.

M.p. of umbelliferone-8-carboxylic acid (dimorphous): lower m.p. 235–237°C., higher m.p. 258–260°C.; m.p. of the mixture of our degradation product with the higher melting form 220–225°C.

(2) Substance C: 190–210°C. (air bath), yellow crystals (45 mgm.); purification by recrystallization from ether under pressure, yellow plates, m.p. 263–265°C. (decomp.). For $C_{11}H_8O_4$ calc.: C, 64.72, H, 3.95%; found: C, 64.83, H, 4.07%.

(*c*) *With 0.5% Alcoholic Potassium Hydroxide*

Substance A yielded the same two products as described under (*b*); the identity was established by melting points and mixed melting points.

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# THE COMPRESSIBILITY OF GASES

## VII. ARGON IN THE TEMPERATURE RANGE 0–600° C. AND THE PRESSURE RANGE 10–80 ATMOSPHERES[1]

By E. Whalley,[2] Y. Lupien, and W. G. Schneider

ABSTRACT

The virial coefficients of argon have been measured in the temperature and pressure range described. "Best" values of the virial coefficients have been computed from all measurements reported in the literature.

The method of measurement has been adequately described previously (6, 11, 12, 15). The two pipettes had volumes of about 220 and 56 ml. The temperature was controlled to ± 0.005° and before each measurement of the pressure was maintained to ± 0.002° for 15 min. by manual adjustment of the control circuit. To maintain 0°C., it was found easier to use a cooling coil in the bath and an intermittent heater than to use ice.

The argon used in the first runs was "commercial argon" supplied by Linde Company and was stated to contain a minimum of 99.8% of argon and a maximum of 0.2% of nitrogen having a purity of 99.99%. The nitrogen was removed by passing the argon slowly several times over heated magnesium until mass spectrometer analysis showed that no nitrogen (< 0.02%) was present. Subsequently, we used "refined argon" stated to contain less than 5 p.p.m. each of hydrogen, oxygen, nitrogen, and carbon dioxide, and less than 3 p.p.m. of water. Runs performed with the two grades at the same temperature showed no difference in compressibility. Frequent checks on the purity of the gas were made during the runs by mass spectrometer analyses. These were kindly performed by Dr. F. P. Lossing and co-workers.

### ANALYSIS OF RESULTS

The pressure of the gas in the large pipette was measured; then the gas was expanded into the small pipette and the pressure measured again. The pressures $P_1$ and $P_2$ before and after expansion are related by the equation

$$[1] \qquad \frac{P_1}{P_2} = N + (N-1)\frac{B}{A}P_1 + \left(N - \frac{P_2}{P_1}\right)\frac{C}{A}P_1^2 + \ldots$$

if the equation of state of the gas can be written

$$[2] \qquad PV = A + BP + CP^2 + \ldots$$

and $N$ is the ratio of the total volume of both pipettes to the volume of the large pipette. The measured values of $P_1/P_2$ and $P_1$ were fitted to Equation [1] by the method of least mean squares described below, and the values of the parameters $N$, $B/A$, and $C/A$ determined. Sufficient terms were used that the minimized sum of the squares of the deviations was not appreciably reduced

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by the addition of another term in the next higher power of $P_1$ and the deviations were randomly distributed. None of the measurements warranted a higher term than $P_1^2$, and from 400° upwards the term in $P_1^2$ was insignificant.

If the isotherms were not linear the $N$ value was determined by a series of expansions with helium which gives a linear isotherm. Equation [1] could then be transformed to

$$[3] \qquad \frac{P_1/P_2 - N}{P_1} = (N - 1)\frac{B}{A} + \left(N - \frac{P_2}{P_1}\right)\frac{C}{A}P_1 + \ldots$$

which is linear if Equation [2] is not of higher order than quadratic. The results were fitted to this equation by a method similar to that described below. The mean of the $B/A$ and $C/A$ values obtained from Equations [1] and [3] was used. In the final runs the $B/A$ and $C/A$ values determined by the two methods agreed within experimental error.

The method used in fitting the measured values of $P_1/P_2$ and $P_1$ to Equation [1] is different from that used in previous papers and has the advantages that the amount of work is considerably lessened, the standard errors of $B$ and $C$ are readily calculated, and the approximation that $(N - P_2/P_1)$ is constant is not made. We therefore include a brief description of the method used. Equation [1] was written in the form

$$[4] \qquad y = a + (a - 1)\,bx + (a - 1/y)\,cx^2,$$

where

$$[5] \qquad \begin{aligned} y &= P_1/P_2,\ x = P_1, \\ a &= N,\ b = B/A,\ c = C/A. \end{aligned}$$

It was assumed that $x$ and $y$ are independent measurements. This is not true as is evident from their definitions, but is sufficiently accurate for our purposes. To check this, the 600°C. runs were fitted to the equation

$$[6] \qquad \frac{1}{P_2} = \frac{N}{P_1} + (N - 1)\frac{B}{A}$$

by the method of least mean squares. There was no significant difference in the values of either $N$ or $B/A$ obtained by using Equations [4] and [6].

The procedure for least mean squares fitting is that described by Deming (3). Approximate values of $a$, $b$, and $c$, say $a_0$, $b_0$, and $c_0$, were obtained from previous measurements of the compressibility or from the graph of $x$ vs. $y$. If

$$[7] \qquad \begin{aligned} a &= a_0 - \alpha, \\ b &= b_0 - \beta, \\ c &= c_0 - \gamma, \end{aligned}$$

the normal equations for computing $\alpha$, $\beta$, and $\gamma$ are written with detached coefficients as follows:

$$[8] \qquad \begin{array}{cccc} \alpha & \beta & \gamma & = \quad 1 \\ \sum \frac{F_a^2}{L} & \sum \frac{F_aF_b}{L} & \sum \frac{F_aF_c}{L} & \sum \frac{F_aF_0}{L} \\ \sum \frac{F_aF_b}{L} & \sum \frac{F_b^2}{L} & \sum \frac{F_bF_c}{L} & \sum \frac{F_bF_0}{L} \\ \sum \frac{F_aF_c}{L} & \sum \frac{F_bF_c}{L} & \sum \frac{F_c^2}{L} & \sum \frac{F_cF_0}{L} \end{array}$$

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Each row but the first is a normal equation and each term is to be multiplied by the parameter in the first row.

The various quantities used in Equation [8] are:

$$[9] \qquad \begin{aligned} F &= y - a - (a-1)bx - (a-1/y)cx^2, \\ F_0 &= y - a_0 - (a_0-1)b_0x - (a_0-1/y)c_0x^2, \\ F_a &= \partial F/\partial a, \text{ etc.}, \\ L &= (F_x^2/w_x) + (F_y^2/w_y), \end{aligned}$$

and $w_x$ and $w_y$ are the weights of $x$ and $y$. Since $F_x$ is of the order $10^{-3} - 10^{-4}$ and $F_y$ is of the order unity and $w_x$ and $w_y$ are of the same order, $F_x^2/w_x$ is negligible in comparison with $F_y^2/w_y$. $F_y$ differs from unity by a maximum of about 1%. Since we are calculating the small quantities $\alpha$, $\beta$, and $\gamma$ four or five figures are sufficient in the normal equations, and since the factor $F_y^2$ appears as a divisor in all the square and cross products of $F_a$, etc., it is quite safe to neglect it. The sensitivity of the piston gauge does not vary much with pressure and we gave each value the same weight. Consequently the $L$ terms are constant and cancel from the normal equations. This considerably reduces the computation required. The minimized sums of squares and the standard error of the parameters are readily calculated by the method described by Deming (3).

The value of $A$ at temperature $T$ is defined by

$$[10] \qquad A = A_0T/273.16$$

where $A_0$ is the value of $A$ at 0°C. $A_0$ is obtained from the identity that if the unit of volume is the normal volume or amagat, then at one atmosphere pressure and 0°C.

$$[11] \qquad PV = 1 = A_0 + B_0 + C_0.$$

$B_0/A_0$ and $C_0/A_0$ are known from the 0°C. isotherm so $A_0$ is readily obtained. The standard error of $A_0$ was obtained from the relation

$$[12] \qquad \sigma(A_0) = \{[\sigma(B_0/A_0)]^2 + [\sigma(C_0/A_0)]^2\}^{\frac{1}{2}},$$

where $\sigma$ denotes the standard errors of the quantities within the round brackets.

## RESULTS

The results are given in Table I. The unit of pressure is the standard atmos-

TABLE I

VIRIAL COEFFICIENTS OF ARGON, N.R.C. VALUES

| $T$, °C. | $A$ | S.E. of $10^6A$ | $10^3B$, amagat/mole | $10^6C$, amagat/mole/atm. | No. of expansions | S.E. of $10^5 \frac{P_1}{P_2}$ |
|---|---|---|---|---|---|---|
| 0 | 1.000999 | 10 | −1.001 ± .010 | 2.37 ± .07 | 33 | 7.1 |
| 50 | 1.184225 | 12 | −0.500 ± .011 | 1.86 ± .11 | 41 | 9.5 |
| 100 | 1.367450 | 14 | −0.194 ± .004 | 1.59 ± .04 | 37 | 2.6 |
| 150 | 1.550676 | 16 | +0.045 ± .006 | 1.27 ± .06 | 41 | 3.9 |
| 200 | 1.733902 | 17 | 0.236 ± .007 | 0.96 ± .05 | 38 | 3.1 |
| 300 | 2.100353 | 21 | 0.481 ± .011 | 0.61 ± .08 | 44 | 3.3 |
| 400 | 2.466805 | 25 | 0.703 ± .005 | | 27 | 6.2 |
| 500 | 2.833258 | 28 | 0.793 ± .006 | | 35 | 5.6 |
| 600 | 3.199708 | 32 | 0.870 ± .006 | | 33 | 4.9 |

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phere and the unit of volume the normal volume. The normal volume $V_n$ is $RT_0/A_0$ and is, from our measurements, 22.3916 ± .0022 l./mole or 22,392.2 ± 2.2 cc./mole.

## COMPARISON WITH PREVIOUS RESULTS

The $P$-$V$-$T$ relations for argon have been measured by Onnes and Crommelin (9) at Leiden; Holborn, Schultze, and Otto (4, 5, 10) at Berlin; Masson, Dolley, and Tanner (7, 13) at Durham; and Michels, Wijker, and Wijker (8) at Amsterdam at high pressures; and by Baxter and Starkweather (1) at low pressures. In Tables III, IV, and V, we compare the various values of $A_0$, $B$, and $C$, respectively, obtained by various workers.

The Leiden data agree badly with the other measurements, apparently because of "side-trapping in one limb of the piezometer after measuring the volume at one atmosphere pressure" (2, 14). They are therefore omitted from this discussion.

The Berlin data cover the temperature range −100° to +400°C. and pressure range 0–100 atm., and measurements were made up to 200 atm. at 0° and 100°C. We have not used the latter results since our measurements are only to 80 atm. As pointed out by Cragoe (2) the results were not worked up correctly and we have considered it worth while to recalculate from the measurements. We have given a rather extended discussion of the Berlin data since the $PVT$ properties of a number of gases below 0°C. and above 150°C. are known only from these measurements.

The experimental procedure was briefly as follows. An unknown mass of gas was confined in a known volume $V$ at a known high pressure and at a known temperature near (± 0.5°) the temperature at which $PV$ was required. The gas was then expanded into a known volume $V_u$ at a pressure $P_u$ of about 1 atm. The following corrections were applied.

1. To $V$− (i) Correct to round values of the temperature 0°, 50°, etc.
   (ii) Correct for dead space not at temperature of measurement.
   (iii) Correct for pressure variation of dead space volume since the pressures inside and outside the dead space were not equal.

The sum of these corrections is about 0.3–0.4% of the total volume and it is difficult to decide whether the corrections were made by assuming the gas to be ideal.

2. To $V_u$− (i) Dead space.
   (ii) $P_u$ and $V_u$ were measured at about 16°C. and $V_u$ corrected to be the volume the gas would occupy at 0°C. and pressure $P_u$.

Again it is difficult to decide whether the corrections were made by assuming the gas to be ideal. For lack of knowledge we have assumed that these corrections were applied correctly, i.e. using real values for $PV$. If this were not done, the results would be appreciably affected.

Holborn and Otto have assumed that

[13] $$P_u V_u = P_0 V_0$$

where $V_0$ is the volume that the gas in the piezometer would occupy at the unit pressure $P_0$ which is 1 m. of mercury. In fact, $P_u$ is usually in the range 65–85

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cm. of mercury and because the gas is not ideal Equation [13] cannot be assumed correct. We have calculated $P_0V_0$ where possible on the basis $P_0 = 1$ atm. making allowance for the difference between $P_u$ and 1 atm. For the 0°, 50°, 100°, 150°, and 200° isotherms this correction was not possible since the values of $P_u$ and $V_u$ were not quoted. We have therefore assumed that $P_u$ was near 1 atm. and that $P_uV_u$ is very close to $P_0V_0$ for $P_0 = 1$ atm. If the values of $P_u$ are similar to those quoted for other runs, this will probably not be a bad approximation.

Then

$$PV/P_0V_0 = A + BP + CP^2 + \ldots . \qquad [14]$$

We analyzed the data according to this equation. At 0°C., by definition of the unit of volume, Equation [11] holds so that

$$\frac{PV/P_0V_0 - 1}{P - 1} = B_0 + C_0(P + 1). \qquad [15]$$

A graph of $\frac{PV/P_0V_0 - 1}{P - 1}$ vs. $P + 1$ gives $B_0$ and $C_0$. Least mean squares were not used since we could not correct $P_uV_u$. The $A_0$ obtained was used to calculate $A$ at any other temperature. The use of the "best" value of $A_0$ (see below) would have made very little difference to the value of $B$ and $C$. For temperatures other than 0°C. the data were evaluated from the equation

$$(PV - A)/P = B + CP. \qquad [16]$$

Least mean squares were used for −100°, −50°, 300°, and 400°C. since at these temperatures we could correct $P_uV_u$ to $P_0V_0$. At other temperatures $B$ and $C$ were evaluated graphically. The 300°C. isotherm gave a very strongly curved line, indicating that the $A$ used was not correct. Using Equation [14] to determine the best values for $A$, $B$, and $C$ by least mean squares, we found $A = 2.10277$. The $A_0$ $(= AT_0/T)$ value derived from this is 1.00215 which is wildly wrong. If we assume that $A_0 = 1.00096$ then we find that the temperature of the runs must have been 300.7°C. This seems the only reasonable explanation of the 300°C. measurements.

TABLE II

VIRIAL COEFFICIENTS OF ARGON FROM THE BERLIN DATA

| $T$, °C. | $10^3 B$ | | $10^3 C$ | |
|---|---|---|---|---|
| | Berlin analysis | Our analysis | Berlin analysis | Our analysis |
| −100 | −2.873 | −2.850 ± .014 | −10.3 | −10.2 ± .6 |
| − 50 | −1.688 | −1.643 ± .007 | +0.79 | −0.845 ± .26 |
| 0 | −0.986 | −0.96 | 2.37 | +2.09 |
| 50 | −0.492 | −0.465 | 1.79 | 1.50 |
| 100 | −0.191 | −0.167 | 1.61 | 1.35 |
| 150 | +0.052 | +0.088 | 1.24 | 0.90 |
| 200 | 0.209 | 0.233 | 1.12 | 1.03 |
| 300.7 | 0.501 | 0.439 ± .003 | 0.46 | 0.90 ± .26 |
| 400 | 0.683 | 0.669 ± .007 | | 0.19 ± .22 |

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The original values of Holborn and Otto, converted directly to $P_0 = 1$ atm., are compared with the results of our analysis in Table II and the corrected values are included in Tables III, IV, and V.

The Durham data were obtained over the temperature range 25–174°C. and pressure range 5–125 atm. The value of $A_0 = 1.00098$ obtained by Holborn and Otto was used. The measured $PV$ values are not quoted; the virial coefficients are given together with the mean deviation of $PV$.

The Amsterdam data were obtained over the temperature range 0–150°C. and pressure range 20–2900 atm. The data up to 80 atm. were fitted to the equation

$$PV = A_\rho + B_\rho\rho + C_\rho\rho^2, \qquad [17]$$

where $\rho$ is the density in amagat units. Exact comparison of this equation with Equation [2] is difficult as they are not exactly equivalent. If both series are carried to a large enough number of terms they become equivalent and the following relationships hold,

$$\begin{aligned} A &= A_\rho, \\ B &= B_\rho/A_\rho, \\ C &= (A_\rho C_\rho - B_\rho^2)/A_\rho^3, \text{ etc.} \end{aligned} \qquad [18]$$

But if the series are carried only to the square term, these relationships cannot hold exactly. In a later paper concerned with the intermolecular potential of argon, we shall be interested in the relation between the constants of Equations [2] and [17] since the constants in Equation [17] are those usually used in discussing the intermolecular potential. It is therefore worth while examining in some detail the validity of Equations [18] when Equations [2] and [17] are restricted to quadratic.

Michels' values of $A_\rho$, $B_\rho$, and $C_\rho$ for argon at 0°C. up to 80 atm. were converted to $A$, $B$, and $C$ using Equations [18]. The virial coefficients do not, unfortunately, have standard errors assigned to them and are quoted to six figures; we have omitted the last three as these are not significant. The original data of Michels' up to 80 atm. which contain the measured values of $PV$ and $P$ were fitted to Equation [2] by the method of least mean squares and the following results were obtained.

| | $A$ | $10^3B$ | $10^6C$ |
|---|---|---|---|
| Equations [18] | 1.00097 | − 0.956 | 1.62 |
| Equation [2] | 1.000963 | − 0.965 ± .007 | 2.02 ± .02 |

From the measurements at 150°C. the following results were obtained.

| | $A$ | $10^3B$ | $10^6C$ |
|---|---|---|---|
| Equations [18] | 1.55065 | 0.062 | 1.13 |
| Equation [2] | 1.550620 | 0.0698 ± .0013 | 0.98 ± .03 |

The $A$ values at 150°C. were obtained from the respective $A_0$'s by using Equation [10]. It is evident that though exact conversion of the constants of one equation to those of the other is not possible, the values obtained using Equations [18] are probably within experimental error. We include in Tables III, IV, and V the values obtained from Michels' data using Equations [18] except the 0° and 150° values which were obtained using Equation [2].

Baxter and Starkweather determined the densities of argon at 0°C. and pressures below 1 atm. The $A_0$ value calculated from their data by Cragoe (2)

TABLE III

COMPARISON OF $A_0$ VALUES FOR ARGON

| | $A_0$, amagat atm. | S.E. of $A_0$, $\times 10^6$ |
|---|---|---|
| This work | 1.000999 | 10 |
| Berlin | 1.000984 | |
| Berlin corrected | 1.00096 | |
| Amsterdam, equation [16] | 1.00097 | |
| Amsterdam, equation [21] | 1.000963 | 7 |
| Baxter and Starkweather | 1.00100 | |

TABLE IV

COMPARISON OF $10^3B$ VALUES OF ARGON, AMAGAT/MOLE

| $T$, °C. | Our values 10–80 atm. | Berlin 0–100 atm. (corrected) | Durham 5–125 atm. | Amsterdam 20–80 atm. |
|---|---|---|---|---|
| −100 | | −2.850 | | |
| − 50 | | −1.643 | | |
| 0 | −1.001 | −0.96 | | −0.9578 |
| 25 | | | −0.730 | −0.703 |
| 50 | −0.500 | −0.465 | −0.513 | −0.502 |
| 75 | | | −0.334 | −0.324 |
| 100 | −0.194 | −0.167 | −0.183 | −0.179 |
| 125 | | | −0.032 | −0.053 |
| 150 | +0.045 | +0.088 | +0.097 | +0.062 |
| 174 | | | +0.166 | |
| 200 | +0.236 | +0.223 | | |
| 300 | +0.481 | +0.439 | | |
| 400 | +0.703 | +0.669 | | |
| 500 | +0.793 | | | |
| 600 | +0.870 | | | |

TABLE V

COMPARISON OF $10^6C$ VALUES OF ARGON, AMAGAT/ATM./MOLE

| $T$, °C. | Our values 10–80 atm. | Berlin 0–100 atm. (corrected) | Durham 5–125 atm. | Amsterdam 20–80 atm. |
|---|---|---|---|---|
| −100 | | −10.2 | | |
| − 50 | | −0.84 | | |
| 0 | 2.37 | 2.09 | | 1.62 |
| 25 | | | 2.19 | 1.66 |
| 50 | 1.86 | 1.50 | 1.91 | 1.70 |
| 75 | | | 1.70 | 1.54 |
| 100 | 1.59 | 1.35 | 1.47 | 1.44 |
| 125 | | | 1.12 | 1.32 |
| 150 | 1.27 | 0.90 | 0.9 | 1.13 |
| 174 | | | 1.0 | |
| 200 | 0.96 | 1.03 | | |
| 300 | 0.61 | 0.90 | | |
| 400 | | 0.2 | | |

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uses the results of only the first paper. We quote in Table III the mean of the results given in both papers.

## ASSESSMENT OF BEST VALUES FOR $B$ AND $C$

Since we do not expect our values of $B$ and $C$ to be very much more accurate than previous measurements, we have combined all the values obtained by various workers at the same temperature to obtain the best values of $B$ and $C$. We based the weights to be assigned to the various values on the following considerations.

1. The Berlin, Amsterdam, Durham, and N.R.C. values have about the same standard error calculated from the internal consistency of the data.

2. The Berlin, Amsterdam, and Durham measurements include a volume and a mass measurement (measurement of $P_0V_0$ is equivalent to a mass measurement) and the temperature of the gas must be exactly at the required value or the measurements must be corrected to it since $A \propto T$. The N.R.C. measurements do not require a volume or a mass measurement and it is not so important that the temperature be exactly the temperature required on the thermodynamic scale. It is true that a volume ratio is needed, but this is obtained from the same measurements that give $B$ and $C$ so its inaccuracy is already included in the standard errors of $B$ and $C$.

3. The Berlin data are subject to uncertainties for reasons outlined above.

4. Low pressure data are less accurate than high pressure data since the relative error in high pressure measurements is smaller than for low pressure measurements.

We have therefore given the following weights to the various measurements.

| | |
|---|---|
| Baxter and Starkweather | 1 |
| Berlin | 1 |
| Durham | 2 |
| Amsterdam | 2 |
| N.R.C. | 4 |

TABLE VI

WEIGHTED MEAN VALUES OF $B$ AND $C$ FOR ARGON

| $T$, ° C. | $A$ | $10^3B$ | | Exptl. − calc. | $10^6C$ | | Exptl. − calc. | $10^9D$ |
|---|---|---|---|---|---|---|---|---|
| | | Exptl. | (Eq. 19) | | Exptl. | (Eq. 20) | | |
| −100 | 0.634539 | −2.850 | −2.846 | −.004 | −10.24 | | | −13 |
| − 50 | 0.817762 | −1.643 | −1.661 | .018 | − 0.84 | | | 22 |
| 0 | 1.000985 | −0.987 | −0.966 | −.021 | 2.23 | 2.24 | −.01 | |
| 25 | 1.092597 | −0.717 | −0.713 | −.004 | 1.93 | 1.97 | −.04 | |
| 50 | 1.184208 | −0.499 | −0.505 | .006 | 1.80 | 1.75 | .05 | |
| 75 | 1.275820 | −0.329 | −0.330 | .001 | 1.62 | 1.57 | .05 | |
| 100 | 1.367431 | −0.185 | −0.181 | −.004 | 1.50 | 1.42 | .08 | |
| 125 | 1.459043 | −0.043 | −0.053 | .010 | 1.22 | 1.29 | −.07 | |
| 150 | 1.550655 | 0.065 | 0.059 | .006 | 1.12 | 1.17 | −.05 | |
| 174 | 1.638602 | 0.166 | 0.153 | .013 | 1.0 | 1.06 | −.06 | |
| 200 | 1.733878 | 0.233 | 0.243 | −.010 | 0.97 | 0.95 | .02 | |
| 300 | 2.100324 | 0.481 | 0.503 | −.022 | 0.61 | 0.58 | .03 | |
| 400 | 2.466771 | 0.703 | 0.675 | .028 | | | | |
| 500 | 2.833217 | 0.793 | 0.794 | −.001 | | | | |
| 600 | 3.199663 | 0.870 | 0.878 | −.008 | | | | |

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The Berlin 300°C. isotherm was rejected because of doubt about the temperature of the measurement (see above). Cragoe (2) points out that there is some doubt about the volume of the high pressure pipette as it shrunk by about 2 parts in $10^3$ during a long series of experiments with argon and other gases. The Berlin 400° isotherm agrees rather badly with ours and the disagreement is of about the right order to be explained by this shrinkage. We have therefore not included the 400° isotherm in our mean values.

The weighted means of $B$ and $C$ are listed in Table VI. It is difficult to state an exact standard error for all the values of $B$ and $C$ since many of the measurements include appreciable constant errors. Standard errors of about $0.01\times10^{-3}$ in $B$ and $0.06\times10^{-6}$ in $C$ seem reasonable.

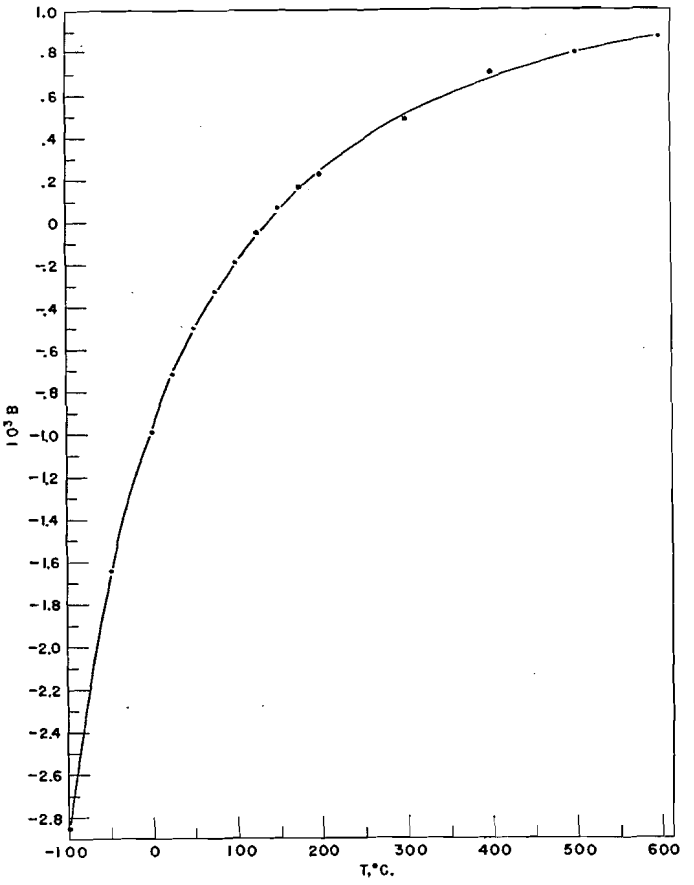



FIG. 1. $B$ vs. $T$ for argon. Values at $-100$ and $-50°$ C. are from Berlin; values from 0 to 200° C. are means; values from 200–600° C. are from this work. The line is Equation [19].

In Figs. 1 and 2 we plot the mean values of $B$ and $C$ respectively against temperature. The size of the dots indicates roughly the standard error. In Figs. 3 and 4 we compare the measured values of $B$ and $C$ obtained by various workers

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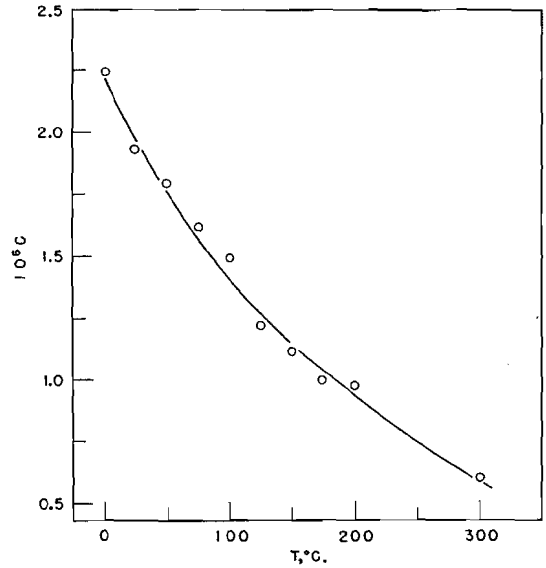



FIG. 2. $C$ vs. $T$ for argon. Values from 0 to 200° C. are means; the 300° C. value is from this work. The line is Equation [20].

with the mean value we have chosen. Outside the temperature range 0–200°C. no duplicate measurements have been included in the chosen values.

The normal volume using the averaged values of $A_0$ is 22,392.5 ± 2.2 cc./mole or 22.3919 ± .0022 l./mole.

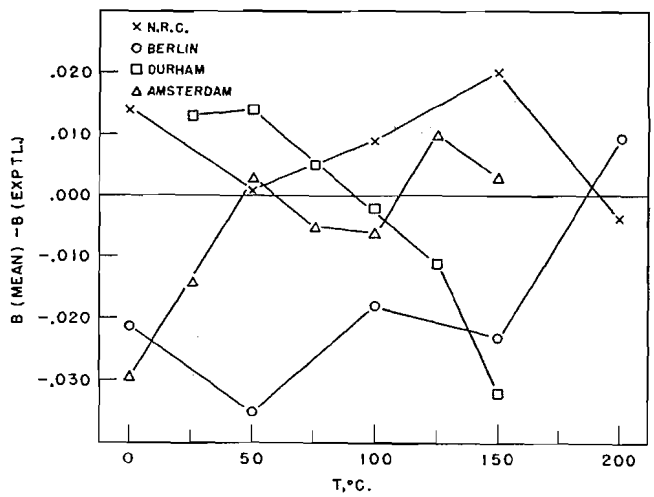



FIG. 3. $B$ (mean)$-B$ (exptl.) for argon.

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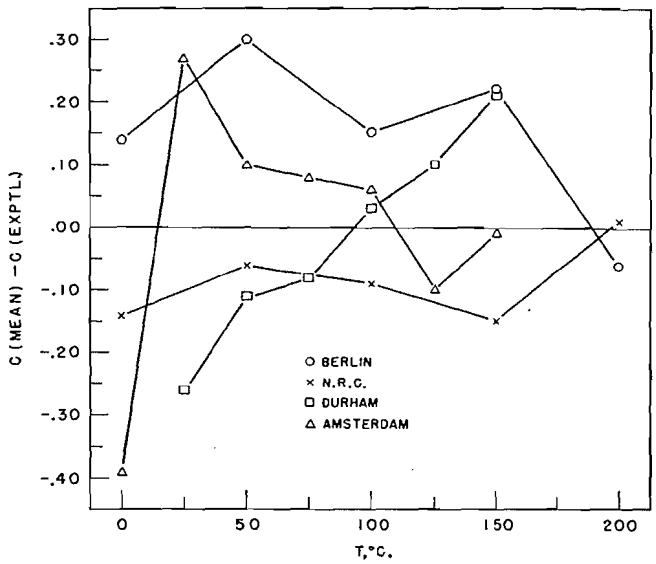



FIG. 4. $C$ (mean) $-C$ (exptl.) for argon.

## TEMPERATURE SERIES FOR $B$ AND $C$

To facilitate interpolation of the virial coefficients and calculations of their derivatives with respect to temperature we have fitted the mean values of $B$ and $C$ to temperature series. Values of $B$ over the range $-100°$ to $+600°$C. were fitted to the series

$$10^3B = a + bT + cT^{-1} + dT^{-3}$$

by the method of least mean squares, giving equal weight to all values. The following equation gave the best fit

[19] $$10^3B = 2.0358 - 3.140\times10^{-4}T - 769.34T^{-1} - 1.990\times10^6T^{-3},$$

with a standard deviation in $10^3B$ of 0.016. The experimental and calculated values using Equation [19] are given in Table VI. In Fig. 1 we compare directly the experimental values and Equation [19]. From Equation [19] and the deviation curve, the Boyle Point (temperature at which $B$ is zero) is $138.2 \pm 2.3°$C.

Values of $C$ over the temperature range 0–300°C. were fitted to the series

$$10^6C = a + bT + cT^{-3},$$

using the method of least mean squares and giving equal weight to all values. The following equation gave the best fit

[20] $$10^6C = 2.191 - 2.97\times10^{-3}T + 1.76\times10^7T^{-3}$$

with a standard deviation in $10^6C$ of 0.06. The experimental and calculated values are given in Table VI. In Fig. 2 we compare directly the experimental values and Equation [20].

## ACKNOWLEDGMENTS

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# THE pH DEPENDENCE OF THE ADSORPTION ISOTHERM AND ABSORPTION SPECTRUM OF METHYL ORANGE BOUND TO HUMAN AND BOVINE SERUM ALBUMIN[1]

By J. Ross Colvin

ABSTRACT

The difference between adsorption isotherms and absorption spectra of methyl orange bound to human and to bovine albumin at pH 6.8, 9.1, and 11.0 has been studied. Exaltation of the spectrum of methyl orange bound to human albumin is not necessarily correlated with total binding capacity. However, above pH 6.8, heterogeneity of the binding sites for methyl orange on human albumin increases so markedly that it is reflected in an appreciable increase in extinction coefficient for the first three or four anions bound. The exaltation is accompanied by an increased $-\Delta F^{\circ}$ of binding. Increase in ionic strength diminishes exaltation, and denaturation of the protein destroys it. These effects were not observed for bovine albumin. Results are interpreted in terms of a limited reversible expansion of the human protein molecules, without unfolding, due to intramolecular, electrostatic repulsion between groups.

## INTRODUCTION

New techniques have recently encouraged the quantitative study of adsorption of ions by proteins in solution (6, 10, 12). These studies indicated that mechanisms of adsorption of organic anions by serum albumins from different species are similar (7). However, significant differences in total binding capacity for anions, and in mode of interaction, have been reported lately between samples of human and bovine serum albumin at pH's above 6.8 (8, 9). Studies reported here confirm and extend these observations.

Klotz, Burkhard, and Urquhart (8, 9) observed that as pH increased, total binding capacity of human and bovine albumin for methyl orange and related dyes increased unexpectedly but the increment was much greater for human albumin. In addition, there was an exaltation of the spectrum of dye anions bound to human albumin while the extinction coefficient of those bound to bovine albumin decreased slightly. Because such differences are important for a better understanding of the mechanism of adsorption reactions, these experiments have been repeated and extended to higher free anion concentrations. Relative heterogeneity of binding sites for methyl orange on human and bovine albumin has also been studied. Results confirm the previous observations on the spectra of methyl orange bound to the two proteins but also show that an exaltation of the spectrum of methyl orange bound to human albumin is not necessarily correlated with an increase of total binding capacity. Furthermore, exaltation of extinction coefficient of methyl orange bound to three or four sites on human albumin is accompanied by greatly increased heterogeneity among the remainder. An alternate interpretation of the original observations is suggested.

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## METHODS AND MATERIALS

Adsorption isotherms were obtained by the method of dialysis equilibrium, which involves determination of the distribution of dye anions between a protein solution on one side of a semipermeable membrane and a buffer solution on the other. Techniques were as described previously (3). Vials were rotated overnight in a water bath which was held at the desired temperature ±0.1°C. Optical densities of the buffer solutions were measured at room temperature by a Beckman spectrophotometer Model DU at 5400Å. The protein concentration was about 0.2% for most experiments, corrected for moisture as determined by drying *in vacuo* at 100° for 16 hr. Molecular weight of all samples of albumin was assumed to be 69,000.

Absorption spectra of protein – methyl orange solutions were determined by a Cary recording spectrophotometer, Model 11M, Serial 95, over the range 3000–6000 Å. When only the absorption spectrum of the anion bound to protein was desired, a solution of the anion in the corresponding equilibrated buffer solution was used as blank. This procedure assumes that, as in dialysis equilibrium, free anion concentrations are equal in both solutions after equilibration.

Human and bovine albumin were denatured by heating solutions at the temperature of boiling water for 30 min. under reflux. At pH levels used in these experiments, both albumins remained in solution.

Intrinsic viscosities of protein solutions were estimated by the techniques outlined by Weissberger (13) using a capillary viscometer at 26.00 ± 0.05°C.

Specific optical rotations of protein solutions were determined with an A. Hilger Ltd. polarimeter, precision ±0.01°; final error of the specific angle was about ±0.5°. Tubes two decimeters long were used at room temperature with a sodium lamp as light source. The recorded estimate was the mean of 10 readings.

A commercial sample of methyl orange was purified by recrystallizing once from water, washing with alcohol, then ether, and subsequently drying the residue over calcium chloride. Extinction coefficient in 0.05 *M* phosphate, pH 6.8 at 4500 Å, 25°C., was 23,000 liters $mole^{-1}$ $cm^{-1}$.

Bovine serum albumin was purchased from Armour and Co., Chicago; Control No. 128–165.

Two samples of human serum albumin were employed. Sample I was prepared by Squibb and Sons, New Jersey, using method six of Cohn *et al.* (2) with the addition of cysteine monohydrochloride to remove mercury present as merthiolate. A 25% solution of this sample was then heated at 68°C. for 10 hr. It was subsequently reworked by fractionation with 10% alcohol and precipitation at pH 4.87 with 40% alcohol. Purity was greater than 99% by electrophoretic analysis. The small amount of impurity appeared to be an alpha globulin. Sample II was prepared by Cutter Laboratories, Calif., according to method six of Cohn *et al.* (2).

Buffers were made by Clark's procedure (1) from reagent grade materials.

## RESULTS

Adsorption isotherms of methyl orange on human serum albumin (Sample I) and on bovine serum albumin were determined at 3° ± 0.1°C. over a wide

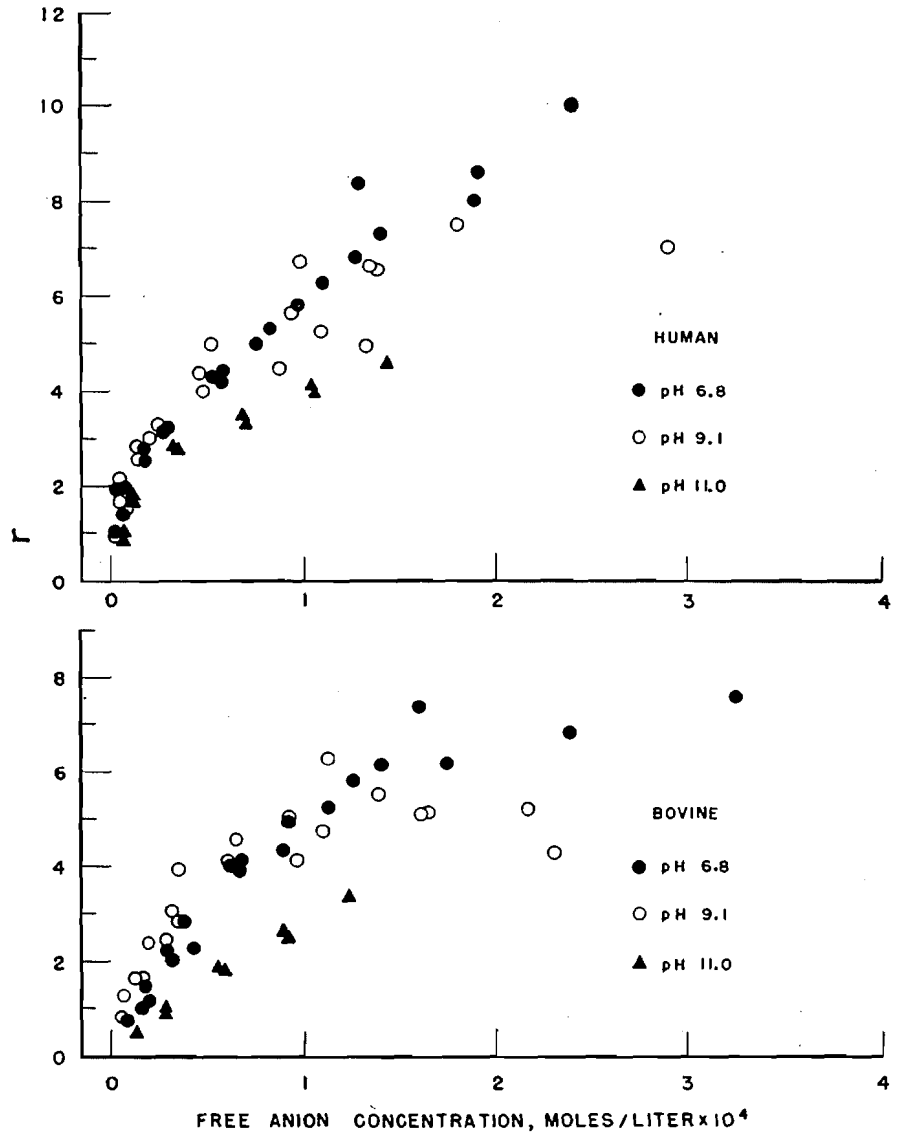



FIG. 1. Adsorption isotherms of methyl orange on human (Sample I) and bovine serum albumin in 0.05 *M* phosphate buffer pH 6.8, 0.05 *M* borate pH 9.1, and 0.07 *M* sodium hydroxide – phosphate buffer pH 11.0, at 3.0° C. The ordinate, *r*, is the average number of anions bound per protein molecule.

range of free dye concentrations for pH 6.8, 9.1, and 11.0 in 0.05 *M* phosphate, borate, and sodium hydroxide – phosphate buffers. Results are given in Fig. 1. Concentrations of free dye are plotted on a linear scale rather than logarithmic to illustrate experimental errors at high concentrations of dye. Contrary to the results of Klotz *et al.* (8, 9), there was no significant change in total binding capacity of either sample of albumin as pH increased from 6.8 to 9.1 but there was a decrease in total capacity for both proteins at pH 11.0. Lack of significant

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change in total binding capacity for both albumins between pH 6.8 and 9.1 was confirmed by a second series at 30°C.

These observations were strengthened by a third series of experiments on Sample II of human albumin. Adsorption isotherms for methyl orange on this sample are shown in Fig. 2, as a function of pH. Clearly, these corroborate

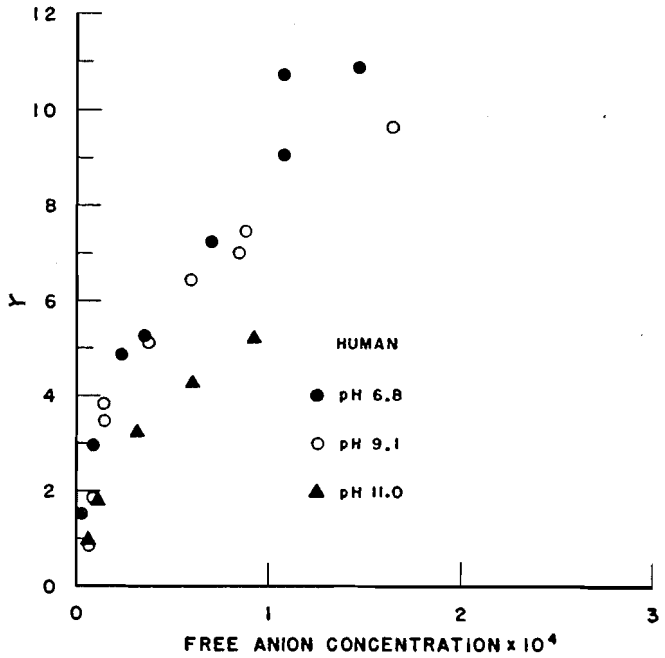



FIG. 2. Adsorption isotherms of methyl orange on human serum albumin (Sample II) in 0.05 *M* phosphate buffer pH 6.8, 0.05 *M* borate pH 9.1, and 0.07 *M* sodium hydroxide – phosphate buffer pH 11.0 at 3°.

the data of Fig. 1. Taken together, both figures show that adsorption capacity of human and bovine serum albumin for methyl orange does not necessarily increase with an increase in pH from 6.8 to 9.1 and that the capacity of both proteins decreases at pH 11.0.

Observations of Klotz *et al.* (8, 9) on the effect of human serum albumin on the spectrum of methyl orange at pH's above 6.8 have been completely confirmed, however. A progressive exaltation of the spectrum of adsorbed methyl orange was observed for both samples of human albumin as pH increased. Typical results are shown in Fig. 3. Although they extend over a wider range, these confirm results previously reported (8). Exaltation increases progressively from pH 6.8 to 9.1 and then remains constant from pH 9.1 to 11.0. This effect was not observed for bovine serum albumin and, as pointed out by Klotz *et al.*, indicates a marked difference in the interaction of organic anions with these two proteins.

Exaltation of the spectrum of methyl orange bound to human serum albumin is dependent on a specific structure of the adsorbent, for heat denaturation

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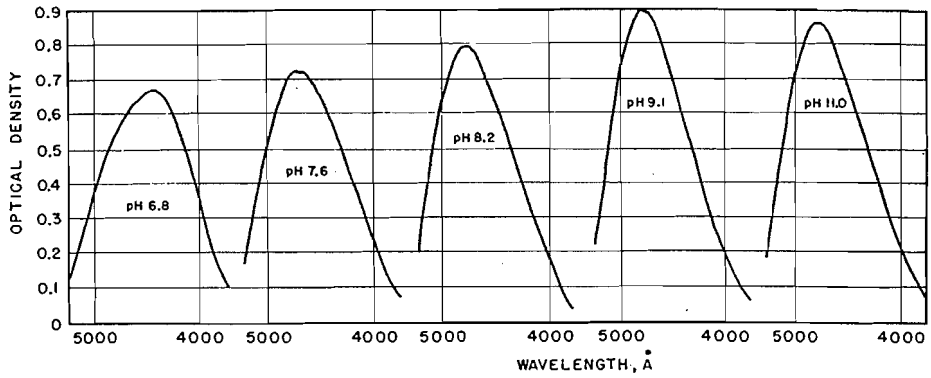



FIG. 3. Absorption spectra of methyl orange – human serum albumin mixtures at increasing pH levels. Concentration of methyl orange in all solutions $0.3 \times 10^{-4}$ $M$; protein concentration of 0.2%.

completely abolished the effect. Although not unexpected, this conclusion could not be assumed since the increase in extinction coefficient might well be due to interaction with stable groups which become more easily available either on denaturation or as pH increased.

The relation between optical density of a solution of bound anions of constant protein concentration and fixed light path, and the number of anions bound per protein molecule may give information about homogeneity of binding sites. For instance, if all anions are bound by identical mechanisms, there will be a direct proportionality between optical density of such a solution and number of anions bound. On the other hand, variations in manner of binding over the range of adsorption may lead to departure from linearity in this relation provided that the protein–anion interaction is strong enough to perturb the light adsorbing portions of the dye. It is impossible, except in special cases, to obtain a solution containing only bound dye anions. However, using the Cary recording spectrophotometer with an equilibrated free anion solution as blank the optical density of such a hypothetical solution may be estimated accurately and plotted against the independently determined $r$ value. This has been done for both bovine and human serum albumin at pH 6.8, 9.1, and 11.0 over the widest practicable concentration range. Results are shown in Figs. 4 and 5. Visual inspection shows that the relation between optical density of bound methyl orange solution and $r$ is linear over the whole concentration range, for both bovine and human serum albumin at pH 6.8. Statistical analysis confirms this (Table I). Therefore, within the limits of this insensitive test, all binding sites of methyl orange on both human and bovine albumin are equal at pH 6.8. This is also true for bovine albumin at pH 9.1 and 11.0, although the data are less reliable at pH 11.0. However, the relation between optical density of bound methyl orange solution and $r$ is curvilinear for human albumin at pH 9.1 and 11.0 (Table I). Inspection of the curves shows that for human albumin at both pH's, average optical density per dye anion bound is greater for the first three anions adsorbed than that for all anions bound at pH 6.8. The average extinction coefficient per anion bound declines at both pH levels as total number bound

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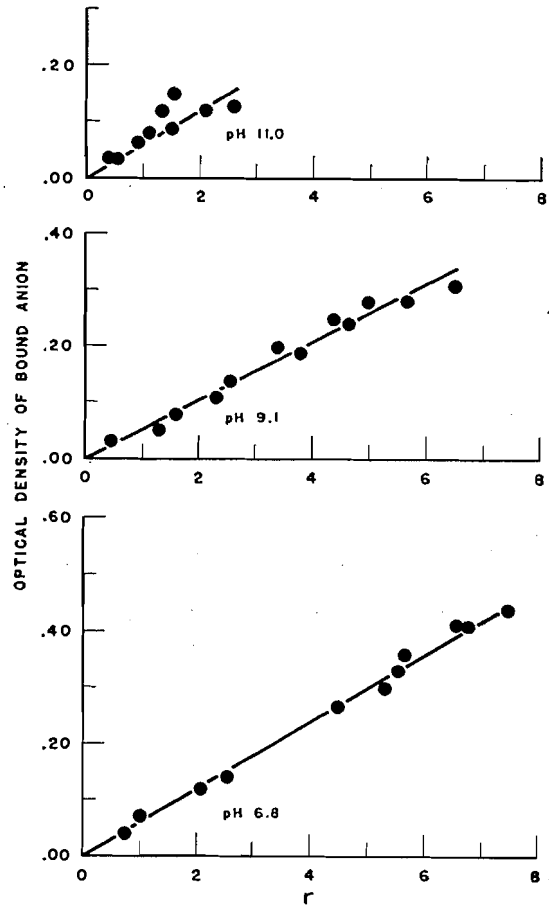



FIG. 4. Relation between optical density of a solution of methyl orange anions bound to bovine serum albumin and $r$, the average number of bound anions per protein molecule, at pH 6.8, 9.1, and 11.0. Protein concentration constant at 0.2%; light path constant at 1 mm.

TABLE I

TEST OF LINEARITY OF RELATION BETWEEN $D$, OPTICAL DENSITY OF SOLUTIONS OF METHYL ORANGE BOUND TO HUMAN OR BOVINE ALBUMIN, AND $r$, AVERAGE NUMBER OF ANIONS BOUND PER PROTEIN MOLECULE, AT pH 6.8, 9.1, AND 11.0; PROTEIN CONCENTRATION 0.2%, LIGHT PATH 1 MM.

| System | pH | No. of deter. | Mean $r$ | Mean $D$ | Slope of $D$ versus $r$ with 95% confidence limits | Ordinal intercept with 95% confidence limits |
|---|---|---|---|---|---|---|
| Bovine – methyl orange | 6.8 | 11 | 4.37 | 0.26 | $0.061 \pm 0.004$ | $-0.004 \pm 0.009$ |
| | 9.1 | 12 | 3.46 | 0.180 | $0.051 \pm 0.006$ | $0.003 \pm 0.012$ |
| | 11.0 | 10 | 1.23 | 0.083 | $0.055 \pm 0.028$ | $0.016 \pm 0.020$ |
| Human – methyl orange | 6.8 | 12 | 5.72 | 0.352 | $0.061 \pm 0.002$ | $0.003 \pm 0.005$ |
| | 9.1 | 12 | 4.11 | 0.244 | $0.050 \pm 0.005$ | $0.037 \pm 0.010$ |
| | 11.0 | 12 | 2.83 | 0.167 | $0.039 \pm 0.008$ | $0.056 \pm 0.010$ |

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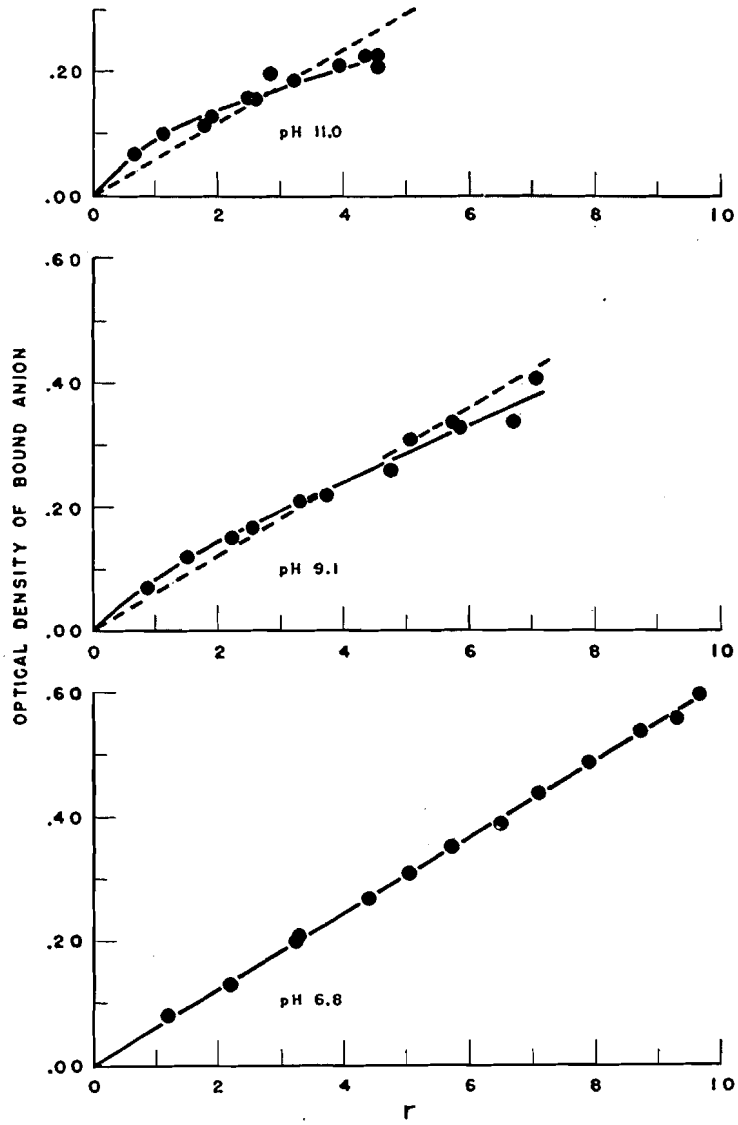



FIG. 5. Relation between optical density of a solution of methyl orange anions bound to human serum albumin and $r$, the average number of bound anions per protein molecule, at pH 6.8, 9.1, and 11.0. Protein concentration constant at 0.2%; light path constant at 1 mm. The dotted line at pH 9.1 and pH 11.0 indicates the relation at pH 6.8.

increases, showing that methyl orange anions must be bound very unequally to human albumin at each of these pH's. Furthermore, considering that the average extinction coefficient of anions bound to bovine albumin decreases as pH increases (Table I), the first three or four anions must be bound with an abnormally large free energy decrease in such a way that they cause an exaltation of the spectrum of bound methyl orange and the remainder cause a decrease.

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In contrast, as shown above, anions are bound relatively equally to bovine serum albumin at all dye concentrations for each pH.

TABLE II

WAVE LENGTHS OF MAXIMUM ABSORPTION OF METHYL ORANGE BOUND TO HUMAN AND BOVINE PLASMA ALBUMIN AS A FUNCTION OF $r$, NUMBER OF ANIONS BOUND PER PROTEIN MOLECULE, AT pH 6.8, 9.1, AND 11.0

| 6.8 | | 9.1 | | 11.0 | |
|---|---|---|---|---|---|
| $r$ | $\lambda_{max}$, Å | $r$ | $\lambda_{max}$, Å | $r$ | $\lambda_{max}$, Å |
| *Human* | | | | | |
| 1.2 | — | 0.9 | 4850 | 0.7 | 4800 |
| 3.3 | 4400 | 2.3 | 4700 | 1.8 | 4750 |
| 4.4 | 4400 | 3.7 | 4600 | 2.6 | 4650 |
| 7.1 | 4350 | 5.0 | 4400 | 3.2 | 4500 |
| 8.8 | 4400 | 5.7 | 4350 | 3.9 | 4350 |
| 9.7 | 4350 | 7.0 | 4350 | 4.4 | 4300 |
| *Bovine* | | | | | |
| 0.8 | 4500 | 0.5 | 4400 | 0 | 4400 |
| 2.1 | 4400 | 1.6 | 4500 | 0.4 | 4400 |
| — | — | 2.6 | 4350 | 0.9 | 4250 |
| 5.3 | 4300 | 3.4 | 4350 | 1.5 | 4300 |
| 5.7 | 4250 | 4.4 | 4300 | 2.1 | 4250 |
| 6.6 | 4300 | 5.0 | 4300 | 2.6 | 4200 |

These conclusions were confirmed by shifts in the absorption maxima of the spectra of the bound methyl orange complexes (Table II). At pH 6.8, wave length of maximum adsorption of methyl orange bound to both human and bovine albumin was nearly independent of average number of anions bound per protein molecule. This was also true of complexes with bovine albumin at pH 9.1 and 11.0. For complexes of methyl orange with human albumin at both pH 9.1 and 11.0, however, $\lambda_{max}$ shifted steadily toward shorter wave lengths as $r$ increased.

Increasing the ionic strength should tend to eliminate the difference in absorption spectra between the two albumins because of the competitive binding of other anions, decrease in internal electrostatic repulsion, and decrease in Donnan pressure (11). Accordingly, the spectrum of methyl orange bound to both samples of human albumin was determined at pH 9.1 and 11.0 in concentrations of sodium chloride varying from zero to 2.0 *M*. Typical spectra are shown in Fig. 6. As expected, optical density of the solution decreases with increasing ionic strength but the rate of decrease is surprisingly small. Clearly, those sites responsible for the exaltation of the spectrum of bound methyl orange are little affected by the presence of ions in the external solution. This is consistent with the abnormally large free energy decrease associated with binding to these sites.

If exaltation of extinction coefficient of methyl orange bound to human plasma albumin were attendant on a major configurational change of the

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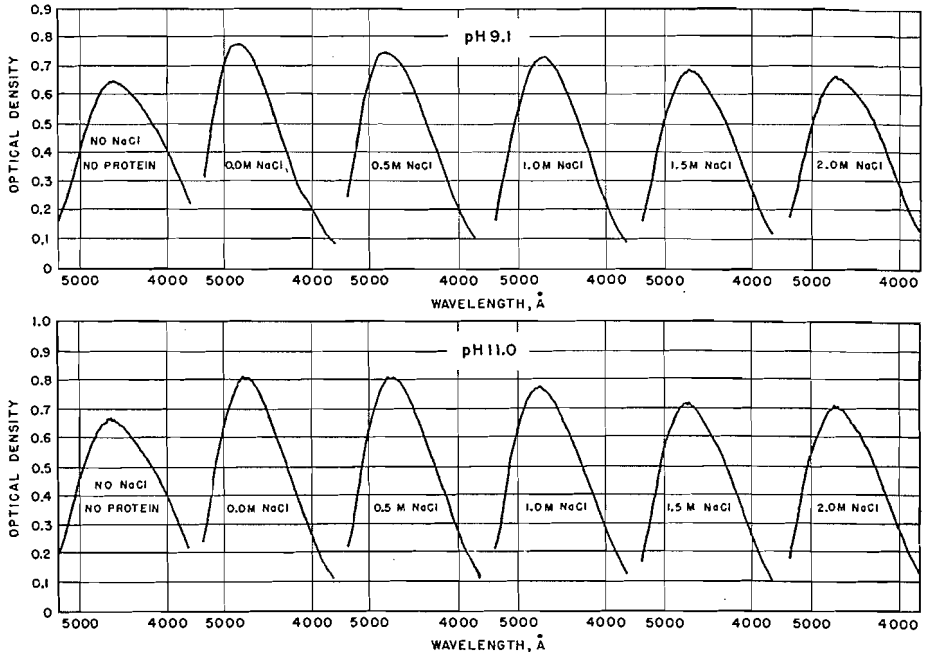



FIG. 6. Absorption spectra of methyl orange – human serum albumin mixtures for increasing sodium chloride concentrations at pH 9.1 and pH 11.0. Methyl orange concentration $0.3 \times 10^{-4}$ $M$; protein concentration 0.2%.

protein, such an alteration might be detectable by a change in intrinsic viscosity or specific optical rotation as pH increased. Since intrinsic viscosity is equal to $(\eta_{sp}/c)_{c\to 0}$(13), such a change with pH should be reflected in a change of slope of a plot of specific viscosity against concentration. Fig. 7 summarizes results of a determination of specific viscosity of human and bovine albumin at pH 6.8 and 9.1 as a function of concentration. Statistical analysis shows that the slopes of the functions, and therefore intrinsic viscosities, are equal at pH 6.8 and 9.1, for both proteins. Likewise, determination of specific optical rotation of both human and bovine albumin in duplicate at pH 5.5, 6.8, and 9.1 yielded values varying from $-55°$ to $-62°$ in agreement with previous work (5) but no significant differences could be observed between the two proteins in the manner in which this parameter varied with pH. Consequently, both types of evidence indicated that any configurational change is minor. This is consistent with the reversibility of the effect (8).

## DISCUSSION

The isotherms of Figs. 1 and 2, together with spectra of Fig. 3, show that there is no general positive correlation of increase in binding capacity of human albumin with increase in extinction coefficient of bound anion as pH increases. On the contrary, as would be expected from electrostatics, total binding capacity decreases while exaltation increases with increasing pH, up to a limit. Furthermore, Fig. 5 shows that after three anions are bound to human albumin at pH

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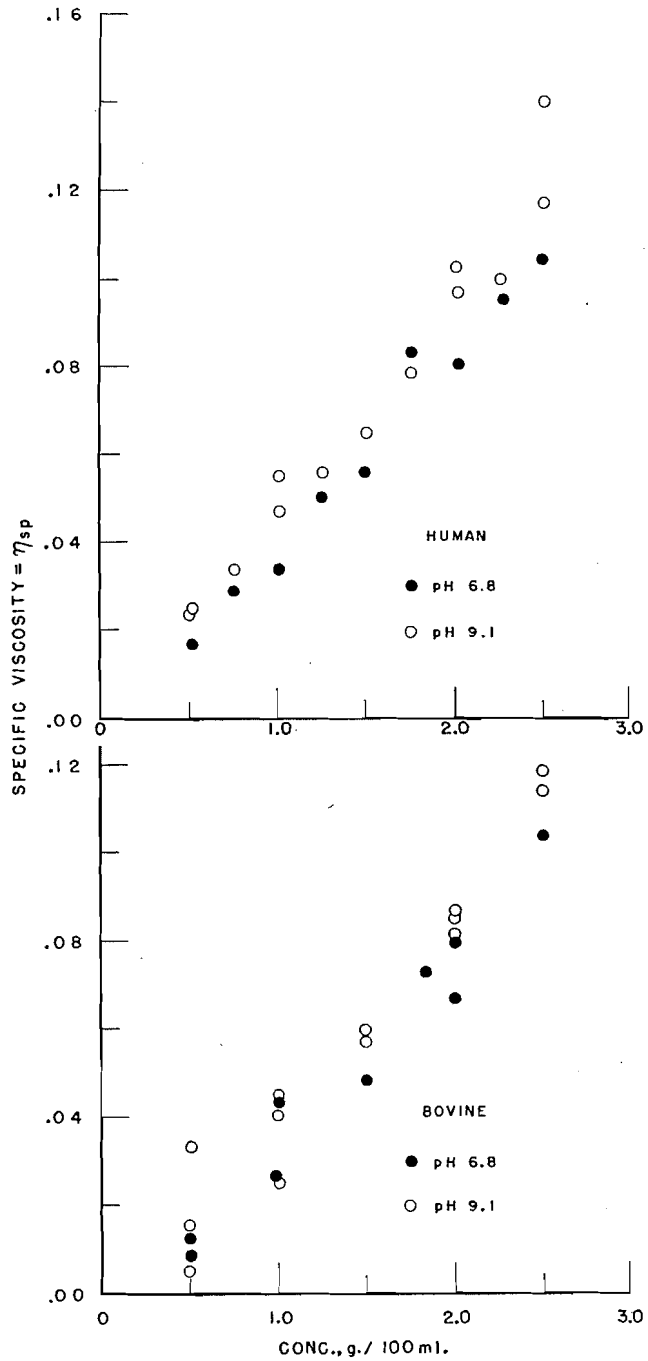



FIG. 7. Plots of the specific viscosity of bovine and human serum albumin against concentration in gm./100 ml. for pH 6.8 and 9.1.

Probability, $P$, that the difference between the intrinsic viscosities of human albumin at pH 6.8 and pH 9.1 would be obtained by chance is 0.2; for bovine albumin between pH 6.8 and 9.1, $P = 0.3$; and for the difference between bovine and human at pH 6.8, $P = 0.7$.

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9.1 or 11.0, the average extinction coefficient per anion bound is progressively less than that of anions bound at pH 6.8. Therefore, only the first few anions bound are responsible for exaltation of the spectrum of the complex. The decrease in average extinction coefficient for anions bound to bovine albumin, as pH increases (Table I), strengthens this conclusion. Consequently, unless all binding sites at pH 6.8 are different from those at pH 9.1, the exaltation is probably not caused by the binding of anions to new sites made available by unfolding of the molecule but by anions bound to a few formerly equivalent sites which have been strongly modified by expansion of the molecule under Coulomb forces (9). In fact, these results can be interpreted as direct evidence for the type of expansion envisaged by Scatchard (11). The heterogeneity of binding shows that this expansion permits suitable groups such as the tyrosine side chain (9) to perturb the light absorbing system of the anions in perceptibly different ways. However, only three or four of these anions are influenced in such a way that their molecular extinction coefficient is increased. Because these anions tend to be bound first, their free energy decrease must be appreciably greater than for remaining positions, in addition to the statistical effect (7).

The strong binding of the first anions to human albumin at pH's above 6.8 is probably responsible for the apparent discrepancy between results of Klotz, Burkhard, and Urquhart (9) and those reported here. Klotz *et al.* determined adsorption isotherms for methyl orange on both human and bovine albumin over a range of $r$ values extending only from zero to four. Consequently, they concluded that exaltation of the spectrum of methyl orange bound to human albumin was generally accompanied by an increase in total binding capacity. Results reported here, which do not confirm this correlation, were foreshadowed by the fact that although their sample 179 — 5X had the greatest adsorption affinity for methyl orange, a second sample from Cyanamid had the largest effect on the spectrum of the anion at pH 7.6.

A similar explanation probably also applies to lack of decrease of exaltation at pH 11.0. In Fig. 4 exaltation increases with pH from 6.8 to 9.1 and then remains constant, although total binding capacity decreases markedly. Those bound anions which are chiefly responsible for exaltation are therefore least affected by increased electrostatic repulsion. This would be expected if they are those bound most strongly. Lack of effect of pH on these sites also suggests that expansion of the molecule must be strictly limited by some strong covalent bonds. Otherwise the suitable spatial relation of given sites would be destroyed by continual expansion and therefore exaltation should decrease. However, since it is not known whether sites occupied first at pH 9.1 are the same as those initially occupied at pH 11.0, this argument cannot be conclusive.

Postulation of such strong covalent bonds also offers a reasonable explanation of the difference between human and bovine albumin at pH's above 6.8. Apparently, for bovine plasma albumin, these covalent links may be strong enough to completely prevent any appreciable modification of binding sites for methyl orange at all pH's. In addition, human albumin may contain three or four more suitably situated hydroxyls, relative to cationic sites. Further investigation is needed to test these possibilities.

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These results appear to provide a direct confirmation of the common assumption that binding sites for methyl orange on bovine serum albumin at pH 6.8 are equivalent (7), in apparent refutation of previous criticisms of the validity of this postulate (3, 4). However, the insensitive test for homogeneity applied in this study could not show effects even of major variations in local topography which did not directly perturb the light absorbing system of the anion. Linearity between optical density of a solution of bound anions and average number of anions bound per protein molecule is a necessary but not a sufficient condition for equality of sites.

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# THE SENSITIVITY OF INITIATOR EXPLOSIVES TO MECHANICAL IMPACT[1]

By N. R. S. Hollies,[2] N. R. Legge,[3] and John L. Morrison

ABSTRACT

An original ball-drop impact apparatus has been constructed and used to test the sensitivities of dextrin lead azide and mercury fulminate to mechanical impact. Ball masses and heights were both varied. Both the net kinetic energy and the change of momentum gave continuous functions with the percentage of detonations. Comparisons of the absolute values of the net kinetic energy and the change of momentum with another reported in the literature suggest that momentum is the more important factor in determining the probability of detonation. Values for the momentum at 50% detonations for lead azide and mercury fulminate are $4.6 \times 10^4$ and $2.6 \times 10^4$ c.g.s. units, respectively, with an area of contact of about 0.08 cm.$^2$ The corresponding times of impact were found to be about $2.2 \times 10^{-4}$ and $1.9 \times 10^{-4}$ sec.

The question of whether the probability of the detonation of an initiator explosive is chiefly determined by the kinetic energy or the momentum of the impacting mass is of theoretical interest in interpreting the process of detonation by impact (8). In their earlier work, Taylor and Weale (9) suggest that kinetic energy is the important factor, although in 1938 (10) they introduce experiments and calculations based on momentum. Taylor and Weale do not mention the rebound of the steel balls used in their impact tests, although the measurement of rebound was introduced decades ago (referred to in Ref. 11). Powell, Skelly, and Ubbelohde (8) measured the momenta and kinetic energies of impact for mercury fulminate and lead styphnate. In their calculations, they assumed without measurement a definite value for the coefficient of restitution of the impacting mass. In the present work, some measurements of the net kinetic energy, change of momentum (hereinafter called impulse), and time of impact for the initiator explosives mercury fulminate and lead azide are reported. The time measurements allowed estimations to be made of the forces involved and these were found to be comparable with those found by Taylor and Weale (10) by an entirely independent method.

## EXPERIMENTAL

### *Materials*

Dextrin lead azide was prepared from sodium azide which had been recrystallized from a water–acetone mixture. Separate 50 ml. aqueous solutions containing 4 gm. sodium azide and 10.2 gm. lead nitrate C.P. were simultaneously added from burettes (delivery time—134 sec.) into 250 ml. of 0.5% aqueous solution of dextrin. Microscopic examination showed that the crystals of lead azide were of the same form as those prepared by Lowndes (6).

[1] *Manuscript received February 24, 1953.*
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Mercury fulminate was prepared by a method given by Davis (5, p. 406).

*Impact Apparatus*

The essential parts of the impact apparatus are shown in Fig. 1. The hammer

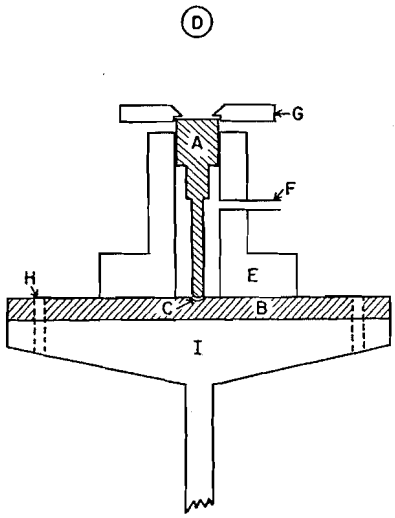



FIG. 1. Impact apparatus (schematic).

| | | |
|---|---|---|
| A—hammer | D—steel ball | G—steel ring for static load |
| B—base plate | E—hardwood guide | H—bolt hole |
| C—cavity in base plate | F—vent to suction | I—I beam |

was made from the rear axle of a 1929 model Pontiac automobile. It rested in a concentric cavity in a 0.5 in. thick steel base plate which had been cut from a high carbon steel road grader blade. The steel base plate was carefully faced and fastened securely by six large bolts to the smoothed upper face of an 18 in. I beam (approx. wt. = 110 lb.). Both the hammer and base plate were hardened by heat treatment and quenching. This arrangement of base plate and I beam ensured a large mass *as well as* the possibility of hardening the anvil. In all the experiments the hammer was under a static load obtained by means of a second class lever. The total load, including the hammer of 211 gm., was 40,098 gm.

Steel balls (S.K.F. ball bearings) of various sizes were dropped on the hammer by release from an electromagnet and their rebound was measured by the shadow cast on a lighted calibrated scale.

The original cavity in the base was obtained by bouncing a $1\frac{1}{2}$ in. diameter ball (larger than any used in the impact tests) on the hammer. Then, in carrying out a series of tests, the smallest balls and heights of fall were used at first, and these were increased in succession. This procedure prolonged the good condition of the base plate cavity and of the hammer. Whenever the end of the hammer became pitted by explosions, it was reshaped on a lathe to a radius of curvature of 5/32 in. with successive emery paper sizes 2, 00, and 0000. This procedure was necessary after 15 to 20 detonations of lead azide. Then the cavity in the base plate was repounded until the normal bounce height was secured.

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In carrying out an impact test, the cavity in the base plate was filled with initiator explosive by dusting with a camel's hair brush. (The initiator was kept over calcium chloride between tests.) The hammer and weight arm were gently lowered on top of the sample and the extra weight was then placed on the weight arm.

There was no difficulty in detecting the occurrence of an explosion, although mercury fulminate exhibited the phenomenon of partials a few times.

*Time of Impact Measurements*

The time of impact was measured in a way similar to that used by Bowden and Tabor (4). A wave controller using a cathode ray oscilloscope was designed and built by Dr. H. E. Johns* and one of us (N.R.S.H.). The controller used a thyratron which was applied to the horizontal plates to produce a linear beam of definite periodicity across the oscilloscope screen. At the same time a transient, which was produced by the closing of a voltage circuit by the impact of the hammer on the base plate, was applied to the vertical plates. The resulting impact wave trace on the oscilloscope screen was photographed with Kodak Verichrome film. The period of the trace was calibrated by photographing the trace of a standard 10,000 or 20,000 cycle sec.$^{-1}$ wave on the same film.

Because of a poor estimate of the expected length of the wave trace, the firing mechanism was inaccurately timed, and the length of the transient was estimated to be as much as 25% too short; that is, the times listed in Table III are at the most about 25% low; however, they are still related relatively.

*Bases of the Calculations*

The percentage of detonations are compared with (*a*) the kinetic energy assuming no rebound of the ball, (*b*) the net kinetic energy, and (*c*) the impulse or change in momentum. These are given by the following equations, respectively:

$$(a)\ mgh,$$
$$(b)\ mg(h_1 - h_2) = 980\, mh_1(1 - e^2),$$
$$(c)\ Ft = m(v_1 - v_2) = 44.3\, m(1 + e)h_1^{\frac{1}{2}},$$

where $m$ = ball mass, $g$ = gravitational constant, $h_1$ = initial fall height, $h_2$ = rebound height, $e = v_2/v_1 = (h_2/h_1)^{\frac{1}{2}}$ = coefficient of restitution, $F$ = force, $t$ = time over which ball goes from $v_1$ to $v_2$, $v_1$ = falling velocity before duration of contact, $v_2$ = rebounding velocity after duration of contact.

## RESULTS AND CALCULATIONS

*Impact Tests*

The results of about 500 impact tests on dextrin lead azide and 300 on mercury fulminate are given in Tables I and II respectively. At least 20 and sometimes 100 trials were made for each ball at each height (the numbers are given in brackets after the percentage detonations). In Figs. 2 and 3 the percentage detonations are plotted against gross kinetic energy, net kinetic energy, and impulse respectively.

*Time of Impact*

The times of impact as measured under various conditions are given in

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TABLE I

SENSITIVITY OF LEAD AZIDE TO KINETIC ENERGY AND IMPULSE

| Ball diam., in. | Ball mass, gm. | Height ($h_1$), cm. | $e$ | Detonations, % | $mgh$, ergs $\times 10^{-6}$ | Net kinetic energy, ergs $\times 10^{-6}$ | Impulse, c.g.s. units $\times 10^{-4}$ |
|---|---|---|---|---|---|---|---|
| 7/8 | 44.66 | 90 | 0.645 | 10.0(20) | 3.94 | 2.30 | 3.10 |
| " | " | 100 | 0.644 | 15.0(20) | 4.37 | 2.56 | 3.26 |
| " | " | 110 | 0.643 | 17.5(40) | 4.82 | 2.81 | 3.42 |
| " | " | 120 | 0.647 | 20.0(20) | 5.25 | 3.07 | 3.58 |
| 1 | 66.68 | 60 | 0.510 | 17.5(40) | 3.92 | 2.90 | 3.46 |
| " | " | 80 | 0.513 | 35.0(40) | 5.23 | 3.86 | 4.03 |
| " | " | 100 | 0.514 | 47.5(78) | 6.54 | 4.83 | 4.51 |
| " | " | 120 | 0.509 | 57.0(100) | 7.84 | 5.79 | 4.93 |
| 1-1/8 | 95.04 | 100 | 0.372 | 70.0(20) | 9.33 | 8.04 | 5.80 |
| " | " | 120 | 0.368 | 87.5(40) | 11.20 | 9.65 | 6.32 |

TABLE II

SENSITIVITY OF MERCURY FULMINATE TO KINETIC ENERGY AND IMPULSE

| Ball diam., in. | Ball mass, gm. | Height ($h_1$), cm. | $e$ | Detonations, % | $mgh$, ergs $\times 10^{-6}$ | Net kinetic energy, ergs $\times 10^{-6}$ | Impulse, c.g.s. units $\times 10^{-4}$ |
|---|---|---|---|---|---|---|---|
| 3/4 | 28.14 | 60 | 0.738 | 15.0(60) | 1.65 | 0.75 | 1.67 |
| " | " | 90 | 0.738 | 31.7(60) | 2.48 | 1.13 | 2.06 |
| " | " | 120 | 0.739 | 43.3(30) | 3.30 | 1.50 | 2.38 |
| 7/8 | 44.66 | 60 | 0.636 | 45.0(60) | 2.62 | 1.58 | 2.50 |
| " | " | 80 | 0.627 | 63.3(60) | 3.50 | 2.12 | 2.89 |
| " | " | 100 | 0.628 | 85.0(60) | 4.38 | 2.65 | 3.23 |

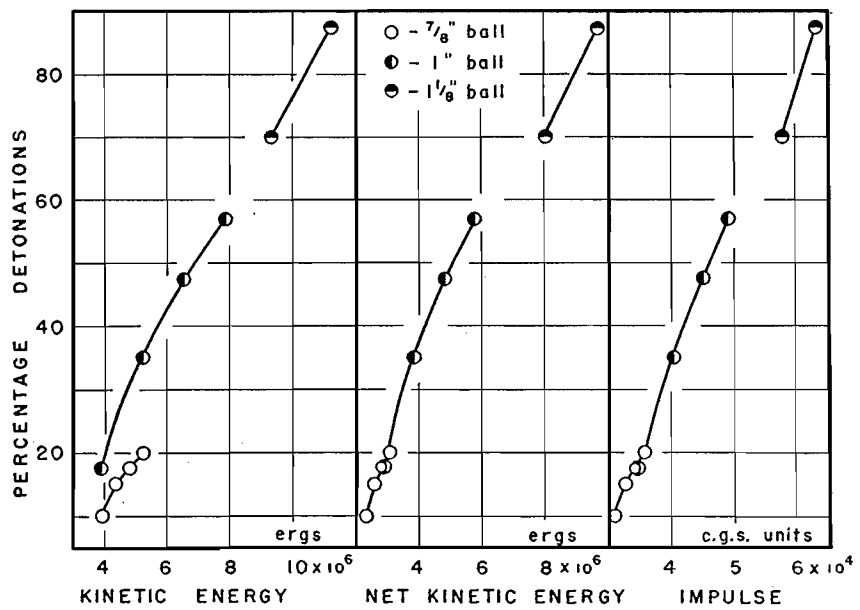



FIG. 2. Comparisons of the percentage of detonations of dextrin lead azide with gross and net kinetic energies and impulse.

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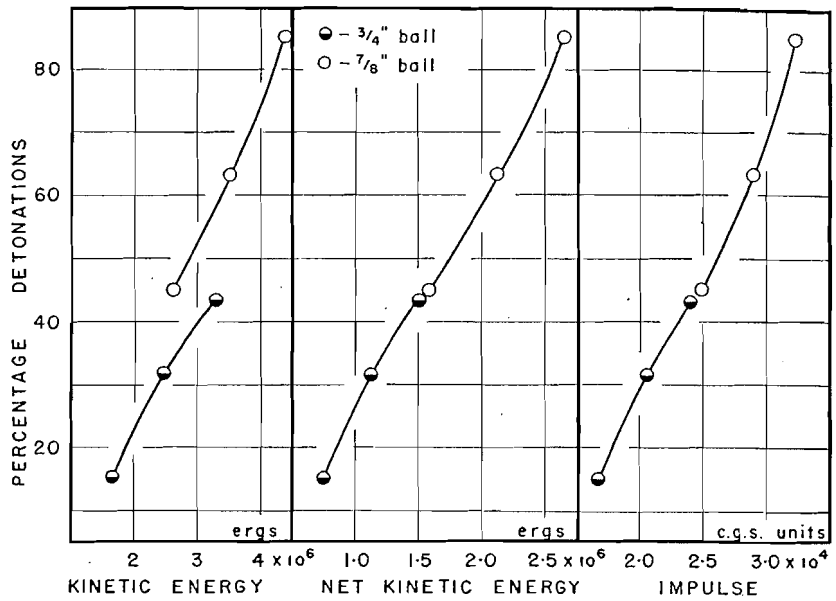



FIG. 3. Comparisons of the percentage of detonations of mercury fulminate with gross and net kinetic energies and impulse.

Table III. Between the tests on lead azide and mercury fulminate the base plate was reground and rehardened. This accounts for the slight change in the coefficient of restitution $e$ of the 7/8 in. ball in Tables I and II. Also, in some of the time experiments, norite was placed in the cavity between the hammer and base plate. The use of norite probably simulated the conditions of impact when initiator crystals rested between the hammer and base.

Hertz's theory of colliding metal pieces (1) shows that $t(rv/m^2)^{1/5} = k$, a constant, where $t$ = time of impact, $r$ = radius of steel ball, $v = v_1$ = velocity before impact, $m$ = ball mass. The constant $k$ has been calculated for the norite time experiments and is included in Table III. The evaluation of $k$ permits an estimation to be made of the time of impact within the lead azide detonation range where norite experiments were not made.

*Calculation of Impulsive Pressures*

Assuming that impulse determines the probability of detonation, an estimate of the impulsive pressure or force per unit area at 50% detonations can be made. The apparent area of contact between the hammer and base plate was 0.10 sq. cm. The hammer was under a static load of 400 kgm. cm.$^{-2}$ Under this compression, the 'true' area of contact with the initiators can be calculated from their crystal densities at known compressions (7). These are 0.88 of the apparent area for mercury fulminate, and 0.75 for lead azide.

*For Mercury Fulminate*

Total impulse at 50% detonations = $2.6 \times 10^4$ c.g.s. units. Time of impact at 50% detonations = $1.9 \times 10^{-4}$ sec. Force = $I/t = 1.37 \times 10^8$ dynes. Impulsive

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TABLE III

TIMES OF IMPACT

| Ball diam., in. | Height ($h_1$), cm. | Time of impact, sec. $\times 10^4$ | |
|---|---|---|---|
| *Original base plate* | | | |
| 7/8 | 90 | 0.62 | |
| " | 100 | 0.72 | |
| " | 110 | 0.88 | |
| " | 120 | 0.94 | |
| 1 | 60 | 1.01 | |
| " | 80 | 1.28 | |
| " | 100 | 1.38 | |
| " | 120 | 1.48 | |
| 1–1/8 | 100 | 1.65 | |
| *Reground base plate* | | | |
| 3/4 | 90 | 0.21 | |
| " | 120 | 0.39 | |
| 7/8 | 60 | 0.39 | |
| " | 90 | 0.54 | |
| " | 120 | 1.08 | |
| 1 | 60 | 0.72 | |
| " | 90 | 0.83 | |
| " | 120 | 1.07 | |
| *Reground base plate with norite* | | | $k$ (Hertz) $\times 10^4$ |
| 3/4 | 60 | 1.49 | 1.25 |
| " | 90 | 1.63 | 1.43 |
| " | 120 | 1.81 | 1.59 |
| 7/8 | 60 | 1.83 | 1.31 |
| " | 90 | 2.01 | 1.49 |
| " | 120 | 2.16 | 1.63 |

pressure = $1.37 \times 10^8/0.88 \times 0.1 = 1.56 \times 10^9$ dyne cm.$^{-2}$ or 11.3 ton in.$^{-2}$

*For Lead Azide*

Total impulse at 50% detonations = $4.6 \times 10^4$ c.g.s. units. Time of impact at 50% detonations (based on norite times and Hertz's formula) = $2.2 \times 10^{-4}$ sec. Impulsive pressure = $2.1 \times 10^8/0.75 \times 0.1 = 2.8 \times 10^9$ dyne cm.$^{-2}$ or 20.3 ton in.$^{-2}$

(Note: As the time of impact may be about 25% low, the above impulsive pressures may be about 25% high.)

*Coefficient of Restitution*

Values of the coefficient of restitution $e$ are included in Tables I and II. Their measurement is a useful method of testing the stability of the impact apparatus. The constancy of $e$ for any one ball over the range of fall heights used is considered an indication of a rigid system (1). The values of $e$ were found to be completely independent of the presence or absence of initiator explosive crystals, or of the occurrence or nonoccurrence of detonations.

The relation between ball weights and $e$ is given in Fig. 4. Shown are the results for (*a*) an earlier, more complex, apparatus which included a ball bearing

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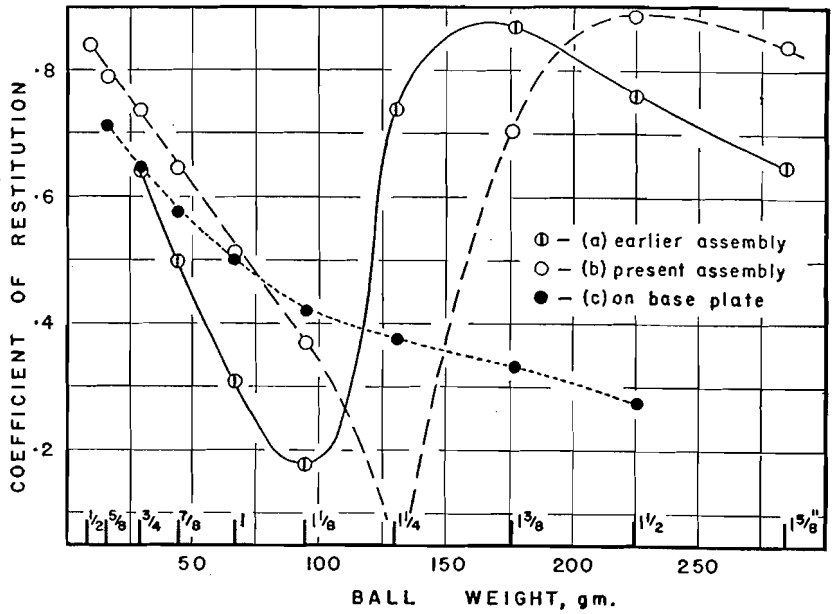



FIG. 4. The relationship between coefficient of restitution and ball weight for various assemblies.

as part of the hammer assembly, (*b*) the present apparatus (Fig. 1), and (*c*) the same balls when dropped directly on the base plate. It would appear that the curious periodic relation between ball weight and *e* arises largely from the hammer part of the apparatus, and may be related to its resonating frequency.

## DISCUSSION

Although the range of fall heights used in the present work was not sufficient to give overlapping in the critical regions of percentage of detonations (Figs. 2 and 3), yet the general trend is quite clear. It is apparent that both the *net* kinetic energy and the impulse are continuous functions of the percentage of detonations. Thus, no discrimination between the relative importance of kinetic energy and impulse in determining the probability of detonation can be made merely by varying the size of balls. If this is true for all impact machines, then one must look in other directions for such a discrimination.

Kinetic energy is dissipated in many directions, whereas impulse is probably conserved in one direction. A comparison of the absolute magnitudes of the net kinetic energy and the impulse for different impact assemblies may provide the basis for a critical test of which is the more important factor in detonation. In the present case, the assembly could have been varied by altering the mass of the hammer—this was not attempted.

Powell, Skelly, and Ubbelohde (8) have also determined the variation of the percentage of detonations with kinetic energy and impulse for mercury fulminate. Their value for the net kinetic energy at 50% detonations was about $8 \times 10^3$ ergs, compared with the present result of $1.7 \times 10^6$ ergs. On the other hand, their value for the impulse at 50% detonations was $1.2 \times 10^4$

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c.g.s. units, which is quite comparable with the present value of $2.6 \times 10^4$ c.g.s. units on the following grounds. Their area of contact appears to be about *one half* of the present one; their drift, containing a 3/16 in. diameter ball bearing, rested on a flat brass disk which was resting in turn on a prepressed sample of the initiator explosive; in the present case, the end of the hammer is the equivalent of a 5/16 in. diameter ball, and it rests on a sample of the initiator which is resting in turn in a cavity concentric with the end of the hammer. Thus, it would appear on the basis of the above comparisons involving radically different impact machines that impulse is the more important factor in initiating detonation.

In their calculations, Powell *et al.* assumed a value of 0.9 for the coefficient of restitution. Moreover, their impact assembly was not rigid: "a fraction of the momentum of the drift is lost owing to imperfect rigidity of the supports for the initiator (i.e. the brass disks, the Hoffman roller, etc.)"—(8, p. 294). It is possible that their results would have been more consistent if they had measured *e* and used a more rigid assembly. In spite of this, the impulses for two different drifts are parallel to each other over the range of percentage of detonations, and only differ by about 20% in the case of mercury fulminate and 12% in the case of lead styphnate.

A hypothesis which favors kinetic energy is that of Bowden and Gurton (2) who, on the basis of work with added grits, come to the conclusion that the initiation of explosives by mechanical impact is a frictional phenomenon. In their words: "The mechanical energy of the blow must first be degraded to heat to form a hot spot of small but finite size. Thermal initiation then occurs at this hot spot." This round-about transfer of energy (i.e. a transfer from mechanical to thermal to chemical energies) is difficult to conceive on thermodynamic grounds. The more direct transfer from mechanical to chemical energies would be suggested if impulse is the factor determining the probability of detonation on impact.

In another paper (3), Bowden and Gurton report what they designate as "the delay between impact and explosion" *times* measured by means of the high speed photography of actual explosions on impact. Practical difficulties prevented the measurement of the times for ordinary lead azide and mercury fulminate but in the presence of a glass grit particle, they were of the order of $1 \times 10^{-4}$ sec. This is very similar to the times of impact reported in the present work, and would suggest that the so-called 'delay'—presumably to allow mechanical energy to be changed to thermal energy and then to detonation—may be none other than the normal time of impact connected with the direct transfer of momentum. For larger crystals of lead azide, Bowden and Gurton found the 'delay' time to be about $1 \times 10^{-5}$ sec., an observation difficult to account for on the basis of their hypothesis, but not so on the basis of the momentum hypothesis.

The magnitude of the impulsive pressures necessary for the detonation of mercury fulminate may be compared with another estimate available in the literature. Taylor and Weale (10) compared the impulse necessary to detonate mercury fulminate with that necessary to indent a lead block. They concluded

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that "the impulsive stress required to initiate a thin layer of mercury fulminate was not less than 7 tons per sq. in." (10, p. 999). Further, they estimated the time of impact to be of the order of $10^{-5}$ sec.

Some realization of the apparatus difficulties involved in this type of work may be seen by an examination of the velocities of impact necessary for the detonation of initiator explosives. Referring to the work of Andrews (1) and of Bowden and Tabor (4), it is apparent that the velocities used here (343 to 486 cm. sec.$^{-1}$) are well beyond the velocity where the plastic deformation of steel sets in. Bowden and Tabor found that for very hard tool steel at higher velocities (100 to 200 cm. sec.$^{-1}$) the conductance curves for the time of impact became asymmetric, showing that plastic deformation occurs. Andrews has shown that Hertz's well-known formula only strictly applies for pure elastic rebound, which only occurs at low velocities of the order of a few cm. sec.$^{-1}$ It would appear, however, from the present results, that the occurrence of some plastic deformation is not too important provided that an otherwise *rigid* assembly is used in impact tests.

ACKNOWLEDGMENTS

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# STUDIES OF LIGNIN BIOSYNTHESIS USING ISOTOPIC CARBON

## II. SHORT-TERM EXPERIMENTS WITH $C^{14}O_2$ [1]

By Stewart A. Brown, K. G. Tanner, and J. E. Stone[2]

ABSTRACT

The formation of lignin in wheat plants from $C^{14}O_2$, during the period of rapid lignification, has been studied over the first few hours of photosynthesis by measuring the incorporation of carbon-14 into the guaiacyl and syringyl portions of the lignin molecule. Plants grown 62 days from seeding were exposed to 20 microcuries of $C^{14}O_2$ in a closed chamber for 20 min., and grown for periods of 1 to 24 hr. in a normal atmosphere before harvesting. Synthesis of lignin is most rapid four to six hours from activation, the syringyl residues apparently being formed more slowly than the guaiacyl. A slower rate of formation persists for the remainder of a one-day period, probably as a result of recycling in the carbon pool. Cellulose acquires carbon-14 more rapidly than lignin during the period immediately following administration of $C^{14}O_2$, but after three or four hours when synthesis of lignin has become rapid, the total carbon-14 content of both components reaches about the same value.

## INTRODUCTION

Earlier studies carried out in this laboratory (5) have traced the incorporation of labelled carbon dioxide into those portions of the wheat straw lignin molecule which yield phenolic aldehydes on nitrobenzene oxidation. The results showed that the total carbon-14 content of the syringaldehyde residue remained substantially constant after the first day, whereas that of *p*-hydroxybenzaldehyde exhibited a gradual decrease. That of the vanillin, after a small initial decline (possibly due to a decrease in more easily oxidizable guaiacyl-type lignans), also reached a constant level. No investigation was made, however, of the rate of incorporation of the $C^{14}$ into lignin during the first day of activation. This paper reports the extension of the previous work to cover this early period.

The principles employed in these experiments were essentially those of the earlier studies, but several refinements in technique were developed. The use of a smaller activation chamber together with hydroponic cultivation of the wheat increased the convenience of activating the plants, and purification of the phenolic aldehydes was facilitated by precipitation as the 2,4-dinitrophenylhydrazones.

Preliminary experiments indicated that when plants were exposed to $C^{14}O_2$ for periods up to 20 min., and then permitted to continue growing in a normal atmosphere for further periods up to about an hour, very little carbon-14 entered the lignin. Considerable amounts appeared, however, after five hours of growth. A series of experiments was therefore carried out in which a group of similar plants were grown for periods of one to seven hours following activation. For comparison, other plants were grown for 24 hr. to obtain the approximate value of the maximum total activity.

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*Contribution from the National Research Council, Prairie Regional Laboratory, Saskatoon, Sask. Issued as N.R.C. No. 3032.*
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## EXPERIMENTAL

### *Cultivation of the Wheat Plants*

The Thatcher wheat plants used in these experiments were grown in aqueous nutrient solution. In addition to providing a reproducible source of inorganic nutrients, this procedure facilitated the use of the comparatively small activation chamber described below. The seeds were planted in moist Vermiculite, and the seedlings were allowed to grow to a height of about 10 cm. The roots were washed free of adhering particles, and placed in opaque jars in 500 ml. of nutrient of the following composition: $CaSO_4$, 136 mgm.; $Ca(NO_3)_2$, 164 mgm.; $KNO_3$, 101 mgm.; $MgSO_4$, 240 mgm.; $KH_2PO_4$, 136 mgm., *or* trace element solution, 0.1 ml.; demineralized water, 1 liter.

The composition of the trace element solution[3] was: $H_3BO_3$, 28 gm.; $ZnSO_4$, 2 gm.; $FeSO_4$, 50 gm.; $MnSO_4$, 20 gm.; $CuSO_4$, 2 gm.; concentrated $H_2SO_4$, 5 ml.; demineralized water, 1 liter.

The seedlings were allowed to grow through holes in the rubber stoppers of the jars, and were supported by cotton wool loosely stuffed in the holes, and later also by rings made from aluminum welding rod. A slow stream of air was passed continuously through the solution, which was changed twice weekly. All plants were grown in a greenhouse.

### *Activation with $C^{14}O_2$*

The plants used for these experiments were 62 days old and well headed out; this age was selected because the rate of lignification is comparatively rapid during this period of growth (7). Before exposure to $C^{14}O_2$ they were kept in darkness for 24 hr.

The activation chamber was constructed of a 2 liter flask with 24/40 and 45/50 joints, and a 6 × 70 cm. vertical glass tube with a 45/50 joint, open at the top. The smaller joint of the flask held a T-tube, one end of which was closed with rubber tubing and a clamp, and the other connected to a 500 ml. siphon bottle. A small side arm just above the center of the large glass tube provided for admission of carbon dioxide from a small generating flask.

Each plant, with its supporting stopper, was removed from the nutrient and placed in the vertical tube. The tube was connected to the flask, the latter containing water into which the roots extended. The open end of the tube was tightly stoppered, and the air-tight assembly was placed in bright sunlight so that the rate of photosynthesis and incorporation of $C^{14}O_2$ would be at a maximum. A partial vacuum was created within by siphoning off as much water as would flow from the closed system. Then 0.2 ml. of 0.03 *M* $Na_2C^{14}O_3$, containing 20 μc. of carbon-14, was introduced by means of a syringe and needle through a serum bottle cap on the generating flask, which already contained 72% perchloric acid. Air was then sucked through a side arm in the carbon dioxide generator to sweep any remaining carbon dioxide into the chamber, and the process was repeated using 0.5 ml. of inactive 0.3% sodium carbonate solution. After 20 min. exposure the air in the chamber was swept out into a gas absorption

[3] *Phosphate and trace elements were added to alternate changes of nutrient; addition of both together resulted in iron deficiency symptoms, presumably due to the complexing of that element by phosphate (2).*

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tower containing sodium hydroxide solution. After five minutes' vigorous sweeping the apparatus was disassembled and the plants replaced in nutrient, where they were allowed to grow in a normal atmosphere for periods of 1 to 24 hr.

*Isolation of Lignin Degradation Products*

Each plant, with heads and roots removed, was cut into 1 cm. lengths. The tissue was then killed rapidly by dropping it into water at about 90° in a Waring blendor and disintegrating for 10 min. The resulting mixture was transferred to a flask, and after a further 10 min. the supernatant was decanted off. The coarse fibrous material which remained was filtered off, sucked free of water, and dried at 105°. It was then extracted with ethanol–benzene, 1:2, in a Soxhlet apparatus until the solvent was colorless, dried thoroughly *in vacuo*, and ground to pass a 60 mesh screen.

Nitrobenzene oxidation of this material and separation of the resulting phenolic aldehydes was done by methods similar to those used in earlier work (6). One and a half milliliters of nitrobenzene and 25 ml. of 2 *N* sodium hydroxide were used per gram of dry plant material, and the 0.5 to 2 gm. samples were oxidized in a hydrogenator bomb. The residue of unattacked cellulose was filtered off on a glass frit, washed with water, and reserved for purification (see below). The filtrate and washings, after separation of the small oil layer, were made up to a convenient known volume (50–100 ml.) and 0.2 ml. was analyzed for phenolic aldehydes (6). To remove some impurities the remainder was extracted overnight with benzene in a continuous liquid–liquid extractor. Then, after acidification to pH 3, the phenolic aldehydes were extracted into benzene in the same way. The benzene was removed *in vacuo* and replaced by ethanol, and the ethanolic solution after concentration to about 1 ml. was chromatographed on three to five sheets of Whatman No. 1 paper, 46 × 57 cm. Ethanol solutions of the aldehydes separated in this way were decolorized with charcoal, concentrated to a volume of 1–2 ml., and treated with an excess of 2,4-dinitrophenylhydrazine reagent.[4] The precipitate of aldehyde 2,4-dinitrophenylhydrazone was filtered off, washed with cold ethanol, and recrystallized once from ethanol–pyridine. Further recrystallization of the active compounds produced no change in specific activity.

As there is some doubt that *p*-hydroxybenzaldehyde originates from lignin in wheat (5, 7) no measurements of its activity were made during this experiment.

*Isolation of Cellulose*

The residue of crude cellulose obtained following the nitrobenzene oxidation was further washed on the frit with ethanol and benzene, to remove adhering nitrobenzene and dissolved impurities. After drying, it was submitted to the series of treatments described by Lewis (3). One such series was usually sufficient to yield a pure white, fluffy cellulose.

To obtain a measure of the cellulose content of the original dry cell wall material, each sample was analyzed by Tettamanzi's modification of the Kürschner-Hoffer method (8). Samples of 10 to 30 mgm. were refluxed for one

[4] *This was prepared as described by Shriner and Fuson (4, p. 97) except that no water was added.*

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hour with 5 ml. of concentrated nitric acid and methanol, in a 1:2 ratio by volume, and the residue of cellulose was filtered off and weighed.

*Determination of Radioactivity*

All samples were counted in the gas flow counting chamber of a Marconi type 138-660 proportional scaler.

The 2,4-dinitrophenylhydrazones were plated from pyridine solution on aluminum disks for counting, and the observed counts were corrected to "infinite thinness" from a self-absorption curve. The cellulose samples were burned in a combustion train, the carbon dioxide was absorbed in a carbonate-free sodium hydroxide solution, and precipitated as barium carbonate. This was plated for counting by filtration on disks of Whatman No. 3 filter paper, the counts being made at "infinite thickness".

In both cases the radioactivity was calculated as microcuries by reference to a carbon-14 standard obtained from the National Bureau of Standards, Washington. This standard, a solution of sodium carbonate, decayed at the rate of 1280 disintegrations per sec. per ml.; and after appropriate dilution it was precipitated and plated as barium carbonate, or plated at "infinite thinness" as sodium carbonate, using a procedure as nearly as possible the same as that used for the unknown samples.

## RESULTS AND DISCUSSION

The changes in the carbon-14 content of vanillin and syringaldehyde during the first 24 hr. after activation of the plants are depicted in Fig. 1. It is evident that radioactive carbon begins to reach the lignin in appreciable quantities only after a lapse of several hours. From about four to five hours in the case of vanillin, and five to six hours in that of syringaldehyde the incorporation of carbon-14 is very rapid, and beyond this time there are indications of a levelling off of the curve. Despite this, however, the net gain of activity during the remainder of the 24 hr. period is about equal to that attained in the first seven hours, so it is evident that a slower incorporation persists until a maximum is reached, presumably near 24 hr. after activation. Whereas during the period of rapid synthesis the total carbon-14 content of the syringaldehyde seems always to lag behind that of the vanillin, this situation may be reversed in the period represented by the broken lines; in one experiment syringaldehyde of appreciably higher total activity was obtained after 24 hr. Such divergent results must represent fluctuations in relative rates of synthesis, and are not unexpected in view of variations among plants, and of the fact that different ones were, of course, used for each experiment. While the necessity for an additional methylation (probably by transmethylation from the methionine system (1)) would satisfactorily account for the early lag in the synthesis of the syringyl residue, direct comparisons with the guaiacyl should be made only with caution, as consistent differences in yield of vanillin and syringaldehyde during the oxidation could conceivably account for part of the difference.

It appears reasonable to conclude that most of the incorporation of carbon dioxide into lignin by the most direct synthetic route occurs during the first seven hours following activation. The slower build-up which continues for

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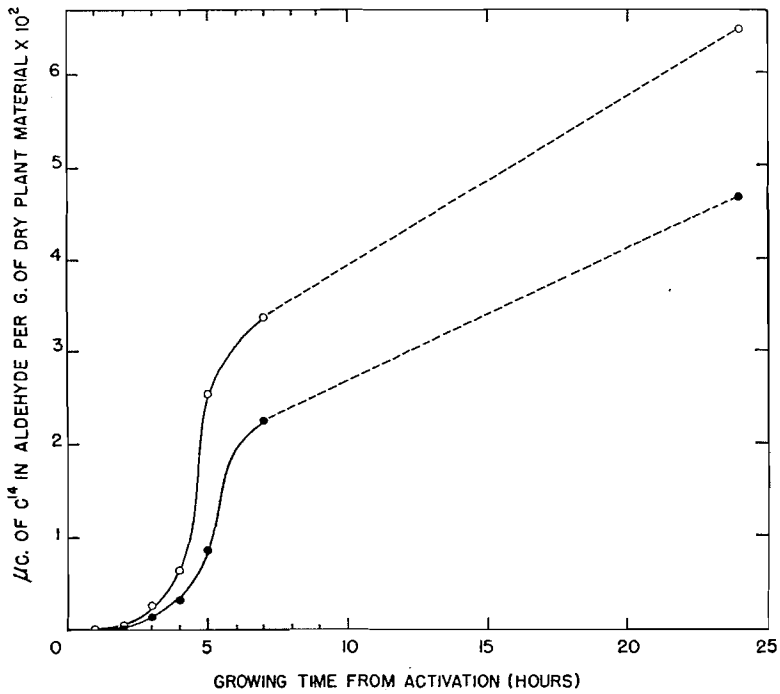



FIG. 1. Incorporation of $C^{14}$ from carbon dioxide into vanillin and syringaldehyde obtained on lignin oxidation. The ordinate values are obtained by multiplying microcuries per millimole of the aldehyde (calculated from the count) by the millimoles of aldehyde per gram of ash-free straw (calculated from assay of the oxidation mixture). ○-Vanillin. ●-Syringaldehyde.

approximately 17 hr. more can be accounted for by the recycling of simple precursors in the plant's carbon pool, a process which would continue until they were respired, or converted into relatively stable compounds such as other cell wall constituents.

Because lignin is a substance of unknown chemical structure, it is not possible to obtain an accurate figure for the radioactive carbon content of the entire lignin fraction, as opposed to that of the derived phenolic aldehydes. In an earlier paper (7) however, a procedure was given for calculating total lignin based on the aldehyde yield from young plants and the 72% sulphuric acid lignin content of mature plants; this method is considered to give the closest approach to the true lignin content. As calculated in this way, the percentage of lignin is equal to the percentage of vanillin at the same age multiplied by a factor which at an age of 62 days equals 6. Consequently, if the total carbon-14 content of vanillin, as shown in Fig. 1, be multiplied by 6, it is possible to arrive at a value for the total carbon-14 content of lignin. The results are shown in the fourth column of Table I. The assumption is made, of course, that lignin is uniformly labelled (5), and it must be emphasized that these figures can be taken to represent only approximate values, as the data used to calculate the above factor were obtained with plants grown under somewhat different conditions.

Table I shows that, except during very early stages of synthesis, the total

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TABLE I

DISTRIBUTION OF $C^{14}$ IN CELL WALL AFTER ADMINISTRATION OF $C^{14}O_2$

| Growing time from activation (hours) | μc. of $C^{14}$ in cell wall derivative per gram of dry cell wall material | | | | |
|---|---|---|---|---|---|
| | Vanillin | Syringaldehyde | Lignin (calc'd from vanillin) | Cellulose | Lignin / Cellulose |
| 1 | $6.7 \times 10^{-5}$ | | $4.0 \times 10^{-4}$ | $8 \times 10^{-3}$ | 0.05 |
| 2 | $4.1 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $2.5 \times 10^{-3}$ | $1.8 \times 10^{-2}$ | 0.14 |
| 4 | $6.40 \times 10^{-3}$ | $3.11 \times 10^{-3}$ | $3.8 \times 10^{-2}$ | $4.5 \times 10^{-2}$ | 0.85 |
| 5 | $2.55 \times 10^{-2}$ | $8.52 \times 10^{-3}$ | $1.5 \times 10^{-1}$ | $1.52 \times 10^{-1}$ | 1.0 |
| 7 | $3.38 \times 10^{-2}$ | $2.26 \times 10^{-2}$ | $2.0 \times 10^{-1}$ | $2.28 \times 10^{-1}$ | 0.9 |
| 24 | $6.48 \times 10^{-2}$ | $4.67 \times 10^{-2}$ | $3.9 \times 10^{-1}$ | $2.68 \times 10^{-1}$ | 1.5 |

carbon-14 entering lignin is roughly the same as that appearing in cellulose. The synthetic route to cellulose is probably the more direct, and it is to be anticipated that the discrepancy in favor of cellulose would be large in the early stages, and would be overcome as the rate of lignin formation from the administered $C^{14}$ increased. It is of interest that even at the stage of maturity investigated, when the rate of lignification is greatest, the amount of carbon dioxide converted to lignin does not exceed that employed in the synthesis of cellulose.

It may also be noted that after 24 hr. the carbon-14 appearing both in lignin and in cellulose is of the order of $1\frac{1}{2}$ to 2% of that administered. The percentage of that actually absorbed by the plant is undoubtedly much higher, but the method of killing did not permit the total $C^{14}$-content to be determined with accuracy.

Further studies of possible intermediates between carbon dioxide and lignin are in progress.

ACKNOWLEDGMENT

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# REARRANGEMENT IN THE REACTION BETWEEN 2-PHENYLETHYLAMINE-1-$C^{14}$ AND NITROUS ACID[1]

By C. C. Lee and J. W. T. Spinks

ABSTRACT

On treatment with sodium nitrite, 2-phenylethylamine-1-$C^{14}$ in aqueous hydrochloric, perchloric, acetic, or glacial acetic acid gives rise to products in which the $C^{14}$ atoms have been rearranged from the C-1 to the C-2 position to an extent of 20.5 to 22.5%. The results are discussed on the basis of carbonium ions as possible reaction intermediates.

## INTRODUCTION

The concept of a carbonium ion as an intermediate in the reaction between a primary amine and nitrous acid was elaborated in 1932 by Whitmore and Langlois (12). It is the basis for the presently accepted mechanistic interpretation of the Demjanow reaction for ring expansion (1). Products arising from rearrangements characteristic of carbonium ion processes have been observed for reactions of primary amines with nitrous acid; for example, the treatment of 2,2-diphenylethylamine with nitrous acid gave benzylphenylcarbinol (3, 6). The application of the tracer technique has recently furnished data, on rearrangements, which were previously unobtainable. Thus insight into the nature of the intermediate formed in interconversion reactions of cyclobutyl, cyclopropylcarbinyl, and allylcarbinyl derivatives was obtained from a study of the reaction of $C^{14}$-labeled cyclopropylcarbinylamine with nitrous acid (8). The migration ratios, with reference to phenyl, of several substituted aryl groups were determined by the nitrous acid induced rearrangement of the corresponding 2,2-diarylethylamine-1-$C^{14}$ (3), and the formation of 1.5% of rearranged product, ethanol-2-$C^{14}$, was found when ethylamine-1-$C^{14}$ was treated with nitrous acid (9).

This paper reports observations on the reaction between 2-phenylethylamine-1-$C^{14}$ and nitrous acid.

## RESULTS AND DISCUSSION

Carboxyl-labeled phenylacetic acid, prepared by carbonation of benzylmagnesium chloride with $C^{14}O_2$, was converted to the amide which in turn was reduced with lithium aluminum hydride to give 2-phenylethylamine-1-$C^{14}$. On oxidation with alkaline potassium permanganate, inactive benzoic acid was produced from the labeled amine, indicating that all the $C^{14}$-activity was in carbon-1.

When the labeled 2-phenylethylamine was dissolved in 10% hydrochloric, 10% perchloric, or 50% acetic acid and treated with an aqueous solution of sodium nitrite, the product isolated was 2-phenylethanol. Attempts to isolate, by fractional distillation, any styrene that might have resulted from possible elimination reactions were not successful. Part of the 2-phenylethanol was

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*Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*



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TABLE I

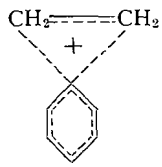
RADIOACTIVITY DATA FROM NITROUS ACID – 2-PHENYLETHYLAMINE-1-$C^{14}$ REACTION

| Compound | Reaction medium | Observed activity,[1] counts/min. | | Corrected activity,[2] counts/min./mM. | | % Rearrangement | |
|---|---|---|---|---|---|---|---|
| | | Run I | Run II | Run I | Run II | Run I | Run II |
| $C_6H_5NHCSNHCH_2CH_2C_6H_5$[3] | | 1185 ± 11.2 | | 303 | | | |
| $C_6H_5COOH$[3] | | 0.5 ± 2.5 | | 0.0 | | | |
| $C_6H_5NHCOOCH_2CH_2C_6H_5$[4] | 10% HCl | 1240 ± 11.2 | 1232 ± 11.3 | 299 | 297 | | |
| $C_6H_5COOH$[4] | " | 530 ± 5.4 | 502 ± 5.3 | 64.6 | 61.2 | 21.6 | 20.6 |
| $C_6H_5NHCOOCH_2CH_2C_6H_5$[4] | 10% $HClO_4$ | 1257 ± 11.3 | 1233 ± 11.2 | 303 | 297 | | |
| $C_6H_5COOH$[4] | " | 552 ± 5.8 | 548 ± 5.8 | 67.3 | 66.8 | 22.2 | 22.5 |
| $C_6H_5NHCOOCH_2CH_2C_6H_5$[4] | 50% HOAc | 1241 ± 11.5 | 1261 ± 11.5 | 299 | 304 | | |
| $C_6H_5COOH$[4] | " | 515 ± 5.7 | 511 ± 5.7 | 62.8 | 62.3 | 21.0 | 20.5 |
| $C_6H_5NHCOOCH_2CH_2C_6H_5$[4] | Glacial HOAc | 1220 ± 11.3 | 1241 ± 11.4 | 294 | 299 | | |
| $C_6H_5COOH$[4] | " | 531 ± 5.6 | 510 ± 5.5 | 64.7 | 62.2 | 22.0 | 20.8 |

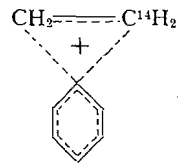
[1] *"Infinitely thick" samples of constant geometry measured in windowless Q-gas counter.*
[2] *Observed activity × molecular weight × $10^{-3}$.*
[3] *From 2-phenylethylamine-1-$C^{14}$ before reaction with nitrous acid.*
[4] *From products of reaction between 2-phenylethylamine-1-$C^{14}$ and nitrous acid.*

converted to its phenylurethan for activity determination. The remainder was oxidized with alkaline permanganate to benzoic acid. The radioactivity in the benzoic acid so obtained indicated a 20.5–22.5% rearrangement of the $C^{14}$-activity from the C-1 to the C-2 position during the conversion of the amine to the alcohol (Table I). When the reaction was carried out in glacial acetic acid and solid sodium nitrite was used, the product was 2-phenylethyl acetate which could be converted to 2-phenylethanol by treatment with lithium aluminum hydride or oxidized directly to benzoic acid with alkaline potassium permanganate. In the oxidation, probably the ester was first hydrolyzed by the alkaline medium. The degree of rearrangement in the acetate was the same as that obtained when the reaction was carried out in aqueous acids (Table I).

Recent interest in the structural representation of "nonclassical" carbonium ions poses the question whether the phenylethyl cation may have a bridged structure, the "ethylenephenonium ion" (I). In the reaction between 2-phenylethylamine-1-$C^{14}$ and nitrous acid, the observed degree of rearrangement appears to have eliminated the possibility of the bridged ion as the only intermediate. If this reaction were to proceed solely and directly through IA, the result-



I



IA

ing product, if isotopic effect were neglected, would consist of equal amounts of 2-phenyl-ethanol-1-$C^{14}$ and 2-phenylethanol-2-$C^{14}$, equivalent to a 50% rearrangement.

To explain the observed results, one may assume that part of the reaction would lead to a rearranged product, arising, for example, from IA as reaction intermediate, and the remainder would proceed via some process or processes without rearrangement. One possible route that would lead to no rearrangement might be the formation of diazophenylethane in the course of the reaction:

$$C_6H_5CH_2C^{14}H_2\overset{+}{N}_2 \xrightarrow{-H^+} C_6H_5CH_2C^{14}HN_2 \xrightarrow{H_2O} C_6H_5CH_2C^{14}H_2OH + N_2.$$

However, Roberts and Yancey (9) have shown that in the ethylamine – nitrous acid reaction, less than 10% of the ethanol could have been formed via a diazohydrocarbon intermediate.

A more probable interpretation of the results is depicted below:

$$C_6H_5CH_2C^{14}H_2\overset{+}{N}_2 \xrightarrow{-N_2} C_6H_5CH_2C^{14}\overset{+}{H}_2 \rightleftarrows IA \rightleftarrows \overset{+}{C}H_2C^{14}H_2C_6H_5$$

$$\text{IIA} \qquad\qquad \text{IIB}$$

$$X = OH \text{ or } OAc \qquad\qquad \downarrow X^- \qquad\qquad \downarrow X^-$$

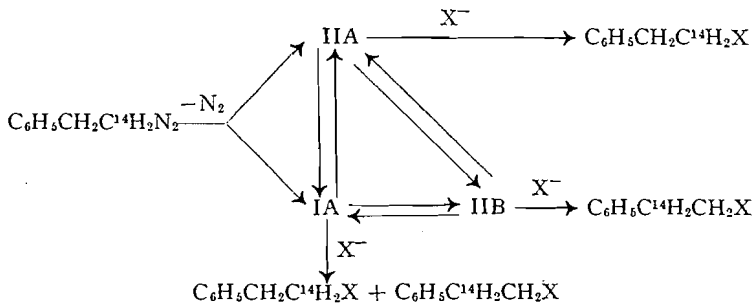
$$C_6H_5CH_2C^{14}H_2X \qquad\qquad C_6H_5C^{14}H_2CH_2X$$

The 2-phenylethyldiazonium ion may first give rise to IIA which can rearrange via IA to IIB. However, IIA may react with the conjugate base of the solvent

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($OH^-$ or $OAc^-$) faster than it can rearrange, resulting in a predominance of products with no rearrangement as observed.

It should be pointed out that the existence of IA or IIB or both cannot be distinguished from radioactivity data alone. Of course, IA may react directly with $OH^-$ or $OAc^-$ to give the final products without proceeding through IIA and IIB. The possibility that IIA may rearrange directly to IIB, though unlikely, is not eliminated by the results from the tracer studies. Moreover, the observed degree of rearrangement can also be explained by assuming that the reaction proceeds partly through IIA and partly through the direct formation of IA. A series of reactions, analogous to that given by Roberts and Yancey (9), which includes all these possibilities is as follows:




It is not likely that these reactions would all take place during the treatment of 2-phenylethylamine with nitrous acid. All of them, however, are possibilities, appropriate combinations of which can satisfactorily account for the observed degree of rearrangement.

It is of interest to note that in the 3-phenyl-2-butanol system, Cram (4) found that with the tosylate of one of the stereoisomers, the ability of phenyl to participate in an intramolecular displacement reaction is about eight times the ability of hydrogen. The same trend is observed from a comparison of the degree of rearrangement reported here for 2-phenylethylamine-1-$C^{14}$ and that reported by Roberts and Yancey (9) for ethylamine-1-$C^{14}$. The ratio of phenyl shift to hydride shift would be 20 to $22/1.5 \simeq 14$.

In view of the finding of Leete and co-workers (7) that an essentially 100% *p*-methoxyphenyl shift occurs in the conversion of *p*-vinylanisole to homoanisaldehyde by oxidation with yellow mercuric oxide and iodine, it would be logical to expand the present studies to include labeled substituted arylethylamines. Dr. J. D. Roberts has kindly informed one of us (C.C.L.) that studies with 2-*p*-nitrophenyl-, 2-*p*-methoxyphenyl-, as well as 2-phenylethylamine-1-$C^{14}$ have been completed in his laboratory and that the results are in press.

## EXPERIMENTAL

### *Phenylacetamide-1-$C^{14}$*

Phenylacetic acid-carboxyl-$C^{14}$ (400 mgm.), prepared according to the method given by Calvin *et al.* (2), and thionyl chloride (2 ml.) were heated on a steam bath under reflux for one-half hour. The excess thionyl chloride was removed *in vacuo*, and the residue taken up in dry ether. Ammonia, generated

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by heating concentrated ammonium hydroxide, was bubbled into the ether solution. The amide, together with some ammonium chloride, precipitated. The product was collected by filtration, the inorganic salt being removed by thorough washing with distilled water. After drying, the colorless crystalline product weighed 288 mgm. (75%), m.p. 155–157°C. (lit. (2) m.p. 155–158°C.).

*2-Phenylethylamine-1-$C^{14}$*

In trial runs with nonlabeled materials, the reduction of phenylacetamide with lithium aluminum hydride according to the method of Uffer and Schlittler (11) required reaction times of 30–40 hr. for runs using 5–10 gm. of the amide. The yields obtained were of the order of 50%. By using a small amount of the amide in a fairly large volume of ether, thus overcoming the difficulties arising from the slight ether solubility of the amide, and isolating the product with the aid of added ordinary 2-phenylethylamine as carrier, the labeled amide was reduced to the amine as follows.

In a three-necked flask fitted with reflux condenser, dropping funnel, and stirrer was placed 400 mgm. of lithium aluminum hydride in 40 ml. of anhydrous ether. To the stirred solution, 250 mgm. of phenylacetamide-1-$C^{14}$ ($3.81 \times 10^4$ counts/min./mgm.,* total activity = $9.53 \times 10^6$ counts/min.) in 250 ml. of dry ether was added. Stirring was continued for six hours. The resulting mixture was decomposed by the addition of an excess of a 10% aqueous solution of sodium hydroxide. The ether was then separated and the aqueous layer extracted with more ether. To the combined ether solution, approximately 5 gm. of ordinary 2-phenylethylamine was added as carrier. After drying over anhydrous sodium sulphate, the ether was removed using an efficient column. The residue was distilled, the product boiling over the range of 195–198°C. (lit. (10) b.p. 198°C.). The recovery was 4840 mgm. ($0.93 \times 10^3$ counts/min./mgm. of the hydrochloride,* total activity = $5.86 \times 10^6$ counts/min.). The yield, based on the total activity recovered, was 61.5%. A further quantity of inactive 2-phenylethylamine was added to give a stock of about 35 gm. of labeled amine which was used in all subsequent reactions.

*N-Phenyl-N'-2-phenylethyl-1-$C^{14}$-thiourea*

The phenylthiourea derivative of 2-phenylethylamine-1-$C^{14}$ was prepared by treating the labeled amine with phenylisothiocyanate according to established methods (10). It melted at 135°C. (lit. (10) m.p. 135°C.). Its activity is recorded in Table I.

*Oxidation of 2-Phenylethylamine-1-$C^{14}$*

One gram of 2-phenylethylamine-1-$C^{14}$, 8 gm. of potassium permanganate, and 5 gm. of sodium hydroxide in 50 ml. of distilled water were placed in a 125-ml. erlenmeyer flask and heated on a steam bath for three hours with occasional shaking. The resulting mixture was cooled, the manganese dioxide removed on a suction filter and thoroughly washed with water. The filtrate and washings were acidified with sulphuric acid. Sodium bisulphite was added in small portions until the excess permanganate was reduced and the solution

**Measured as "infinitely thin" samples in a windowless counter.*

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became colorless. The product was then extracted from the aqueous solution with ether. Removal of the solvent from the ethereal extract gave a colorless residue. Recrystallization from water gave 0.76 gm. (84%) of benzoic acid, m.p. 121°C. It was not radioactive (Table I) indicating that all the activity of the labeled amine was in the C-1 position.

*Reaction between 2-Phenylethylamine-1-$C^{14}$ and Nitrous Acid*

A. *In Aqueous Acids*

In a 125-ml. erlenmeyer flask equipped with a magnetic stirrer was placed 3.63 gm. (0.03 mole) of 2-phenylethylamine-1-$C^{14}$. Ten per cent hydrochloric acid, 10% perchloric acid, or 50% acetic acid was added until all the amine was dissolved and the solution was acid to bromophenol blue. The flask was then immersed in an ice bath and agitated while a solution of 4.14 gm. (0.06 mole) of sodium nitrite in 10 ml. of water was added portionwise, more acid being introduced at the same time to keep the reaction medium acidic. The ice bath was then removed and the reaction mixture stirred at room temperature for one hour. During this period of stirring, an additional 2.07 gm. (0.03 mole) of solid sodium nitrite was added, together with more acid when necessary to maintain an acidic medium. The resulting mixture was finally heated on a steam bath for 10 min. before it was cooled and extracted with ether. The extract, after being washed with dilute acid, alkali, and water and being dried over anhydrous sodium sulphate, was concentrated until all the ether had been removed. The residue was distilled at atmospheric pressure in a distillation flask with a long side arm serving as air condenser. The product, 2-phenylethanol, boiled at 215–218°C. (uncorrected), $n_D^{25}$ 1.5318; phenylurethan, m.p. 79–80°C. (lit. (5) $n_D^{16.8}$ 1.5337; phenylurethan, m.p. 79–80°C.). The yields from various runs are listed below. Trial distillations under reduced pressure showed little, if any, improvement in the yield.

| Reaction medium | % Yield |
|---|---|
| 10% HCl | 61, 66 |
| 10% $HClO_4$ | 50, 54 |
| 50% HOAc | 76, 78 |

B. *In Glacial Acetic Acid*

To a stirred solution of 3.63 gm. (0.03 mole) of 2-phenylethylamine-1-$C^{14}$ in 30 ml. of glacial acetic acid was added portionwise 6.21 gm. (0.09 mole) of solid sodium nitrite. Stirring was continued for one-half hour. The mixture was then heated on the steam bath for an additional one-half hour. After cooling, the resulting material was poured into ice–water and extracted with ether, the extract being thoroughly washed with alkali and distilled water. Distillation of the residue, after removal of the ether by evaporation from the dried extract, gave 2-phenylethyl acetate, b.p. 218–220°C. (uncorrected), $n_D^{25}$ 1.5064 (lit. (5) $n_D$ 1.5108). The yields on duplicate runs were 2.96 gm. and 3.15 gm. (69% and 73%). The material did not react with phenylisocyanate.

An ether solution of 3.00 gm. of the acetate was added dropwise to 0.75 gm. of lithium aluminum hydride in 50 ml. of anhydrous ether. The mixture was stirred for two hours and then decomposed with dilute hydrochloric acid. The

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product was worked up by ether extraction and distillation of the residue from the extract. The 2-phenylethanol recovered weighed 1.70 gm. (68%), $n_D^{25}$ 1.5321. With phenylisocyanate, it gave the phenylurethan, m.p. 79–80°C., in 90% yield.

*Phenylurethan of 2-Phenylethanol*

Equal weights (0.5 to 1.0 gm. scale) of 2-phenylethanol and phenylisocyanate and a few drops of pyridine, placed in a 10 ml. erlenmeyer flask, were heated on the steam bath for 15 min. The resulting mixture was cooled in an ice bath. A few milliliters of petroleum ether, b.p. 30–60°C., was added and the flask rubbed with a stirring rod whereby the urethan readily crystallized. It was collected by filtration and thoroughly washed with petroleum ether, the yields being of the order of 90%. On recrystallization from chloroform – petroleum ether mixture, it melted at 79–80°C. (lit. (5) m.p. 79–80°C.). The radioactivity data are recorded in Table I.

*Oxidation of 2-Phenylethanol or 2-Phenylethyl Acetate*

The oxidation of the products of reaction between 2-phenylethylamine-1-$C^{14}$ and nitrous acid in the various acid media used was carried out in alkaline potassium permanganate. The conditions were the same as given above for the oxidation of 2-phenylethylamine-1-$C^{14}$, the amine being replaced by the alcohol or the acetate. The yields of recrystallized benzoic acid ranged between 70 and 80%. Measurements of the activity of various samples are tabulated in Table I.

ACKNOWLEDGMENT

We are grateful for the financial assistance given by the National Research Council of Canada.

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## A NOTE ON THE PREPARATION OF CHLORINE GAS CONTAINING $Cl^{36}$ [1]

By F. Brown, A. Gillies,[2] and W. H. Stevens

On several occasions in this laboratory, it has been important to obtain chlorine gas in practically quantitative yield from either potassium chloride or dilute hydrochloric acid containing $Cl^{36}$. The standard methods for obtaining chlorine gas from these compounds, for example, oxidation by $KMnO_4$, $MnO_2$, or $K_2Cr_2O_7$, in acid solutions, do not give high yields.

A method for obtaining a 95–100% yield of radioactive chlorine gas from $NaCl^{36}$ was recently reported by Woeber (1). The procedure consisted of adding cold fuming sulphuric acid to sodium chloride dissolved in ice-cold superoxol and sweeping the chlorine evolved out of the generator with an inert gas.

Previous to this, we had developed a somewhat similar method which we feel is more easily controlled and perhaps less hazardous when applied to larger scale preparations.

The method is as follows: Two to three equivalents of potassium peroxysulphate are added to either an approximately 0.5 *N* hydrochloric acid solution or an equivalent potassium chloride – sulphuric acid solution. An inert gas stream is gently bubbled through the mixture and the mixture is heated at 70–75°C. The production of chlorine gas is easily controlled by cooling or warming the reaction mixture. Practically no reaction occurs below 65°, and at 70–75° the reaction proceeds quite smoothly. If the chlorine is required dry, the gas stream may be passed through concentrated sulphuric acid. The chlorine gas may be frozen out of the carrier gas stream (e.g. argon, or helium), if desired, using a liquid nitrogen cooled trap. Some oxygen is also evolved during the reaction from decomposition of peroxysulphate by water, but below 75°C. this reaction is quite slow.

On a one millimole scale, the reaction requires 10 to 15 min. On a hundred millimole scale, the reaction requires one half to three quarters of an hour.

The yield of chlorine, determined in several inactive runs by absorbing the chlorine in potassium iodide solution and titrating the iodine liberated with thiosulphate, was 98–100%. Tracer experiments were also done to determine the completeness of the chloride oxidation. Solutions of hydrochloric acid containing $Cl^{36}$ were counted using a dipping geiger tube. After reaction, the residual solutions were again counted. Only $1\frac{1}{2}$–2% of the original radioactivity remained in the solution.

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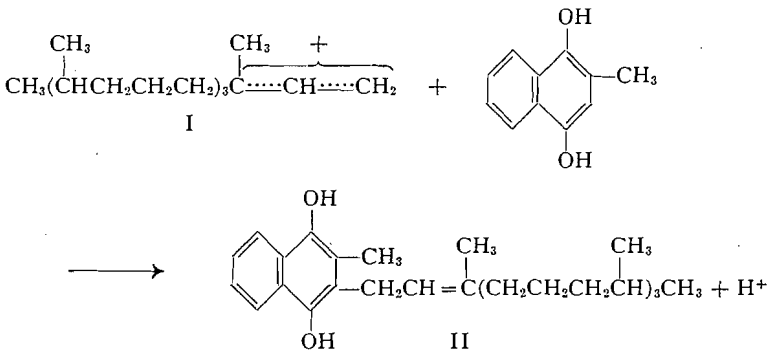
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## VITAMIN $K_1$ LABELED WITH $C^{14}$

By C. C. Lee, F. C. G. Hoskin, L. W. Trevoy, L. B. Jaques, and J. W. T. Spinks

Vitamin $K_1$, labeled with $C^{14}$, was synthesized using a method developed by Dr. Otto Isler of F. Hoffman-La Roche, A. G., Basle (4), with modifications suited to small-scale synthesis. It involves the reaction between isophytol (3,7,11,15-tetramethyl-1-hexadecen-3-ol) and 2-methyl-1,4-naphthohydroquinone with boron trifluoride as catalyst. Isophytol is known to isomerize readily in the presence of phosphorus tribromide and ligroin to give phytyl bromide (5, 8), and Dr. Isler (4) found that it can successfully replace phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol) in Fieser's (2, 3) well-known vitamin $K_1$ synthesis. One may suggest that in the presence of the acid catalysts used, an identical cationoid intermediate, I, is derived from either phytol or isophytol, which then reacts with 2-methyl-1,4-naphthohydroquinone through an electrophilic displacement to give the hydroquinone of vitamin $K_1$ (II).



In the Hoffmann-La Roche process, the reaction product was hydrogenated using a special palladium on calcium carbonate catalyst which was found suitable for reducing vitamin $K_1$ to its hydroquinone (6). This treatment eliminates any loss of the hydroquinone product through oxidation, during the course of the reaction, to the liquid quinone (vitamin $K_1$ itself) which would be washed away during the isolation of the solid hydroquinone. After the hydrogenation, the isolated hydroquinone is taken up in ether and oxidized to vitamin $K_1$ with silver oxide.

In the radiochemical synthesis, the starting material was 2-methyl-$C^{14}$-1,4-naphthohydroquinone prepared from $C^{14}$-labeled vitamin $K_3$ (7) according to the method of Fieser (3). The activity of this starting material was $1.56 \times 10^5$ counts/min./mgm.* or $2.68 \times 10^7$ counts/min./mM. (approximately 40 $\mu$c./mM.). The resulting 2-methyl-$C^{14}$-3-phytyl-1,4-naphthoquinone (vitamin $K_1$) had an activity of $5.82 \times 10^4$ counts/min./mgm. or $2.62 \times 10^7$ counts/min./mM. With alcoholic potassium hydroxide, the labeled vitamin $K_1$ gave a positive Dam-Karrer color test (2). Its ultraviolet absorption

*Measured as infinitely thin samples in a windowless Q-gas counter.*

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spectrum, measured in alcoholic solution using a Beckmann quartz spectrophotometer, was practically identical with that of an authentic sample and agreed with that recorded by Ewing and co-workers (1). The radiochemical purity was further demonstrated by its conversion to a solid derivative, the diacetate of 2-methyl-$C^{14}$-3-phytyl-1,4-naphthohydroquinone (2). Applying the principles of isotopic dilution, the diacetate, on two successive recrystallizations, accounted for 94.3% and 96.0%, respectively, of the vitamin $K_1$ activity used in the preparation of the derivative.

## EXPERIMENTAL

A mixture of 500 mgm. of 2-methyl-$C^{14}$-1,4-naphthohydroquinone, 400 mgm. of isophytol, and 0.1 ml. of 45% boron trifluoride in ethyl ether (Eastman Organic Chemicals) was dissolved in 2 ml. of dry dioxane. The solution, under a nitrogen atmosphere in a small glass-stoppered flask, was mechanically shaken at room temperature for 24 hr. The resulting dark brown solution was taken up in 20 ml. of ether and washed first with 10 ml. of distilled water to remove the dioxane, then with three 10-ml. portions of 2% aqueous potassium hydroxide, containing 5% sodium hydrosulphite, to remove the unreacted 2-methyl-$C^{14}$-1,4-naphthohydroquinone. The yellow alkaline washings were combined and extracted once with ether. This extract was, in turn, washed with aqueous alkali containing sodium hydrosulphite before it was added to the original ether solution. After the ethereal solution was dried over anhydrous sodium sulphate, it was concentrated to a small volume for transfer to the flask used in the subsequent hydrogenation.

The reaction product was placed in a 15 ml. hydrogenation bottle, fitted with a magnetic stirrer, and was subjected to evacuation by the water pump to remove all the remaining ether. To the viscous residue, 3 to 4 ml. of petroleum ether and about 100 mgm. of palladium catalyst were added. The mixture was hydrogenated at room temperature under ordinary pressure for one-half hour. The hydroquinone of vitamin $K_1$ separated as a white voluminous precipitate. It was transferred under nitrogen into a 15 ml. centrifuge tube, with the aid of an additional few milliliters of cold petroleum ether, and centrifuged after thorough cooling in an ice–salt bath. The brown supernatant liquid was drawn off and the solid hydroquinone washed two or three times with a few milliliters of cold petroleum ether, the washings being removed by centrifugation. The final washing was only slightly colored. The washed product was dissolved in 10 ml. of dry ether, the catalyst suspended in the ether solution being easily removed by centrifugation.

To the ether solution of the hydroquinone, 500 mgm. of silver oxide was added and the mixture agitated by means of a magnetic stirrer for one-half hour. A small quantity of anhydrous sodium sulphate was then added as drying agent. The resulting ethereal solution of vitamin $K_1$ was separated from the oxidizing and drying agents by centrifugation. With the removal of the solvent, finally *in vacuo*, 146 mgm. of vitamin $K_1$ was obtained as a clear yellow oil. A small droplet dissolved in 95% alcohol gave, with alcoholic potassium hydroxide, an intense indigo blue color which changed with time

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to purple and finally to dull red, a positive Dam-Karrer test. The ultraviolet absorption spectrum of an alcoholic solution of the product was practically identical with that of an authentic sample (Merck and Co.) (1). The maximum peak of absorption occurring at 249 mμ had an optical density of 0.800 for a concentration of 2 mgm. of vitamin $K_1$ in 100 ml. of 95% alcohol. The bulk of the labeled vitamin was dissolved in sesame oil, approximate concentration 10 mgm./ml., for administration to experimental animals.

From the alkaline washings of the original reaction mixture, 224 mgm. of unreacted 2-methyl-$C^{14}$-1,4-naphthohydroquinone was recovered. The 146 mgm. of labeled vitamin $K_1$ obtained thus represents a yield of 20% based on the used 2-methyl-$C^{14}$-1,4-naphthohydroquinone. This compares favorably with the reported yield of Fieser (3) which, based on the hydroquinone of vitamin $K_3$, would be of the order of 15%.

The unreacted 2-methyl-$C^{14}$-1,4-naphthohydroquinone was recovered through acidification of the alkaline washings with sulphuric acid followed by extraction with ether. The ethereal extract was shaken with 10% aqueous sodium hydrosulphite to keep the desired material in the reduced form, dried over anhydrous sodium sulphate, and evaporated to about one milliliter. Sulphur, which resulted from the decomposition of the hydrosulphite when the washings were acidified, separated out on cooling. It was filtered off and washed with a small volume of cold ether to leach out all the hydroquinone of vitamin $K_3$. On addition of petroleum ether to the sulphur-free ether solution, the unreacted 2-methyl-$C^{14}$-1,4-naphthohydroquinone separated as a grayish powder and was collected by filtration. Further purification was effected by dissolving the recovered material in ether, shaking with 10% hydrosulphite solution, drying, and again adding petroleum ether to the concentrated ethereal solution. The purified hydroquinone of vitamin $K_3$ thus recovered weighed 224 mgm. It was of sufficient purity for use in vitamin $K_1$ synthesis. When treated with silver oxide in ether, it reverts readily to vitamin $K_3$, isolated by sublimation, m.p. 103–104°C. (uncorrected) (lit. (7), m.p. 103–104°C.).

A weighed quantity (147.6 mgm.) of the sesame oil solution of labeled vitamin $K_1$, together with 497.6 mgm. of ordinary vitamin $K_1$ (Merck and Co.), was subjected to reductive acetylation with acetic anhydride and zinc dust in the presence of a small amount of pyridine according to the procedure given by Fieser (2). The colorless diacetate, crystallized from methanol, weighed 420 mgm. On recrystallization from ethanol, it melted at 59–60°C. (uncorrected) (lit. (2), m.p. 59–60°C.). Radioactivity measurements showed that the diacetate, after one and then two recrystallizations, accounted for 94.3% and 96.0%, respectively, of the vitamin $K_1$ activity used.

## ACKNOWLEDGMENTS

We should like to express our sincere appreciation to Dr. Otto Isler for transmitting the details of his process, which was modified for this synthesis, and to Messrs. Hoffman-La Roche Inc., Nutley, N.J., for a generous supply

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## N-*BIS*-(β-N-ARYLCARBAMYLOXYETHYL)ARYLAMINES[1]

BY A. F. MCKAY and W. G. HATTON

Some new N-*bis*-(β-N-arylcarbamyloxyethyl)arylamines (II) have been prepared by the reaction of arylisocyanates with N-*bis*-(β-hydroxyethyl)arylamines (I). The properties of these compounds are given in Table I.

$$\underset{\text{I}}{\text{R–N(CH}_2\text{CH}_2\text{OH)}_2} + 2\text{R}'\text{–N=C=O} \rightarrow \underset{\text{II}}{\text{R–N(CH}_2\text{CH}_2\text{OC(O)NHR}')_2}$$

### EXPERIMENTAL[2]

*N-bis-(β-Hydroxyethyl)benzylamine*

N-*bis*-(β-Hydroxyethyl)benzylamine (b.p.$_{0.5\text{ mm.}}$ 140–142°C.; $n_D^{24.8}$ 1.5355) was prepared in 95% yield by the addition of ethylene oxide to benzylamine. The procedure was similar to the previously described method (3) of preparation of *bis*-(β-hydroxyethyl) *n*-butylamine. Gabriel and Stelzner (2) report a boiling point of 225–225.5°C. at 40 mm. pressure for N-*bis*-(β-hydroxyethyl)benzylamine.

*N-bis-(β-Hydroxyethyl) p-Anisidine*

Fifty grams (0.406 mole) of *p*-anisidine were dissolved in 100 cc. of methanol and brought to reflux. During a period of eight hours, 39.4 gm. (0.895 mole) of ethylene oxide were introduced under the surface of the amine solution. After removal of solvent and excess ethylene oxide, 84.5 gm. (99.2%) of crystalline N-*bis*-(β-hydroxyethyl) *p*-anisidine (m.p. 67.5–70°C.) was obtained. This compound was purified by trituration with petroleum ether and filtration. A final melting point of 72.5°C. was obtained. N-*bis*-(β-Hydroxyethyl) *p*-anisidine prepared from ethylene chlorohydrin and *p*-anisidine has been described (1, 4) as melting at 73°C. A mixed melting point determination between samples prepared by both methods gave no depression.

*Preparation of di-N-Arylcarbamyl Derivatives of N-bis-(β-Hydroxyethyl)arylamines*

Two mole equivalents of the arylisocyanate are added to one mole equivalent

[1] *Issued as D.R.C.L. Report No. 125.*
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[1] *Issued as D.R.C.L. Report No. 125.*
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of N-*bis*-(β-hydroxyethyl)arylamine in dry benzene. After addition is complete, the benzene solution may be warmed to bring the reaction to completion. In this manner the reaction products were prepared in quantitative yields. Purification was effected by crystallizing from 95% ethanol. The compounds obtained by this procedure are described below in Table I.

TABLE I

$RN(CH_2CH_2OC(O)NHR')_2$

| R | R' | M.p., °C. | C | | H | | N | | Cl | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| *p*-Anisyl | *p*-Chlorophenyl | 144.5–145 | 57.91 | 58.28 | 4.86 | 5.10 | 8.11 | 8.25 | 13.67 | 13.80 |
| *p*-Anisyl | *p*-Tolyl | 140–140.5 | 67.92 | 67.57 | 6.54 | 6.48 | 8.80 | 9.10 | | |
| *p*-Anisyl | Phenyl | 102–102.5 | 66.82 | 67.15 | 6.06 | 6.16 | 9.35 | 9.44 | | |
| *p*-Anisyl | Benzyl | 86–86.5 | 67.92 | 67.77 | 6.54 | 6.41 | 8.80 | 8.95 | | |
| Benzyl | *p*-Chlorophenyl | 112–112.2 | 59.76 | 59.45 | 5.02 | 5.21 | 8.37 | 8.24 | 14.11 | 14.36 |

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# THE HYDROGENOLYSIS OF 3-HYDROXYMETHYLINDOLE AND OTHER INDOLE DERIVATIVES WITH LITHIUM ALUMINUM HYDRIDE[1]

BY EDWARD LEETE[2] AND LÉO MARION

ABSTRACT

Indole-3-aldehyde, indole-3-carboxylic acid and its ethyl ester were reduced by excess lithium aluminum hydride to skatole. The expected reduction product, 3-hydroxymethylindole, was obtained by the action of sodium hydroxide on gramine methiodide. It and its alkyl ethers were readily reduced to skatole. 3-Hydroxymethylindole underwent self-condensation to 3,3′-di-indolylmethane in neutral and alkaline media, and with acidic reagents was converted to an oxygen-free polymeric substance. The mechanism of these reactions and of the hydrogenolysis is discussed.

In the course of the investigation of various indole alkaloids anomalous products were obtained on reduction of 3-substituted indole derivatives with lithium aluminum hydride. Thus the action of this reagent on simple indole compounds was investigated with the rather surprising result that indole-3-carboxylic acid, its ethyl ester, and indole-3-aldehyde were reduced in ether solution under very mild conditions to skatole. It was also found that 3-acetylindole was reduced to 3-ethylindole.

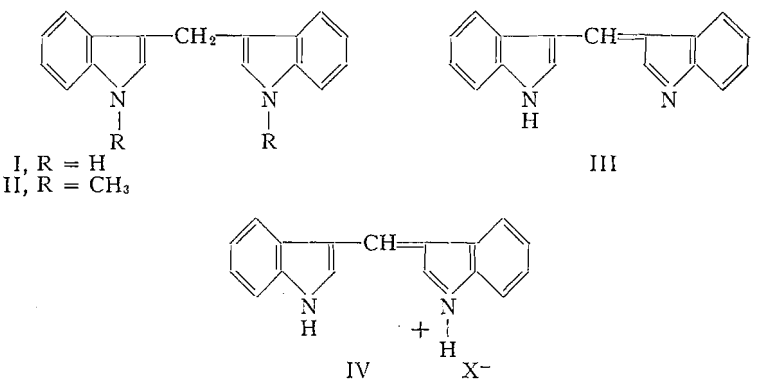
There have been a few isolated reports of the hydrogenolysis of acids and carbonyl compounds with lithium aluminum hydride to methyl or methylene groups. Witkop (40) found that an *o*-aminoketone (*spiro*cyclopentane-1,2′-pseudoindoxyl) was reduced to an oxygen-free amine. Conover and Tarbell (7, 8) showed that various benzene and thiazole acids and carbonyl derivatives underwent hydrogenolysis when there was an amino group *ortho* or *para* to the group being reduced. Jones and Kornfeld (15) reported the hydrogenolysis of a carbethoxy group to a methyl in a pyridine derivative. Many of these reductions, however, were carried out for a prolonged time and at a high temperature, and it was possible to isolate the expected alcohol by employing less vigorous conditions. But with 3-carbethoxyindole, even when less than the theoretical amount of lithium aluminum hydride to cause reduction to the alcohol was employed, the only products isolated were skatole and unreduced ester. It was thus of interest to prepare by another method the 3-hydroxymethylindole which was apparently very readily reduced by lithium aluminum hydride.

[1]*Manuscript received April 24, 1953.*
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[2]*Holder of a Postgraduate Travelling Fellowship from the Goldsmiths' Company of London, England.*



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This compound was first obtained by Mingoia (23) by the action of trioxymethylene on indole magnesium bromide. He described it as a stable substance melting at 158°. Repetition of this experiment yielded only high melting glassy material. Madinaveitia (21), who claimed to have obtained it by the action of methyl iodide in methanol on gramine and by the catalytic reduction of indole-3-aldehyde, described it as a substance very sensitive to acids melting at 90°. All attempts to hydrogenate indole-3-aldehyde with a variety of catalysts were unsuccessful in our hands. Derivatives of 3-hydroxymethylindole have been recorded in the literature (14, 29, 31) but they were not well characterized and their instability in air was noted. 2-Hydroxymethylindole and its derivatives have recently been prepared (12, 39) by the reduction of the corresponding carbethoxy compound with lithium aluminum hydride. Thus the hydroxymethyl group is apparently stable to attack by this reagent when in the 2-position of the indole nucleus. This has also proved to be the case with more complex indole derivatives (2). The ON-diacetyl derivative of 3-hydroxymethylindole has recently been prepared by the action of acetic anhydride and sodium acetate on gramine (11). Attempted hydrolysis of this ON-diacetyl derivative with boiling 10% sodium hydroxide yielded a resinous product from which we isolated an oxygen-free compound. The analytical figures suggested that this compound might be 3,3′-di-indolylmethane (I), a suggestion supported by its ultraviolet absorption spectrum which was similar to that of skatole (Fig. 1). The identity was confirmed by direct comparison with an authentic sample of 3,3′-di-indolylmethane synthesized from indole, paraformaldehyde, and zinc chloride. This compound obtained by the reduction of di-indolylmethine (III) was recorded briefly (26) without mention of any properties. It is a colorless substance very sensitive to acids




in the presence of air, rapidly becoming deep red in color presumably due to the formation of di-indolylmethine salts (urorosein) (IV)(13). Hydrolysis of ON-diacetyl-3-hydroxymethylindole with sodium hydroxide in methanol at room temperature leads to the formation of 3-methoxymethylindole and in ethanol to 3-ethoxymethylindole. Treatment with hydrochloric acid produced a dark red resinous mass. From these results it was apparent that 3-hydroxymethylindole was unstable in hot alkali and sensitive to acids.

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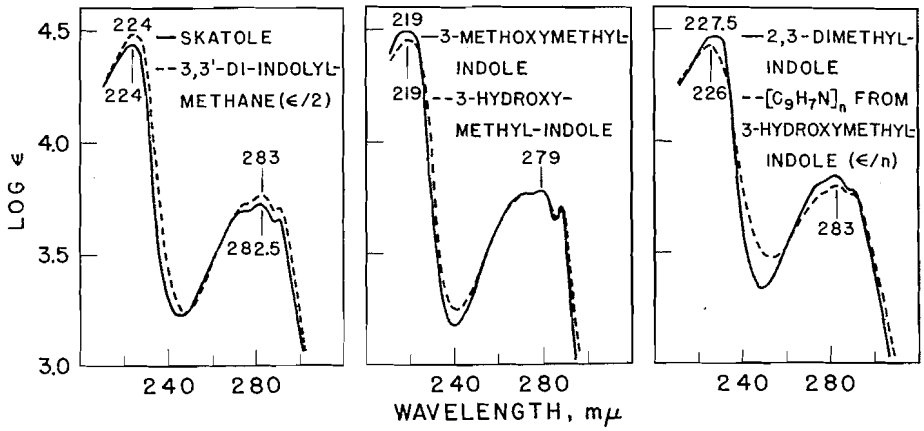



FIG. 1. Ultraviolet absorption spectra taken in 95% ethanol with a Beckman quartz spectrophotometer.

The nucleophilic attack of gramine methiodide by hydroxide ions appeared to be a possible route to 3-hydroxymethylindole, the cationoid activity of this quaternary salt being well known (11, 34, 36, 37). Accordingly an aqueous solution of authentic gramine methiodide (11) was shaken in the presence of ether with sodium hydroxide. The ether layer was found to contain 3-hydroxymethylindole. A small quantity of substance insoluble both in water and ether was also obtained in this reaction (see experimental). The 3-hydroxymethylindole, obtained in 70% yield, melted at 99–100°. The authenticity of the product was confirmed by the analytical results, molecular weight determination, and the similarity of its ultraviolet spectrum with that of 3-methoxymethylindole (Fig. 1). Its infrared absorption spectrum in nujol suspension showed an intense peak at 3360 cm.$^{-1}$ due to the NH stretching vibration, and a broad peak at 3270 cm.$^{-1}$ presumably due to a hydrogen bonded hydroxyl group. A peak similar to the former, attributable to the NH stretching vibration, was present in the infrared spectra of skatole (3395 cm.$^{-1}$), 2,3-dimethylindole (3370 cm.$^{-1}$), and 3,3′-di-indolylmethane (3395 cm.$^{-1}$), whereas the latter broad absorption peak was absent in the spectra of these alkyl indoles.

3-Hydroxymethylindole was a relatively unstable substance slowly becoming brown in air. In boiling water in which it was appreciably soluble, it underwent self-condensation giving rise to the sparingly soluble 3,3′-di-indolylmethane (I) which separated out of the hot solution. This property explains the failure to obtain 3-hydroxymethylindole by the alkaline hydrolysis of its acetyl derivative and recalls the self-condensation of the 2-hydroxymethylpyrroles to give dipyrrylmethanes (9). The production of 1,1′-dimethyl-3,3′-di-indolylmethane (II) on boiling 1-methylgramine methiodide with sodium hydroxide (35) is presumably due to the intermediate formation of 1-methyl-3-hydroxymethylindole which then undergoes self-condensation. Attempts to acylate 3-hydroxymethylindole or to prepare its picrate were unsuccessful and resulted in considerable darkening of the reaction mixtures. 3-Hydroxymethylindole

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was also found to be very sensitive to acids. Thus, addition of hydrochloric acid to its aqueous solution resulted in the separation of an amorphous white precipitate which slowly became pink in the acid medium, but was quite stable after addition of ammonia to the suspension. This precipitate could not be induced to crystallize from any solvent, and it was purified by dissolving in benzene and precipitating with petroleum ether. It contained no oxygen and the analytical results were in agreement with the empirical formula $C_9H_7N$. The properties of the compound, its indefinite melting point and low solubility in organic solvents, indicated a polymeric substance. A structure such as IX is suggested and it is supported by the ultraviolet spectrum of the compound which is very similar to that of 2,3-dimethylindole (Fig. 1). Further evidence for such a structure is found in the infrared absorption spectrum of the polymer particularly in the region 600–800 cm.$^{-1}$ (Fig. 2).

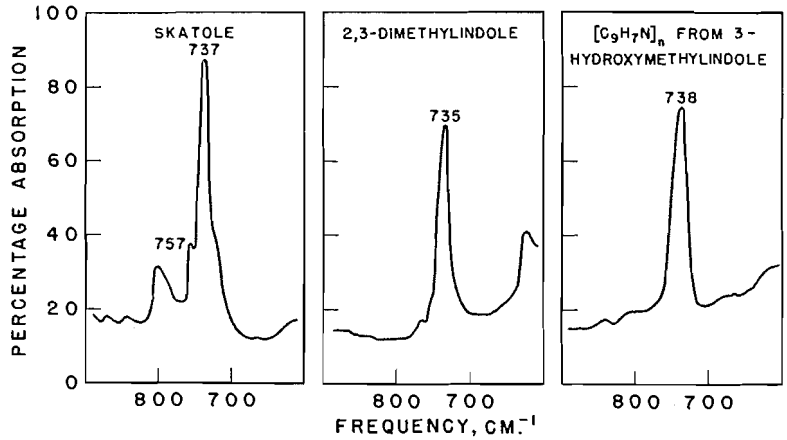


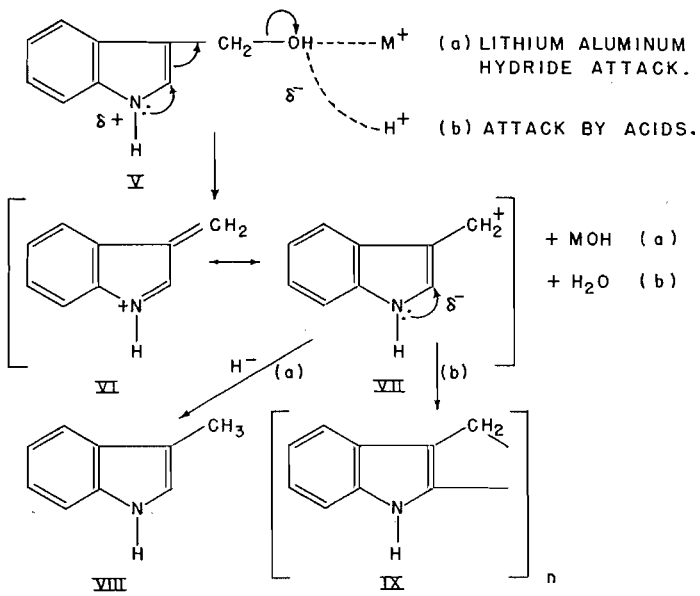

FIG. 2. Infrared absorption spectra measured as nujol mulls on a Perkin-Elmer double beam infrared spectrophotometer, Model 21 with sodium chloride prism.

The absorption in this region has been attributed to the out-of-plane bending vibration of the CH bonds in an aromatic system (1, 6). The strong absorption at 735–738 cm.$^{-1}$ has been assigned to the CH vibrations in an *ortho* substituted benzene ring as in indole. It has also been found that an absorption peak at 757 cm.$^{-1}$ always occurs in alkyl indoles in which the 2-position is unsubstituted (e.g. skatole), so that this peak may be tentatively assigned to the out-of-plane bending vibration of the CH bond in the 2-position of the indole nucleus. As shown in Fig. 2 this absorption peak is absent in both the spectra of 2,3-dimethylindole and of the polymeric compound. The infrared absorption spectrum shows the expected peak at 3370 cm.$^{-1}$ due to the NH stretching vibration.

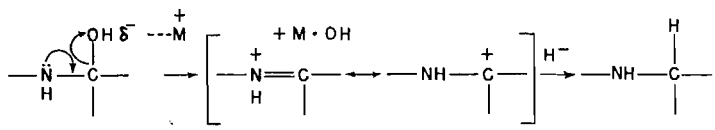
As expected, 3-hydroxymethylindole was readily reduced by lithium aluminum hydride to give skatole. It was not, however, reduced in alcohol solution by hydrogen in the presence of Adams' catalyst. Its methyl and ethyl ethers were also reduced to skatole by lithium aluminum hydride. This reagent apparently acts as a nucleophilic reagent furnishing in solution anions such

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as $AlH_4^-$ (5) or actually the hydride anion ($H^-$), at least in diethyl ether solution (27, 28). However, the 3-position of indole has a high electron density made evident from its chemical properties and indicated by molecular orbital calculations (20). This high electron density at the 3-position would be expected to retard attack by the hydride anion, and it is suggested that the first attack is by a positive ion ($M^+$) such as $Li^+$ or $AlH_2^+$ eliminating the hydroxyl group to form in the ether solution a nonionized salt M–OH and leaving the carbonium cation (VI↔VII) which rapidly picks up a hydride anion to give the final hydrogenolysis product (VIII). A similar mechanism has been proposed for the reduction of the *ortho* and *para* amino aromatic acids and carbonyl derivatives (7). It is considered that the attack by acids proceeds by a similar mechanism, the proton extracting the hydroxyl group and thus giving rise to the carbonium ion VII which undergoes self-condensation at the free electronegative 2-position to produce the polymer IX.




The facile reduction of amino-aldehydes with lithium aluminum hydride to give oxygen-free amines (10, 24, 25) presumably proceeds by a similar mechanism.



3-Hydroxymethylindole may be regarded as the vinylogue of an amino-aldehyde. The reduction of the tosyl derivatives of alcohols (16, 17, 18, 19, 30, 33) with lithium aluminum hydride has also been interpreted (33) as proceeding through an elimination of the tosylate group to leave a carbonium cation which then picks up a hydride anion from the solution.

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## EXPERIMENTAL[3]

*O,N-Diacetyl-3-hydroxymethylindole*

This was prepared essentially by the method of Geissman and Armen (11) with, however, a marked increase in yield. Gramine (10 gm.) and dry sodium acetate (20 gm.) were refluxed in a metal bath with freshly distilled acetic anhydride (100 ml.) for four hours. The mixture was cooled and poured into a stirred mixture of ice and sodium carbonate solution. After stirring for one hour the yellow amorphous precipitate was filtered off, washed, and dried *in vacuo* (12.3 gm., 88% yield). Crystallization from ethanol (charcoal) yielded the acetyl derivative as pale yellow needles, m.p. 89–90°, (11.0 gm.).

*Attempted Hydrolysis of O,N-Diacetyl-3-hydroxymethylindole*

(*a*) *With Aqueous Sodium Hydroxide (3,3′-Di-indolylmethane I)*

The diacetyl derivative (5.0 gm.) was refluxed with 10% sodium hydroxide solution (200 ml.) on a metal bath for 18 hr. A brown tar separated on the surface of the liquid; it was removed by decantation and on cooling set to a solid (2.96 gm.). This product was dissolved in hot benzene (20 ml.) and the filtered solution on cooling deposited a brown amorphous substance (1.03 gm.), m.p. 135–160°, which was crystallized from benzene (charcoal). 3,3′-Di-indolylmethane thus obtained consisted of colorless plates melting at 164–165°, either alone or in admixture with an authentic synthetic sample. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37; mol. wt., 246.3. Found: C, 83.11; H, 5.67; N, 11.42%; mol. wt. (Rast) 251. In contrast to skatole it was almost odorless and sublimed unchanged *in vacuo* (150° at $10^{-4}$ mm.) very slowly. In air it became brown and on treatment with acids became pink and finally bright red. Attempts to prepare a picrate or an acetyl derivative were unsuccessful. In the Ehrlich test it gave a red color which became orange-red on standing.

(*b*) *With Alcoholic Sodium Hydroxide*

To a suspension of O,N-diacetyl-3-hydroxymethylindole (5.0 gm.) in ethanol (25 ml.), 10% sodium hydroxide (17 ml.) was added. All the diacetyl derivative dissolved and in the course of about half an hour colorless prisms had separated, the quantity of which was increased by the addition of water. The precipitated substance was filtered and dried (3.27 gm.), m.p. 60–65°, and recrystallized from petroleum ether (b.p. 50–80°) from which it separated as colorless prismatic needles, m.p. 63–64°, not depressed by admixture with 3-ethoxymethylindole (3, 11). Calcd. for $C_{11}H_{13}ON$: C, 75.40; H, 7.48. Found: C, 75.32; H, 7.69%. When the reaction was carried out in methanol the product was 3-methoxymethylindole, obtained as colorless prismatic needles from benzene – petroleum ether, m.p. 94–95°.

*3,3′-Di-indolylmethane (I)*

To indole (4.0 gm.) and paraformaldehyde (0.2 gm.) melted together on the steam bath, powdered zinc chloride (1.0 gm.) was added and the mixture heated on the steam bath for 15 hr. After cooling, unchanged indole was extracted with petroleum ether and the residue extracted with hot benzene. The benzene extract on cooling deposited an amorphous solid (0.34 gm.),

[3]*All melting points are corrected.*

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m.p. 138–140°, which crystallized from benzene and after several recrystallizations from the same solvent consisted of colorless plates (0.12 gm.), m.p. 164–165°. The melting point of this sample of 3,3′-di-indolylmethane was not depressed by admixture with the product obtained by the hydrolysis of O,N-diacetyl-3-hydroxymethylindole. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 83.34; H, 5.60; N, 11.16%.

*3-Hydroxymethylindole* (*V*)

Of several modifications the following method was found to give the highest yield of 3-hydroxymethylindole. Gramine methiodide (5.0 gm.), prepared according to Geissman and Armen (11), was dissolved in cold water (200 ml.) and added slowly to a rapidly stirred mixture of 10% sodium hydroxide (200 ml.) and ether (200 ml.). A small amount of white precipitate was produced and as soon as all the gramine methiodide had been added (10 min.) this was filtered off (0.24 gm.) and the ether layer separated from the filtrate. The residual aqueous layer was extracted several times with further quantities of ether and the combined ether extract was dried over sodium sulphate and distilled at room temperature *in vacuo*. A white crystalline solid (2.18 gm.) was left which crystallized from benzene. 3-Hydroxymethylindole thus obtained (1.54 gm., 66% of theory) consisted of colorless leaflets, m.p. 99–100°. Calcd. for $C_9H_9ON$: C, 73.45; H, 6.16; N, 9.52; mol. wt., 147.2. Found: C, 73.49, 73.64; H, 6.09, 6.18; N, 9.47, 9.38; mol. wt. (Rast) 150. Variations in this experimental procedure such as the reverse addition of the sodium hydroxide to the gramine methiodide lead to an increase in the amount of insoluble white precipitate obtained. This product was sparingly soluble in alcohol and almost insoluble in other organic solvents. It melted indefinitely at 190–210°, contained iodine, and may have been formed by the attack of gramine methiodide by the 3-indolylmethylene carbonium ion.

3-Hydroxymethylindole was readily soluble in alcohol and ether, moderately soluble in cold water, and sparingly soluble in petroleum ether. It gave a reddish violet color in the Ehrlich test. Attempts to prepare a picrate or acyl derivatives resulted only in the formation of amorphous resinous products.

*Self-condensation of 3-Hydroxymethylindole*

(*a*) *In Neutral Solution*

3-Hydroxymethylindole (0.10 gm.) was refluxed in water (50 ml.) for six hours in a current of nitrogen which was ultimately bubbled through a solution of dimedone (5,5-dimethylcyclohexane-1,3-dione). On cooling, the solution deposited a pale brown microcrystalline product (0.056 gm.) which on crystallization from benzene afforded colorless plates, m.p. 162–163°, not depressed by admixture with 3,3′-di-indolylmethane. No precipitate was detected in the dimedone solution indicating that no formaldehyde was liberated. The aqueous solution obtained after removal of the di-indolylmethane when treated with mercuric chloride gave a white precipitate of mercurous chloride indicating the presence of formic acid.

(*b*) *Effect of Heat*

3-Hydroxymethylindole (0.20 gm.) was heated in a dry tube in a current

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of nitrogen for three hours at 200°. The nitrogen was ultimately passed into a solution of dimedone in which a small amount of crystalline precipitate was produced (20 mgm.), m.p. 189–190°, either alone or in admixture with dimedone–formaldehyde condensate. The residue in the reaction tube was soluble in benzene but could not be induced to crystallize.

(*c*) *Effect of Alkali*

3-Hydroxymethylindole (1.0 gm.) was refluxed with 10% sodium hydroxide (100 ml.) for one hour. The solution was cooled, neutralized with carbon dioxide, and filtered. The filtered substance (0.52 gm.) was crystallized from benzene to yield glistening plates of 3,3′-di-indolylmethane, m.p. 163–164°.

(*d*) *Effect of Acid*

When 3-hydroxymethylindole (0.20 gm.) was dissolved in cold water (100 ml.) and concentrated hydrochloric acid (40%, 1 ml.) was added, an almost white precipitate immediately separated which became pink after a few minutes. The mixture was alkalized with ammonia, the precipitate filtered off and washed well with water. The product after drying *in vacuo* weighed 0.177 gm. and melted at 150–170°. It was boiled with benzene and the solution filtered to remove a small amount of insoluble material. To the filtrate petroleum ether was added, which caused the separation of a white precipitate, m.p. 160–200°, becoming red at 140°. Calcd. for $C_9H_7N$: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.33, 83.47; H, 5.57, 5.52; N, 10.62, 10.49%. It was insoluble in most of the common organic solvents, sparingly soluble in ethanol, and moderately soluble in benzene.

*General Method of Reduction of the Indole Derivatives with Lithium Aluminum Hydride*

The indole derivative (0.5–2.0 gm.) was dissolved or suspended in sodium-dried ether (50–200 ml.) and a definite amount of lithium aluminum hydride in ether solution was added to the stirred suspension or solution. The mixture was then refluxed in a nitrogen atmosphere for one-half to three hours. After cooling, the excess lithium aluminum hydride was decomposed by the addition of wet ether, the mixture filtered, and the filtrate evaporated to dryness *in vacuo*. The residue was heated to 80° at 0.2 mm. when the alkyl indoles readily sublimed. The usual product of reduction was skatole which was characterized by its melting point (94–95°) and by the formation of its picrate, m.p. 177–178° (red fibrous needles), not depressed by admixture with authentic skatole picrate. Reduction of 3-acetylindole (32) yielded 3-ethylindole, leaflets from petroleum ether, m.p. 42°. Calcd. for $C_{10}H_{11}N$: C, 82.72; H, 7.64. Found: C, 82.41; H, 7.52%. The picrate was obtained as red needles from benzene, m.p. 120° in agreement with that recorded in the literature (4). Details of the reduction of the indole derivatives are summarized in Table I.

*Attempted Catalytic Reduction of 3-Hydroxymethylindole*

3-Hydroxymethylindole (0.100 gm.) was shaken in ethanol (20 ml.) with freshly reduced Adams' catalyst (0.100 gm.) for six hours in the presence of

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TABLE I

REDUCTION EXPERIMENTS

| Compound* | Time of reflux in hours | Molecular equivalents of $LiAlH_4$ used** | Reduction product (yield) |
|---|---|---|---|
| Indole-3-aldehyde (38) | 3 | 2 | Skatole, 84% |
| Indole-3-carboxylic acid (22) | 3 | 3 | Skatole, 67% |
| 3-Carbethoxyindole (22) | 0.5 | 2 | Skatole, 92% |
| 3-Carbethoxyindole (22) | 0.5 | 0.5 | 3-Carbethoxyindole, 90%<br>Skatole, 5% |
| 3-Acetylindole (32) | 3 | 2 | 3-Ethylindole, 72% |
| 3-Hydroxymethylindole | 0.5 | 2 | Skatole, 87% |
| 3-Methoxymethylindole | 3 | 2 | Skatole, 71% |
| 3-Ethoxymethylindole | 0.5 | 1 | Skatole, 80% |

**Numbers after the compounds are references to methods of preparation of those indole derivatives which are not described in the experimental.*

***The strength of the lithium aluminum hydride solution was determined by measuring the volume of hydrogen evolved when a known volume of the solution was treated with cold water.*

hydrogen. No hydrogen, however, was absorbed and 3-hydroxymethylindole was isolated unchanged from the reaction mixture.

ACKNOWLEDGMENT

The authors are indebted to Dr. R. N. Jones and to Mr. R. Lauzon of these laboratories for the infrared spectra.

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# SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

## VII. DEUTERATED 3-PENTANONES[1]

By L. C. Leitch[2] and A. T. Morse[2]

ABSTRACT

The following deuterated 3-pentanones were synthesized, in some cases by modifications of the methods reported in the literature, and in others by deuterium exchange:

3-pentanone-$d_{10}$, 3-pentanone-1,5-$d_6$,
3-pentanone-2,4-$d_4$, 3-pentanone-1-$d_3$,
3-pentanone-1,2,4-$d_7$, and 3-pentanone-1,2-$d_5$.

## INTRODUCTION

The deuterated pentanones I to VI were recently synthesized for investigations in chemical kinetics (12) and infrared spectroscopy (11).

| | |
|---|---|
| $CD_3CD_2COCD_2CD_3$ I | $CD_3CH_2COCH_2CH_3$ IV |
| $CH_3CD_2COCD_2CH_3$ II | $CD_3CD_2COCD_2CH_3$ V |
| $CD_3CH_2COCH_2CD_3$ III | $CD_3CD_2COCH_2CH_3$ VI |

These compounds, as well as the starting materials and intermediates from which they were obtained, are all believed to be new. They were prepared by well-known reactions modified on account of the peculiar difficulties associated with the synthesis of organic deuterium compounds.

Ivanoff (5) has reported the synthesis of several aliphatic ketones from alkyl halides without isolating the intermediate acids. In the present work 3-pentanone-$d_{10}$ (I) was prepared from ethyl-$d_5$ bromide by the same reactions:

$$CD_3CD_2Br \xrightarrow{Mg} CD_3CD_2MgBr \xrightarrow{CO_2} CD_3CD_2CO_2MgBr \longrightarrow CD_3CD_2COCD_2CD_3.$$

The important feature of this synthesis is that the isolation of deuterated propionic acid is avoided, rendering unnecessary either the subsequent preparation of the barium salt or the replacement of hydrogen by deuterium in the carboxyl group before pyrolysis.

Preliminary experiments with ordinary ethyl bromide indicated that the yield of 3-pentanone-$d_{10}$ depended largely upon the design of the reactor in which the pyrolysis of propionoxymagnesium bromide was carried out. In a reactor of the dimensions specified by Ivanoff, the yields of 3-pentanone-$d_{10}$ were consistently 70% or more based on the ethyl bromide, as he had claimed.

Ethyl-$d_5$ bromide was prepared by photochemical addition of deuterium bromide to ethylene-$d_4$ which was obtained as described in an earlier paper of this series (7). The halide contained 96.8 mole % $C_2D_5Br$. The vapor pressure

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of ethyl-$d_5$ bromide was measured at several temperatures as shown in Table I. These data were used to plot the vapor pressure of ethyl-$d_5$ bromide shown in Fig. 1. The line representing the vapor pressure of normal ethyl bromide was plotted from values reported in International Critical Tables. The Grignard reagent was prepared from the halide and carbonated in the

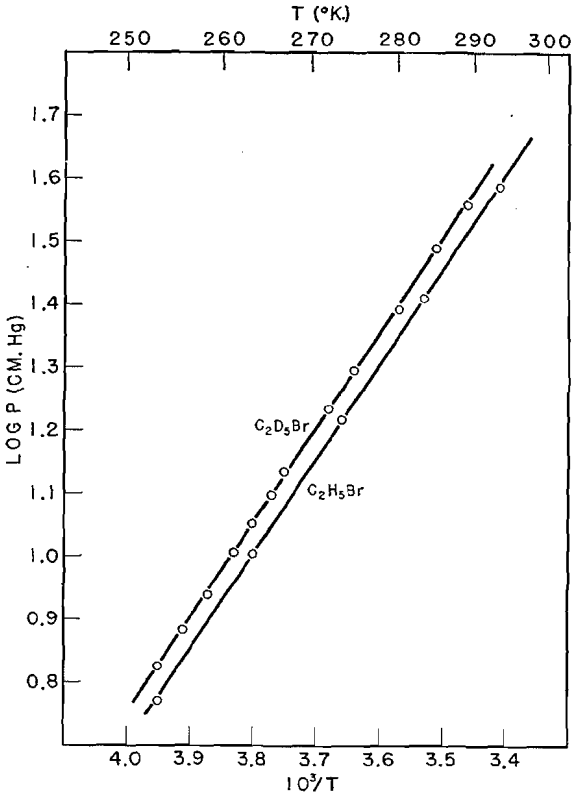



FIG. 1.

TABLE I

VAPOR PRESSURES ($P$) OF ETHYL BROMIDE AND ETHYL-$d_5$ BROMIDE

| $C_2H_5Br$ | | $C_2D_5Br$ | | $C_2D_5Br$ | |
|---|---|---|---|---|---|
| Temp., °C. | $P$, cm. | Temp., °C. | $P$, cm. | Temp., °C. | $P$, cm. |
| −20.0 | 5.90 | −20.0 | 6.70 | −6.0 | 13.65 |
| −10.0 | 10.10 | −17.0 | 7.63 | −1.0 | 17.14 |
| 0.0 | 16.50 | −14.5 | 8.69 | +1.5 | 19.72 |
| +10.0 | 25.69 | −12.0 | 10.14 | +7.0 | 24.66 |
| +20.0 | 38.59 | −10.0 | 11.27 | +12.0 | 30.83 |
| | | −7.5 | 12.53 | +16.0 | 36.14 |

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usual way. On pyrolysis, 3-pentanone-$d_{10}$ (I) was obtained which analyzed 70.4 mole % $C_5D_{10}O$ by mass spectrometry.

The 3-pentanone-$d_{10}$ obtained by direct synthesis was further enriched in deuterium by repeated exchange with deuterium oxide containing a trace of anhydrous sodium carbonate. The final product analyzed 85.8 mole % $C_5D_{10}O$. Since only the exchange of hydrogen atoms adjacent to a carbonyl group in ketones is base-catalyzed, it would seem that most of the residual hydrogen is now in the methyl groups. The appearance of hydrogen in these positions indicates exchange took place during pyrolysis—a circumstance considered irremediable.

An alternative synthesis of 3-pentanone-$d_{10}$ is the sequence of reactions:

$$2C_2D_5MgBr \xrightarrow{HCO_2C_2H_5} \begin{matrix} C_2D_5 \\ C_2D_5 \end{matrix}\!\!>\!CHOMgBr \longrightarrow C_2D_5CH(OH)C_2D_5 \longrightarrow C_2D_5COC_2D_5.$$

The deuterated pentanol was obtained in 80% yield as described by Lewis (9). In order to prevent the loss of deuterium in the methylene groups by exchange, the oxidation of the pentanol must be carried out in a neutral anhydrous medium. These conditions were met by employing a modified Oppenauer oxidation (6). When the alkoxide of the deuterated pentanol was treated with benzophenone, 3-pentanone-$d_{10}$, which analyzed 59.1 mole % $C_5D_{10}O$, was formed. The deuterium content was raised to 98.92 atom % or 90.5 mole % 3-pentanone-$d_{10}$ by three exchanges with deuterium oxide in the presence of sodium carbonate.

3-Pentanone-2,4-$d_4$ (II) was prepared by exchanging ordinary 3-pentanone with deuterium oxide in the same manner. After 10 exchanges, the deuterium content remained practically constant at 92.5 mole % $CH_3CD_2COCD_2CH_3$. Conversely, 3-pentanone-$d_{10}$ was exchanged with ordinary water containing a trace of carbonate to give 3-pentanone-1,5-$d_6$ (III). The final product analyzed 88.7 mole % $CD_3CH_2COCH_2CD_3$.

3-Pentanone-1-$d_3$ (IV) was prepared by the following reactions:

$$CD_3C{\equiv}CD \xrightarrow{NaNH_2} CD_3C{\equiv}CNa \xrightarrow{C_2H_5Br} CD_3C{\equiv}CCH_2CH_3,$$

$$2CD_3C{\equiv}CCH_2CH_3 \xrightarrow[H_2O]{H^+} CD_3CH_2COCH_2CH_3 + CD_3COCH_2CH_2CH_3.$$

The starting material, propyne-$d_4$, was prepared by the method of Leitch and Renaud (8) and converted into 2-pentyne-1-$d_3$ by alkylation of the sodium derivative as described by Greenlee (3). Hydration of the alkyne gave a mixture of isomeric pentanones (10) which were separated by means of saturated aqueous sodium bisulphite (4). The methyl ketone forms an addition compound about twenty times faster than the 3-pentanone.

The pentanone (V) was obtained by exchanging (IV) with alkaline deuterium oxide. It analyzed 85.4 mole % $CD_3CD_2COCD_2CH_3$.

The synthesis of (VI) was attempted, partly to complete the series and partly to find out whether or not such a compound would equilibrate thus:

$$CD_3CD_2COCH_2CH_3 \rightleftharpoons CD_3CHDCOCHDCH_3 \quad (VII).$$

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The desired compound was obtained almost isotopically pure in the following way:

$$CD_3CD_2Br \xrightarrow{Mg} CD_3CD_2MgBr \xrightarrow{CH_3CH_2CHO} CD_3CD_2CH(OH)CH_2CH_3,$$

$$CD_3CD_2CH(OH)CH_2CH_3 \xrightarrow{Al} \begin{matrix} CD_3CD_2 \\ CH_3CH_2 \end{matrix}\!\!>\!CHO \xrightarrow[Al/3]{(C_6H_5)_2CO} CD_3CD_2COCH_2CH_3.$$

Deuterated 3-pentanol-1,2-$d_5$ was made in the usual manner from ethyl-$d_5$ magnesium bromide and propionaldehyde. In order to avoid the acid- or base-catalyzed rearrangement of the ketone shown in (VII), the pentanol had to be oxidized in an anhydrous neutral medium. This objective was realized by again employing a modified Oppenauer oxidation (6). When the alkoxide of 3-pentanol-1,2-$d_5$ was treated with benzophenone, 3-pentanone-1,2-$d_5$ was formed. The mass spectrum of the ketone showed 86.5 mole % $C_5H_5D_5O$; from an examination of the fragments, however, it appeared that the product contained a small amount of rearranged ketone.

Exchange with deuterium oxide gave the ketone (V) while exchange with ordinary water gave ketone (IV). Mass spectra indicated that the isotopic purity of these compounds exceeded that of the products obtained from propyne-$d_4$.

## EXPERIMENTAL

### *Ethyl-$d_5$ Bromide*

Ethylene-$d_4$ was prepared as described in an earlier paper (7). The reactor there described was fitted with a quartz window and, after evacuation, deuterium bromide and ethylene-$d_4$ were introduced in a ratio of 1:1. The mixture was irradiated with ultraviolet light from a Hanovia lamp. A trap kept at −40°C. was placed under the receiver at the bottom of the reactor to condense the ethyl-$d_5$ bromide as it was formed. The ethyl-$d_5$ bromide was washed with ice-cold water and distilled on a vacuum line, first through soda-lime and then through phosphorus pentoxide. The yield of product analyzing 96.8 mole % (99.3 atom % D; $n_D^{20}$ 1.4211) was nearly quantitative. Its vapor pressure was measured between −20°C. and +20°C. in an apparatus similar to that used by Booth and Swinehart (1).

### *3-Pentanone-$d_{10}$ (I) (via Pyrolysis)*

Ethyl-$d_5$ magnesium bromide was prepared by adding slowly, with stirring, a solution of 15 ml. of ethyl-$d_5$ bromide in 25 ml. of absolute ether to 5.0 gm. of magnesium turnings suspended in 50 ml. of absolute ether. After the reaction mixture had been refluxed for 45 min., it was cooled to −20°C. while dry argon was passed through the apparatus; dry carbon dioxide was then introduced during one hour. Finally, the reaction mixture was brought to room temperature under an atmosphere of argon. After the ether was distilled off, the residue was gradually heated to 200°C. and kept at that temperature for one hour while argon was passed through the apparatus. When the residue had cooled to room temperature, it was rapidly transferred, preferably in a dry box, to a reactor of the dimensions specified by Ivanoff

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(5). It was slowly heated to 250°C. under reduced pressure to remove traces of ether and, after a Dewar flask of dry ice and acetone at −78°C. had been placed under the receiver, the temperature of the reactor was slowly raised to 380°C. and kept there for one hour. The apparatus was then filled with argon and allowed to cool.

The crude deuterated pentanone in the trap was shaken with 10 ml. of deuterium oxide and distilled off on the vacuum line through Drierite into a receiver cooled in dry ice and acetone. Yield: 6.9 gm. (74%), $n_D^{20}$ 1.3890. It analyzed 70.4 mole % $C_5D_{10}O$ (94.9 atom % D).

It was further enriched in deuterium by exchange at 80°C. with an equal volume of deuterium oxide containing 10 mgm. of anhydrous sodium carbonate in a tube with a break-off seal. The transfer of deuterium oxide and 3-pentanone-$d_{10}$ before and after each exchange was made on a vacuum manifold so that at no time were the reactants exposed to atmospheric moisture. After four exchanges, the 3-pentanone-$d_{10}$ analyzed as follows:

| | |
|---|---|
| $C_5D_{10}O$ | 85.8 mole % |
| $C_5D_9HO$ | 8.80 mole % |
| $C_5D_8H_2O$ | 3.64 mole % |
| $C_5D_7H_3O$ | 0.8 mole % |

$n_D^{20}$ 1.3889.

This corresponds to a deuterium content of 97.2 atom %. The residual hydrogen in the methyl groups would not be exchangeable for deuterium under the conditions employed.

*3-Pentanol-1,2,4,5-$d_{10}$*

A stirred solution of ethyl-$d_5$ magnesium bromide in ether (prepared from 7.0 gm. (0.287 mole) of magnesium turnings, 31.0 gm. (0.272 mole) of ethyl-$d_5$ bromide, and 100 ml. of absolute ether) was cooled to −15°C. and treated with 10.5 gm. (0.142 mole) of ethyl formate over a period of 10 min. After stirring for a further period of 15 min., 30 ml. of water were slowly added, followed by a cold solution of 12 ml. of concentrated sulphuric acid in 60 ml. of water. The lower aqueous layer was drawn off, extracted with a little ether, and the ether extract added to the main portion. The residue from the ether, on fractionation, gave 10.6 gm. (0.108 mole) of deuterated 3-pentanol, b.p. 113–4.5°C., $n_D^{20}$ 1.4050. Yield: 79.5%.

*3-Pentanone-$d_{10}$ (via Grignard Synthesis)*

A mixture of the deuterated 3-pentanol (5.0 ml.), aluminum shot (0.550 gm.), and a trace of mercuric chloride was heated with a low flame under reflux on an open vacuum manifold until hydrogen ceased to be evolved. Unreacted pentanol was then recovered by distillation under reduced pressure and reused in another run. Molten benzophenone (18 gm.) was added to the alkoxide while stirring with a magnetized bar. The 3-pentanone-$d_{10}$ was condensed in a trap elsewhere on the line, cooled to −78°C. Yield: 3.0 ml., $n_D^{20}$ 1.3892, 94.3 atom % D. The unreacted pentanol (2.0 ml.), oxidized in the same manner, gave 0.5 ml. more of the ketone, $n_D^{20}$ 1.3897, 93.4 atom % D. The total yield was therefore 3.5 ml. of ketone from 5.0 ml. of 3-pentanol.

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This product was further enriched in deuterium by three exchanges with deuterium oxide in the presence of traces of sodium carbonate. It now analyzed:

| | |
|---|---|
| $C_5D_{10}O$ | 90.5 mole % |
| $C_5D_9HO$ | 7.58 mole % |
| $C_5D_8H_2O$ | 1.70 mole % |
| $C_5D_7H_3O$ | 0.36 mole % |

Atom % D, 98.9; $n_D^{20}$ 1.3888

*3-Pentanone-2,4-$d_4$ (II)*

Redistilled 3-pentanone (10 ml.) was exchanged with alkalized deuterium oxide (10 ml.) as already described until its deuterium content reached an optimum. After 10 exchanges the compound analyzed as follows:

| | |
|---|---|
| $C_5H_5D_5O$ | 2.78 mole % |
| $C_5H_6D_4O$ | 92.5 mole % |
| $C_5H_7D_3O$ | 3.7 mole % |
| $C_5H_8D_2O$ | 0.78 mole % |

Atom % D, 40.0; $n_D^{20}$ 1.3918.

*3-Pentanone-1,5-$d_6$ (III)*

3-Pentanone-$d_{10}$ was exchanged three times with water containing a trace of sodium carbonate. The product then analyzed as follows:

| | |
|---|---|
| $C_5D_7H_3O$ | 0.73 mole % |
| $C_5D_6H_4O$ | 88.7 mole % |
| $C_5D_5H_5O$ | 8.25 mole % |
| $C_5D_4H_6O$ | 2.61 mole % |

Atom % D, 58.9; $n_D^{20}$ 1.3904.

*2-Pentyne-1-$d_3$*

Sodium amide was prepared by adding sodium (5.7 gm.) to 100 ml. of liquid ammonia in a 300 ml. round-bottomed flask with a stirrer, addition tube, and a tin spiral condenser cooled with dry ice and acetone (3). Propyne-$d_4$ (5.0 l.) prepared as in Reference 8 was distilled into the stirred suspension of sodium amide. Ethyl bromide (30 gm.) was added as rapidly as possible to the sodium methyl-$d_3$ acetylide and the reaction mixture was stirred for six hours. Water (200 ml.) and toluene (20 ml.) were added dropwise. The toluene layer was separated, treated as described by Greenlee (3), and fractionated in a short Stedman column ($\frac{3}{8}$ in. × 18 in.). The pentyne was collected between 54 and 56°C. Yield: 91%.

*3-Pentanone-1-$d_3$ (IV)*

The pentyne (13.0 gm.) from the previous experiment was stirred at 0°C. with 69 ml. of 80% sulphuric acid for two hours and the reaction mixture was poured into ice water. The yield of mixed ketones, analyzing 37.4% 2-pentanone and 62.6% 3-pentanone, as determined by mass spectrometry, was 18.5 ml. (82% yield).

The mixed ketones were distilled on a vacuum line into a suspension of 16 gm. of sodium bisulphite in 24 ml. of water and the mixture was shaken several minutes by hand. The unreacted ketone was distilled off and collected in a trap cooled with dry ice and acetone. After repeating the treatment with water and sodium bisulphite five more times, the volume of ketone had shrunk

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to 8 ml. It was then distilled through a tube containing pellets of sodium hydroxide to remove sulphur dioxide. This product gave only a trace of iodoform on standing in sodium hypoiodite solution and analyzed as follows:

| | |
|---|---|
| $C_5H_{10}O$ | 3.17 mole % |
| $C_5H_9DO$ | 7.67 mole % |
| $C_5H_8D_2O$ | 4.92 mole % |
| $C_5H_7D_3O$ | 82.2 mole % |
| $C_5H_6D_4O$ | 0.21 mole % |

Atom % D, 26.5; $n_D^{20}$ 1.3914.

*3-Pentanone-1,2,4-$d_7$ (V)*

3-Pentanone-1-$d_3$ (2.0 ml.) was exchanged three times with deuterium oxide (10.0 ml.) as already described. The final product analyzed as follows:

| | |
|---|---|
| $C_5D_8H_2O$ | 0.045 mole % |
| $C_5D_7H_3O$ | 85.4 mole % |
| $C_5D_6H_4O$ | 7.07 mole % |
| $C_5D_5H_5O$ | 2.60 mole % |
| $C_5D_4H_6O$ | 3.1 mole % |
| $C_5D_3H_7O$ | 0.74 mole % |

Atom % D, 67.3; $n_D^{20}$ 1.3901.

*3-Pentanol-1,2-$d_5$*

Freshly distilled propionaldehyde (10.0 ml.) was added to a solution of ethyl-$d_5$ magnesium bromide prepared as described above from 10.0 ml. ethyl-$d_5$ bromide and 3.0 gm. of magnesium, and the reaction mixture was worked up in the usual manner (2). The yield of deuterated pentanol, b.p. 111–113°C., was 10.2 ml. (71%).

*3-Pentanone-1,2-$d_5$ (VI)*

A mixture of 3-pentanol-1,2-$d_5$, aluminum shot (0.81 gm.), and a trace of mercuric chloride was heated with a low flame under reflux on an open vacuum line until hydrogen ceased to be evolved. Unreacted pentanol was then removed by distillation under reduced pressure. Molten benzophenone (25 gm.) was added to the residue of aluminum alkoxide while stirring. The 3-pentanone evolved was condensed in a trap elsewhere on the vacuum line, cooled to −78°C. The yield of product was 6.7 ml. (75%). It analyzed:

| | |
|---|---|
| $C_5H_4D_6O$ | 3.72 mole % |
| $C_5H_5D_5O$ | 86.5 mole % |
| $C_5H_6D_4O$ | 6.45 mole % |
| $C_5H_7D_3O$ | 3.49 mole % |

Atom % D, 49.0; $n_D^{20}$ 1.3903.

When this product was exchanged with alkalized deuterium oxide, it gave 3-pentanone-1,2,4-$d_7$ (V) which had been obtained as described above by an alternative method. The product now described analyzed as follows:

| | |
|---|---|
| $C_5D_8H_2O$ | 0.67 mole % |
| $C_5D_7H_3O$ | 87.5 mole % |
| $C_5D_6H_4O$ | 8.55 mole % |
| $C_5D_5H_5O$ | 3.29 mole % |
| $C_5D_4H_6O$ | 1.30 mole % |

Atom % D, 69.3; $n_D^{20}$ 1.3892.

Its deuterium content was slightly higher than that of the product obtained

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from propyne-$d_4$. This result is not unexpected since the ethyl-$d_5$ bromide was of higher isotopic purity than the propyne-$d_4$.

Similarly, 3-pentanone-1,2-$d_5$ was exchanged with ordinary water to give 3-pentanone-1-$d_3$ (IV) which had also been obtained by an alternative method (p. 790). The present product analyzed:

| | |
|---|---|
| $C_5D_4H_6O$ | 0.63 mole % |
| $C_5D_3H_7O$ | 96.0 mole % |
| $C_5D_2H_8O$ | 2.97 mole % |
| $C_5DH_9O$ | 0.57 mole % |

Atom % D, 29.7; $n_D^{20}$ 1.3912.

The isotopic purity of this material is also superior to that of the compound described earlier for the reason mentioned above.

## ACKNOWLEDGMENTS

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# CRYSTALLINE XYLANS FROM STRAWS[1]

By C. T. Bishop

ABSTRACT

Hemicelluloses, extracted from barley, flax, oat, rye, and wheat straw holocelluloses, were composed predominantly of anhydro-D-xylose units, with small amounts of L-arabinose and D-glucuronic acid. The hemicelluloses had degrees of polymerization ranging from 55 for oat to 185 for rye and were shown to be linear polysaccharides. Autoclaving in distilled water at 120°C. yielded crystalline xylans from barley, rye, and wheat straw hemicelluloses. The basic structure of the hemicellulose was maintained in the crystalline xylans, which gave identical X-ray diffraction patterns and had similar, linear structures. The crystallization procedure was found to degrade the hemicellulose, removing D-xylose, L-arabinose, and D-glucuronic acid as components of hydrolytic fragments and leaving a pure xylan one sixth to one third the length of its parent hemicellulose. Depending on uronic acid content, the five hemicelluloses in water gave pH values ranging from 2–5 with consequent variations in resistance to hydrolysis during autoclaving.

## INTRODUCTION

Polysaccharides composed predominantly of anhydro-D-xylose units (xylans) are found in many natural products and have been the subjects of a number of structural investigations. The uncertainties and complexities arising from these investigations were discussed in a recent publication by Adams (1). In 1949 Yundt (17) crystallized a xylan by autoclaving a hemicellulose fraction of barley straw. The crystalline xylan was composed entirely of anhydro-D-xylose units and, based on a comparison of specific rotations, was very similar to Haworth's esparto xylan (18). However, no structural study of the crystalline xylan was made nor was the possible degradative effect of autoclaving on the hemicellulose investigated.

The purpose of the present investigation was to determine the effect of autoclaving on hemicelluloses of five cereal straws and to examine the constitutions of the xylans produced, if any.

## RESULTS AND DISCUSSION

Hemicelluloses were prepared from barley, flax, oat, rye, and wheat holocelluloses (2) as described in the experimental section. Molar compositions of the hemicelluloses are shown in Table I.

TABLE I

MOLAR COMPOSITIONS OF HEMICELLULOSES

| Hemicellulose | D-Xylose | L-Arabinose | Uronic acid |
|---|---|---|---|
| Barley | 50 | 6 | 1 |
| Rye | 16 | 3 | 1 |
| Wheat | 21 | 3 | 1 |
| Flax | 7 | — | 1 |
| Oats | 10 | 3 | 1 |

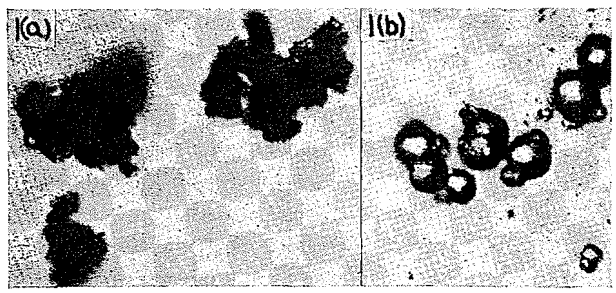
[1] *Manuscript received May 20, 1953.*
*Contribution from the Division of Applied Biology, National Research Council, Ottawa. Issued as N.R.C. No. 3042.*

Successive autoclavings in distilled water and separation of the products yielded crystalline xylans from barley, rye, and wheat hemicelluloses. The hemicelluloses of flax and oats were completely degraded to products soluble in 75% ethanol. Table II shows the pH values of the hemicelluloses in water and the yields of crystalline xylans obtained from each. The acid properties exhibited were inherent in the molecules because all hemicelluloses were

TABLE II

pH OF HEMICELLULOSES AND YIELDS OF CRYSTALLINE XYLANS

| Hemicellulose | pH in water | Yield of crystalline xylan (% of hemicellulose) |
|---|---|---|
| Barley | 5.0 | 29.4 |
| Wheat | 5.0 | 23.7 |
| Rye | 3.5 | 8.5 |
| Oat | 2.0 | Nil |
| Flax | 2.0 | Nil |



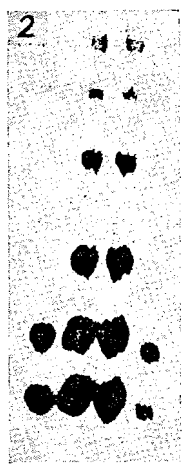




FIG. 1. (*a*) Wheat straw hemicellulose, (*b*) crystalline wheat xylan, magnification 604×.
FIG. 2. Chromatogram of ethanol solubles from autoclavings of straw hemicellulose.

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prepared at the same time and by exactly the same procedures. It is also apparent that the decrease in pH of the hemicelluloses bears a direct relationship to the increase in uronic acid contents. Hydrolysis of the crystalline xylans, followed by chromatographic examination of the hydrolyzate showed that D-xylose was the only constituent sugar. No traces of L-arabinose or D-glucuronic acid originally present in the hemicellulose as single unit side chains (1) could be found, even when the papers were heavily spotted. This confirmed, by a more sensitive method, Yundt's (18) observation that crystalline barley xylan was composed entirely of anhydro-D-xylose units.

The crystallinity of the xylans was confirmed by microscopic examination and by X-ray diffraction. Photomicrographs of amorphous wheat straw hemicellulose and the crystalline xylan obtained from it are shown in Fig. 1. The X-ray powder diagrams of the three crystalline xylans were identical; the hemicelluloses gave no diffraction patterns. Crystallizations were carried out in 0.2% aqueous solutions, hence it is unlikely that the crystals were oligosaccharides because they would be soluble at that concentration. A precedent for the crystallization of a polysaccharide is found in the work of Schoch (13) who crystallized an amylose fraction from starch.

Table III shows the relative degrees of polymerization (D.P.) of the

TABLE III

D.P.'S OF HEMICELLULOSES AND CRYSTALLINE XYLANS
(Calculated from viscosity measurements $K_m = 5 \times 10^{-4}$)

| | Hemicelluloses | Crystalline xylans | |
|---|---|---|---|
| Barley | 179 | 60 | (1/3) |
| Wheat | 150 | 33 | (1/5) |
| Rye | 185 | 30 | (1/6) |

hemicelluloses and corresponding crystalline xylans as determined by viscosity measurements on their solutions in cupriethylenediamine. Whether the values are absolute or not depends on the validity of the constant $K_m = 5 \times 10^{-4}$ (9). The results show that autoclaving degraded the hemicelluloses, shortening the chains one third to one sixth their original length. Adams and Castagne (3) have shown that approximately 50% of wheat straw hemicellulose can be obtained homogeneous in chemical constitution and molecular size. Therefore, the low yields of crystalline xylans, the complete removal of L-arabinose and D-glucuronic acid branch units, and the large (78%) decrease in D.P. make it highly probable that a degradation rather than a fractionation occurred during autoclaving.

Periodate oxidation can often be used to determine whether the structure of a polysaccharide is linear or branched (5). Table IV shows the periodate consumptions of the hemicelluloses and crystalline xylans. These results indicated the presence of linear structures because a straight chain xylan, linked 1–4 (1), would consume one mole of periodate for each anhydro-D-

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TABLE IV

PERIODATE CONSUMED BY HEMICELLULOSES AND CRYSTALLINE XYLANS
(Moles periodate/mole polysaccharide)

| | Hemicelluloses | Crystalline xylans |
|---|---|---|
| Barley | 0.92 | 0.94 |
| Wheat | 0.90 | 0.92 |
| Rye | 1.08 | 0.93 |

xylose unit, plus an extra mole at each end of the chain. In a long, straight chain the effect of end groups is diminished and periodate consumption approaches one mole per mole of polysaccharide. The similarities in periodate consumptions showed that the basic structure of the hemicellulose was maintained in the crystalline xylan. The uniformity of the specific rotations (Table V) was further confirmation of this fact and the high negative values indicated a predominance of $\beta$-glycosidic bonds.

TABLE V

SPECIFIC ROTATIONS OF HEMICELLULOSES AND CRYSTALLINE XYLANS

| | $[\alpha]_D^{26}$ ($c$ = 1.0 in 2% aqueous potassium hydroxide | |
|---|---|---|
| | Hemicellulose | Crystalline xylans |
| Barley | − 95.6° | − 85.2° |
| Wheat | − 81.6° | − 79.3° |
| Rye | − 87.1° | − 83.4° |

Some features of the structures of the crystalline xylans were now evident. Based on periodate consumptions and specific rotations the crystalline xylans were linear polysaccharides linked by $\beta$-glycosidic bonds probably in the 1–4 positions (1). When periodate oxidized xylan was hydrolyzed no D-xylose could be found in the hydrolyzate. Had a branch point existed in the xylan chain, the anhydro-D-xylose unit at which the branching occurred would not have been attacked by periodate and would have been detected after hydrolysis.

In periodate oxidation of a linear xylan three moles of formic acid should be produced; two from the reducing end and one from the nonreducing end of the chain, and it is possible to calculate a molecular weight on this basis (5). Table VI shows the amounts of formic acid produced by periodate oxidation of the crystalline xylans and the D.P.'s calculated from these results. D.P.'s calculated from viscosity measurements and reducing power determinations are also included. The D.P.'s based on formic acid production were calculated

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on the assumption that the xylans were linear. Good agreement among the three independent estimates validated this assumption and indicated that the values found were probably correct.

TABLE VI
DEGREES OF POLYMERIZATION OF CRYSTALLINE XYLANS

| Crystalline xylan | Formic acid produced by periodate oxidation (mole/mole) | D.P. (formic) | D.P. (viscosity) | D.P. (reducing power) |
|---|---|---|---|---|
| Barley | 0.069 | 44 | 60 | 50 |
| Wheat | 0.099 | 30 | 33 | 28 |
| Rye | 0.120 | 25 | 30 | 32 |

Methylation of crystalline barley xylan, followed by hydrolysis, as described in the experimental section, yielded a mixture of reducing sugars having the following composition: (*a*) 2,3,4-trimethyl-D-xylose, 2.0%, (*b*) 2,3-dimethyl-D-xylose, 97.1%, (*c*) monomethyl-D-xylose, 0.9%. The tri- and dimethyl-D-xylose derivatives were identified chromatographically by comparison with known compounds run on the same paper. The monomethyl-D-xylose was not identified. The amount of 2,3,4-trimethyl-D-xylose corresponded to approximately 50 residues per nonreducing end group, a value in good agreement with those found by other methods (Table VI). The 2,3-dimethyl-D-xylose was derived from a long chain of D-xylose units linked 1–4 by glycosidic bonds. The small amount of monomethyl-D-xylose must have resulted either from a branch point in the xylan chain or from incomplete methylation. A constant methoxyl content of 36.8% was obtained after nine methylations of the crystalline barley xylan, a value slightly lower than the theoretical methoxyl content of 38.7% for a dimethyl xylose. Because of the difficulty of complete methylation and because of the other evidence indicating a straight chain polysaccharide, it is probable that the monomethyl-D-xylose resulted from incomplete methylation.

From the evidence obtained it was apparent that the autoclaving of straw hemicelluloses produced a mild hydrolysis, degrading the polysaccharide chain and removing L-arabinose and D-glucuronic acid as components of hydrolytic fragments. The degree of degradation depended on uronic acid content, and its progressive removal by successive autoclavings finally left a pure xylan completely resistant to further hydrolysis by water at 120°C. Removal of the single unit side chains of L-arabinose and D-glucuronic acid must have enabled the xylan chains to associate with each other and crystallize. The similar properties and behavior of the five straw hemicelluloses indicated that they all possessed the same basic structure (1) varying only in uronic acid content and chain length.

Fig. 2 shows a paper chromatogram of the soluble fragments produced by autoclaving the straw hemicelluloses. In addition to D-xylose and L-arabinose,

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a series of oligosaccharides was present. An investigation of these oligosaccharides will form the subject of a further communication.

## EXPERIMENTAL

### *Chromatographic Procedures*

All chromatograms were run on strips of Whatman No. 1 filter paper, 13.4 × 57.0 cm. The following solvent systems were used: (*a*) pyridine: ethyl acetate: water—1: 2: 2 (10), (*b*) methyl ethyl ketone: water—2: 1 (4), (*c*) butanol: ethanol: water: ammonia—40: 10: 49: 1 (11). Sugars were located on the papers by spraying with aniline hydrogen phthalate (12).

### *Preparation of Hemicelluloses*

Extractive-free, chlorite holocelluloses (2) of barley, flax, oat, rye, and wheat straws were chosen as sources of hemicelluloses. Holocellulose (30.0 gm.) was stirred for 24 hr. at room temperature with 5% aqueous sodium hydroxide (1 liter). Three extractions were made and the combined extracts, brought to pH 7.5 by acetic acid, were concentrated under diminished pressure to 750 ml. Addition of 3 volumes of ethanol precipitated crude hemicelluloses which were purified by dialysis against running distilled water for 48 hr. After reprecipitation by ethanol the hemicelluloses were dried through solvent exchange with ethanol and ether and finally by pumping to constant weight over phosphoric anhydride and paraffin at 0.05 mm. The final products were white powders containing 1–2% ash. Yields, based on holocellulose, ranged from 24–26%.

### *Crystallization Procedure*

Dry hemicellulose (5 gm.) was made into a thick paste with water (10 ml.) and heated for four hours at 120°C. in an autoclave. Ethanol (30 ml.) was added to the cooled mixture to precipitate high molecular weight material which was removed by centrifuging and autoclaved again. This procedure was repeated until no more ethanol soluble material was produced, four autoclavings being required. The ethanol solubles were stored for later examination. The precipitated polysaccharide was dissolved by heating for 15 min. at 120°C. in sufficient water to make a 0.2% solution (18). When this solution was cooled slowly to room temperature the polysaccharide separated as microcrystals which were removed by centrifuging and dried by washing with ethanol and ether.

### *Determination of Constituent Sugars*

Polysaccharides were hydrolyzed to constant reducing power by 2.5% sulphuric acid at 97°C. Individual sugars in the neutralized hydrolyzates were estimated by quantitative paper chromatography (7) using solvent (*a*). Uronic acids were estimated before hydrolysis by the method of Tracy (15).

### *Viscosity Measurements*

Hemicelluloses and crystalline xylans were dissolved in cupriethylenediamine to give 0.5% solutions from which 0.25%, 0.125%, and 0.0625% solutions were prepared by dilution. Flow times of freshly prepared solutions

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were measured in an Ostwald-Cannon-Fenske type viscometer (ASTM 100) in a water bath maintained at 25 ± 0.02°C. Degrees of polymerization were calculated from intrinsic viscosities using the Staudinger equation with $K_m = 5 \times 10^{-4}$ (9).

*Periodate Oxidation*

Samples (100 mgm.) of the hemicelluloses and crystalline xylans were suspended in water (120 ml.) to which was added 30 ml. of periodic acid solution (6.9 gm. periodic acid in 120 ml. water, neutralized to methyl red indicator by sodium hydroxide). All oxidations were carried out in a dark room at 16°C. At various time intervals analyses were carried out for periodate consumption and formic acid production (6). After periodate oxidations of the crystalline xylans were complete, excess periodate was destroyed by butylene glycol. The solutions were dialyzed against running distilled water for 48 hr. and then concentrated to sirups. These sirups were hydrolyzed by heating their solutions in water (5 ml.) with Amberlite IR 120 (0.5 gm.) in a sealed tube at 110°C. for 18 hr. (16). The resin was removed by filtration and paper chromatography of the filtrate, using solvent (*a*), showed no sugars. Preliminary experiments showed that the hemicelluloses and crystalline xylans were completely hydrolyzed by the resin, Amberlite IR 120, under the conditions reported.

*Reducing Power Determinations*

Samples (20 mgm.) of the hemicelluloses and crystalline xylans were covered with water (5 ml.) and allowed to stand at 5°C. for 96 hr. until thoroughly wet. Somogyi copper reagent (5 ml.) was then added and the determination was carried out in the usual manner (14).

*Methylation of Crystalline Xylan*

Crystalline barley xylan (0.722 gm.) was methylated with dimethyl sulphate (7.5 ml.) and 40% aqueous sodium hydroxide (15 ml.) in an atmosphere of nitrogen. After five methylations by this procedure the sirupy product was methylated four times with Purdie's reagents (methyl iodide and silver oxide) raising the methoxyl content to 31.7%. This product was fractionally precipitated from chloroform by adding petroleum ether. The most soluble fraction (0.344 gm.) was a white powder having MeO = 36.8%. This methoxyl content was not changed by three more methylations with Purdie's reagents.

*Hydrolysis of Methylated Xylan*

Methylated xylan (300 mgm.) was sealed in a tube with an equal weight of Amberlite IR 120 and anhydrous methanol (15 ml.). The tube was then shaken at 110°C. for 18 hr. Methanol was removed from the opened tube by evaporation and replaced by water (15 ml.). The tube was resealed and heated as before. Removal of the resin by filtration and evaporation of the filtrate left a mixture of reducing sugars. Qualitative and quantitative (8) examinations of this mixture were done by paper chromatography using authentic samples of 2,3-dimethyl-D-xylose and 2,3,4-trimethyl-D-xylose for identifications and using solvent systems (*b*) and (*c*).

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*Soluble Products from Autoclavings*

The ethanol solubles, produced by autoclaving the hemicelluloses, were chromatographed on paper using solvent (*a*). The developed chromatogram is shown in Fig. 2 in the discussion section.

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# ESTIMATION OF CARBOXYL, ALDEHYDE, AND KETONE GROUPS IN CHROMIUM TRIOXIDE OXYSTARCHES[1]

By A. C. Ellington[2] and C. B. Purves

ABSTRACT

Under identical conditions, corn starch amylose was more readily oxidized than the amylopectin by chromium trioxide dissolved in acetic acid – acetic anhydride, which was a nonswelling system. These differences in rate nearly vanished for samples dried through solvent exchange when the oxidant was dissolved in a swelling medium, 0.2 *M* aqueous sulphuric acid. The absolute rate of oxidation, however, was greatly reduced.

Carboxyl groups in the oxystarches were satisfactorily estimated either by ion-exchange with calcium acetate or sodium bromide solutions, or by direct titration to about pH 8.5 with aqueous alkali. The samples retained chromium compounds which grossly interfered with the determination of total carbonyl groups by condensation with hydroxylamine hydrochloride; condensation with excess sodium cyanide, and estimation of the ammonia from the hydrolysis of the cyanohydrins, gave better results.

Aldehyde groups in an oxystarch containing 0.16 M. of carboxyl and 0.14 M. of carbonyl groups were selectively oxidized with chlorous acid or alkaline hypoiodite, or were selectively condensed with sodium bisulphite solution. All three estimations indicated that about one-third of the carbonyl groups were aldehydes probably occupying the sixth positions in the glucose residues. The cyanohydrin of the oxystarch, when saponified and then hydrolyzed and reduced with boiling hydriodic acid, yielded the lactone of 2-methyl-4-hydroxyhexanoic acid, the recovery of which showed that at least 17% of the carbonyl groups occurred as 2-ketoglucose residues.

## INTRODUCTION

Publications regarding the action of diverse oxidizing agents on starches number well over 250, and have been reviewed in several standard books (17, 27, 36). For the most part, the literature is concerned with the preparation and physical properties of the industrially valuable "soluble" and "thin boiling" modifications of starch (dextrins) rather than with the chemistry of the oxidations. The researches dealing with chromic acid oxystarches, for example, revealed little of the chemical nature of the products beyond the facts that they contained acidic (15, 28, 39) and reducing or "alkali-labile" groups (14), were degraded, were difficult to free from chromium compounds, and sometimes yielded furfural when distilled (3, 19) with mineral acids. The supposition was that the furfural originated from glucuronic acid residues produced in the oxidation (17). Oxycelluloses, however, have been studied more intensively (38) and this background of knowledge formed the basis of the present research. A purified, commercial corn starch was used throughout, and the oxidant, chromium trioxide, was dissolved either in 0.2 *M* aqueous sulphuric acid or in acetic acid kept anhydrous by admixture with acetic anhydride. Although the oxidizing power of both solutions remained constant for many hours and was readily estimated iodometrically, the accessibility of the starch to the former was greatly increased by swelling,

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*Contribution from the Division of Industrial and Cellulose Chemistry, McGill University and Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from a Ph.D. thesis submitted to the University in September 1948 by A. C. E.*
[2] *National Research Council Student 1946-47 and 1947-48.*

whereas the latter was a nonswelling system producing negligible oxidation in unbroken, dried starch granules (9).

## DETERMINATION OF CARBOXYL AND CARBONYL GROUPS

Most of the methods for estimating carboxyl groups in acidic oxystarches depend upon ion-exchange with a soluble salt, MX.

$$\text{Starch COOH} + \text{MX} \longrightarrow \text{Starch COOM} + \text{HX}.$$

Elizer (7) employed silver *o*-nitrophenolate or cupric acetate as the salt MX and measured the decrease in silver or cupric ion in the supernatant liquor. The silver reagent at least would probably give inaccurate results with chromium trioxide oxystarches owing to their content of chromium ash (6) and reducing groups (5). The use of sodium chloride and titration of the acid liberated in the liquor (14) was probably free from these objections, and a similar method employing 1 *N* sodium bromide (35) gave the results shown in column 4 of Table I. These results agreed within ± 6%

TABLE I

CARBOXYL CONTENT OF CHROMIUM TRIOXIDE AND CHROMIC ACID OXYSTARCHES

| Sample | Milliatoms O consumed[a] | Millimoles carboxyl[a] | |
|---|---|---|---|
| | | By $Ca(OAc)_2$ | By NaBr |
| *Oxidation with $CrO_3$ in acetic acid – anhydride at 21°C.* | | | |
| I | 260 | 81 | 78 |
| | 260 | 85 | 80 |
| II | 278 | 90 | 94 |
| | 278 | 85 | 90 |
| III | 265 | 85 | 92 |
| | 265 | 80 | 90 |
| *Oxidation with $CrO_3$ in 0.2 M sulphuric acid at 21°C.* | | | |
| IV | 310 | 81 | 86 |
| | 310 | 79 | 84 |
| V | 570 | 158 | 162[b] |
| | 570 | 162 | 166[b] |

[a] *Per anhydroglucose unit.*
[b] *Values by direct electrometric titration against standard alkali to pH 8.3, 159, 157 mM.*

with those obtained with 0.5 *N* calcium acetate, another standard method for oxycellulose (9, 22, 23, 37, 41), and also with others based on the electrometric titration of the acidic oxystarch suspension to pH 8.3 with standard alkali. The last method required more extensive checking, because the existence of a Donnan equilibrium rendered it inapplicable to oxycelluloses (38). Fortunately Mattisson and Legendre (21) have independently confirmed the validity of a similar procedure.

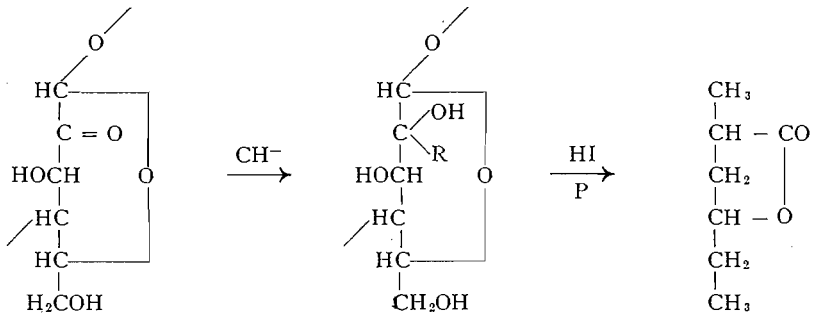
Apart from the reducing power and some colorimetric tests, the estimation

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of carbonyl groups in oxystarches and oxycelluloses depended on condensation to oximes with a solution of hydroxylamine hydrochloride initially near pH 5,

$$> C = O + H_2NOH.HCl \longrightarrow > C = NOH + H_2O + HCl,$$

followed by a potentiometric titration of the hydrochloric acid liberated (9, 22, 31). This highly buffered system made the titration of low accuracy when the content of carbonyl groups was small, and the presence of adsorbed chromium compounds caused serious interference (see below). The aldehyde and ketone groups in simple sugars, however, could be estimated satisfactorily by hydrolyzing the corresponding cyanohydrins and noting the amount of ammonia produced (2). Structure II illustrates the principle of the method for the oxystarch unit I, in which the carbonyl group was arbitrarily assigned to the second position.




I II R = CN → $CONH_2$ → COOH + $NH_3\uparrow$ III

When the sodium cyanide solution was added to the sample at a pH of 8 or more, the suspension turned purple and then orange, although no further deepening in color occurred on standing. This evidence of degradation made it desirable to form the cyanohydrin at the lowest convenient pH. Since Head (11) found that the tetraaldehyde produced by oxidizing methyl-β-cellobioside with periodic acid changed only very slowly when kept in a buffer at pH 9.5, although rapidly in one at pH 10.5, the lower value was chosen for the present estimation. The condensation of 1-gm. samples of the oxystarch with 40 cc. volumes of 0.38 *M* sodium cyanide was carried out at 20°C., and in one case the millimoles of cyanide consumed per glucose residue were 70, 81, 86, 90, 85, and 92 after 3, 6, 9, 12, 18, and 24 hr., respectively. A time of at least 12 hr. was chosen, and the reproducibility of the estimation was assessed as ± 4% for oxystarches in which carbonyl groups were plentiful.

If it was assumed that all of the carboxyl groups originated from primary alcohol units in the starch, each group represented the consumption of 2 atoms of available oxygen from the chromium trioxide. Table II, column 4, expresses the results of estimations with calcium acetate as a percentage of the oxidant reduced in the preparation of various oxyamyloses, oxyamylopectins, and oxystarches. Column 6 records the similar percentages recovered as carbonyl groups, each of which required only 1 atom of oxygen in its

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TABLE II

ESTIMATION OF CARBONYL GROUPS BY THE CYANOHYDRIN METHOD

| Sample | Milliatoms O consumed[a] | COOH by $Ca(OAc)_2$ | | CO by HCN | | Recovery of oxidant, | Ash, |
|---|---|---|---|---|---|---|---|
| | | mM.[a] | % | mM.[a] | % | % | % |
| *Oxidation with $CrO_3$ in acetic acid – anhydride at 21°C. for 1 hr.*[b] | | | | | | | |
| Amylose | 400 | 113 | 56 | 118 | 30 | 86 | 0.3 |
| Amylose | 200 | 52 | 52 | 88 | 44 | 96 | 0.4 |
| Amylopectin | 80 | 35 | 87 | 14 | 18 | 105 | 0.6 |
| *Oxidation with $CrO_3$ in 0.2 M sulphuric acid at 21°C.*[c] | | | | | | | |
| Amylose | 300 | 66 | 44 | 102 | 34 | 78 | 0.4 |
| Amylose | 130 | 34 | 52 | 62 | 48 | 100 | 0.2 |
| Amylopectin | 520 | 158 | 60 | 131 | 25 | 85 | 4.8 |
| Amylopectin | 300 | 81 | 54 | 99 | 33 | 87 | 2.5 |
| Starch | 580 | 163 | 56 | 151 | 26 | 82 | 5.6 |
| Starch | 540 | 158 | 58 | 140 | 26 | 84 | — |
| Starch | 540 | 160 | 60 | 138 | 26 | 86 | — |
| Starch | 400 | 120 | 60 | 102 | 26 | 86 | — |
| Starch | 300 | 81 | 54 | 92 | 31 | 85 | 3.1 |
| Starch | 200 | 60 | 60 | 68 | 34 | 94 | 1.2 |
| Starch[d] | 540 | 40 | 15 | 99 | 18 | 33 | 3.8 |

[a] *Per anhydroglucose unit.*
[b] *Yields 102 to 104% uncorrected for ash.*
[c] *Yields 95 to 98% uncorrected for ash.*
[d] *Recovered in 85% yield after electrodialysis.*

formation. Since the total recovery of oxidant (column 7) as carboxyl plus carbonyl groups was 90% of the amount used (within a cumulative analytical error of perhaps ± 10%) and since the yield of the oxidized products was nearly quantitative, it appeared that the cyanohydrin estimation of carbonyl groups contained no gross systematic error. The recovery of only 33% of the oxidant in the last experiment noted in the table was left out of consideration, because the ash in this oxystarch had been reduced from 6% to 3.8% by electrodialysis, and the yield was only 85%. Degradation of the starch to acidic, reducing, dialyzable substances was therefore considerable during the oxidations. Concurrent estimations of carbonyl groups by the hydroxylamine hydrochloride method, made on the acidic samples and not shown in the table, were usually about 90% of the cyanohydrin value when the ash contents were 0.4% or less (column 7), but were only 30% to 60% with ash of 2.5% or more. Negative values were occasionally observed with acidic amylopectins of very high ash content.

The suggestion in Table II, lines 2 and 3, that amylopectin consumed the oxidant from acetic acid – acetic anhydride solution much more slowly than amylose was confirmed in a similar experiment employing 200 milliatoms of available oxygen per anhydroglucose unit and samples from which water had been removed by direct drying *in vacuo*. After one hour, the amylose

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had consumed 195 milliatoms of the available oxygen and had acquired 45 mM. of carboxyl groups, while the corresponding figures for the amylopectin were 90 milliatoms and 39 mM. These results were not significantly altered when the samples were dried through methanol and benzene instead of directly. In more drastic oxidations, carried out for two hours with 600 milliatoms of available oxygen, the amylose consumed 400 and the amylopectin only 120 milliatoms, and the production of carboxylic acid was 113 and 40 mM., respectively. The greater reactivity of amylose in acetic acid – acetic anhydride had been previously observed by Hirst, Plant, and Wilkinson (12) during experiments on acetylation with chlorine gas as a catalyst. These differences in reactivity probably had a physical origin because they practically disappeared when samples dried through solvent-exchange were oxidized in 0.2 *M* aqueous sulphuric acid, a swelling agent. Fig. 1, Plot A, which illustrates

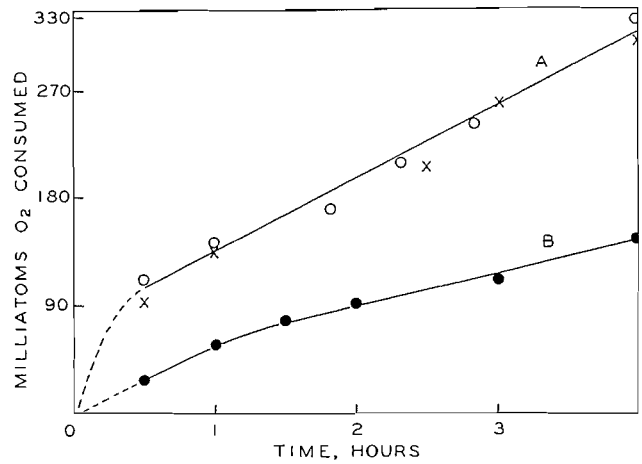



FIG. 1. Rates of oxidation in 0.2 *M* sulphuric acid with 600 milliatoms of available oxygen from chromium trioxide per glucose residue. Plot A, amylopectin, X, and amylose, O, dried through methanol–benzene. Plot B, amylose, ●, dried directly.

this point, also represents the behavior of amylopectin dried directly from water at room temperature. Amylose was peculiar in that direct drying markedly reduced its reactivity (Plot B), perhaps because it was rendered almost insoluble in water and incapable of being dispersed again. Direct drying did not have this effect on amylopectin. Felton, Farley, and Hixon (8) observed that aqueous bromine in the presence of barium carbonate oxidized a soluble "beta-amylose" fraction four times as rapidly as the corresponding "alpha-amylose". A comparison with the present result could not be made because the physical state of these fractions and their relationship to amylose and amylopectin were not specifically studied.

## DIFFERENTIATION OF ALDEHYDE AND KETONE GROUPS

Although acidic sodium chlorite solution had no significant effect on unmodified starch or cellulose, or on ketose sugars, Jeanes and Isbell (16) showed that the reagent oxidized aldoses quantitatively to aldonic acids.

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Reasonable results were obtained when the decrease in total carbonyl, and the increase in the carboxyl content, caused by the reoxidation of oxycelluloses with chlorous acid, was attributed to aldehyde functions (22, 23, 38). A similar reoxidation of two samples of chromium trioxide oxystarch (Table III)

TABLE III

ESTIMATIONS OF ALDEHYDE GROUPS IN STARCHES WITH ACID SODIUM CHLORITE

| Reoxidation[a] | Oxystarch A | | Oxystarch B | |
|---|---|---|---|---|
| | COOH[b] | CO[c] | COOH[b] | CO[c] |
| Before | 162 | 151 | 89 | 96 |
| After | 200 | 110 | 121 | 64 |
| Increase or decrease | +38 | −41 | +32 | −32 |
| Apparent aldehyde | 39/151 = 26%. | | 32/96 = 33%. | |

[a]*With excess 4% sodium chlorite at pH 2.5 and 25°C. for one hour.*
[b]*Millimoles per glucose unit by calcium acetate method.*
[c]*Millimoles per glucose unit by cyanohydrin–ammonia method.*

gave a quantitative recovery of the products, and the increase in carboxyl was neatly balanced by the decrease in total carbonyl content, as was expected. The inference was that 26% to 33% of the total carbonyl groups were aldehydes.

Another method of differentiating aldehydes from ketones was based on the work of Siggia and Maxcy (32), who estimated simple aldehydes by condensing them with standard bisulphite solution and titrating the excess bisulphite potentiometrically with standard alkali

$$> C = O + NaHSO_3 \rightleftarrows > C(OH)SO_3Na.$$

Similar titrations in the presence of ketones differed in having no pronounced end point, perhaps because the above equilibrium was far to the left for ketones instead of being far to the right. Other workers (34) showed that the specific rotation of glucose, but not of fructose, was greatly changed in aqueous sodium bisulphite, while Davidson (4) observed that more bisulphite was bound by periodate oxycellulose (a dialdehyde structure) than by a dichromate oxycellulose at a comparable level of oxidation. Nevell (23) noted the combination with nitrogen dioxide oxycelluloses. The application of Siggia and Maxcy's method to two samples of oxystarch indicated that 29% to 37% of the total carbonyl content was aldehydic (Table IV). These reasonable results, however, must still be regarded as tentative.

The third method of differentiation depended upon the selective oxidation of aldoses, as opposed to ketoses, by alkaline hypoiodite (1), and the conditions chosen, pH 9.7 for two and one-half hours, were similar to those successfully used for hydrocelluloses (20, 29). Control experiments with unmodified starch were necessary. Since the hypoiodite estimated only 34% of the carbonyl groups (Table IV) found in the oxystarches by the cyanohydrin method (also at pH 9.7), it seemed likely that degradation by the alkalinity did not

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TABLE IV

ESTIMATIONS OF ALDEHYDE GROUPS WITH SODIUM BISULPHITE AND WITH ALKALINE HYPOIODITE

| Method | Oxystarch C,[a] millimoles CO | Oxystarch D,[b] millimoles CO |
|---|---|---|
| *Bisulphite*[c] | 41, 39 | 34, 34 |
| Apparent aldehyde[d] % | 29, 28 | 37, 37 |
| *Hypoiodite*[e] | 48 | 32 |
| Apparent aldehyde[d] % | 34 | 34 |

[a]*Originally 141 mM. CO per glucose unit by cyanohydrin method.*
[b]*Originally 93 mM. CO.*
[c]*Excess 1 M sodium bisulphite at pH 7.5 for three hours, then titration to pH about 9.5.*
[d]*Quotient of 41 by 141 mM., etc.*
[e]*Sodium hypoiodite, 0.1 N, at pH 9.7 and 25°C. for two and one-half hours.*

interfere seriously and that the oxidation was restricted to the original aldehyde groups. Although the gross over-oxidation reported for oxycelluloses (24) suggested that the hypoiodite method was of doubtful reliability, in the present case it supported the conclusion from the other two methods that approximately one-third of the carbonyl groups in the oxystarches were aldehydes, presumably occupying the sixth positions in the anhydroglucose units in starch. The remaining two-thirds were therefore ketone groups in the second and third positions.

## DETECTION OF ANHYDRO-2-KETOGLUCOSE UNITS

If the oxystarch contained any glucose residues oxidized to ketone in the second position (Structure I), cyanohydration followed by saponification would yield a branched chain heptonic acid unit (II, R = COOH). Complete hydrolysis of this product with constant-boiling hydriodic acid would then liberate the acid (II) with an aldehyde group in the first position, but the simultaneous reduction would change the aldehyde to a methyl unit and replace hydroxyl groups with hydrogen atoms. The product would be 2-methylhexanoic acid or its lactone (III). This was the method used by Kiliani to locate the ketone group in fructose, and the yield of the lactone (III) from this source was recently raised to about 70% of theory (26). In the same way, any 3-keto unit in oxystarch would yield 2-ethylpentanoic acid, and the product from a 6-aldehydo unit would be *n*-heptanoic acid or lactone.

The chromium trioxide oxystarch used was prepared in 0.2 *M* sulphuric acid, and averaged 158 mM. of carboxyl and 141 mM. of carbonyl groups per glucose unit. After the formation and saponification of the cyanohydrin, the acidic product containing (II) was isolated in nearly quantitative yield, but the carboxyl content was only 265 mM., or only 85% of the expected value of (158 + 141) 299 mM. The reason for this discrepancy was not determined. Hydrolysis with boiling 0.5 *N* sulphuric acid then made it possible to separate the unoxidized portion of the oxystarch as glucose, and to recover the acidic portions as barium salts in 50% yield by weight. This yield, and the barium content of 21.0% corresponded to 0.98 equivalents of barium for each carboxyl

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group (0.265 M.) retained after the cyanohydrin synthesis but the analysis was not that of a single chemical individual. Hydrolysis with boiling 1 *N*, instead of 0.5 *N*, sulphuric acid reduced the yield of these salts to about 35% by weight of the original oxystarch, presumably because some of the uronic acid units were decarboxylated. The barium content of the salts, and the fact that the reducing power of the hydrolyzates increased to only 50% as glucose, suggested that most of the product consisted of difficultly hydrolyzable aldobiuronic acids.

The above barium salts were then reduced with constant-boiling hydriodic acid in the presence of red phosphorus, and the acidic portion of the product was freed from a little combined iodine by hydrogenation. After recovery, the pale yellow oil was at first methylated with diazomethane and fractionally distilled, but analyses showed the fractions to be mixtures of ester and lactone. In later experiments the oil was converted to its white barium salt, whose composition as that of a monohydroxyheptanoic acid was unchanged by reprecipitation from aqueous alcohol. This salt amounted to 13.2% by weight of the carbohydrate barium salts from which it was derived, and its barium content of 32.3% accounted for only 20% of the original carboxyl groups. Since no trace of a barium hexanoic acid was discovered, it was inferred that any remaining uronic acid residues in the oxystarch had been lost by decarboxylation during the reduction with boiling hydriodic acid. On this basis the 13.2% yield corresponded to 6% by weight of the oxystarch, or to about one-third of the 141 mM. of carbonyl groups it contained.

In a final experiment, 30 gm. of the oxystarch yielded 14 gm. of carbohydrate barium salts after cyanohydration, saponification, and hydrolysis, and the acidic oil from the reduction and deiodination was fractionally distilled at 1.5 mm. pressure. The main fraction, 0.5 gm., had the composition of a heptanoic lactone and yielded the crystalline hydrazide of 2-methyl-4-hydroxyhexanoic acid (III), the identity of which was confirmed by comparison with an authentic sample. Since 2.9 gm. of the lactone could be theoretically expected from 141 mM. of carbonyl group in the oxystarch, the observed recovery of 0.5 gm. showed that 17% of these groups were 2-keto units. This estimate was a minimum, because the recovery from pure fructose was only about 70% of theory (26), and the proper value was probably at least 25%. Aldehydo and 2-keto units therefore accounted for at least one half of the carbonyl groups in the oxystarch examined; no 3-keto units were detected, and the remaining carbonyl groups perhaps escaped identification because they were located on glucose residues oxidized in more than one way. Since the 2,3-dialdehyde structure produced by highly selective oxidants like periodic acid (38) was amost certainly absent from the oxystarch, the aldehyde units found were restricted to the 6-positions of the glucose residues.

## EXPERIMENTAL

### *Materials*

A commercial, air-dry corn starch was freed of fat by extractions with 85% aqueous methanol (30), and the amylose was isolated by dispersing 30 gm.

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of the product in 1 l. of water in which 1.3 gm. of thymol and 1 gm. of sodium chloride had been dissolved (10). Yield 6.3 gm., or 21%. Stirring for one hour with 4 gm. of absorbent cotton removed traces of amylose (25) from the mother liquor, which was then concentrated under diminished pressure and diluted with 4 volumes of methanol. The precipitated amylopectin, after being dried through methanol and benzene, amounted to 23 gm., or 79%.

The whole starch employed in later experiments was extracted for one week at room temperature with 10 volumes of 97% acetic acid, and for a second week with an equal volume of fresh acid. Work carried out at the Massachusetts Institute of Technology in 1942 by our former colleague, Dr. G. E. Murray, for the Corn Industries Research Foundation, showed that this treatment removed much of the ash, fat, and nitrogen compounds, but caused no acetylation and no visible change in the starch granules. Although the product was of the thin boiling variety, the hydrolytic action of the reagent was so slight that eight days were required for a 50% hydrolysis of sucrose, and methyl-$\alpha$-glucopyranoside was unaffected after six months.

Pure thiophene-free benzene freshly distilled from sodium, and methanol dried and distilled from magnesium, were used to dry the samples through solvent-exchange, and stock acetic acid was boiled under reflux with 2% of chromium trioxide to remove any reducing impurities (13). The acetic anhydride was purified by fractional distillation without adding chromium trioxide, the presence of which caused an explosion or fire.

*Oxidation of the Starch Samples*

(*a*) Thirty grams of the dried starch, defatted with 97% acetic acid, was reprecipitated with ethanol after dispersion in 1 l. of water about 70°C., and was solvent-exchanged into glacial acetic acid. Without previous drying, the product was immersed in 1 l. of a cold 4:1 mixture of glacial acetic acid and acetic anhydride containing the required amount of chromium trioxide, and the oxidation was followed iodometrically as described in the parallel work with cellulose (9). After being stirred mechanically at room temperature until an aliquot gave a negative test for the chromate ion with aqueous lead acetate, the oxystarch was recovered and was usually steeped in glacial acetic acid to remove some of the adsorbed chromic compounds. The product was freed of acetic acid *in vacuo* over solid sodium hydroxide, was washed with methanol and benzene, and was stored *in vacuo* over phosphorus pentoxide and solid sodium hydroxide.

Six-gram samples of the amylose and amylopectin were oxidized in 300 cc. volumes of the acetic acid – acetic anhydride mixture containing 0.74 gm. of chromium trioxide, an amount which afforded 0.3 atoms of available oxygen for each glucose unit. After being mechanically stirred for one hour, the products were recovered on a filter and the filtrate, plus the glacial acetic acid washings, was titrated with 0.125 *N* sodium thiosulphate in presence of excess potassium iodide to determine the oxidant consumed. The products were partially de-ashed and were isolated as already described. Attempts to remove ash with 10% instead of glacial acetic acid reduced the yield for oxyamylose

from 102% to 88% (including residual chromium ash), and of oxyamylopectin from 104% to 85%, both products being gelatinous and difficult to filter.

(*b*) A 60-gm. sample of the defatted starch was dispersed in 1 l. of distilled water at 80°C., and, after cooling, sufficient 20% sulphuric acid was added to make the mixture 0.2 *M*. The required amount of chromium trioxide, dissolved in 100 cc. of 2*M* sulphuric acid, was added and the mixture was stirred mechanically at room temperature until the oxidant was completely reduced. The slightly green colored product was precipitated by adding 2 volumes of methanol, was washed repeatedly in the same liquid, and was dried through benzene. Yield, 95% to 98%. An attempt to reduce the ash in a 55 gm. sample of the oxystarch by electrodialysis yielded only 47 gm. with an ash content (3.8%) that was still high. A three-compartment dialyzer with platinum electrodes operating at 110 volts and 0.5 to 0.15 amp. was used in this experiment.

*Analytical Methods*

The original articles described sources of error in these methods.

(*a*) Carboxyl groups were estimated by immersing the acidic oxystarch, 0.5 gm., in 50 cc. of 0.5 *N* calcium acetate previously adjusted to pH 8.2 (9) or in 50 cc. of 1 *N* sodium bromide (35). In each case the acid displaced in the ion-exchange was determined after 24 hr. by titration with 0.1 *N* sodium hydroxide to the pH of the blanks, and was accepted as equivalent to the carboxyl content (Table I). When this titration was carried out potentiometrically, the plot for a sodium bromide estimation practically coincided over the pH range 4 to 12 with the plot for the oxystarch suspended in distilled water, the maximum inflection occurring near pH 8.

(*b*) Carbonyl groups were estimated by the method just published for fructose (2). A solution of 0.3 gm. of the oxystarch in 20 cc. of 0.38 *N* sodium cyanide, buffered to pH 9.5 with aldehyde-free glacial acetic acid, was kept in a tightly stoppered vessel for 24 hr. After the addition of 8 cc. of 30% sodium hydroxide, the ammonia liberated from the hydrolysis of the cyanohydrin was quantitatively steam-distilled from a semimicro Kjeldahl apparatus into a 2% solution of boric acid containing a mixture of bromocresol green and methyl red as indicator (18). The time of distillation was standardized at 10 min., the final titration was with 0.01 *N* hydrochloric acid, and a blank determination was necessary to correct for the ammonia liberated from the excess cyanide.

(*c*) Aldehydes were differentiated from ketone groups by reoxidizing 6.5 gm. of the oxystarch, immersed in 145 cc. of 30% acetic acid, for one hour at pH 2.5 and 25°C. with 6 gm. of pure sodium chlorite dissolved in the minimum amount of water (22). The product was recovered by precipitation into 2 volumes of alcohol, and while in the centrifuge cup it was de-ashed by three quick extractions with a large excess of cold 70% methanol made 0.05 *N* with respect to hydrochloric acid. Any adsorbed chloride ion was thoroughly extracted with 70% methanol, and the reoxidized starch was dried through methanol and benzene. Yield 6.5 gm. or 100%. This product was then analyzed for carboxyl and carbonyl groups as described in (*a*) and (*b*).

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In the second method of differentiation, 50 cc. of 1 *M* sodium sulphite, 0.5 gm. of oxystarch, and 5 cc. of 1 *M* sulphuric acid were mixed together and kept in a stoppered flask for three hours (32). Aliquots, 25 cc., were then withdrawn and titrated potentiometrically with 0.1 *N* sodium hydroxide, the break in the plot near pH 9.5 being accepted as the end point. The result, when corrected for a blank containing no oxystarch, was taken to represent the moles of aldehyde *plus* carboxyl groups, and the latter were estimated separately as described in (*a*).

The third differentiation involved oxidizing a 0.3 gm. sample, suspended in 30 cc. of a 0.1 *N* sodium carbonate – bicarbonate buffer at pH 9.7, with 25 cc. of 0.1 *N* iodine in 2% potassium iodide (20, 29). The oxidation was for 2.5 hr. at 25°C. Ten cubic centimeters of 0.4 *N* sulphuric acid was then added and the liberated iodine was titrated with 0.1 *N* sodium thiosulphate to a starch end point. The mixture was agitated at intervals during the titration and at the end was colorless, although some purple deposits of the starch–iodine complex remained. It was necessary to carry out a blank titration in which the addition of acid immediately followed that of the iodine to the oxystarch sample.

*Preparation and Hydrolyses of Oxystarch Cyanohydrin*

(*a*) In a typical experiment 3.0 gm. of oxystarch averaging 0.141 carbonyl and 0.158 carboxyl groups per glucose unit was mixed with 100 cc. of 0.38 *N* sodium cyanide buffered to pH 9.5 with acetic acid. After standing at room temperature for 24 hr., the orange colored colloidal solution was concentrated under reduced pressure to expel ammonia, a procedure which caused no further increase in the color. The residual liquor was neutralized with dilute hydrochloric acid and the distillation continued for another hour to remove excess hydrogen cyanide. The product was then precipitated by pouring the liquor into 5 volumes of cold methanol made 0.05 *N* with hydrochloric acid and was thoroughly washed on the centrifuge with 0.05 *N* acid in 70% aqueous methanol. Washing was continued with neutral 70% methanol until the filtrate was free of chloride ion, and drying was done through absolute methanol and benzene. Yields varied from 96% to 104%. Found: COOH by the calcium acetate method, 0.265 M. A sample, 0.5 gm., was hydrolyzed in 500 cc. of boiling *N* sulphuric acid under reflux and at 30 min. intervals the copper reducing power of the solution was estimated, as glucose, by the Shaffer-Hartmann-Somogyi (33) method. A value of about 50% of theory was reached after hydrolysis for two and one-half hours, and further increase was only very slow. The same result was attained after about five hours' hydrolysis with 0.5 *N* sulphuric acid. As previously known (40), cyanide ion had to be removed prior to these estimations.

(*b*) The above cyanohydration was repeated on a 10-fold scale (30 gm. of oxystarch) with the exception that sulphuric instead of hydrochloric acid was used prior to the distillation of excess hydrogen cyanide. More sulphuric acid was added to increase the normality to 0.5 *N* and the product was hydrolyzed to glucose and sugar acids by heating for five and one-half hours

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under reflux on a steam bath. Two volumes of 95% ethanol were added to precipitate sodium sulphate and after its removal next day, the clear light red filtrate was freed of alcohol by distillation *in vacuo*. The residue, now 400 cc., was kept under reflux near 100°C. with barium carbonate for three or four hours, and the excess, together with barium sulphate, was removed on the centrifuge and thoroughly washed with water. Washings and filtrate, now about 2.5 l., were clarified with 8 gm. of absorbent charcoal and the clear yellow, neutral liquor was evaporated under diminished pressure to about 80 cc. and was poured into 2 volumes of 95% ethanol to precipitate the barium salts of sugar acids. After recovery next day, these salts were dissolved in the minimum amount of water, the solution was clarified with absorbent carbon, and the white salts were reprecipitated with ethanol and were dried *in vacuo* at 50°C. Yield: 14.5 gm. with a barium content of 20.8, 21.1%. A smaller-scale experiment gave a yield corresponding to 15.3 gm.

*Reduction to 2-Methyl-4-hydroxyhexanoic Acid*

(*a*) A published method was followed (26). Fourteen grams of the above barium salts, 6 gm. of red phosphorus, and 150 cc. of freshly distilled, constant boiling hydriodic acid (b.p. 127°C.) were heated together under gentle reflux for four hours. The dark mixture was cooled and extracted continuously with ether for 12 hr. to remove 14 gm. of a dark brown, acidic oil, which was recovered by evaporating the ether at atmospheric pressure. This oil was dissolved in 150 cc. of *N* sodium hydroxide, and combined iodine was reduced by high-pressure hydrogenation over 4 gm. of Raney nickel catalyst for two hours at 135°C. After recovery by extracting the strongly acidified solution with ether, 3.2 gm. of a yellow oil remained. Distillation of this product at 1.5 mm. pressure yielded 0.5 gm. of a pale yellow oil boiling at 54° to 58°C. and with a refractive index of $n_D^{21}$ 1.4350. Found: C, 65.0, 65.4%; H, 9.5, 9.4%; neutralization equivalent 128, 129, 126.5. Calcd. for $C_7H_{12}O_2$: C, 65.6%; H, 9.4%; neut. equiv., 128. A second fraction, 0.2 gm., consisted of a thick yellow syrup distilling at 130°C. and 1 mm. pressure and with $n_D^{18}$ 1.4680. Although crystals appeared to form in this fraction, the amount was too small to permit isolation. The more volatile fraction, 0.4 gm., when boiled under reflux for two hours with 1 cc. of hydrazine hydrate and 2 cc. of ethanol, deposited crystals which were recrystallized from chloroform. These crystals, 0.15 gm., melted at 115° to 122°C., undepressed by admixture with an authentic sample of 2-methyl-4-hydroxyhexanoic hydrazide, m.p. 123°C., kindly supplied by A. S. Perlin.

(*b*) Another reduction, carried out on 10 gm. of the above barium salts, yielded 2.6 gm. of the de-iodinated yellow acid oil. The crude barium salt of this oil, however, was found to contain barium iodide, which was removed by double decomposition of the aqueous solution with 3 gm. of silver sulphate. After removal of silver ion as the sulphide, careful neutralization of the filtrate with barium hydroxide, and the use of adsorbent charcoal, the liquor was evaporated to small volume. A pure barium salt, 0.85 gm., separated after several days. Found: C, 39.1, 39.3%; H, 5.9, 6.0%; Ba, 31.8, 32.0%. Calcd.

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for the barium salt of a hydroxyheptanoic acid, $(C_7H_{13}O_3)_2Ba$: C, 39.5%; H, 6.1%; Ba, 31.7%. Treatment of the filtrate with 2 volumes of acetone recovered a further 0.47 gm. (Found: Ba, 32.1, 32.4%) of this salt, and increased the total yield to 1.32 gm., or to about 50 mM. per anhydroglucose unit in the original oxystarch.

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# A METHOD FOR THE IDENTIFICATION OF THE MONO-*O*-METHYLGLUCOSES[1]

By R. U. Lemieux and H. F. Bauer[2]

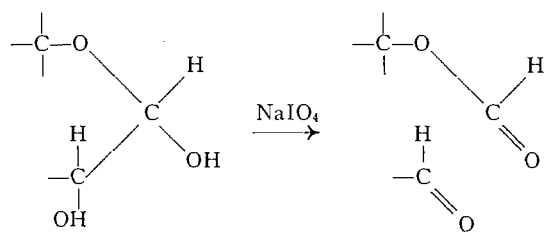
ABSTRACT

Periodate oxidation of any one mono-*O*-methylglucopyranose and alkaline hydrolysis of the product yields a substance which can be positively distinguished by paper chromatography from the products formed under the same conditions from the other mono-*O*-methylglucopyranoses. Thus, the components of a mixture of the mono-*O*-methylglucopyranoses can be readily identified. The method appears useful for the identification of di-*O*-methylglucoses. Reduction with sodium borohydride prior to periodate oxidation renders the method useful for the identification of tri-*O*-methylglucoses. The potential value of the method, which can be used on a microscale, is illustrated by an application to the characterization of the *O*-methylglucoses derived from a water-soluble *O*-methylcellulose.

A method for the identification of the components of mixtures of mono-*O*-methylglucoses was required as an aid in determining the extent and nature of acetyl group migrations during methylation with silver oxide and methyl iodide. This communication describes a method suitable for this purpose which may find useful application in studies on the composition of *O*-methylated polysaccharides.

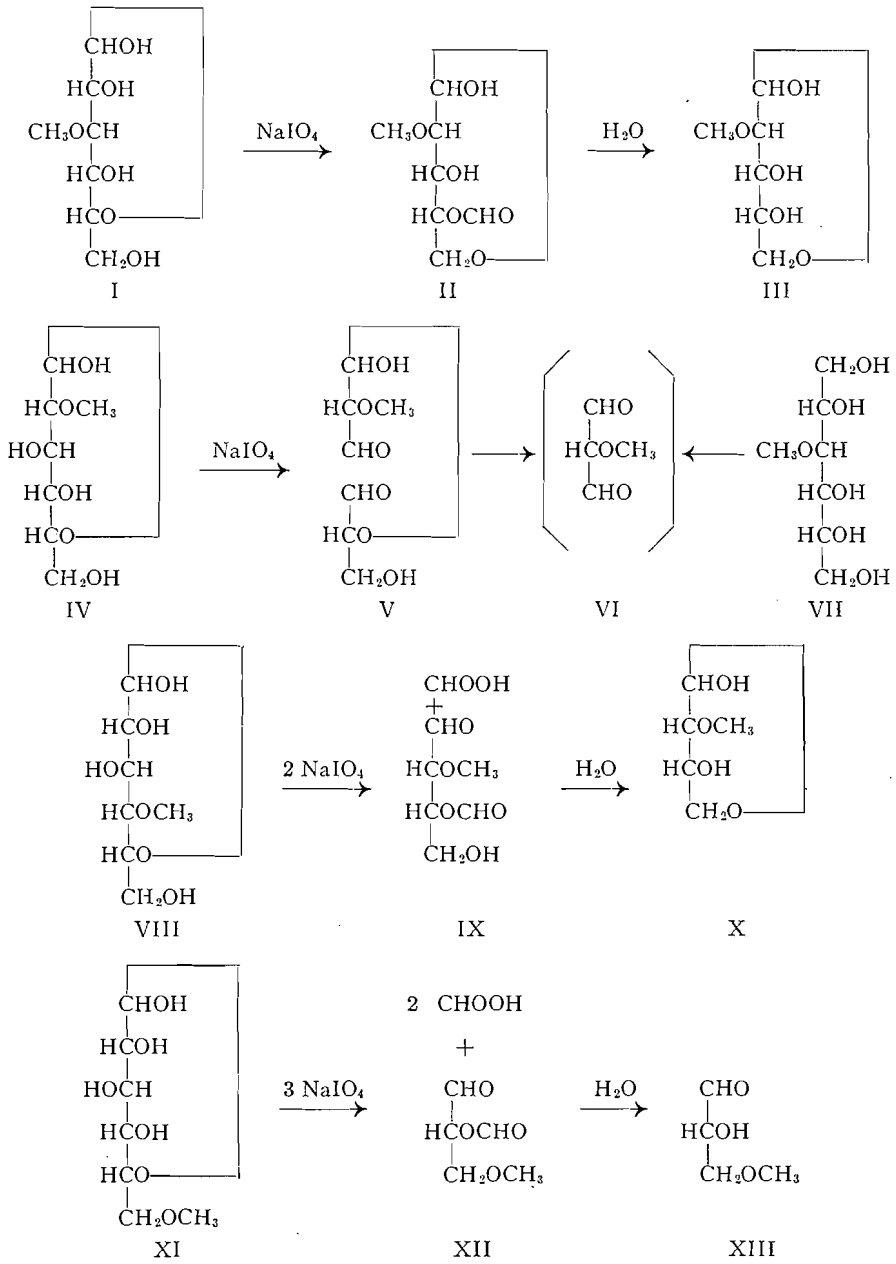
The position-isomers for a partially *O*-methylated sugar are not usually separable by unidimensional partition paper chromatography. For example, although a mono-*O*-methylglucose fraction which contained three different mono-*O*-methylglucoses was examined (chromatogram 1, Fig. 1), no information on the chemical heterogeneity of the fraction was obtained. Although the solution to the problem could have been approached by application of two-dimensional paper chromatography, it was felt that the following method would yield more decisive information and be of more general application. The method developed involves periodate oxidation of the mixture of *O*-methylglucoses, alkaline hydrolysis of the formyl esters formed, and characterization of the products by unidimensional paper chromatography.

It is now firmly established (1, 4, 5, 12, 16) that the periodate oxidation of reducing sugars may be attended by the formation of formyl esters. The *O*-formyl groups are derived from the lactol carbon atom, as shown below, and are sufficiently stable in slightly acid media to serve as blocking groups toward further periodate oxidation. Recently, the periodate oxidation of




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[2] *National Research Council of Canada Postdoctorate Fellow.*

3-*O*-methyl-D-glucopyranose (I) has been shown (1) to yield mono-*O*-formyl-2-*O*-methyl-D-arabinose (II). It is of interest to note that the success met (3) in limiting the consumption of periodate by starch and cellulose, when the oxidation mixture is controlled within the limits of pH 2.05–4.8, to one mole of oxidant per glucose residue is in all probability related to the formation of formyl esters at the reducing ends of the polysaccharide chains.




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In the light of the above-described behavior of reducing sugars toward periodate, it was to be expected that the course of oxidation followed on periodate oxidation of an *O*-methylglucose would vary considerably with variation of the position of the methyl group. It could be expected that the first product formed on periodate oxidation of 2-*O*-methyl-D-glucopyranose (IV) would be the trialdehyde (V). However, the course of further oxidation could not be predicted. Oxidation of the 4-*O*-methyl (VIII) and 6-*O*-methyl (XI) derivatives of D-glucopyranose would be expected to yield the mono-*O*-formyl-2-*O*-methyl-D-erythrose (IX) and mono-*O*-formyl-3-*O*-methyl-D-glyceraldehyde (XII), respectively. Identification of the products II, IX, and XII by paper chromatography could then serve as a means for identifying the

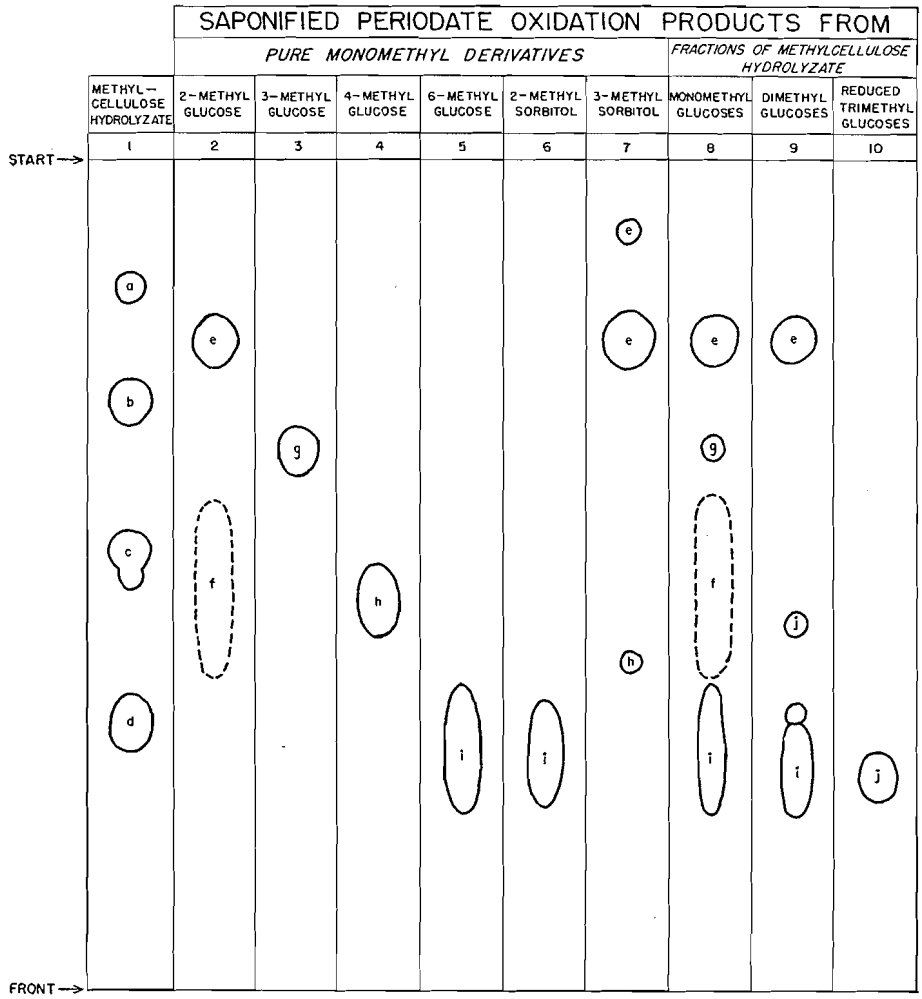


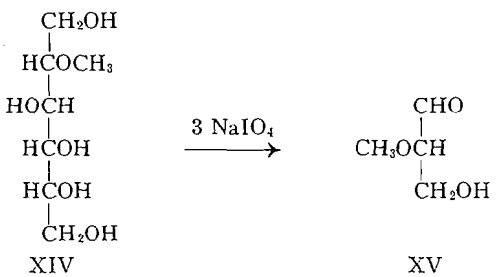

FIG. 1. Paper chromatograms developed with butanol–ethanol–water (6) and sprayed with aniline phthalate solution (15). *a*—glucose, olive brown. *b*—mono-*O*-methylglucoses, plum. *c*—di-*O*-methylglucoses, plum. *d*—tri-*O*-methylglucoses, plum. *e*—lemon yellow. *f*—faint canary yellow. *g*—2-*O*-methylarabinose, plum. *h*—citrine. *i*—canary yellow. *j*—olive brown.

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mono-*O*-methylglucose oxidized. This appeared to be the case. However, since the formyl esters underwent hydrolysis during the chromatography, the resulting chromatograms were ill-defined. When the *O*-formyl groups were saponified prior to chromatography, the well-defined chromatograms shown in Fig. 1 were obtained.

The chromatograms shown in Fig. 1 were developed with the butanol–ethanol–water system (6) and the reducing compounds were detected with the aniline phthalate reagent (15). The periodate oxidations were carried out for one hour at 0°C. with an excess of reagent. Ethylene glycol was added to destroy the excess periodate and the solution was neutralized to phenolphthalein before application to the chromatogram. The dark spots formed at the starting point through reaction of the aniline spray reagent with the sodium iodate were not included in Fig. 1.

The main product from 2-*O*-methyl-D-glucopyranose (IV) gave a strong lemon yellow spot in the cold. Since a material was formed on periodate oxidation of 3-*O*-methylsorbitol (VII) which possessed the same $R_f$ value (compare chromatograms 2 and 7, Fig. 1) and which gave the same color reaction, it seems likely that the substance is derived from methoxymalonaldehyde (VI). This conclusion is supported by the appearance of this spot on the chromatogram (Fig. 1, 9) for the oxidation products from the di-*O*-methylglucose fraction of the *O*-methylcellulose hydrolyzate. 2,6-Di-*O*-methyl-D-glucopyranose would also be expected to yield methoxymalonaldehyde (VI) on periodate oxidation. Attempts are being made to characterize the substance actually responsible for the color reaction. A diffuse band of greater $R_f$ value also appeared on the chromatogram of the product from 2-*O*-methylglucose. This complication may be serious should it be desired to identify 4-*O*-methylglucose (see Fig. 1, 4) in the presence of large amounts of 2-*O*-methylglucose. 3-*O*-Methyl-D-glucopyranose (I) gave only 2-*O*-methyl-D-arabinose (III) (1). The $R_f$ value for the product obtained from 4-*O*-methyl-D-glucopyranose is of the order expected for 2-*O*-methyl-D-erythrose (X). The product from 6-*O*-methyl-D-glucopyranose (XI) appeared to be 3-*O*-methyl-D-glyceraldehyde (XIII) since a substance of similar $R_f$ value was obtained from 2-*O*-methylsorbitol (XIV) (compare chromatograms 5 and 6 in Fig. 1). This substance should yield 2-*O*-methyl-L-glyceraldehyde (XV). 5-*O*-Methylglucose was not tested.




XIV XV

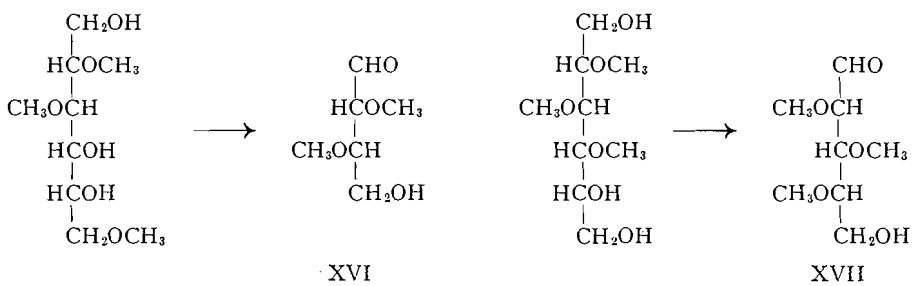
Inspection of chromatograms 2 to 5 in Fig. 1 shows that the method allows a ready and definite identification of a pure mono-*O*-methylglucose which

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possesses the methyl group at positions 2, 3, 4, or 6. Furthermore, the method allows the identification of these substances in the presence of one another except, as noted above, for some interference between the 2- and 4-substituted compounds.

The potential value of the method is illustrated by the following application to the methylglucoses derived from a technical cold-water-soluble *O*-methylcellulose. The *O*-methylcellulose was completely hydrolyzed (see Fig. 1, 1) and the hydrolyzate was fractionated by means of preparative paper chromatography to yield the fractions of mono-, di-, and tri-*O*-methylglucoses. The tri-*O*-methylglucose fraction crystallized immediately to yield 2,3,6-tri-*O*-methyl-D-glucose. Application of the procedure to the mono-*O*-methylglucose fraction showed clearly the presence of the 2-, 3-, and 6-substituted glucoses. Although it could undoubtedly be accomplished, no attempt was made to put the method on a quantitative basis for analysis. Nevertheless, a comparison of chromatogram 7 with chromatograms which contained varying amounts of the products from the individual mono-*O*-methylglucoses indicated that the ratio of mono-*O*-methylglucoses was approximately 10:1:5 for the glucoses substituted at positions 2, 3, and 6, respectively. This conclusion is in agreement with the conclusions reached by several investigators (18) that, at least under certain conditions of methylation, the 2-position of cellulose is considerably more reactive than the primary position and that the 3-position is quite unreactive (11). On the basis that the 2- and 6-positions are much more reactive toward methylation than the 3-position, it must be expected that the main di-*O*-methylglucose in the *O*-methylcellulose hydrolyzate would be the 2,6-di-*O*-methylglucose. Inspection of chromatogram 9 of Fig. 1 leaves little doubt that this was the case and that only relatively small amounts of the 2,3- and 3,6-di-*O*-methylglucoses were present. Timell (19) has established analytical methods for determining the distribution of the methyl groups in a partially methylated cellulose (20).

The method should be of value as an aid in the identification of methylated sugars. For example, it could be shown in a very simple manner that the tri-*O*-methylglucose derived from the *O*-methylcellulose hydrolyzate was 2,3,6-tri-*O*-methylglucose. Only a few milligrams of material were required. The substance was unchanged by the periodate treatment (4). This result obviously eliminated 3,4,6-tri-*O*-methylglucose. The substance was reduced with sodium borohydride and the tri-*O*-methylsorbitol was subjected to the procedure. The reducing substance formed (see Fig. 1, 10) must be 2,3-di-*O*-




XVI XVII

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methyl-L-threose (XVI). 2,3,4-Tri-*O*-methyl-D-glucose would have yielded 2,3,4-tri-*O*-methyl-L-xylose (XVII) of higher $R_f$ value and 2,4,6-tri-*O*-methyl-D-glucose would have resulted in the periodate resistant 2,4,6-tri-*O*-methylsorbitol.

## EXPERIMENTAL

### *Materials*

The 2-*O*-methyl-β-D-glucopyranose (10, 2), 3-*O*-methyl-α-D-glucopyranose (7, 8), and 6-*O*-methyl-α-D-glucopyranose (9) used in this work were pure crystalline compounds. Although the 4-*O*-methyl-D-glucopyranose was a sirup (14), it was prepared from pure crystalline 4-*O*-methyl-D-glucose dibenzyl mercaptal (17).

### *Periodate Oxidations*

The *O*-methylglucose or *O*-methylglucose mixture, 1 mgm., was dissolved at 0°C. in 0.120 ml. of 0.5 *N* sodium metaperiodate solution. After one hour at 0°C., 2–3 mgm. of ethylene glycol was added and the solution was warmed to room temperature. After five minutes the solution was made alkaline to phenolphthalein by titration with 0.5 *N* sodium hydroxide solution to a stable pink end point. After five minutes, the solution, 2–30 cu.mm., was applied by means of a microburette to Whatman No. 1 paper for chromatography. The spots were kept to about 6 mm. in diameter. The same procedure was used for the *O*-methylsorbitols.

### *Chromatography*

A descending chromatographic procedure was used with the butanol–ethanol–water system (6). Aniline phthalate solution was used as spraying reagent (15). The results obtained are summarized in Fig. 1. Table I lists the sensitivity of the color test for the products formed from the mono-*O*-methylglucoses.

TABLE I

SENSITIVITY OF THE ANILINE PHTHALATE REAGENT IN DETECTING THE PERIODATE OXIDATION PRODUCTS FROM THE MONO-*O*-METHYLGLUCOSES

| Mono-*O*-methylglucose oxidized | Color of spot | Approximate $R_f$ | Sensitivity in μgm. of *O*-methylglucose |
|---|---|---|---|
| 2-Methyl | Lemon yellow | 0.22 | 2–3 |
| 3-Methyl | Plum | 0.35 | 2–3 |
| 4-Methyl | Citrine | 0.53 | 12–15 |
| 6-Methyl | Canary yellow | 0.71 | 5–7 |

### *O-Methylsorbitols*

The *O*-methylglucose, 25 mgm., and 10 mgm. of sodium borohydride were dissolved in 0.2 ml. of water. After one hour at room temperature, the excess sodium borohydride was destroyed with acetic acid and the solution was deionized in the usual manner (21). The products from the 2- and 3-mono-*O*-

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methyl-D-glucoses and from the 2,3,6-tri-*O*-methyl-D-glucose were nonreducing sirups.

*Hydrolysis of O-Methylcellulose*

A technical *O*-methylcellulose, soluble in cold water, 26.3% methoxyl, 1.56 methyl groups per glucose residue, 1.0 gm., was dissolved in 25 ml. of concentrated hydrochloric acid, and the solution was left at room temperature for 24 hr. Water, 100 ml., was added and the clear solution was heated on the steam bath for 1.5 hr. The nearly colorless solution was evaporated *in vacuo* below 40°C. to a sirup which was dissolved in 25 ml. of water. The solution was left at room temperature overnight before the remaining hydrochloric acid was removed by passage through a column of Amberlite IR4B. Evaporation gave 1.0 gm. of colorless sirup. Chromatogram 1 of Fig. 1 shows that hydrolysis was complete.

*Preparative Paper Chromatography*

The *O*-methylglucoses in the above *O*-methylcellulose hydrolyzate were separated into the mono-*O*-methyl-, di-*O*-methyl-, and tri-*O*-methylglucose fractions by preparative partition chromatography (13). A 20% aqueous solution of the sirup was streaked across 47 × 57 cm. sheets of Whatman No. 3 MM paper using a mechanical device which ensured a uniform distribution over the whole length of the streak. In this way 100–120 mgm. of the sirup was applied to each sheet. The chromatograms were developed as described above. The positions of the bands were located by spraying strips cut out from each end of the sheets. The *O*-methylglucoses were extracted from the paper strips simply by stirring in water.

ACKNOWLEDGMENT

The 3-*O*-methylglucose was kindly provided by Dr. A. C. Neish of this laboratory.

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# CYCLIC METHYLENE ACETAL STABILITIES IN DIANHYDRO-HEXITOLS[1]

By Samuel B. Baker[2]

ABSTRACT

Ring closure at the 1,4-3,6-positions in monomethylenated mannitol and iditol imparts considerable lability to the cyclic methylene acetal group. The two derivatives, 1,4-3,6-dianhydro-2,5-methylene-D-mannitol and 1,4-3,6-dianhydro-2,5-methylene-D-iditol, are easily cleaved at the 2,5-methylene positions by highly dilute acid and differ distinctly in this respect from 2,5-methylene-D-mannitol.

The cyclic methylene acetal bridge in 2,5-methylene-D-mannitol (I) is quite stable to dilute acids. The methylene bridge does not cleave unless rather drastic acid treatment is carried out. In comparison to benzylidene and ethylidene acetals and isopropylidene ketals methylene acetals are surprisingly stable. It is therefore valid to assume that the acetal ring in 2,5-methylene-D-mannitol is a low energy structure. Sterically, the mannitol carbon chain can fold in such a manner as to diminish distortion within the methylene carbon valence bonds. Benzylidene, ethylidene, and isopropylidene groups are in reality methylene groups in which one phenyl, one methyl, and two methyl groups replace hydrogen atoms respectively. Folding of the carbon chain may be more difficult, owing to steric forces, so that the inherent energy may be large enough to make benzylidene, ethylidene, and isopropylidene acetals act in a normal manner, that is, they are unstable in acidic solution.

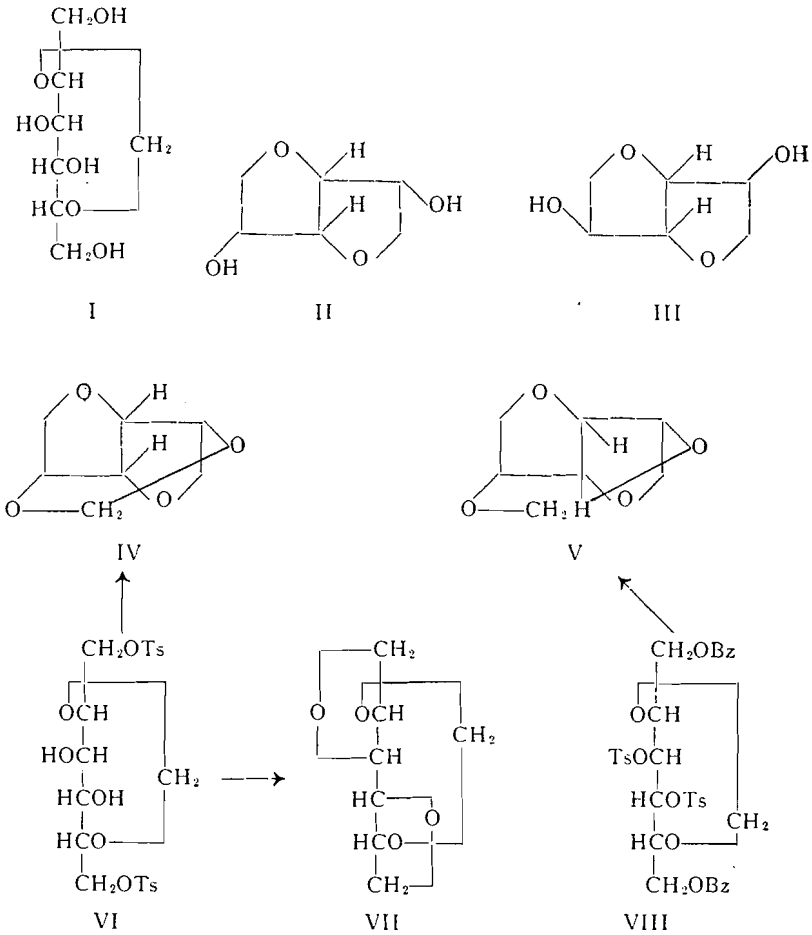
Mannitol and iditol readily form fused tetrahydrofuran rings as shown by the formation of 1,4-3,6-dianhydro-D-mannitol (II) (1, 4) and 1,4-3,6-dianhydro-L-iditol (III) (2, 6). These dianhydrohexitols (II) and (III) have been prepared by the above-mentioned authors by means of simple acid-catalyzed dehydration of D-mannitol and L-iditol respectively. The 1,4-3,6-dianhydro rings in the mannitol (II) and iditol (III) derivatives are fused tetrahydrofuran systems that are *cis*-oriented, thus imparting considerable stability to the two substances, (II) and (III).

A methylene acetal bridge across C-2 and C-5 in (II) and (III) should be under considerable strain inasmuch as the valence bond angular distortion cannot be diminished by folding of the rigid tetrahydrofuran ring structures. 1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV) and 1,4-3,6-dianhydro-2,5-methylene-D-iditol (V) were synthesized to compare the stability of the methylene acetals in the latter two dianhydrohexitols, (IV) and (V), to the identical group in 2,5-methylene-D-mannitol (I). The mannitol derivative(IV) proved to be very labile to 0.001 *N* hydrochloric acid and even to hot water. The iditol derivative (V) required somewhat more drastic treatment to cleave the acetal ring. Hot water had no effect whatsoever and 0.01 *N*, but not 0.001 *N*, hydrochloric acid cleaved the acetal ring in a few minutes. Although

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[2] *In charge, Division of Organic Chemistry.*



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Bz = Benzoyl
Ts = *p*-Toluenesulphonyl

the iditol derivative (V) was less labile than the mannitol derivative (IV), both were extremely labile when compared to 2,5-methylene-D-mannitol (I).

Saponification of 2,5-methylene-1,6-ditosyl-D-mannitol (VI) with alcoholic potassium hydroxide or sodium methoxide solution yielded a dianhydromethylene hexitol. It is now generally accepted that detosyloxylation followed by ring closure occurs through the transitory formation of a carbonium cation. Ring closure occurs when the transitory carbonium cation has a hydroxyl or presumptive hydroxyl group in a *trans* position and the ring closes on the side of the molecule where the reacting hydroxyl group is situated. Therefore the dianhydromethylene hexitol can be formulated either 1,4-3,6-dianhydro-2,5-methylene-D-mannitol (IV) or 1,3-4,6-dianhydro-2,5-methylene-D-mannitol (VII). The latter structure can be dismissed on steric grounds. Removal of the methylene group with either hot water or 0.001 *N* hydrochloric acid yielded a product identical with the known isomannide. It is unlikely

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that a methylene acetal group can shift under the experimental conditions used to prepare the dianhydromethylene mannitol. This is therefore further unequivocal proof of the 1,4-3,6-dianhydro-D-mannitol (II) structure for isomannide.

The iditol derivative was prepared by sodium methoxide saponification of 1,6-dibenzoyl-2,5-methylene-3,5-ditosyl-D-mannitol (VIII). Again, for the same reasons as above, it is only possible to formulate the hexitol derivative as 1,4-3,6-dianhydro-2,5-methylene-D-iditol (V). Removal of the methylene acetal with 0.01 *N* hydrochloric acid yielded a product that was identical with the known isoidide. This then is additional proof for the 1,4-3,6-dianhydro ring structure for isoidide.

## EXPERIMENTAL

*2,5-Methylene-1,6-ditosyl-D-mannitol (VI)*

2,5-Methylene-D-mannitol (5) (50 gm.) was dissolved in hot pyridine (500 cc.). The solution was cooled (0°C.) and *p*-toluenesulphonyl chloride (100 gm.), dissolved in pyridine (200 cc.), was added over a period of 30 min. with stirring. The reaction mixture was then allowed to stand overnight at room temperature and was finally concentrated *in vacuo* to remove most of the pyridine. The remaining sirupy mass was suspended in a large volume of cold water and the sirup soon crystallized. It was filtered, washed well with cold water, and air-dried. The crude product was recrystallized once from methanol after decolorizing with charcoal. An additional recrystallization gave 94 gm. (73%) of a pure product melting at 148–149°C. and rotating $(\alpha)_D^{20°C.} -22.8°$. These constants agreed with those found by Haskins, Hann, and Hudson (3).

A sample of the above (3 gm.) was dissolved in pyridine (20 cc.), *p*-toluenesulphonyl chloride (2.4 gm.) was added, and the solution allowed to stand 72 hr. at 40°C. The reaction mixture was cooled to 20°C. and then added to a large volume of cold water. The product separated as an oil and it slowly solidified. After the solid had been allowed to stand overnight it was broken up, filtered, and washed with cold water. The air-dried material was recrystallized from 99% ethanol and after desiccation it weighed 3.3 gm. (68%) and melted at 176–177°C. A mixed melting point determination with authentic 2,5-methylene-1-3,4,6-tetratosyl-D-mannitol was not depressed.

*1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV)*

*Sodium Methoxide Method*

2,5-Methylene-1,6-ditosyl-D-mannitol (20 gm.) was dissolved in chloroform (200 cc.). A sodium methoxide solution (50 cc.) containing 1.9 gm. sodium was added and, within one minute, a gel formed. The gel was soon replaced by glistening crystals of sodium *p*-toluenesulphonate. The small excess of sodium methoxide was converted to sodium carbonate by means of carbon dioxide and the separated salts removed by filtration. The slightly colored filtrate was concentrated *in vacuo* and the gummy residue mixed with hot chloroform (100 cc.). The turbid solution was filtered and the solvent

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again removed *in vacuo* at 30°C. The solid residue was dissolved in hot ether (300 cc.) and the ethereal solution was decolorized with charcoal, then filtered. The filtrate was concentrated to one-half volume and cooled to −20°C. Long needlelike crystals separated in a yield of 5 gm. (80%). They were recrystallized twice more when the melting point of 84–85°C. became constant and the rotation was $(\alpha)_D^{24°C.}$ 133.7° ($CHCl_3$; *c*, 10.4304; 1, 2).

*Potassium Hydroxide Method*

2,5-Methylene-1,6-ditosyl-D-mannitol (20 gm.) was dissolved in ethanolic potassium hydroxide (5.3 gm. in 250 cc.). The highly alkaline reaction mixture became neutral to phenolphthalein on heating under reflux. Heating was continued an additional 30 min. and the mixture was then concentrated *in vacuo* at 30°C. The gummy mass was thinned with chloroform (300 cc.) and the mixture filtered to remove potassium *p*-toluenesulphonate in quantitative yield. The chloroform solution was then concentrated *in vacuo* and the residual solid dissolved in hot ether (300 cc.) and the latter solution decolorized with activated charcoal. The solution, after filtration, was concentrated to one-half volume and on cooling to −20°C. needlelike crystals separated in a yield of 5.6 gm. (90%). An additional recrystallization from ether gave a pure product melting at 84–85°C. and rotating $(\alpha)_D^{24°C.}$ 133.2° ($CHCl_3$; *c*, 8.631; 1, 2). A mixed melting point determination with a sample of the substance obtained by the sodium methoxide method, above, was not depressed.
Anal. Calc. for $C_7H_{10}O_4$; C, 53.16; H, 6.33. Found: C, 53.09; H, 6.46.

*Methylenation of 1,4-3,6-Dianhydro-D-mannitol (II)*

1,4-3,6-Dianhydro-D-mannitol (4 gm.) was dissolved in anhydrous dioxane (175 cc.) containing paraldehyde (5 gm.) and anhydrous calcium sulphate (20 gm.). The mixture was heated in a sealed bomb tube in a steam bath for 10 hr. The tube was cooled to 20°C. and the contents removed in the fume cabinet. Chloroform (380 cc.) was added and the mixture filtered. The filter was washed with a little chloroform and the combined filtrates concentrated to dryness *in vacuo*. A sirup resulted which was partially soluble in ether and it was therefore heated under reflux with anhydrous ether (300 cc.) for one hour. The ethereal solution was decanted from the undissolved sirup and the latter was triturated with a little ethyl acetate. The sirup crystallized immediately and after one recrystallization from ethyl acetate it weighed 2 gm. (50% recovery) and melted at 87–88°C. A mixed melting point determination with authentic 1,4-3,6-dianhydro-D-mannitol was not depressed.

The ethereal solution, above, was concentrated to about 75 cc. and filtered from a faint turbidity. The clear, colorless solution was cooled to −20°C. and crystals which separated in a yield of 1.2 gm. (27%) melted at 84–85°C. A mixed melting point determination with 1,4-3,6-dianhydro-2,5-methylene-D-mannitol obtained above was not depressed.

*Acetolysis of 1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV)*

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (1 gm.) was added to an acetolyzing (5) mixture (5 cc.) at 0°C. The solid dissolved immediately and

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the solution was allowed to stand 18 hr. at 5°C. The reaction mixture was added slowly with stirring to an excess of cold (5°C.) saturated potassium bicarbonate solution. The aqueous solution was then concentrated to dryness *in vacuo* at 15°C. The dry residue was extracted with warm chloroform (100 cc.) and after filtration, the solvent was removed *in vacuo*. The remaining colorless sirup was distilled at 130–133°C. at 0.08 mm. and gave 0.9 gm. of a viscous sirup. This yield was equivalent to 64% based on 2,5-diacetyl-1,4-3,6-dianhydro-D-mannitol. The specific rotation was $(\alpha)_D^{23°C.}$ 119.8° ($CHCl_3$; *c*, 1.602; 1, 2) and refractive index $\eta_D^{23°C.}$ 1.4840. A few drops of the product when heated with dilute hydrochloric acid did not give a test for formaldehyde, signifying that the methylene acetal was cleaved by the acetolyzing mixture.

The presumed 2,5-diacetyl-1,4-3,6-dianhydro-D-mannitol (0.6 gm.) was dissolved in chloroform (25 cc.). Sodium methoxide solution (5 cc. of 0.01 *N*) was added and the solution allowed to stand overnight at 5°C. Carbon dioxide gas was passed in and the mixture was then concentrated *in vacuo*. The dry residue was heated with a small volume of ethyl acetate. The latter solution was concentrated to one-half volume and after cooling to −10°C. the concentrate was inoculated with a crystal of 1,4-3,6-dianhydro-D-mannitol. Immediate crystallization occurred and the product was recrystallized once more from ethyl acetate yielding 0.39 gm. (77%) and melting at 87.5–88°C. A mixed melting point determination with authentic 1,4-3,6-dianhydro-D-mannitol was not depressed.

*Effect of Hot Water on 1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV)*

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (1 gm.) was dissolved in distilled water (25 cc.) and the solution was distilled slowly through a 150 mm. glass column. The distillate was collected in an excess of ice-cold 2,4-dinitrophenylhydrazine hydrochloride solution. Immediate precipitation of formaldehyde-2,4-dinitrophenylhydrazone occurred and distillation was continued until 15 cc. distillate was collected. The water was replaced and distillation continued. This process was repeated six times so that practically all the formaldehyde was removed. The voluminous 2,4-dinitrophenylhydrazone was filtered, washed with a little water, and air-dried. The yield was 1.2 gm. (89%) and the melting and mixed melting points with an authentic sample were 164–167°C.

The above was repeated but the distillate was added to an excess of 5,5-dimethyl-1,3-cyclohexanedione. The dimethone of formaldehyde separated in nearly quantitative yield and melted at 187–189°C. A mixed melting point determination with an authentic sample showed 188–189°C.

The residues in both distilling flasks were combined and concentrated to dryness *in vacuo* and the gummy product dissolved in a small volume of hot ethyl acetate. The slightly colored solution was decolorized with charcoal, filtered, and then allowed to cool. The crystalline product that separated was removed by filtration and it was recrystallized once more giving 1.3 gm. (77%) melting at 87–88°C. This proved to be 1,4-3,6-dianhydro-D-mannitol as determined by a mixed melting point.

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*1,4-3,6-Dianhydro-2,5-dibenzoyl-*D*-mannitol*

1,4-3,6-Dianhydro-2,5-methylene-D-mannitol (IV) (2 gm.) was dissolved in 0.001 *N* hydrochloric acid (75 cc.) and the solution distilled *in vacuo* at 50°C. The sirupy residue was dried by distilling ethanol from it. This was repeated four times. The partially crystalline mass was then dissolved in anhydrous pyridine (25 cc.), the solution cooled to 0°C., and benzoyl chloride (4 cc.) was added. The reaction mixture was allowed to stand for two hours at 24°C., then concentrated *in vacuo*. The remaining sirup was mixed with cold water and after it had been allowed to stand overnight at 5°C. the sirup solidified. The air-dried material was dissolved in about 20 cc. ethanol and the solution decolorized with charcoal. The solution was cooled and crystallization occurred. Two additional recrystallizations from ethanol raised the melting point to 131–132°C. and rotation to $(\alpha)_D^{24°C.}$ 224.8° ($CHCl_3$; *c*, 0.6649; 1, 2). Fletcher and Goepp (2) report m.p. 132.0–132.4°C. and $(\alpha)_D^{20°C.}$ 225.7° ($CHCl_3$).

*1,6-Dibenzoyl-2,5-methylene-3,4-ditosyl-*D*-mannitol (VIII)*

1,6-Dibenzoyl-2,5-methylene-D-mannitol (5) (25.2 gm.) was dissolved in anhydrous pyridine (90 cc.). The solution was cooled to 0°C. and *p*-toluenesulphonyl chloride (26.4 gm.) was added. The reaction mixture was allowed to stand for three days at 40°C. and then concentrated *in vacuo* to remove most of the pyridine. The dark-brown residue was mixed with a large volume of cold water and the sirup soon solidified. The solid mass was broken up, filtered, and washed with cold water. The air-dried crude material was recrystallized from methanol yielding perfect hexagonal plates. The partially purified material was recrystallized once more from the same solvent and the yield was 40.6 gm. (91%). It melted at 112–113°C. and rotated $(\alpha)_D^{24°C.}$ 13.7° ($CHCl_3$; 1, 2; *c*, 7.2828).

Anal. Calc. for $C_{35}H_{34}S_2O_{12}$; C, 59.15; H, 4.78; S, 9.01. Found: C, 59.21; H, 4.83; S, 9.0.

*1,4-3,6-Dianhydro-2,5-methylene-*D*-iditol (V)*

1,6-Dibenzoyl-2,5-methylene-3,4-ditosyl-D-mannitol (VIII) (27.3 gm.) was dissolved in dry chloroform (200 cc.). Sodium metal (1.8 gm.) was dissolved in methanol (65 cc.) and the solution was added to the chloroform solution. The mixture was allowed to stand at room temperature (24°C.) for 24 hr. The slight excess of sodium methoxide was converted to carbonate with carbon dioxide gas and the mixture filtered to remove the sodium salts. The filtrate was concentrated *in vacuo* at 40°C., the residue was dissolved in chloroform (100 cc.), and the solution treated with decolorizing charcoal to remove a trace of color and turbidity. The colorless sirup that remained after solvent removal was dissolved in a little ethyl acetate and crystallization occurred after several hours' standing at room temperature. The crystalline mass was recrystallized from ethyl acetate and it weighed 4.6 gm. (76%), melted at 83–84°C., and rotated $(\alpha)_D^{22°C.}$ −152.1° ($CHCl_3$; 1, 2; *c*, 0.4108). Mixed melting point determinations with 1,4-3,6-dianhydro-2,5-methylene-D-mannitol and with isomannide were depressed over 20°C.

Anal. Calc. for $C_7H_{10}O_4$; C, 53.16; H, 6.33. Found: C, 53.11; H, 6.41.

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*Effect of Hot Water on 1,4-3,6-Dianhydro-2,5-methylene-*D*-iditol (V)*

The above (V) (0.5 gm.) was heated under reflux for two hours with distilled water (50 cc.) in a stream of nitrogen. The gas was passed through cold (5°C.) water (250 cc.). Formaldehyde could not be detected. The water was then removed from the reaction mixture *in vacuo* at 50°C. and the sirup, after drying with ethanol, was dissolved in a small volume of ethyl acetate. The solution was seeded and after two hours, crystals of 1,4-3,6-dianhydro-2,5-methylene-D-iditol (V) separated as shown by a mixed melting point determination with an authentic sample.

*Effect of Dilute Hydrochloric Acid on 1,4-3,6-Dianhydro-2,5-methylene-*D*-iditol (V)*

The above (V) (0.5 gm.) was dissolved in 0.001 *N* hydrochloric acid (50 cc.). A stream of nitrogen was passed through the solution, while it was heated under reflux for 30 min. The gas was passed into cold (5°C.) water (250 cc.). A test for formaldehyde was negative. The solution was then taken up with more hydrochloric acid to give a normality of 0.01 *N* and heating continued. Formaldehyde was detected after 10 min. by means of 2,4-dinitrophenylhydrazine hydrochloride. The acidic solution was then concentrated *in vacuo* at 50°C. and the remaining colorless sirup was dried by distilling ethanol from it. The dried sirup was dissolved in a small volume of ethyl acetate and allowed to stand overnight at 22°C. after which tufts of crystals separated. After filtration and desiccation the yield was 0.18 gm. (40%) and the product melted at 63–64°C. A mixed melting point determination with authentic 1,4-3,6-dianhydro-D-iditol was not depressed.

*1,4-3,6-Dianhydro-2,5-dibenzoyl-*D*-iditol*

The filtrate from the above isolation of 1,4-3,6-dianhydro-D-iditol was concentrated *in vacuo* and the resulting sirup (0.23 gm.) dissolved in anhydrous pyridine (4 cc.). The solution was cooled to 0°C. and benzoyl chloride (0.5 cc.) was added. The reaction mixture was allowed to stand overnight at 22°C., then poured into cold water (50 cc.). Cold saturated potassium bicarbonate solution was added to dissolve benzoic acid and the sirup solidified after standing for three days at 5°C. The solid was broken up, filtered, and washed. It was dried in air and recrystallized twice from butanol-1. The yield was 0.34 gm. and the product melted at 110–111° and rotated $(\alpha)_D^{22°C.}$ −140.6° ($CHCl_3$; 1, 2; *c*, 0.7724). The reported (1) constants for the enantimorph are m.p. 111.0–111.3°C. and $(\alpha)_D^{25.2°C.}$ 141.9° ($CHCl_3$).

ACKNOWLEDGMENT

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# THE FLOW PROPERTIES AND MESOMORPHIC BEHAVIOR OF ANHYDROUS SOAPS AT ELEVATED TEMPERATURES

## PART I. SODIUM STEARATE ABOVE 200°[1]

By B. D. Powell[2] and I. E. Puddington

ABSTRACT

Although there is a large body of literature dealing with the transition temperatures of the alkali metal salts of the fatty acids, it has not always been possible to feel confidence in their graphical determination. Hitherto few measurements have been made of the viscosity of soaps as a function of temperature and rate of shear, though such measurements promise to prove useful, as sharp changes have been observed in the regions of previously reported transition points. The viscosity apparatus is described and the results obtained with anhydrous sodium stearate given, from the aspect of transition temperatures and as a study of flow properties.

## INTRODUCTION

Fatty acid soaps belong to that interesting class of compounds which exhibit mesomorphism, first observed in 1888 by Reinitzer (4), and on heating pass through a series of transitions before melting to isotropic liquids. Though the intermediate phases have sometimes been described as liquid crystalline, the term is probably not a good one, since these phases have the properties of true liquids with the ability to flow.

The conditions favorable to the formation of mesomorphic phases, given by Bernal and Crowfoot (1), are these.

(*a*) The molecule should be geometrically anisotropic.

(*b*) The molecule should contain only one strongly polar group, though weakly polar groups may also be present.

That the alkali metal salts of the fatty acids are mesomorphic is therefore not surprising.

The transitions manifest themselves by sharp changes in appearance, most conspicuous when seen between crossed nicols in the polarizing microscope, in electrical conductivity, density, thermal capacity, and, as will be shown below, in viscosity, as the temperature varies.

The evaluation of a transition point is dependent upon plotting the property under observation against temperature and determining by inspection the position of a change in slope. This is a difficult thing to do accurately and objectively, especially where large changes do not occur. Some transition temperatures appear to have been assigned on rather meager evidence when a single property is being considered and therefore there is not complete agreement in the interpretation of results. For instance, using the dilatometer, some authors (8) found transitions at 90° and 117°, whereas others did not (6). Table I contains transition temperatures collected from published work.

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TABLE I

REPORTED TRANSITION TEMPERATURES OF ANHYDROUS SODIUM STEARATE

| Name of transition | Calorimetric (9) *g* | Electrical conductivity (10) *h* | Dilatometer | | Viscosity (5) *k* | Hot wire | |
|---|---|---|---|---|---|---|---|
| | | | Vold (8) *i* | Stainsby (6) *j* | | Vold (7) *l* | Vold (8) *m* |
| *A.* | 70 | *b* | *a* | *a* | 65 | *a* | *a* |
| *B.* Curd to supercurd | 93 | *b* | 90 | *a* | *a* | *a* | *a* |
| *C.* Supercurd to subwaxy | 116 | *b* | 117 | *a* | 110 | *a* | *a* |
| *D.* Subwaxy to waxy | 132 | *b* | 132 | 135 | 125 | 132 | 130 |
| *E.* Waxy to superwaxy | *d* | *b* | 167 | *a* | *b* | 167 | 166 |
| *F.* Superwaxy to subneat | 209 | *b* | 198 | 199 | *b* | 203 | 205 |
| *G.* Subneat to neat | 226 | 255 | 257 | 262 | *b* | 257 | 260 |
| *H.* Melting point | *b* | 278 | 288*e* | *a* | *b* | *c* | *c* |

*Notes:*

*a. No transition observed.*
*b. No observation made.*
*c. Not clear from paper whether a or b.*
*d. Too small to be observed. Vold's sample II data (9).*
*e. Confirmed visually (8). Named transitions have been observed visually.*

*References in literature cited:*

*g. Table I in Vold (9).*
*h. Table II in Vold and Heldman (10).*
*i. Table I in Vold, Macomber, and Vold (8).*
*j. From Fig. 2 in Stainsby, Farnand, and Puddington (6).*
*k. From Fig. 3 in Southam and Puddington (5).*
*l. Table I in Vold (7).*
*m. Table II in Vold, Macomber, and Vold (8).*

Since previous work (5) had indicated that the viscous behavior of anhydrous sodium stearate is quite sensitive to phase transition at lower temperatures, it was decided to study this property in the higher temperature region to determine whether it had advantages over methods previously employed in indicating transitions and could contribute useful information as to the nature of the changes that occur in soap as it is heated to the temperature where isotropic liquid is formed.

## EXPERIMENTAL

To determine the viscosity of sodium stearate in the range 285° to 336° a modified Poiseuille method was used with an apparatus constructed from Pyrex glass. Calculation showed that under the conditions of the experiments the correction sometimes necessary for the kinetic energy of the liquid leaving the capillary section was negligible. The Couette correction was also small, since the measured viscosity of a mineral oil* agreed well with the known value of 6.95 poises, as will be seen in Table II.

A diagram of cell III is shown in Fig. 1. While this differed slightly in the design of the end bulbs from cells I and II, it is representative of the apparatus used. The cell was filled with powdered sodium stearate between $A$ and $A'$, placed in an inverted position (i.e., side tubes $CA$ and $A'C'$ above the capillary section) in an electric furnace (25 cm. long and 7 cm. diameter, internal) and heated to 320° under a hard vacuum. Thereby, the soap is rendered anhydrous

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TABLE II

CELL DIMENSIONS

| | Length, cm. | Radius, cm. | Viscosity of oil, poises |
|---|---|---|---|
| Cell I | 8.9 | 0.0521 | * |
| Cell II | 10.0 | 0.0848 | 7.12 |
| Cell III | 10.5 | 0.102 | 6.92 |
| Cell *A* | 3.3071 | 0.0824 | — |
| Cell *B* | 2.6111 | 0.03683 | — |

*No determination.

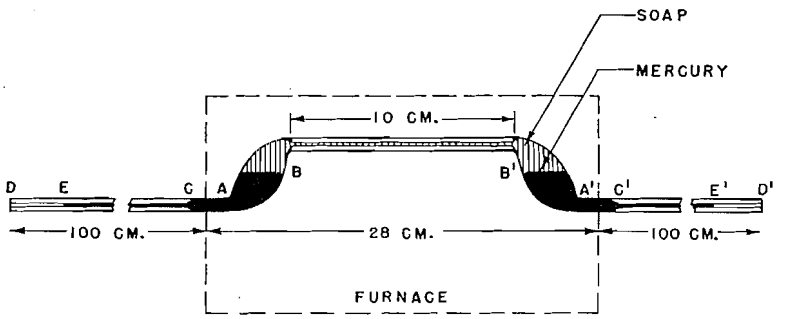



FIG. 1. Cell III in "normal" position with index tubes attached at *C* and *C'*. Not to scale.

(6). The furnace was allowed to cool to room temperature and the soap solidified, filling the cell, which was then restored to its normal position. Meter lengths of capillary tubing *DC* and *C'D'* were sealed on to the cell at *C* and *C'* and well-boiled mercury distilled in under vacuum ($10^{-5}$ mm.) until the apparatus was filled from *E* to *B* and *B'* to *E'*. The furnace temperature was again raised to the required value, giving a volume of liquid sodium stearate, free and isolated from air and water. This was caused to flow by applying nitrogen under pressure from a cylinder to *D* or *D'*, at a rate which could be calculated from the observed movement of the end of the mercury thread in the index tubes, and the pressure was read from a mercury manometer. Before making determinations of the rate of flow as a function of the pressure, the furnace was allowed a day in which to come to thermal equilibrium. The pressure required to overcome the viscous resistance of the mercury ($\eta = 0.015$ poises) in the index tubes, which are at room temperature, is so small in comparison with that required to cause the flow of the soap that it can be neglected.

The glass apparatus was not considered safe at temperatures below 280°, because of the pressures involved, and an extrusion viscometer (3) was brought into use: a steel cylinder 18 cm. in length and 2.5 cm. internal diameter carried a pressure fitting at its upper end and one of the two interchangeable capillary tubes at its lower end. In Table II are given the dimensions of the capillaries; the apparatus when set up with the wider capillary is called cell *A* and with the narrower, cell *B*. The pressure fitting con-

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nected via a manifold and a 10 liter ballast vessel to a nitrogen cylinder and calibrated gauges on the manifold, and a mercury manometer, connected to it, enabled accurate measurement of pressure to be made. An automatically controlled furnace in which the cylinder was mounted gave temperatures constant to ± 0.5° C.

The apparatus was flushed with nitrogen, and dry sodium stearate put into the cylinder and well shaken down; after which the piston, 1 cm. in depth, was inserted and the pressure fitting replaced. Following further flushing with nitrogen the temperature was raised to the required value.

When the temperature had been steady for an hour, the sodium stearate was extruded at different rates, by varying the pressure, and collected in weighing bottles. At a given temperature and pressure several samples were taken to secure an accurate determination of the rate of flow and to demonstrate that it was independent of time.

The lower limit of usefulness of the apparatus was about 210°; when the viscosity of the sodium stearate becomes high, about $10^5$ poises, and the nitrogen forces its way between the piston and the cylinder walls, forming channels through the soap and escaping from the capillary.

The soap used in the experiments was prepared by titration from stearic acid having a melting point of 68°–69° C.

## RESULTS

Rate of flow against pressure applied is plotted in Figs. 2, 3, 4, and 5, for cell I, cell II, cell III, and cell A* respectively, and the units of rate of flow are cubic centimeters per second, excepting in Fig. 5 where they are grams per second; and of pressure, dynes per square centimeter.

The apparent viscosity, calculated from Poiseuille's equation, is plotted as a function of inverse rate of flow in Figs. 6, 7, and 8 for cell II, cell III, and cell A,* respectively.

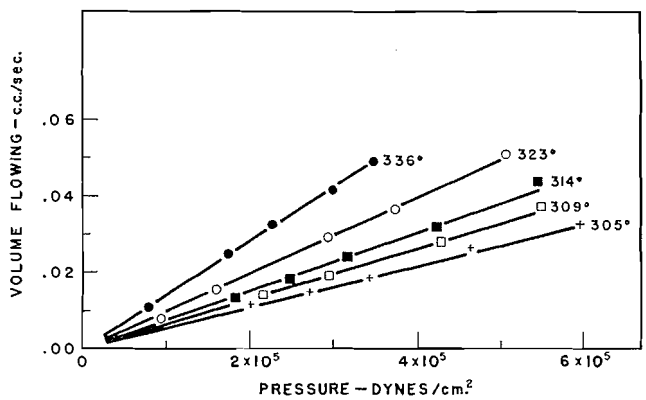



FIG. 2. Rate of flow – pressure curve. Anhydrous sodium stearate in cell I.

*Results for cell B were similar and are not shown.*

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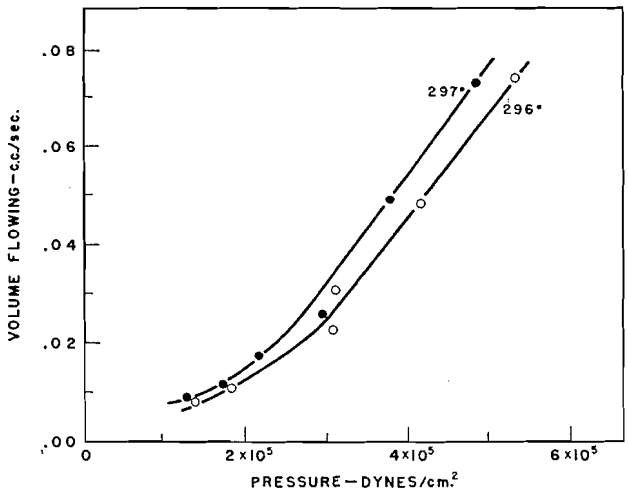



FIG. 3. Rate of flow – pressure curve. Anhydrous sodium stearate in cell II.

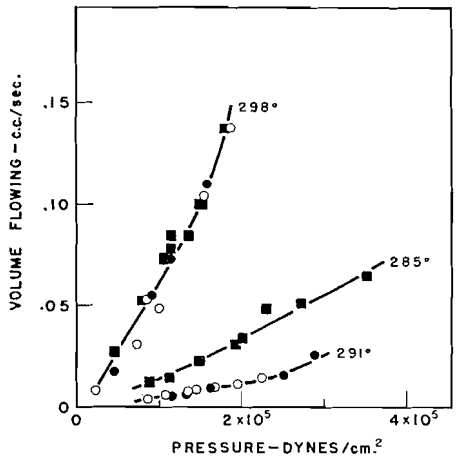



FIG. 4. Rate of flow – pressure curve. Anhydrous sodium stearate in cell III.

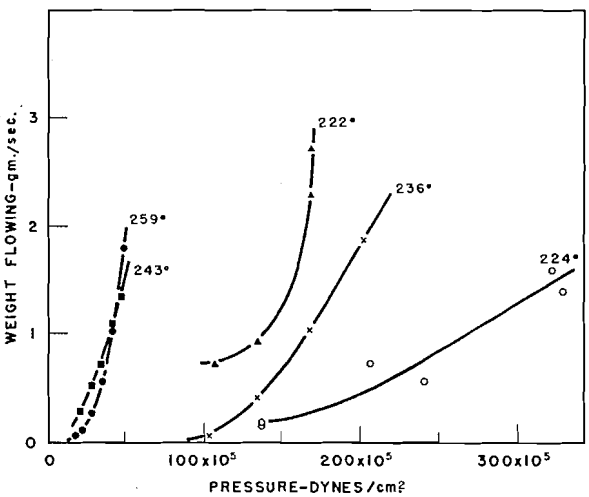



FIG. 5. Rate of flow – pressure curve. Anhydrous sodium stearate in cell *A*. Ordinate for 224° curve shown $\times 10^{-1}$.

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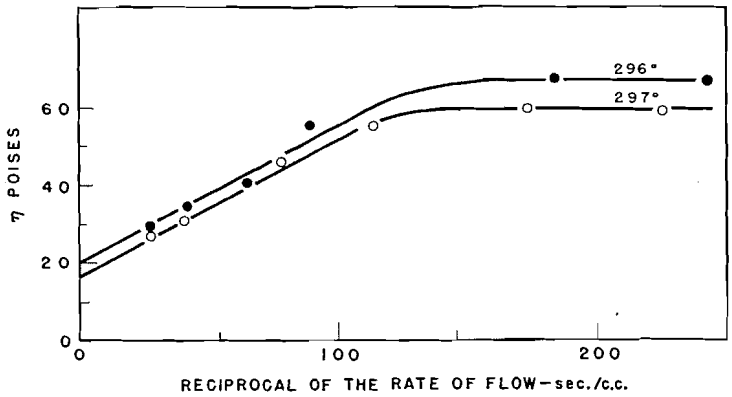



FIG. 6. Apparent viscosity – reciprocal rate of flow curve. Anhydrous sodium stearate in cell II.

The viscosity above 305°, as determined by cell I, is independent of the rate of flow, unlike that at lower temperatures, and the plot of viscosity against reciprocal rate of flow is a straight line of zero slope and is accordingly not reproduced.

In Fig. 9, viscosity at infinite rate of shear, as read by extrapolation from Figs. 6, 7, and 8, is plotted against temperature.

## DISCUSSION

At temperatures above 305° the volume of sodium stearate flowing per second is directly proportional to the pressure, giving a straight line consistency curve which passes through the origin (Fig. 2), demonstrating that the flow is that of a Newtonian liquid. Knowing the constants of the viscosity apparatus, the slope of the pressure – rate of flow curve, and using the Poiseuille equation, the viscosity of sodium stearate is readily calculated and it is seen from Fig. 9 to decrease gradually with rise of temperature.

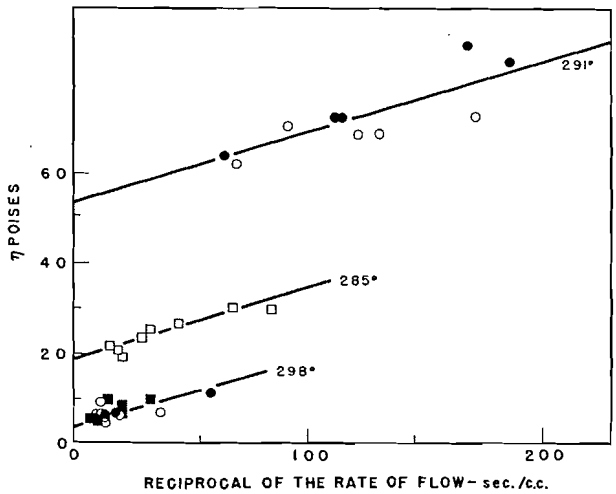



FIG. 7. Apparent viscosity – reciprocal rate of flow curve. Anhydrous sodium stearate in cell III.

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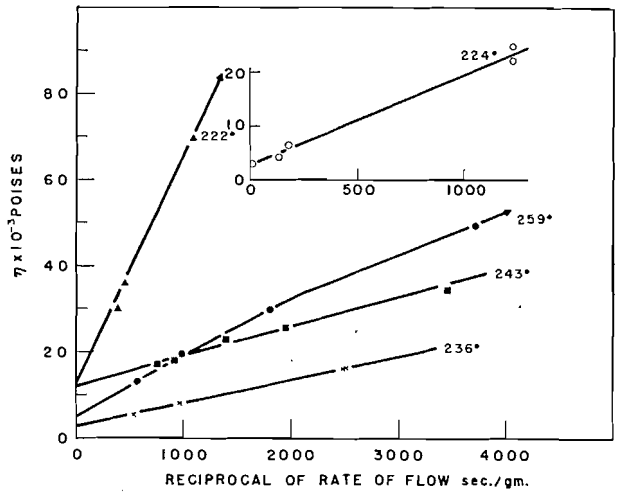



FIG. 8. Apparent viscosity – reciprocal rate of flow curve. Anhydrous sodium stearate in cell *A*. Ordinate for 236° curve shown × 10.

Plastic flow sets in at temperatures below 298°, the rate not being proportional to the pressure, with the consistency curves concave toward the rate axis; it is non-Newtonian. Neither do the curves extrapolate to the origin, but show a tendency to intercept the pressure axis—that is to say, sodium stearate has a yield value and is behaving as a Bingham body. For non-Newtonians we can calculate, again by the Poiseuille equation, the *apparent* viscosity, at a given temperature and a certain rate of flow, which is the viscosity the sodium stearate would have were it Newtonian.* While apparent viscosity is unreal, it is useful, and the definition has been accepted by many

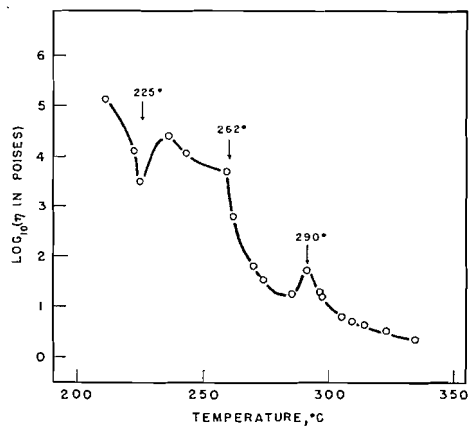



FIG. 9. Residual viscosity – temperature curve. Anhydrous sodium stearate.

**In Fig. 8, curves for 243° and 259° indicate the uselessness of single point determinations of viscosity, which, had they been made here, at the intersection of the curves, would have led to the conclusion that the values were identical at these temperatures. The residual viscosities are quite different.*

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rheologists. Plotting apparent viscosity against the reciprocal of the rate of flow gives a curve which is linear, initially, with a positive slope (e.g. Fig. 7), eventually approaching a steady value (e.g. Fig. 6), when observations could be made at a sufficiently low rate (high reciprocal rate) of flow. The viscosity at a given temperature falls with increasing rate of flow and the sodium stearate can be considered thixotropic.

While no over-all satisfactory explanation of thixotropy has been given, it is safe to assert that it depends upon structure which has rigidity, and the hypothesis of Goodeve and Whitfield (2), put forward originally for suspensions of carbon black in mineral oil, seems applicable: the rate of structural build-up is proportional to the structural concentration and equals, at equilibrium, the rate of structural breakdown, itself proportional to the rate of flow ($S$). Further, the structural concentration is assumed to be proportional to the difference between the apparent and residual viscosities; the former ($\eta$) has been defined above, and the latter ($\eta_0$) is the viscosity at infinite rate of flow when the structure is completely broken up. This theory leads to the equation:

$$\eta = \eta_0 + \theta/S$$

where $\theta$ is the coefficient of thixotropy, and also predicts that as $1/S$ increases, the apparent viscosity rises more and more slowly and bends toward a steady value (Fig. 6).

The coefficient of thixotropy is a function of time and structural strength, and is equal to the yield value intercept of the consistency curve. There is some confusion because these authors say that $\theta$ is not a yield value, but such a value can be, though not necessarily, due to thixotropy.

Residual viscosity, the viscosity at infinite rate of flow, read from the extrapolated curves of apparent viscosity and reciprocal rate of flow, is seen to vary in a discontinuous manner with temperature* in Fig. 9, covering the range 211° to 336°. There are transitions at 225°, 262°, and 290°, the second corresponding to the transition subneat to neat, for which previously reported values are 255°, 257°, 258°, 260°, and 262° respectively (Table I), and the third, to the melting point—hitherto found at 278° and 288° (Table I). It should be recalled that anhydrous sodium stearate is thixotropic, some 8° above the melting point, at 298°, Newtonian when the temperature has risen to 305°, and the change from plastic to Newtonian flow does not appear to take place at the melting point. Vold (9) assigned the transition that he observed at 226° to the subneat to neat phase change, but since the authors find transitions at 225° and 262°, the generally accepted temperature for this change, it is evident that there is a further transition within the subneat phase at 225°.

It is intended to account theoretically for the phase changes in a subsequent publication.

## CONCLUSIONS

1. A viscosity method has been shown to be of use in studying the transition temperatures of anhydrous sodium stearate.

**The plots at 305° and all higher temperatures are for anhydrous sodium stearate as a Newtonian liquid, and the viscosity is, of course, the same at all values of the flow rate.*

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2. The transition subneat to neat occurs at 262°, and the true melting point at 290°, in agreement with those put forward by earlier workers.

3. A transition within the subneat phase has been found at 225°.

4. Anhydrous sodium stearate exhibits thixotropy over the range 211° to 298°, just above the melting point, and the results agree well with the Goodeve and Whitfield model of this phenomenon.

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# PREPARATION OF DINITRO-*n*-ALKYL PHENOLS[1]

By G. G. S. Dutton, T. I. Briggs,[2] B. R. Brown,[3] and R. K. Powell[4]

ABSTRACT

The preparation of a series of dinitro-*n*-alkyl phenols is described. The dinitrophenols were characterized as their piperidine, morpholine, and cyclohexylamine salts. In the course of the work some new derivatives of these *n*-alkyl phenols and intermediate hydroxyketones were obtained.

## INTRODUCTION

The use of dinitroalkyl phenols as insecticides and herbicides has been widely reported and in order to investigate the variation in their toxicity with chemical structure, a series of dinitro-*n*-alkyl phenols was required in which the alkyl group had from two to eight carbon atoms. Kagy (5) reports the testing of some such compounds but the preparation of such a series has not previously been described.

The preparation of the *n*-alkyl phenols was based on the method of Sandulesco and Girard (8) who subjected the phenyl esters to the Fries rearrangement and reduced the resulting hydroxyketones by the method of Clemmensen. We have found that the intermediate hydroxyketones and resulting phenols were more easily characterized by the derivatives described herein rather than as in the original paper (7). The *n*-alkyl phenols were then nitrated and converted to their amine salts as previously described (3).

One typical synthesis is reported and the relevant data on the cognate preparations are given in Tables I–V.

## EXPERIMENTAL*

### *n-Butyryl Chloride*

*n*-Butyryl chloride was prepared by the method of Helferich and Schaefer as given in Organic Syntheses (4). The commercial acid and thionyl chloride used were each distilled before use.

### *Phenyl-n-butyrate*

To pure phenol (1 mole) in a 1 liter flask, fitted with a reflux condenser and a hydrogen chloride trap, was added *n*-butyryl chloride (1.1 mole) over half an hour. The reaction mixture was heated on a steam bath for half an hour and then distilled. After a small forerun of excess acid chloride essentially pure material passed over. The ester was then redistilled, yielding phenyl-*n*-butyrate boiling at 192° C. Yield, 90%.

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**All melting and boiling points are uncorrected.*



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TABLE I

PHENYL ESTERS

| Ester | Yield, % | B.p., °C. | $n_D^{25°C}$ |
|---|---|---|---|
| Phenyl acetate | 85 | 192 | 1.5017 |
| Phenyl propionate | 80 | 206 | 1.5092 |
| Phenyl-*n*-butyrate | 82 | 224 | 1.4934 |
| Phenyl-*n*-valerate | 75 | 160 (14 mm.) | 1.4869 |
| Phenyl-*n*-caproate | 75 | 260 | 1.4840 |
| Phenyl-*n*-heptylate | 90 | 120 (2 mm.) | 1.4829 |
| Phenyl-*n*-caprylate | 85 | 136 (2 mm.) | 1.4810 |

*2- and 4-Hydroxy-n-butyrophenone*

Aluminum chloride (4 moles) was placed in a two-necked 2-liter flask and heated to 70° C. Phenyl-*n*-butyrate (warmed to 40° C.) was then added as quickly as possible, when the temperature of the mixture rose to 110° C. The reaction mixture was then brought rapidly to 140° C. and kept there for three quarters of an hour. The reaction mixture, which was a glassy mass, was cooled to room temperature and hydrolyzed by the addition of 1500 ml. ice cold 6 *N* hydrochloric acid. Hydrolysis was completed by warming to 70° C. for a quarter of an hour, when a viscous red oil separated. This oil was sepa-

TABLE II

HYDROXYKETONES HO-$C_6H_4$-COR

| Compound | Yield, %* | B.p., °C. | M.p., °C. | $n_D^{25°C}$ | 2,4-Dinitrophenylhydrazone | | |
|---|---|---|---|---|---|---|---|
| | | | | | M.p., °C. | Nitrogen, %** | |
| | | | | | | Calc. | Found |
| 2-Hydroxyacetophenone | 36[a] | 45 (0.1 mm.) | .. | 1.5570 | 210 | .. | .. |
| 4-Hydroxyacetophenone | 50[a] | 160 (1.0 mm.) | 107 | .. | 225 | .. | .. |
| 2-Hydroxypropiophenone | 48[a] | 54 (0.1 mm.) | .. | 1.5485 | 189 | .. | .. |
| 4-Hydroxypropiophenone | 40[a] | 164 (1.0 mm.) | 146 | .. | 232 | .. | .. |
| 2-Hydroxybutyrophenone | 36[b] | 64 (0.1 mm.) | .. | 1.5379 | 203 | .. | .. |
| 4-Hydroxybutyrophenone | 34[b] | 171 (1.0 mm.) | 91 | .. | 215 | .. | .. |
| 2-Hydroxyvalerophenone | 37[b] | 74 (0.1 mm.) | .. | 1.5310 | 178 | 15.65 | 15.58 |
| 4-Hydroxyvalerophenone | 41[b] | 160 (1.0 mm.) | 62 | .. | 182 | 15.65 | 15.59 |
| 2-Hydroxycaprophenone | 45[c] | 83 (0.1 mm.) | .. | 1.5262 | 153† | .. | .. |
| 4-Hydroxycaprophenone | 30[c] | 167 (1.0 mm.) | 60 | .. | 184 | .. | .. |
| 2-Hydroxyheptophenone | 51[c] | 94 (0.1 mm.) | .. | 1.5211 | 153† | 14.50 | 14.48 |
| 4-Hydroxyheptophenone | 34[c] | 171 (1.0 mm.) | 90 | .. | 174 | 14.50 | 14.41 |
| 2-Hydroxycaprylophenone | 41[c] | 104 (0.1 mm.) | .. | 1.5170 | 140 | 14.00 | 13.96 |
| 4-Hydroxycaprylophenone | 34[c] | 183 (1.0 mm.) | 59 | .. | 171 | 14.00 | 13.99 |

**In carrying out the Fries rearrangement of the phenyl ester, the ester was warmed to (a) 25° C., (b) 40° C., (c) 60° C. before addition to the aluminum chloride which was heated to 70–80° C. in all cases.*

***Analyses quoted for new compounds only.*

*†Mixed melting point gave depression of 9° C.*

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rated, washed with 6 *N* hydrochloric acid, water, and dried. The dried oil was then fractionated under vacuum using a Bruehl receiver. The 2-hydroxy-*n*-butyrophenone distilled as an oil boiling at 63–65° C. (0.1 mm.) and then 4-hydroxy-*n*-butyrophenone as an oil boiling at 161° C. (1 mm.), which rapidly solidified. The two isomers were then separately redistilled and the 4 isomer on recrystallization gave a melting point of 91° C. Data on the other hydroxyketones are recorded in Table II.

In order to confirm the orientation of the hydroxyketones and hence the phenols derived therefrom by reduction, a sample (1 gm.) of the lower boiling hydroxy-*n*-butyrophenone was dissolved in caustic potash solution and methylated with methyl sulphate. The methyl ether thus formed was oxidized with alkaline permanganate and there was isolated an acid which, on recrystallization from carbon tetrachloride, melted at 101° C., unchanged on admixture with an authentic sample of *o*-methoxybenzoic acid. In a like manner a sample (1 gm.) of the higher boiling, solid hydroxy-*n*-butyrophenone was methylated and oxidized, yielding an acid, m.p. 184–185° C., unchanged on admixture with an authentic sample of anisic acid. Similar oxidations were carried out with each pair of hydroxyketones recorded in Table II.

*2- and 4-n-Butylphenol*

2-Hydroxy-*n*-butyrophenone and the 4 isomer were separately reduced by the Clemmensen method (1, 2) using concentrated hydrochloric acid and amalgamated zinc. In order to reduce the time of refluxing the Martin modification (6) was used whereby some glacial acetic acid was added in order to

TABLE III

*n*-ALKYL PHENOLS

| Phenol | Yield, % | B.p., °C. (1 mm.) | $n_D^{25°C}$ | 3,5-Dinitrobenzoate | | |
|---|---|---|---|---|---|---|
| | | | | M.p., °C. | Nitrogen, % | |
| | | | | | Calc. | Found |
| 2-Ethyl | 72 | 60 | 1.5352 | 107 | .. | .. |
| 4-Ethyl | 75 | 76 | M.p. 45°C. | 139 | .. | .. |
| 2-*n*-Propyl | 60 | 65 | 1.5280 | 96 | 8.48 | 8.51 |
| 4-*n*-Propyl | 72 | 82 | 1.5220 | 123 | 8.48 | 8.54 |
| 2-*n*-Butyl | 65 | 75 | 1.5182 | 97 | 8.14 | 8.16 |
| 4-*n*-Butyl | 67 | 88 | 1.5160 | 92 | 8.14 | 8.17 |
| 2-*n*-Amyl | 88 | 89 | 1.5141 | 98 | 7.82 | 7.82 |
| 4-*n*-Amyl | 80 | 97 | 1.5107 | 94 | 7.82 | 7.84 |
| 2-*n*-Hexyl | 84 | 103 | 1.5090 | 95 | 7.52 | 7.51 |
| 4-*n*-Hexyl | 81 | 112 | 1.5055 | 87 | 7.52 | 7.55 |
| 2-*n*-Heptyl | 86 | 115 | 1.5058 | 92 | 7.25 | 7.26 |
| 4-*n*-Heptyl | 75 | 123 | 1.5040 | 97 | 7.25 | 7.28 |
| 2-*n*-Octyl | 86 | 126 | 1.5032 | 93 | 7.00 | 7.01 |
| 4-*n*-Octyl | 63 | 134 | M.p. 42°C. | 91 | 7.00 | 7.05 |

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TABLE IV

DINITRO-*n*-ALKYL PHENOLS AND THEIR PIPERIDINE SALTS

| Phenol | Yield on nitration, % | B.p., °C. (0.1 mm.) | M.p., °C. | Piperidine salt* | | | |
|---|---|---|---|---|---|---|---|
| | | | | Formula | M.p., °C. | Nitrogen, % | |
| | | | | | | Calc. | Found |
| 4,6-Dinitro-2-ethyl | 64 | 120 | 36 | $C_{13}H_{19}N_3O_5$ | 214 | 14.14 | 14.20 |
| 2,6-Dinitro-4-ethyl | 60 | 130 | 36 | $C_{13}H_{19}N_3O_5$ | 234 | 14.14 | 14.06 |
| 4,6-Dinitro-2-*n*-propyl | 71 | 128 | .. | $C_{14}H_{21}N_3O_5$ | 186 | 13.50 | 13.62 |
| 2,6-Dinitro-4-*n*-propyl | 50 | 141 | 41 | $C_{14}H_{21}N_3O_5$ | 193 | 13.50 | 13.56 |
| 4,6-Dinitro-2-*n*-butyl† | 67 | 140 | .. | $C_{15}H_{23}N_3O_5$ | 148 | 12.92 | 12.92 |
| 2,6 Dinitro-4-*n*-butyl | 58 | 152 | 47 | $C_{15}H_{23}N_3O_5$ | 140 | 12.92 | 13.03 |
| 4,6-Dinitro-2-*n*-amyl† | 60 | 145 | .. | $C_{16}H_{25}N_3O_5$ | 138 | 12.39 | 12.53 |
| 2,6-Dinitro-4-*n*-amyl | 61 | 166 | .. | $C_{16}H_{25}N_3O_5$ | 137 | 12.39 | 12.50 |
| 4,6-Dinitro-2-*n*-hexyl† | 60 | 162 | .. | $C_{17}H_{27}N_3O_5$ | 123 | 11.89 | 11.96 |
| 2,6-Dinitro-4-*n*-hexyl | 49 | 175 | .. | $C_{17}H_{27}N_3O_5$ | 154 | 11.89 | 11.97 |
| 4,6-Dinitro-2-*n*-heptyl | 60 | 171 | .. | $C_{18}H_{29}N_3O_5$ | 121 | 11.44 | 11.39 |
| 2,6-Dinitro-4-*n*-heptyl | 52 | 184 | .. | $C_{18}H_{29}N_3O_5$ | 157 | 11.44 | 11.56 |
| 4,6-Dinitro-2-*n*-octyl† | 51 | 178 | .. | $C_{19}H_{31}N_3O_5$ | 125 | 11.02 | 11.10 |
| 2,6-Dinitro-4-*n*-octyl | 45 | 192 | .. | $C_{19}H_{31}N_3O_5$ | 141 | 11.02 | 11.04 |

**All the salts are red, orange, or yellow.*
†*Ref.* (7).

TABLE V

MORPHOLINE AND CYCLOHEXYLAMINE SALTS OF DINITRO-*n*-ALKYL PHENOLS*

| Dinitrophenol | Morpholine salt | | | | Cyclohexylamine salt | | | |
|---|---|---|---|---|---|---|---|---|
| | M.p., °C. | Formula | Nitrogen, % | | M.p., °C. | Formula | Nitrogen, % | |
| | | | Calc. | Found | | | Calc. | Found |
| 4,6-Dinitro-2-ethyl | 191 | $C_{12}H_{17}N_3O_6$ | 14.05 | 14.02 | 176 | $C_{14}H_{21}N_3O_5$ | 13.50 | 13.49 |
| 2,6-Dinitro-4-ethyl | 217 | $C_{12}H_{17}N_3O_6$ | 14.05 | 14.05 | 190 | $C_{14}H_{21}N_3O_5$ | 13.50 | 13.57 |
| 4,6-Dinitro-2-*n*-propyl | 167 | $C_{13}H_{19}N_3O_6$ | 13.42 | 13.56 | 185 | $C_{15}H_{23}N_3O_5$ | 12.92 | 12.96 |
| 2,6-Dinitro-4-*n*-propyl | 165 | $C_{13}H_{19}N_3O_6$ | 13.42 | 13.40 | 178 | $C_{15}H_{23}N_3O_5$ | 12.92 | 12.90 |
| 4,6-Dinitro-2-*n*-butyl | 169 | $C_{14}H_{21}N_3O_6$ | 12.84 | 12.82 | 175 | $C_{16}H_{25}N_3O_5$ | 12.38 | 12.45 |
| 2,6-Dinitro-4-*n*-butyl | 134 | $C_{14}H_{21}N_3O_6$ | 12.84 | 12.84 | 148 | $C_{16}H_{25}N_3O_5$ | 12.38 | 12.44 |
| 4,6-Dinitro-2-*n*-amyl | 158 | $C_{15}H_{23}N_3O_6$ | 12.32 | 12.47 | 164 | $C_{17}H_{27}N_3O_5$ | 11.90 | 11.84 |
| 2,6-Dinitro-4-*n*-amyl | 132 | $C_{15}H_{23}N_3O_6$ | 12.32 | 12.32 | 154 | $C_{17}H_{27}N_3O_5$ | 11.90 | 11.91 |
| 4,6-Dinitro-2-*n*-hexyl | 155 | $C_{16}H_{25}N_3O_6$ | 11.83 | 11.90 | 176 | $C_{18}H_{29}N_3O_5$ | 11.44 | 11.35 |
| 2,6-Dinitro-4-*n*-hexyl | 150 | $C_{16}H_{25}N_3O_6$ | 11.83 | 11.93 | 135 | $C_{18}H_{29}N_3O_5$ | 11.44 | 11.49 |
| 4,6-Dinitro-2-*n*-heptyl | 146 | $C_{17}H_{27}N_3O_6$ | 11.38 | 11.46 | 175 | $C_{19}H_{31}N_3O_5$ | 11.02 | 11.08 |
| 2,6-Dinitro-4-*n*-heptyl | 148 | $C_{17}H_{27}N_3O_6$ | 11.38 | 11.49 | 125 | $C_{19}H_{31}N_3O_5$ | 11.02 | 11.04 |
| 4,6-Dinitro-2-*n*-octyl | 148 | $C_{18}H_{29}N_3O_6$ | 10.97 | 11.02 | 158 | $C_{20}H_{33}N_3O_5$ | 10.63 | 10.60 |
| 2,6-Dinitro-4-*n*-octyl | 135 | $C_{18}H_{29}N_3O_6$ | 10.97 | 11.04 | 120 | $C_{20}H_{33}N_3O_5$ | 10.63 | 10.65 |

**All the salts are red, orange, or yellow.*

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increase the solubility of the hydroxyketone. The yield of 2-*n*-butylphenol was 65% and of the 4 isomer 67%. Details of these and the other phenols are given in Table III.

*Dinitro-n-alkyl Phenols*

The *n*-alkyl phenols were nitrated in glacial acetic acid as described in a previous communication (3). Most of the nitro compounds were liquids and these were characterized by conversion to piperidine, morpholine, and cyclohexylamine salts (3). See Tables IV and V for details.

ACKNOWLEDGMENTS

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# AN APPARATUS FOR THE MICROANALYSIS OF GAS MIXTURES[1]

By M. J. Marshall[2] and G. Constabaris[3]

ABSTRACT

An apparatus for the microanalysis of gas mixtures is described with which volumes of gases as low as 5 cu. mm. at N.T.P. can be analyzed in the dry way. Two applications of the method are presented; the first is for carbon dioxide, the second is for the use of the diffusion of hydrogen through palladium in the presence of either carbon monoxide or methane for the analysis of hydrogen.

## INTRODUCTION

Marshall and Findlay (5) have briefly described an apparatus for the microanalysis of gas mixtures by dry methods. The purpose of this paper is to describe in more detail this apparatus in an improved form, and to present its application for the analysis of carbon dioxide, and of hydrogen in the presence of carbon monoxide or methane.

The apparatus described here was designed to be used in the volume range of 5 to 40 cu. mm. It will be evident from the description to be given that this range can be moved in either direction by altering the dimensions of the gauge. The method of analysis lends itself most readily to the study of gases occurring in high-vacuum systems, but its use could be made quite general with the development of suitable methods for introducing small gas samples into the apparatus.

## APPARATUS AND METHOD

The apparatus is shown in Fig. 1. It consists of a McLeod gauge which has as its small volume the leg *A* of a three-way capillary stopcock *S*. The leg *C* leads to high vacuum or air through the aligned ground-glass joints *J*. (This type of connection permits the easy removal and reassembly of the gauge whenever cleaning is necessary.) The leg *B* is pulled down in a straight taper as close to the barrel of the stopcock as possible. This taper forms the inner part of a ground-glass connection, the outer part of which is the main line to which the analysis tips are connected, by means of the small ground-glass joints *D*, *E*, *F*, *G*, *H*. The analysis assembly is shown in Fig. 2. The ground-glass joints were hand made. They are identical in size to the tapered part of an ordinary lead pencil. The accessory pumps and lines are not shown.

The inner part of joint *D* is soft glass, into which is sealed a small palladium tube closed at the upper end. The tube is about 5 cm. in length, 1 mm. I.D., 2 mm. O.D. The tube is heated by a small heater made from a few turns of nichrome wire on a quartz sheath which fits fairly loosely over the palladium tube. The temperature is measured with a thermocouple inserted into the heater so that its junction is close to the tube. The inner part of joint *E* is connected very close to the microstopcock which in turn is connected through

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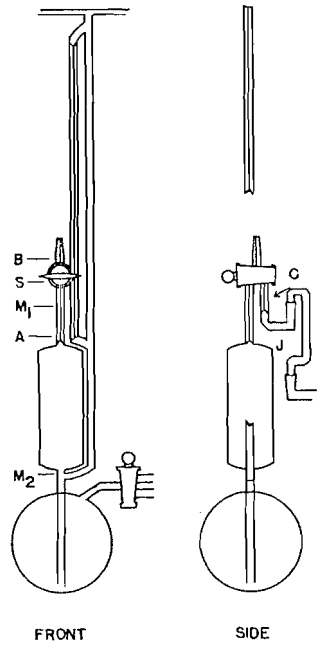



FIG. 1. Modified McLeod gauge as a micro gas analysis apparatus.

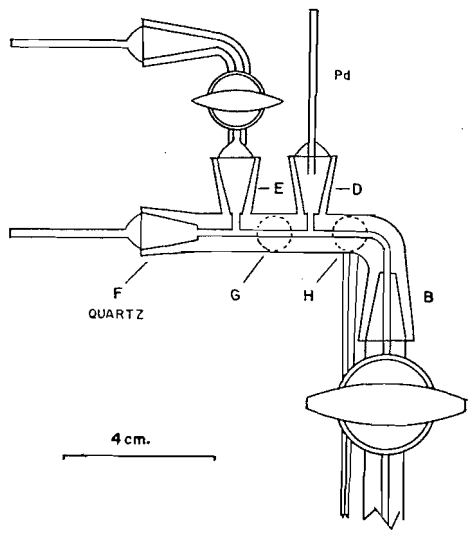



FIG. 2. Detail of analysis assembly.

a ground-glass joint to an analysis tip containing an intimate mixture of silver oxide and hopcalite. The inner part of *F* is made from quartz tubing. This analysis tip holds a small piece of copper wire with its surface oxidized. The tip is heated with a small air-gas flame. The inner part of joint *G* is connected

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to a pyrex tip containing a dry solid solution of lithium, sodium, and potassium hydroxides. This tip is heated with a heater similar to the one described for the palladium tube. The inner part of $H$ is drawn down to a very fine capillary about 8 in. long. This tip is bent into a vertical position and is used as a liquid air trap. The ground-glass joints are sealed with picene and the precision made stopcock $S$ is lubricated with Apiezon "L". (Apiezon wax "W" would be an excellent substitute for the picene. The Apiezon lubricants are available from James G. Biddle and Co., Philadelphia, Pa.; the picene is distributed by Schrader and Ehlers, 239 Fourth Avenue, New York City.) The total volume above the stopcock is 1.39 cc.

The McLeod gauge was calibrated in the accepted manner. The total volume of the gauge is 216.6 cc. and the volume from the plug of the stopcock to the zero mark on leg $A$ of $S$ is 0.0983 cc. This mark is shown as $M_1$ on Fig. 1. A pressure of 1 cm. of mercury read at $M_1$ at 20° C. represents 1.205 cu. mm. at N.T.P. The upper limit of gas volume when read at $M_1$ is 40 cu. mm. but this can be greatly extended by the use of a zero mark further down leg $A$.

The general method of operating the apparatus is as follows. A gas sample is introduced into the highly evacuated apparatus, and its pressure read by raising the mercury to $M_1$ with $S$ closed. The mercury is then lowered a safe distance and $S$ is opened. The mercury is periodically raised and lowered a bit to move the gas about the analysis train while the analysis process is taking place. The mercury is never allowed to run through the plug of $S$. When the analysis process is completed the mercury is lowered carefully to the gauge cutoff $M_2$, and is left in this position for a few minutes. $S$ is closed and the new pressure is read at $M_1$. The change in pressure reading represents the fraction of the constituent being analyzed.

This method of operation involves an error arising from the volume of the analysis assembly, since part of the residual gas remains in the analysis tips. For this apparatus the error is approximately 0.5%. This is the reason that the volume of the analysis assembly must be kept as small as possible. However, there is no error caused by this volume if, when the sample is first admitted to the gauge, the mercury is held at $M_2$, $S$ is opened for a short time, then closed, and the initial pressure read at $M_1$. This procedure, which changes the pressure volume relation given above slightly, can be used if none of the constituents react in the analysis assembly at room temperature. Alternatively, if a constituent does react at room temperature the error can be lessened by separating the particular analysis tip by a microstopcock.

In any case, two other circumstances lead to the necessity of a small analysis assembly volume. First, the lower limit of gas volume that can be analyzed rises with the volume of the tips. Second, it is desirable to carry out the analysis processes at as high a pressure as possible. It is evident that the pressure during analysis varies inversely as the volume of the analysis assembly.

It is seen that the analysis reactions must be carried out in the dry way; water vapor cannot be tolerated in the system.

The older forms of this apparatus used neither ground-glass connections nor the stopcock $S$ (5). The use of the stopcock greatly reduces the quantity of gas that can be analyzed. The use of the small ground-glass joints is not only

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convenient for the removal of the analysis tips but is also necessary in any analysis process requiring the heating of the tip. When the picene is heated it decomposes, admitting gases to the system at a rate proportional to the area exposed to the vacuum. In a ground-glass joint this area is negligible; in this apparatus the picene has given no trouble. This was not the case before ground-glass connections were used.

## THE ANALYSIS OF CARBON DIOXIDE

In this apparatus the best method for the analysis of carbon dioxide is by condensation at liquid air temperature in the analysis tip connected at *H*. After the initial pressure is read and *S* is opened, the liquid air is placed so that its level is about 2 in. above the bottom of the tip. After a few minutes the liquid air level is raised an inch or so and this procedure is continued until the complete vertical portion of the tube is submerged. If the whole tip is submerged immediately, the carbon dioxide will solidify at the liquid air level and will clog the capillary. This does not permit the uncondensed portion of the gas to reach an area of sufficiently low temperature to solidify. The method is accurate and quick but its main disadvantage is that it is not selective.

A selective reagent for carbon dioxide is alkali metal hydroxide. However, the dry hydroxide must be melted before it will absorb carbon dioxide, and at the high melting points of these hydroxides their rate of attack on the glass analysis tip is great. The advantage of hydroxide absorption over liquid air condensation was great enough to warrant a search for a mixture of hydroxides that would melt at a low temperature. A very brief investigation by means of cooling curves of ternary systems of almost dry hydroxides showed that a mixture could be obtained with a melting point under 100° C., at which temperature the rate of glass attack was not marked. The method of preparing the reagent was to fuse together 2.6% lithium hydroxide, 23.6% sodium hydroxide, and 73.8% potassium hydroxide. The melt was allowed to cool to 75° C. and was held at this temperature for an hour. The supernatant liquor was decanted from the solid phase that had settled out. On cooling a few degrees the liquor solidified. The solid was the absorption reagent used. When first put in the analysis tip it must be outgassed in a molten condition to remove the water it absorbs while being handled. Carbon dioxide was prepared by subliming commercial dry ice into a thoroughly outgassed storage bulb.

Preliminary tests led to the following observations. The slight amount of water vapor given off on melting readily reabsorbed in the reagent when it solidified. Therefore, the correct procedure in an analysis was not to lower the mercury from $M_1$ to $M_2$ until the reagent had solidified. Also, the reagent absorbed carbon dioxide extremely slowly at room temperature. The absorption rate did not become significant until a temperature of 65° C. was reached. This showed that there was no necessity of separating the reagent from the main analysis line by means of a microstopcock. At 70° C. 20 cu. mm. of carbon dioxide at S.T.P. would absorb in five minutes.

A comparison of the analysis of carbon dioxide in mixtures with air, by liquid air condensation and hydroxide absorption, is given in Table I. The absorption temperature was 70° C.–100° C. The time at temperature was

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TABLE I

COMPARISON OF ANALYSIS OF CARBON DIOXIDE BY HYDROXIDE ABSORPTION AND BY CONDENSATION

| Sample volume, cu. mm. at N.T.P. | % $CO_2$ by absorption | % $CO_2$ by condensation |
|---|---|---|
| 18.9 | 61.9 | 62.5 |
| 18.2 | 35.7 | 35.7 |
| 17.8 | 67.2 | 68.0 |
| 16.3 | 78.5 | 78.5 |
| 13.5 | 51.2 | 51.2 |
| 13.3 | 39.1 | 39.1 |
| 10.3 | 57.5 | 57.5 |
| 3.2 | 83.5 | 82.0 |

five minutes and the mercury was not lowered until five minutes after the heater was turned off.

It is apparent that the reagent is satisfactory with regard to analysis, attack on glass, and time for analysis.

## ANALYSIS OF HYDROGEN BY DIFFUSION THROUGH PALLADIUM

Smithells (6) states that the rate of diffusion of hydrogen through palladium becomes appreciable only at temperatures above 260° C. and that at 500° C. the palladium slowly loses its permeability. The use of palladium for the analysis of hydrogen in the presence of carbon monoxide, methane, and stopcock grease apparently presents some difficulties. Stopcock greases and hydrocarbons have been shown to poison the diffusion process (1). Fleiger (3) constructed an analysis apparatus with which the analysis of hydrogen by diffusion through palladium was attempted. It was found that an accurate determination of hydrogen in the presence of carbon monoxide and methane could be obtained only if not over 5% of methane or 9% of carbon monoxide were in the gas mixture. These limitations were attributed to the following reactions catalyzed by palladium at 300° C.: (1) $2CO = CO_2 + C$; (2) $CO + 3H_2 = H_2O + CH_4$; (3) $CH_4 = C + 2H_2$. However, Taylor and McKinney show that reactions (1) and (3) do not occur on massive palladium at 300° C. (7).

The apparatus described here uses quite low pressures of reactants, and the greases used have very low vapor pressures. For these reasons, it was believed the above considerations would not apply under the analysis conditions of this apparatus and the analysis of hydrogen could be effected in the presence of methane and carbon monoxide.

Hydrogen was obtained by the reaction of water on potassium. A small piece of clean potassium was sealed into a side tube connected by a narrow arm to a small reaction vessel in the vacuum system. The potassium was distilled, with the pumps on, into the reaction tube. The side tube was removed by collapsing the narrow arm, and pure water vapor was admitted to the reaction vessel. The hydrogen was expanded into an outgassed storage bulb through a liquid air trap. Its purity by copper oxide oxidation, and by diffusion through palladium, was 99.9%.

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Methane was prepared from methyl magnesium iodide. The Grignard reagent, in an ether solution, was placed in a side tube connected to the vacuum system. The solution was frozen with liquid air and the side tube was sealed. The system was well evacuated and the liquid air removed and placed on another side tube into which the ether then distilled. The residue in the first tube was a colorless amorphous solid. The frozen ether was removed by collapsing the side arm and water vapor was admitted to the solid methyl magnesium iodide. The resulting methane was expanded into an evacuated storage bulb through a liquid air trap. The purity of the methane was 99.6% by copper oxide oxidation and condensation of the carbon dioxide by liquid air.

Carbon monoxide was prepared by the method of Thompson (8). Formic acid vapor was passed through outgassed phosphorus pentoxide. The carbon monoxide produced was passed through a liquid air trap into an outgassed storage bulb. Inexplicably the carbon monoxide so produced contained about 2% by volume of hydrogen. This impurity was shown to be hydrogen by a shrinkage in volume on copper oxide oxidation, the products of which condensed completely at liquid air temperature, and by the same shrinkage when subjected to the heated palladium tube. The last effect could not be due to reaction (1) above because no carbon dioxide was produced, nor could the shrinkage be increased by prolonged reaction times. After the hydrogen had been removed by diffusion through palladium the carbon monoxide was 99.9% pure. The data given below show conclusively that reaction (2) did not occur during this process.

The initial experiments with pure hydrogen showed that at an initial pressure of hydrogen of 1.5 cm. of mercury 15 min. was sufficient to remove completely 20 cu. mm. of hydrogen.

TABLE II

ANALYSIS OF HYDROGEN IN THE PRESENCE OF METHANE OR CARBON MONOXIDE

| % by volume | | | Sample vol., cu. mm. at N.T.P. | Time, min. | Temperature, °C. | % $H_2$ found |
|---|---|---|---|---|---|---|
| $H_2$ | CO | $CH_4$ | | | | |
| 41.7 | | 58.3 | 21 | 10 | 410 | 42.2 |
| 69.8 | | 30.2 | 20.6 | 10 | 370 | 71.7 |
| 2.4 | | 97.6 | 6.5 | 5 | 360 | 3.9 |
| 70.0 | | 30.0 | 22.0 | 6 | 340 | 70.0 |
| 35.3 | | 64.7 | 20.8 | 15 | 310 | 35.3 |
| 80.8 | | 19.2 | 31.5 | 15 | 310 | 80.8 |
| 85.7 | 14.3 | | 8.6 | 7 | 380 | 85.7 |
| 82.9 | 17.1 | | 9.6 | 20 | 310 | 82.9 |
| 78.1 | 21.9 | | 4.2 | 5 | 380 | 78.1 |
| 67.0 | 33.0 | | 5.0 | 6 | 385 | 67.0 |
| 59.8 | 41.2 | | 5.5 | 3 | 390 | 59.8 |
| 52.0 | 48.0 | | 6.5 | 6 | 390 | 52.0 |
| 50.0 | 50.0 | | 7.8 | 3 | 370 | 50.0 |
| 44.3 | 55.7 | | 12.2 | 11 | 310 | 44.3 |
| 43.6 | 56.4 | | 8.0 | 6 | 360 | 43.6 |
| 34.3 | 65.7 | | 10.8 | 3 | 380 | 35.1 |
| 33.3 | 66.7 | | 9.9 | 3 | 430 | 31.5 |

Standard mixtures of hydrogen and methane, and of hydrogen and carbon monoxide were made and analyzed for hydrogen under varying conditions of concentration and temperature. The results are given in Table II. The time noted is that taken to give constant readings for the final pressure on the McLeod gauge.

It is evident that hydrogen can be accurately analyzed in this apparatus in the presence of carbon monoxide over the entire concentration range. If hydrogen is analyzed in the presence of methane by this method accurate determinations can be made over the concentration range by not using the palladium tube at a temperature higher than 325° C. Higher temperatures lead to high hydrogen results because of the decomposition of the methane.

The following points of interest concerning this apparatus are stated without presenting data. The use of copper oxide as an oxidant in gas analysis is well known and its use is successful in this particular apparatus. The oxidation of carbon monoxide at room temperature by a silver oxide – hopcalite mixture has been used with good results in the older form of the apparatus (2). More recently red mercuric oxide has been proposed for this purpose (4).

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# ON THE MECHANISM OF THE DISSOLUTION OF MAGNESIUM IN ACIDIC SALT SOLUTIONS

## I. PHYSICAL CONTROL BY SURFACE FILMS[1]

By E. J. Casey and R. E. Bergeron

ABSTRACT

A kinetic study and analysis has been made of the effects of ionic strength, acid activity, temperature, and salt type on the dissolution of magnesium in acidic salt solutions. This is an example of the simplest type of corrosion involving hydrogen evolution. The results are interpreted in terms of the effects of the various factors on the structure of a surface film which must be magnesium oxide and/or hydroxide even in acidic solutions. The importance of internal dissolutions in the film at high concentrations of attacking reagent, for this and other cases, is shown. Owing to complex formation, under certain conditions an odd case of "chemical control" of the dissolution rate in this simplest case becomes evident. Corrosion potential measurements aid in the interpretation.

## INTRODUCTION

According to King and co-workers (12), who support a modification of the diffusion-layer theory originally due to Noyes and Whitney (18), and Nernst (17), the experimental support for probable diffusion control of the rate of dissolution of metals in acidic aqueous solutions rests on the following facts. For convenience these are reproduced in part from the recent paper by Roald and Beck (19).

1. Different solids dissolve at nearly the same rate in the same reagent under the same conditions.

2. Increased stirring increases the rate. That the rate of dissolution in many cases is a linear function of linear velocity, except at very low linear velocity, has been demonstrated for some cases by the data of King *et al.* (12), Garrett and Cooper (5), Roald and Beck (19), and others. The rate is usually expressed as the constant of the first order rate expression

$$dn/dt = k.A.c,$$

where $c$ is the acid concentration, $A$ the area of the specimen, $dn/dt$ the dissolution rate.

3. The rate of dissolution has been found for many cases to be nearly inversely proportional to the viscosity of the solution for a number of solutions.

4. The rates of dissolution in acid solutions seem to follow the diffusion coefficients of the acid through the solution, perhaps even more closely than they follow the acid strength.

5. Temperature coefficients have been found by many investigators to be of the order usually associated with a controlling step which is some physical transport process. Temperature coefficients are usually of the order of 3000 to 5000 cal./mole.

It should be noted that these criteria do not eliminate all but diffusion control. These criteria could apply equally well to any type of mass transfer

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step which is part of the dissolution process. That the rates follow roughly the diffusion coefficients of the acid through the solution indicates that the control of the process is related in some manner to the physical structure of the solutions. However, the rate of dissolution might well be controlled by any physical step whose rate, in turn, is dependent upon the changing structure of the surface film. Each of the criteria listed above refers indirectly to the effects produced by changes in the properties of this surface layer. For instance, King and Cathcart (11) measured (*a*) the diffusion coefficient of the acid, and (*b*) the rates of dissolution of magnesium in a series of solutions. The diffusion coefficients of the acids in the bulk solution were found to increase as the rates of dissolution increase. This was interpreted by the authors as indicating that the rate is controlled by diffusion of hydrochloric acid through the solution, but might perhaps better be interpreted more broadly as being evidence that the molecular structure of the surface film is being reflected by the structure of the bulk solution: the diffusion coefficient of any particle through the film, if it could be measured, would reflect the rate of the dissolution process, since changes in the rate of passage of any particle through the film reflect changes in the structure of the film. Hence, in the over-all process of dissolution, any one of the successive steps whose rate is affected by changes in the physical and electrical properties of the film, by the above criteria, may be in fact the rate-determining step.

A consideration of the first order rate constants listed in various papers indicates that in some cases the values taken at different intervals of time are subject to drift, and that in other cases the values listed are for less than 20% of complete reaction. In either case this would indicate that, although the calculated first order rate constants give a fairly accurate method of measuring temperature coefficients, for example, the evidence for first order dependence (in time) of rate on acid concentration is not good, and, in some cases, poor. Also in previous work there does not seem to be any attempt to isolate the effect of acid strength from the ionic strength of the solution. Hence, a further study of the dissolution of a base metal in acidic solutions with these factors in mind seemed to be indicated.

Consider the simplest case involving hydrogen evolution where only one anodic process and one cathodic process occur.* The anodic process may be pictured as being the sum of the following steps:

(*a*) $M \rightarrow M^{n+} + ne^-$,

(*b*) $M^{n+} + nX^- \rightarrow MX_n$,

(*c*) $X^-_{\text{soln.}} \xrightarrow{\text{diffusion}} X^-_{\text{metal–film interface}}$,

(*d*) $MX_n$ (or $M^{n+} + nX^-)_{\text{at electrode}} \xrightarrow{\text{diffusion}} MX_n$ (or $M^{n+} + nX^-)_{\text{soln.}}$.

The corresponding cathodic process may be pictured as being the sum of the following steps:

**That dissolution of such metals is electrochemical in nature, that is that local anodes and cathodes exist on the metal surface during dissolution, is now well established since the work of Thiel and Eckell, Müller, and others (15).*

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(*a*) $H^+_{\text{solvated, in soln.}} \xrightarrow{\text{diffusion}} H^+_{\text{solvated, metal–soln. interface}}$,

(*b*) $H^+_{\text{solvated, metal–soln. interface}} \xrightarrow{\text{adsorption}} H^+_{\text{adsorbed}}$,

(*c*) $H^+_{\text{ads.}} + e \rightarrow H_{\text{ads.}}$,

(*d*) $2H_{\text{ads.}} \xrightarrow{\text{recombination}} H_{2\text{ ads.}}$,

(*e*) $nH_{2\text{ ads.}} \xrightarrow{\text{desorption}} nH_{2\text{ dissolved}}$,

(*f*) $H_{2\text{ dissolved}} \xrightarrow{\text{hydrogen removal}} H_{2\text{ into the atmosphere}}$.

When the over-all process is physically controlled, a consideration of the local anodic steps indicates that either (*c*) or (*d*) could be the step which controls the over-all rate. In the case of local cathodes the only steps which are probably not physical in nature are (*b*), (*c*), and (*d*), the exact mechanisms of which comprise also the familiar and difficult problem of hydrogen overvoltage. Where physical control is indicated, any of the remaining cathodic steps might control the over-all rate. In such cases, because of the interdependence of the various steps, the film-type of polarizations which determine the rate must in turn be determined by the rates of the various steps which produce and destroy the film. Since the rate of each step is so critically dependent upon the rates of the rest, and since this type of steady state must involve many transport steps proceeding at nearly the same rate, a change in conditions which affects the slowest step could easily result in a readjustment in which some other step becomes rate-determining in a new steady-state condition. Both minor and major readjustments of the structure of the rate-controlling film are to be expected with changing conditions. Hence the physical properties of the surface film, and the polarizations of local anodes and cathodes, may vary quite markedly with changing experimental conditions of temperature, pressure, electrolyte, electrolyte concentration, metal impurities, etc.

Analogous cases or conditions in which the indications are that the controlling step is not some physical process are uncommon. Thus, Abramson and King (1) found that under conditions of very high linear velocity of the dissolving metal, where the rate of stirring was phenomenally high, iron dissolves in acidic salt solutions at rates which are "chemically" controlled, if activation energies of the order of 12 kcal./mole be the criterion; at low linear velocities the activation energies for the iron dissolution are those of a physically controlled process, with temperature coefficient $\sim$ 5000 cal./mole. In their studies of depolarizers Hochberg and King (8) found cases where both chemical control and physical control seemed to be indicated by the velocity of the reactions.

In cases in which the rate of the dissolution is physically controlled by the film, under any conditions of dissolution the film must be composed of anodic reaction products, $MX_n$, and/or gas nuclei and bubbles. Hence a knowledge of the factors which influence the structure of the surface film would help in an attempt to elucidate the mechanism of this "simplest case" of corrosion involving hydrogen evolution. The work of Whitby (23), which showed that in acid solutions magnesium corrodes without oxygen consumption, and the

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present work, which includes corrosion rates measured by both weight loss and hydrogen evolution techniques, have indicated that the dissolution of magnesium in acidic salt solutions, at least under the conditions chosen for this work, is an example of the simplest case, involving only one anodic process (liberation of magnesium) and only one cathodic process (hydrogen gas evolution).

## EXPERIMENTAL METHODS

The magnesium used was the commercially pure, distilled metal obtained from Dominion Magnesium, Ltd., Haley, Ontario. Specimens were prepared by first filing, then mechanically polishing with 00 emery paper, and then etching in 0.5 *N* hydrochloric acid until the surface was bright and clear and the polycrystalline structure of the magnesium clearly visible. Surfaces prepared in this manner gave quite reproducible results on the same metal piece, but pieces with different crystalline faces visible showed the expected small differences in rates of dissolution. These differences have been eliminated experimentally in the data recorded. A surface coating (#323 Stop-Off Lacquer, made by United Chromium, Inc.) was used to protect those portions of the magnesium samples which were not to undergo corrosion.

Solutions were prepared from reagent grade salts and were made up to the desired acid concentration by adding small quantities of the respective acid. Thus nitric acid was used to adjust the pH of the potassium nitrate solutions, and hydrochloric acid for the potassium chloride and magnesium chloride solutions. Thus the pH could be adjusted without the addition of any foreign anion to the solution. Measurements were made with the use of a Beckman Glass Electrode pH Meter, Model H2.

Different types of magnesium samples were used in the dissolution experiments in which weight losses were recorded.

1. A magnesium cylinder was spun at a linear velocity of 40 cm. sec.$^{-1}$ in an overflowing solution, which was continuously being replenished with fresh solution fast enough to maintain a constant pH. For this work the magnesium sample was 0.38 cm. in radius, and 1.20 cm. in length; the neck was smaller in diameter. The bottom of the cylinder and the neck were protected by the surface coating.

2. Round, flat magnesium pieces were placed in 40 ml. portions of unstirred solutions and the horizontal face allowed to dissolve for certain time intervals. The pH of the solutions was recorded before and after each experiment. The round, flat samples were approximately 1.5 cm. in diameter and 0.6 cm. thick. The sides and bottoms of these pieces were lacquered.

3. Similar experiments to those described in 2 were carried out using square, flat magnesium pieces. The dimensions of these pieces were 1.7 cm. $\times$ 1.7 cm. $\times$ 0.60 cm., with sides and bottom lacquered so that corrosion could take place only from the upper horizontal face.

4. For the combined rate–corrosion potential measurements, oblong magnesium sticks were used. These were 3.5 cm. long and 0.4 cm. square in cross section, and were partially immersed vertically in 40 ml. of the stagnant solutions.

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To check the weight loss method, a gas evolution technique was employed. In these experiments, square, flat magnesium pieces corroded in 40 ml. stagnant solutions of magnesium chloride and in each case the volume of water displaced by the evolved gas was recorded as a function of time. Again in these experiments, only one horizontal face was exposed to the solution.

The corrosion potentials of magnesium pieces were measured against silver – silver chloride probe electrodes containing 1 *N* potassium chloride. The probe electrodes were used to prevent any contamination of the magnesium by dissolved silver chloride. The potentials measured were reduced approximately to the hydrogen scale, an activity correction having been made by the Nernst equation; the liquid junction potential, probably of the order of a few hundredths of a volt, was ignored.

A conductivity bridge made by Industrial Instruments Inc., Jersey City, N.J., Model RC-8, was used for conductivity measurements. For salt concentrations below 0.1 molal, a conductivity cell with a constant of 0.0538 was used, while for concentrations above 0.1 molal a cell with a constant of 49.7 was used.

In the overflow system employed for the spinning cylinder, the rates are true initial rates since fresh solution was continually being supplied to the corrosion chamber. In the cases of stationary metal pieces and unstirred solutions, it was found that, in the short times needed for the measurement of the initial rate in potassium chloride, potassium nitrate, and dilute magnesium chloride solutions, the pH of the solutions did not change by more than one or two tenths of a pH unit, and hence the rate through zero time truly referred to the rate of the original pH. The odd effects found in high concentrations of magnesium chloride are considered in the discussion section.

## EXPERIMENTAL RESULTS AND DISCUSSION

### *Potassium Chloride Solutions*

Using the constant flow and spun cylinder technique the dependence of rate upon concentration of potassium chloride, at constant acid strength, was obtained. At pH = 3.5 and at linear velocity of 40 cm./sec. the weight losses were of the convenient order of a few milligrams, and the rates obtained as a function of concentration are shown in Fig. 1. That the maximum in the curve is not a function of the physical structure* of the solution was indicated by the fact that the conductivity measurements on the same solutions (Fig. 1) showed no such concentration dependence. That the inhibition of the corrosion at higher concentrations must be simply a modification of the physical step which controls the over-all dissolution was shown by the temperature dependence of the dissolution rate, Table I. The general shape of this type of rate vs. concentration curve is well known from the work of Abramson and King (1), and the present data are plotted in this same sense in Fig. 2. The information from Fig. 3 shows that the smallest activation energies exist at the concentration corresponding to maximum rate at each temperature.

**For discussions on the extent and nature of associations and cross-linkages in water and its solutions, and their effects on rates of transport processes, the reader is referred to the original work of Bernal and Fowler (3), to the recent papers of Weyl (22), and to the modern interpretations of Glasstone, Laidler, and Eyring (6).*

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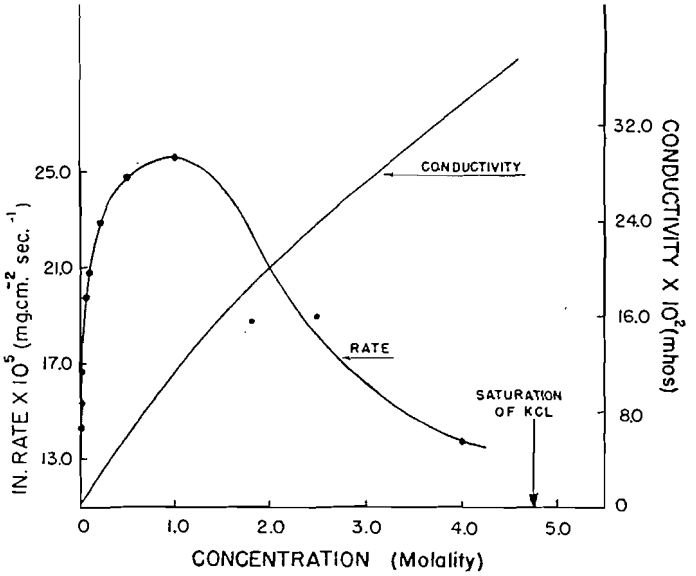



FIG. 1. Initial rate of dissolution and conductivity of solution as a function of salt concentration for magnesium cylinder spun at linear velocity of 40 cm./sec.; constant flow technique, pH = 3.5. Temperature 25°C.

TABLE I

| Molality KCl | Initial rate of dissolution × $10^{+3}$ (mgm. cm.$^{-2}$ sec.$^{-1}$)*, pH = 2.0 | | | |
|---|---|---|---|---|
| | 0°C. | 25°C. | 40°C. | 55°C. |
| 0 | 1.50 | 2.30 | 3.03 | 3.91 |
| 1.0 | 1.85 | 2.78 | 3.53 | 4.38 |
| 3.0 | 0.92 | 1.48 | 1.87 | 2.25 |

**The rates recorded are average values of three to five experimental determinations.*

That the depression of rate of dissolution at high concentrations is not some mechanical effect due to the spinning cylinder was shown by the fact that this same trend occurs in unstirred solutions when the metal piece was held stationary. Since the rates are considerably lower than in the spun-cylinder experiments at pH = 3.5, acid strength of pH = 2.0 and horizontal flat pieces of magnesium were used consistently. Typical data for initial rates as a function of concentration in unstirred solution at pH = 2.0 are shown in Fig. 4. That the depression of rate at high concentration of salt is not a unique function of chloride ion concentration was shown by the fact that the same trend occurs also in potassium nitrate solution. At this temperature, 25°C., the complexing agent versene was found, oddly enough, simply to depress the dissolution rate at all concentrations, although there is slight indication that in 3 molal solution versene had less of a depressing effect. The nonionic surface-active agent triton NE simply increased the rate in all concentrations, perhaps the lower concentrations more than the higher.

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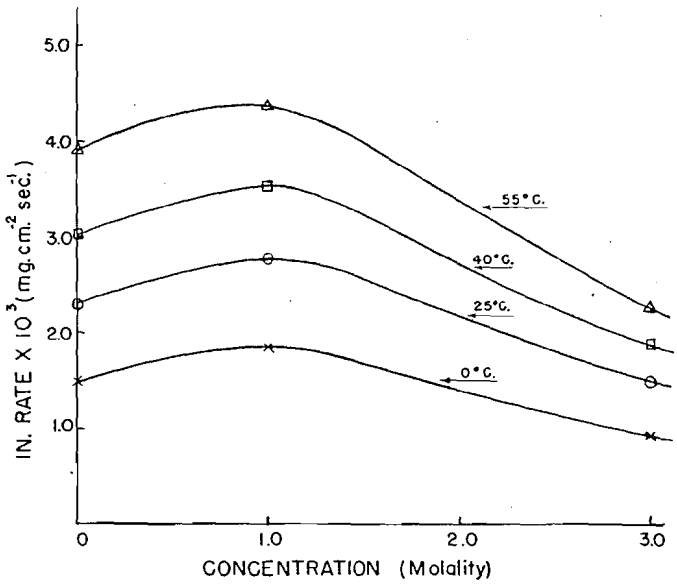



FIG. 2. Initial rate of dissolution as a function of salt concentration for spinning magnesium cylinder in solutions at various temperatures. Constant flow technique, pH = 2.0.

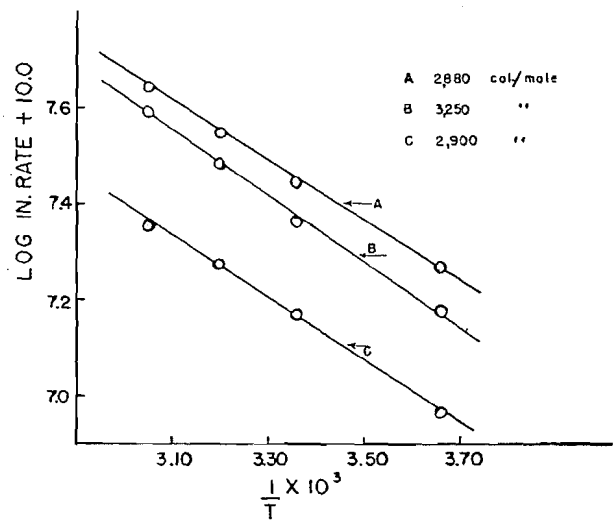



FIG. 3. Arrhenius plots of initial rates of dissolution in potassium chloride solutions; spinning cylinder, constant flow technique, pH = 2.0. A: 1.0 molal potassium chloride; B: 0.0 molal potassium chloride; C: 3.0 molal potassium chloride.

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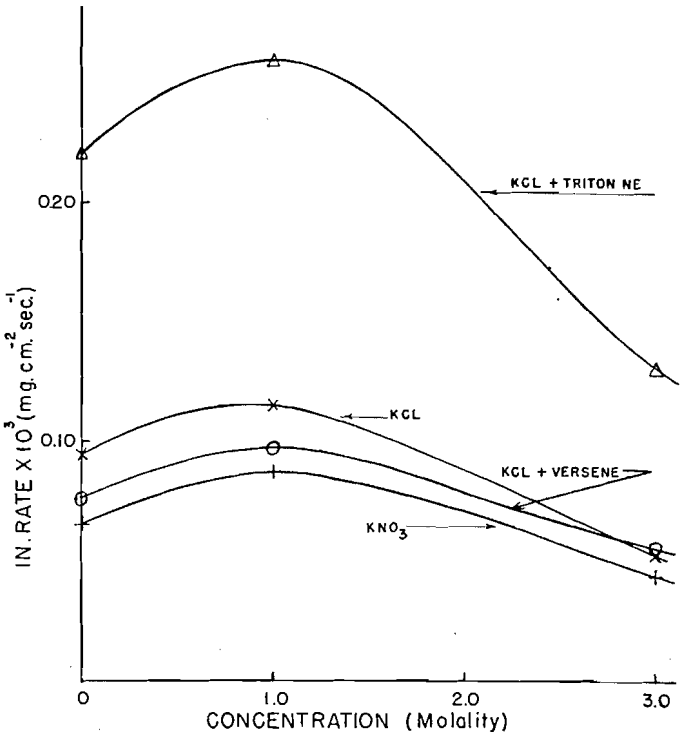



FIG. 4. Initial rate of corrosion of flat, horizontal faces of magnesium as a function of concentration for unstirred potassium chloride and potassium nitrate solutions. Temperature 25°C.

The existence of a maximum in the rate–concentration curve for magnesium in potassium chloride solutions was apparently first noted by Hughes (10) who ascribed the phenomenon to "the catalytic effect of the salt". Since then a similar maximum has been noted in other cases, of which perhaps the most complete figures are reported by Abramson and King (1) on the dissolution of iron in acidic solutions. The apparent dependence of rate of dissolution of magnesium upon the solubility of magnesium hydroxide was suggested by Whitby (24) from work on potassium hydroxide, potassium sulphate, potassium chloride, and other salt solutions. Huber (9) has recently shown by X-ray diffraction and electron diffraction studies that the anodic process of magnesium, in alkaline solutions at least, proceeds by the series of steps $Mg \rightarrow MgO \rightarrow Mg(OH)_2$, that the production of MgO is the primary step.

The facts noted above—the increase, the maximum, and the decrease in rate of dissolution with increasing salt concentration (or increasing ionic strength)—are quite consistent with the assumption that during dissolution the rate is controlled by a surface film of magnesium oxide and/or hydroxide, for it is known (14) that (*a*) the solubility of magnesium hydroxide in water increases with increasing concentration of various salts, and yet (*b*) magnesium hydroxide is much less soluble in the presence of saturated solutions of salts

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such as sodium chloride and potassium nitrate. Thus a maximum exists in the curve of solubility of magnesium hydroxide vs. salt concentration in solutions of many salts. That the controlling film must be liquidlike, perhaps gelatinous in nature is seen from the fact that the activation energies are all of the order of 3000 cal./mole. Thus, if one assumes that the rate of solution of the film is proportional to its solubility, the facts shown in Figs. 1, 2, and 4 can be qualitatively explained in terms of a diffusion layer which is essentially magnesium oxide and/or magnesium hydroxide, even in a bulk solution which is acidic at pH = 2. The work of other investigations has indicated similar effects. For example Müller (16) has discussed corrosion data on iron and aluminum in terms of porous films of oxide and/or hydroxide in acid concentrations even as high as 4 *N* hydrochloric acid.

Further insight into the nature of the rate-determining step and the nature of the film was obtained from a study of the dependence of the rate of dissolution upon acid activity at constant ionic strength. As noted in the introduction, the evidence for first order dependence of rate on acid strength is unconvincing in many cases. Consequently, initial rates were obtained in salt concentrations high enough so that the acid which was added to adjust the pH contributes a negligible fraction to the ionic strength of the electrolyte, in order to determine the true order (13) of the reaction with respect to acid concentration. Since Initial Rate = $k\,c^n$, the slope of a plot of log Initial Rate vs. log $c$ is the true order with respect to acid concentration. For 1 molal and 3 molal potassium chloride solutions the data, with probable errors, are listed in Table II, and

TABLE II

| pH | Initial rate × $10^4$ (mgm. cm.$^{-2}$ sec.$^{-1}$) | |
|---|---|---|
| | 1.0 molal KCl | 3.0 molal KCl |
| 1.6 | 10.9 ± 1.0* | 5.3 ± 0.4 |
| 2.0 | 2.78 ± 0.09 | 0.73 ± 0.15 |
| 2.5 | 0.49 ± 0.13 | 0.14 ± 0.03 |
| 3.0 | 0.083 ± 0.011 | 0.042 ± 0.024 |

**Maximum probable deviation from the average values, as determined from repeat determinations and the weighing error.*

are shown in Fig. 5. Definite curvature exists. The slopes indicative of first order and second order dependence are indicated. At low acid concentrations the order seems to be close to unity. At higher acid concentrations the order definitely increases, and in both cases approaches, if not exceeds, two. It is suggested that this behavior is another case (4), now believed by the authors to be common in film-controlled processes, in which internal dissolution of the film becomes increasingly important with increasing strength of the material which attacks and dissolves the film, in this case the acid. In a process which is diffusion controlled the rate of the controlling step is given by Fick's law, $dc/dt = D.A.\ dc/dx$, where $dc/dt$ is the rate of diffusion, $A$ the area of cross section, $dc/dx$ the concentration gradient of the diffusing substance, and $D$

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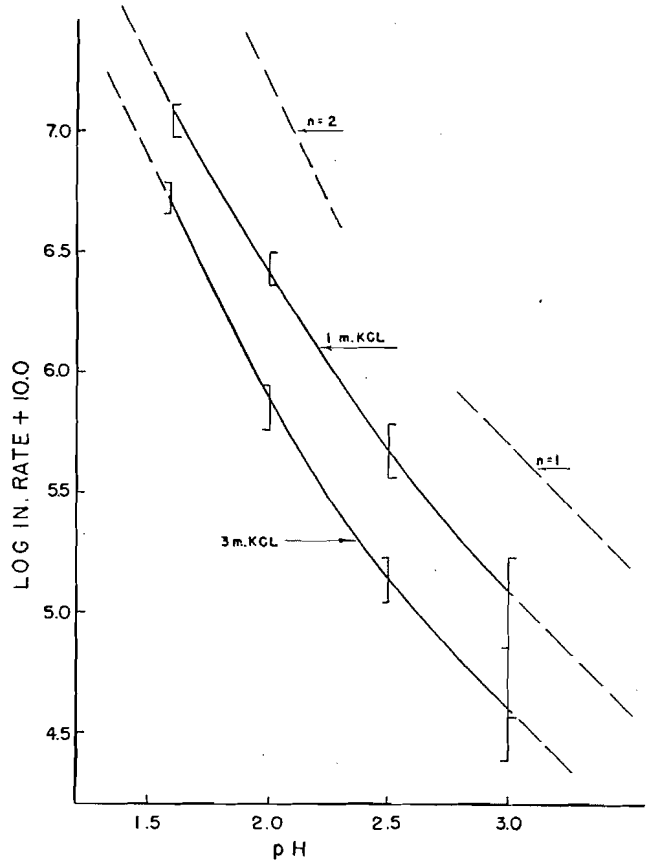



FIG. 5. Dependence of initial rate of dissolution of flat, horizontal faces upon acid strength in unstirred 1 molal and 3 molal potassium chloride. $n$ is true order of the reaction with respect to acid activity. Temperature 25°C.

the diffusion coefficient of the diffusing substance. Since the diffusion coefficient reflects the structure of the surface film, the effect of acid on the film is of critical importance. In the case where the solution has low acid concentration the acid available at the film–solution interface would be small, and most would be expected to be used up dissolving the film at the film–solution interface. Also, in the low acid concentrations the stirring provided by the gas bubbles is small. Hence the amount of acid in the film, diffusing toward the electrode, would be small, and changes of the structure due to internal dissolution of the film would be small. Thus at low concentration of acid, since $D$ would be essentially independent of acid concentration, the rate of the diffusion process would depend upon $dc/dx$ only, and be first order with respect to acid concentration. In the case of stronger acid solution, however, owing in part to increased driving force for the cathodic process, which provides increased agitation by bubbles, and in part to increased diffusion and the onset of convection and eddy currents, acid molecules would get into the film and cause

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internal dissolution of the film. The film thus weakened would now be more easily penetrable; the diffusion coefficient, $D$, is thus an increasing function, $F(c)$, of acid concentration. Hence at high acid concentrations the rate of the diffusion through the film is given by

$$dc/dt = A.F(c).dc/dx$$

and is seen to be of order greater than unity with respect to acid concentration. In terms of Müller's film theory, increased internal dissolution would be expressed as increased pore area per unit area of film.

In the case of the strongly acidic solutions, a possible method of supplying acid to the metal-film interface, alternative to pure diffusion aided by increased internal dissolution or reduced film thickness, could be diffusion augmented by other mass transport processes such as convection and local mass flow provided by the increased bubble formation and liberation. However, transport of acid directly to the metal surface by processes other than diffusion seems to be unlikely when consideration is taken of (*a*) the results of schlieren experiments on the "diffusion layer", (*b*) the state of our knowledge of the electrical double-layer, and (*c*) the success which has been achieved in describing mass transport along the surface in terms of kinetic theory of laminar flow. Pure diffusion aided by internal dissolution seems to account better for the facts obtained.

Presumably because of the poor solubility of magnesium hydroxide in 3 molal potassium chloride, the rate of dissolution of magnesium in 3 molal potassium chloride is less than in 1 molal potassium chloride. In terms of the above considerations this would mean that an effectively thicker or less porous film exists in 3 molal potassium chloride. One would expect that a small amount of internal dissolution in the film could exert more effect the more solidlike or the less porous the film. Consistent with this idea, greater curvature is noted in the curve (Fig. 5) for 3 molal potassium chloride, and the rate tends toward the higher order dependence at a lower concentration of acid than does the rate in 1 molal potassium chloride solutions.

The similar higher order dependence noted by Straumanis and Brakss (21) during studies of the dissolution of aluminum in sodium hydroxide solutions is quite conveniently explainable in terms of this internal dissolution theory, as were data obtained previously (4) on anodic processes occurring on zinc in caustic solutions. The similar data of Roald and Beck (19) on dependence of rate of dissolution of magnesium on acid strength are explainable in the same terms. Thus, the information obtained provides strong support for the internal dissolution theory and for the belief that the rate of the over-all process is either primarily or secondarily controlled by diffusion of acid into the film, since it is the rate of this step which controls the structure and the characteristics of the surface film upon which the rates of all the other mass transport processes are so critically dependent. However, it should be noted that it seems impossible to decide unequivocally, from the experimental information available in this or other researches, whether the slowest and rate determining step of the dissolution process is actually the diffusion of acid

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into the film; the actual slowest step might indeed be any one of the other transport processes, one associated with hydrogen removal and liberation, perhaps, whose rate must depend so closely upon the structure of the surface film.

*Magnesium Chloride Solutions*

Further support for the postulate that the film is actually magnesium oxide or magnesium hydroxide is contained in information obtained on magnesium chloride solutions. Fig. 6 shows that, at the same pH over the same

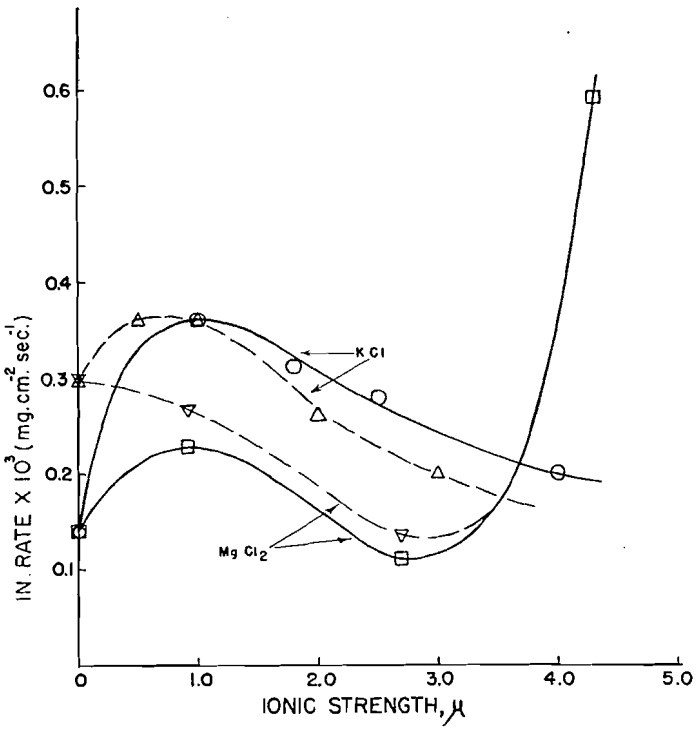



FIG. 6. Initial rate of dissolution as a function of ionic strength in potassium chloride solutions up to saturation, and in solutions of magnesium chloride of low concentration. Bold curves; flat, horizontal corroding faces. Broken curves; corroding rectangular bars.

range of ionic strength ($\mu = \frac{1}{2}\sum_i c_i z_i^2$), the rate of dissolution of magnesium follows closely the trends noted in potassium chloride solutions. The one notable difference is that all the rates in magnesium chloride solutions are lower. This further depression is interpreted as being a result simply of common ion depression of the solubility of magnesium hydroxide.

In Fig. 6, rates are shown for both round, flat, horizontal pieces and for oblong, vertical pieces. The difference, presumably a convection or an edge effect, shows up rather strikingly as a buffer to the various electrolyte effects. This phenomenon was not studied further.

At ionic strength 4.75 potassium chloride is saturated at 25°C., and depression of the rate with increasing ionic strength of salt was noted nearly up

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to saturation. However, beyond ionic strength of about 3 in magnesium chloride solutions (that is, at concentrations greater than 1 molal), the rate of the dissolution process increases very rapidly with increasing concentration, and goes through another maximum. This is shown in Fig. 7, the data being listed in Table III. This behavior can also be explained in terms of the pro-

TABLE III

| Molality of $MgCl_2$ | Initial rate $\times 10^3$ (mgm. $cm.^{-2}$ $sec.^{-1}$) at 25°C. |
|---|---|
| 0 | 0.15 |
| 0.31 | 0.23 |
| 0.90 | 0.11 |
| 1.44 | 0.59 |
| 2.26 | 1.15, 0.95* |
| 3.03 | 1.38 |
| 4.00 | 1.48, 1.52* |
| 5.44 | 1.13, 1.13* |

**By hydrogen evolution. Each recorded initial rate by weight loss method is an average value of 4–10 experimental determinations.*

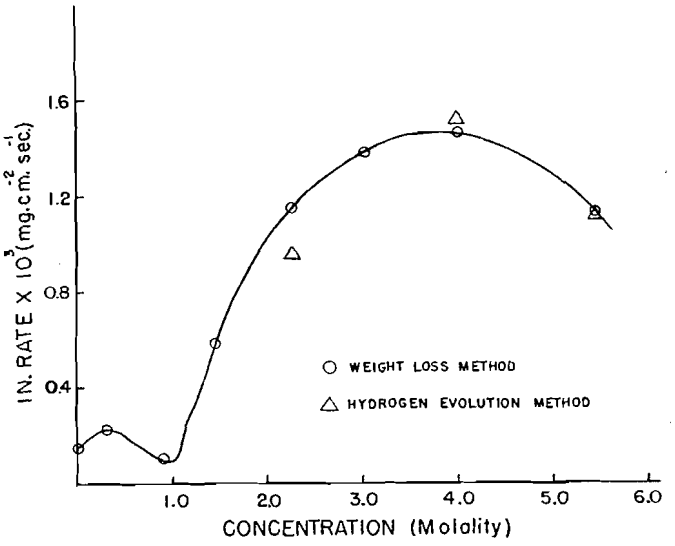



FIG. 7. Initial rate of dissolution of flat, horizontal corroding faces as a function of concentration of magnesium chloride, pH = 2.0, temperature 25.0°C. The curve below 1 molal magnesium chloride is enlarged in Fig. 6.

perties of magnesium hydroxide, for in this region of ionic strength the solubility of magnesium hydroxide is known to be augmented by the presence of magnesium salts. The values given by Robinson and Waggaman (20) for the solubility of magnesium oxide in aqueous magnesium chloride solutions as a function of magnesium chloride concentration follow very closely the sense of the rate values (Fig. 7) in the regions of concentration 1.0 to 4.0 molal

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magnesium chloride. This enhanced solubility is presumably a result of the formation of the soluble oxychloride which was indicated by the solubility and potentiometric titration work of d'Ans and Katz (2). In this regard it is interesting to note that the greater the concentration of magnesium chloride used for the rate determination the more difficult it was to obtain an initial rate of reaction which actually referred to the starting pH. That is, in this region of concentration very little acid need be added to a magnesium chloride solution to adjust the pH to 2, and consequently very little reaction need occur before the pH had risen to 6 or 7. This region of pH, 2 to 7, seemed to be a potentiometric titration inflection point, presumably of the neutralization reaction

$$Mg(OH)_2 + HCl \rightarrow Mg(OH)Cl + H_2O.$$

The amalgamation technique used by Hoar and Farthing (7) provided further evidence that (*a*) a surface film exists in magnesium chloride solutions of $\mu < 3$, and that (*b*) this surface film is increasingly more soluble or less solidlike in magnesium chloride solutions of concentration above $\mu = 3$. In a solution of 0.3 molal magnesium chloride a flat piece of magnesium would corrode away slowly and be untouched by droplets of mercury allowed to fall on the surface. In fact, the metal would be unattacked if left sitting on a pool of mercury, even when the solution was shaken vigorously in order that the magnesium be not held away from the mercury by hydrogen bubbles. In contrast, when the same experiment was done in 4 molal magnesium chloride, after a few seconds of corrosion amalgamation of the magnesium had started and the mercury attack was spreading over the surface. The surface was thus protected by a surface film in solutions of $\mu < 3$, and this protective film was either very weak or nonexistent in 4 molal magnesium chloride.

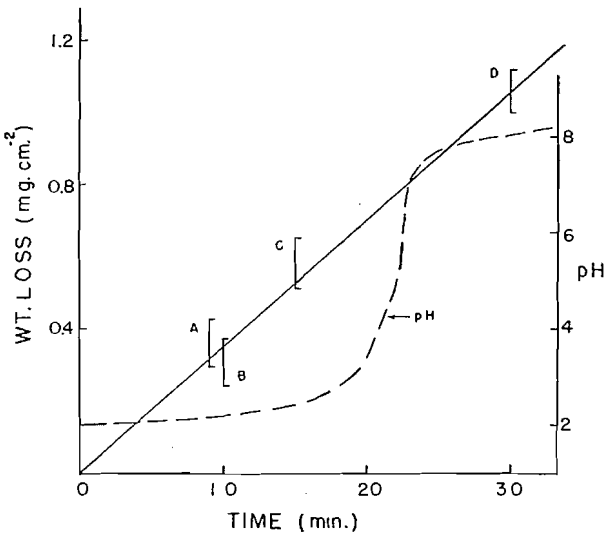



FIG. 8. In 1.44 molal magnesium chloride solution, weight loss and pH of solution vs. time. pH of each solution after the rate determination: A, 2.21; B, 2.25; C, 2.42; D, 8.1. Temp. 25°C.

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The dependence of rate of the dissolution upon concentration of acid in those regions of salt concentration greater than 1 molal could not be determined directly because of the inflection point behavior noted above. However it was shown indirectly that the rate of the dissolution process is essentially independent of pH in this region; Fig. 8 shows weight loss – time data for 1.44 molal magnesium chloride, the highest concentration at which it was possible to be sure that the initial rate actually referred to pH = 2. The pH of the solution after the dissolution run had been done is noted for each determination. That a straight line, within the experimental error, passes through zero time and all the points must indicate that the rate is essentially independent of acid concentration, for if the pH dependence were strong, as in the case of $\mu < 3$ (Fig. 5), the weight loss vs. time curve would flatten off as time proceeds. Further actual measurements of the pH during dissolution in a solution of 1.44 molal magnesium chloride as a function of time of dissolution are dotted in to indicate the time dependence of pH of the solution during dissolution, the time base having been adjusted to correct for the necessary extra stirring since the two experiments could not be done simultaneously.

TABLE IV

| Temperature (°C.) | Initial rate $\times 10^3$ (mgm. cm.$^{-2}$ sec.$^{-1}$) in 4 molal $MgCl_2$, pH = 2.0 |
|---|---|
| 0.0 | $0.23 \pm 0.015$ |
| 25.0 | $1.48 \pm 0.21$ |
| 55.0 | $7.76 \pm 0.69$ |

In 4.0 molal magnesium chloride at pH = 2 the temperature coefficient of initial rate was found to be 11.2 kcal./mole (Table IV, Fig. 9). Apparently the complexing of the film substance is so strong and so fast that no effective surface layer in fact exists in these higher concentrations of magnesium chloride. In 4 molal solutions, where the rate is nearly independent of magnesium chloride concentration, independent of acid concentration, and the activation energy for the process is 11.2 kcal./mole, one must now be measuring a step which is not physical at all but rather one of the chemical-type steps relating perhaps to the complex formation reaction or to hydrogen discharge and evolution. King and co-workers noted apparent chemical control of the dissolution process in the dissolution of iron at extremely high linear velocity where the stirring is sufficient to dissolve the surface film, and also noted apparent chemical control of the dissolution of metals in solutions containing depolarizers. But the case reported here is believed by the authors to be the first case of chemical control noted with stationary metal pieces where the cathodic reaction is all hydrogen evolution.

Solubility data available indicate no maximum in the solubility of magnesium hydroxide at 4 molal, but rather a gentle increase in higher concentrations of magnesium chloride. The definite depression of the rate at concentrations

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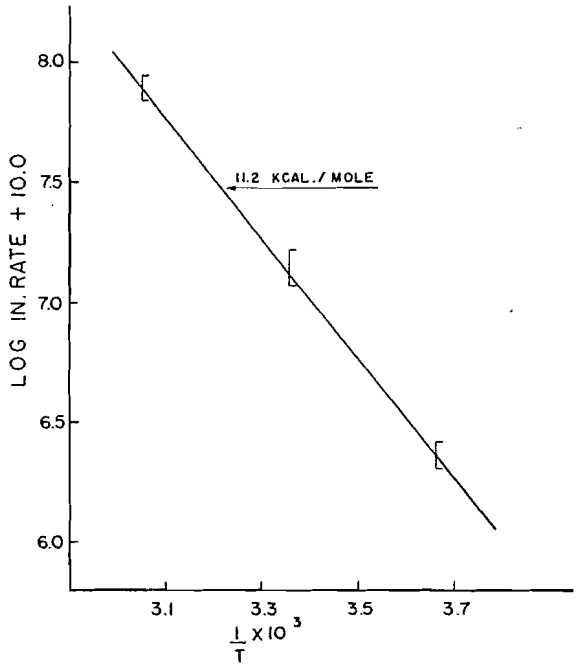



FIG. 9. Arrhenius plot of initial rates of dissolution of flat, horizontal faces of magnesium in 4.0 molal magnesium chloride. Initial pH = 2.0.

above 4 molal is interpreted tentatively as being due perhaps to salting-out of the complex in the vicinity of the electrode where the pH is high.

*Mixed Potential Measurements*

Measurements of corrosion potentials as measured against 1 molal silver – silver chloride electrodes are listed in Table V. Measurements were made on

TABLE V

| Salt | Concentration (molality) | $E_{\text{Mg-Ag/AgCl}}$ (measured), volts | $E^{\text{mixed}}_{\text{Mg-hydrogen}}$ (corrected), volts | Corrosion rate $\times 10^3$ (mgm. cm.$^{-2}$ sec.$^{-1}$) |
|---|---|---|---|---|
| KCl | 0 | 1.840 | 1.497 | 0.295 |
| | 0.5 | 1.890 | 1.700 | 0.36 |
| | 1.0 | 1.960 | 1.725 | 0.36 |
| | 2.0 | 1.967 | 1.749 | 0.26 |
| | 3.0 | 1.960 | 1.752 | 0.20 |
| $MgCl_2$ | 0 | 1.840 | 1.497 | 0.295 |
| | 0.31 | 1.790 | 1.62 | 0.23 |
| | 0.90 | 1.870 | 1.646 | 0.122 |
| | 1.44 | 1.93 | 1.73 | 0.58 |
| | 2.26 | 1.93 | 1.75 | 1.15 |
| | 3.03 | 1.92 | 1.77 | 1.38 |
| | 4.0 | 1.94 | 1.82 | 1.50 |
| | 5.44 | 1.91 | 1.83 | 1.13 |

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oblong pieces of magnesium half submerged in the electrolyte. For potassium chloride solutions the points of the last two columns are plotted on a polarization diagram, Fig. 10, which shows the polarization of both local anodes and

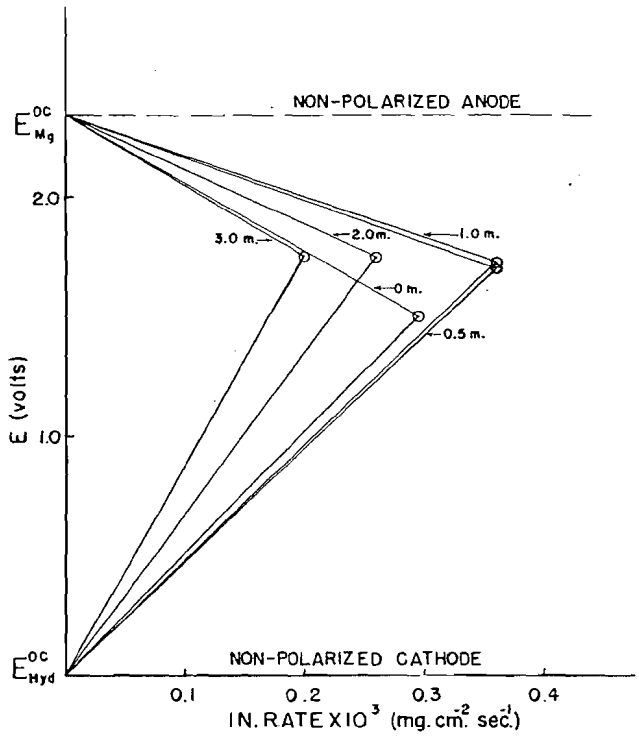



FIG. 10. Mixed potential – corrosion rate data for corroding rectangular bars of magnesium; pH = 2.0; temperature = 25°C. Straight lines joining $E^{oc}$ to $E^{mixed}$ are first approximations of the anodic and cathodic polarizations as a function of local corrosion current.

local cathodes, the mixed potential and the local current for autocorrosion. The information available in general on polarizations as functions of current indicates that in fact a curvature exists in the trace which joins the open circuit potential, $E^{oc}$, with the mixed potential, $E^{mixed}$. Since the curvature would not be expected to change markedly with change in concentration of solution, and since the curvature in the known systems is not large in any case, a first approximation is a straight line joining $E^{oc}$ with $E^{mixed}$. For the hypothetical case where the local current could be controlled, then, the relative polarizations in different solutions at the same rate of corrosion can be estimated from the graph. The relative polarizations $E^{oc} - E$ obtained in this manner for local anodes and cathodes are shown plotted against ionic strength for both magnesium chloride and potassium chloride in Fig. 11. The ordinate is only relative, of course, since the values plotted are for one chosen current. Fig. 11 shows that the polarizations at local anodes and local cathodes as functions of ionic strength of the solutions express in other

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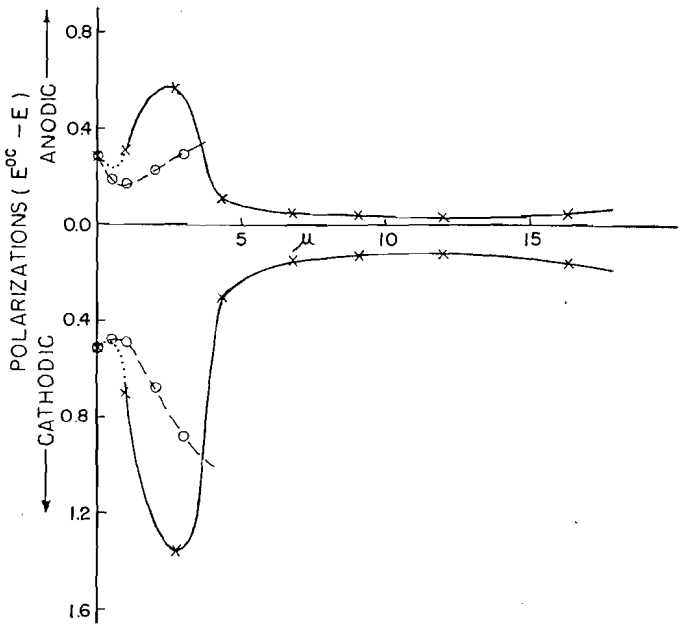



FIG. 11. Relative local anodic and cathodic polarizations on magnesium corroding in acidic (pH = 2.0) solutions of potassium chloride (○) and magnesium chloride (×) as a function of ionic strength of solutions. Values refer to local current of $1.0 \times 10^{-4}$ mgm. cm.$^{-2}$ sec.$^{-1}$.

terms the trends in the rate noted in Figs. 6 and 7. The extra depression of solubility of the magnesium hydroxide film by the presence of the common ion in magnesium chloride solution shows up markedly at $\mu \cong 2$; and the remarkable reduction of the polarizations at $\mu > 3$ is very evident. In all cases, the polarizations of the local cathodes are considerably greater than the polarizations of the local anodes, but this may be just an indication that the total area of the local cathodes is much less than the total area of the local anodes, that the cathode current density is higher than the anode current density.

## ACKNOWLEDGMENT

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# THE FRACTIONAL PRECIPITATION OF GR-S

## THE EFFECT OF CONCENTRATION OF THE SOLUTION ON THE EFFICIENCY OF FRACTIONATION[1]

By L. H. Cragg and D. F. Switzer[2]

ABSTRACT

A careful study was made of the fractionation of GR-S (commercial poly(butadiene-*co*-styrene)) by stepwise precipitation, from solution in benzene, with the precipitant 50:50 (by volume) methanol–benzene. To determine the reproducibility of fractionation, particularly in the high-molecular-weight region, three runs were made with 2% solutions; and to determine the effect of concentration on efficiency, comparable fractionations were performed from solutions of three different concentrations—1, 2, and $3\frac{3}{4}$ gm./100 ml. respectively. In each of the fractions the value of intrinsic viscosity, the viscosity slope constant $\beta$, and the viscosity-average molecular weight were determined. These provide conclusive evidence that in such a primary fractionation a much cleaner separation is accomplished from a dilute solution (1% or less).

## INTRODUCTION

Although the various molecular species comprising a linear high polymer may differ in several respects, molecular chain length is usually much the most significant one. The distribution of chain lengths (and therefore of molecular weights) in a given sample depends on its history but is usually broad enough that for many purposes it is desirable or necessary to separate the sample into fractions more nearly homogeneous with respect to chain length. Although several means of accomplishing this are available (5), the one most commonly used is fractional precipitation (progressively decreasing the solvent power of the solvent).

Although there have been remarkably few studies of fractional precipitation per se, several of the many investigators who have used this means of obtaining fractions have stated that fractionation is most efficient when the solution is very dilute. Moreover, the theoretical treatments of solubility and fractional precipitation, developed in recent years by Schulz, Flory, Huggins, Gee, and Scott,* all tend likewise to the conclusion that the initial concentration of the solution should be low (less than 1%). Unfortunately, precipitation from such low concentrations requires more time, more materials, and more cumbersome apparatus. For these reasons, and because the conclusion was based on observations that were more or less incidental and on theories that embodied simplifying assumptions, Morey and Tamblyn in 1946 made an experimental study of the effect of concentration on efficiency (16). They concluded that "the effect of initial concentration on the efficiency of fractionation by precipitation

[1] *Manuscript received April 9, 1953.*
*Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario. Much of the work was presented in a paper at the Canadian High Polymer Forum, Hamilton, Ont., June 10, 1949.*
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* *Theories of fractionation are ably reviewed by Morey and Tamblyn (17), Hildebrand and Scott (10), Bawn (1), and Frith and Tuckett (9).*

is minor". The same conclusion was reached by Rehner (cited in Reference (17)) from his experience with fractionations of butyl rubber.

This contradiction between theoretical predictions and experimental results emphasized the need for further experimental work. Accordingly, we decided to make a careful test of the effect of concentration on the efficiency of the fractional precipitation of GR-S (poly(butadiene-*co*-styrene)) using benzene as solvent and methanol as precipitant. This polymer was chosen both because of its own importance and because it represents the rubberlike polymers, and benzene–methanol was chosen as the solvent–nonsolvent system because it is the one almost always used in fractionating GR-S.

## EXPERIMENTAL

### 1. *Materials*

The polymer was normal production GR-S (poly(butadiene-*co*-styrene)) obtained from Polymer Corporation Ltd., Sarnia, a portion of lot S-2503. The analysis supplied with it was as follows:

| | | | |
|---|---|---|---|
| Intrinsic viscosity | 2.14 ± 0.02 | Free fatty acid | 4.95 ± 0.04% |
| Mooney viscosity | 52.5 ± 1.0 | Antioxidant | 1.53 ± 0.03% |
| Total ash | 0.66 ± 0.08% | ETA extract* | 7.34 ± 0.05% |
| Soluble ash | 0.51 ± 0.07% | Bound styrene | 23.5 ± 0.1% |
| Free soap | 0.22 ± 0.03% | | |

The polymer was stored in the dark in air. It was free of gel when received and showed no change in either gel content or intrinsic viscosity over the whole period of experimentation. It was used without purification.

The *antioxidant* used was phenyl-β-napthylamine (PBNA), technical-grade material obtained from Polymer Corporation. For convenience in use, it was dissolved in benzene to form a 10% solution (gm./100 ml.).

The *solvent* was benzene, ASTM Industrial Grade, Steel Company of Canada, distilled and dried over sodium, b.p. 80.1° C., $n_D^{25}$ 1.49744, $d^{25}$ 0.8739 gm./ml.

The *nonsolvent* was methanol, synthetic, Carbide and Carbon Chemical Co., used as received (since drying and distilling did not alter its refractive index), b.p. 64.7° C., $n_D^{25}$ 1.3262, $d^{25}$ 0.7864 gm./ml.

The precipitant was a 50:50 (by volume) solution of the benzene and methanol, accurately prepared and kept in a ground-glass-stoppered bottle, $n_D^{25} = 1.4110$.

### 2. *Apparatus*

The *fractionation vessel* was a 1-liter Pyrex Squibb separatory funnel modified by the addition of a vertical side arm. The stem of the funnel was cut off just below the stopcock. Above it, the funnel was graduated for the first 100 ml. so that the volume of the precipitated phase could be measured (roughly) in the vessel. During precipitation the vessel was sealed with cork stoppers. Through the one in the side arm was inserted the tip of the burette from which

* *Portion soluble in ethanol–toluene azeotrope.*

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precipitant was added; through the one in the neck of the funnel was inserted the shaft of the stirrer equipped with a grease seal to prevent the escape of vapor. During equilibration these stoppers were replaced with standard-taper glass stoppers.

The *viscometers* were of the Ostwald-Cannon-Fenske type, ASTM Series 50.

Two *constant-temperature baths* were used, a large one of the aquarium type for precipitating and equilibrating fractions and for viscosity measurements, and a smaller cylindrical glass jar for redissolving and reprecipitating fractions. In both, water was the bath liquid and its temperature was maintained at 25.0 ($\pm$ 0.01)° C. by a cooling coil and heaters controlled by a sensitive thermoregulator.

*3. Procedure*

*Preparation of Solutions*

As noted above, the GR-S was used without further treatment. In preliminary experiments the polymer was extracted with ethanol–toluene azeotrope containing 10% water (12), but the product either contained varying amounts of extractant or, if drying conditions were rigorous enough to remove the extractant completely, varying amounts of insoluble gel. This separate extraction step was shown to be unnecessary because in each stage of the fractionation the extractable material remained in the supernatant liquid. (The precipitated phases were colorless—like solutions of extracted GR-S—and in one fractionation that was carried to completion it was found that the liquid from which no more polymer could be precipitated left, on drying, a residue corresponding closely in weight to the extractable material in the original sample.)

A solution was prepared by allowing the sample of polymer, cut into fine pieces, to stand in contact with benzene in the dark, with occasional gentle shaking. After dissolution was complete, the solution was filtered through a coarse sintered-glass disk, and its density determined. Its concentration was then determined by slowly evaporating aliquot portions, the final drying to constant weight being done in an oven at 100° C.

*Fractionation Procedure*

About 400 ml. of the solution was introduced into the fractionation vessel and allowed to come to thermal equilibrium in the bath at 25.0° C. Then, with vigorous stirring, the precipitant was added, slowly enough to prevent the formation of curds of rubber, until the solution became just turbid enough that the stirrer shaft could not be seen when viewed in line with a 100-watt bulb behind the bath. (This criterion was only a rough guide, especially with the high fractions, but could be modified with experience to make possible the obtaining of fractions of the desired size.)

The vessel was then transferred to the smaller bath, and its contents were heated slowly, with stirring, until the cloudiness just disappeared and then cooled slowly to 25.0° C., with constant stirring to maintain near-equilibrium conditions. The system was left undisturbed at this temperature until the two liquid phases had separated completely (24–46 hr.) and the denser precipi-

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tated phase ("coacervate") was drawn off into a weighed volumetric flask, with suitable precautions to ensure an uncontaminated "precipitate". (The first three or four fractions separated so slowly that it was better to make a first rough separation and then replace the vessel in the bath for several hours to allow the rest of the very viscous coacervate to drain down from the sides.)

The coacervate was immediately weighed, treated with antioxidant (0.1 to 0.4 ml. of the 10% solution of PBNA), and diluted with benzene to a volume of 100 ml. After the weight, and hence the density, of this solution was determined, weighed aliquot portions were carefully evaporated to determine the concentration of polymer in the solution and therefrom the weight of polymer in the fraction.

Various methods of obtaining the fraction free of solvent were tried, including freeze-drying, but all resulted in the formation of insoluble gel, particularly in the first few fractions. Fortunately, a solution of the fraction was all that was necessary for our purpose—intrinsic viscosity determination. When the solution was stored in tightly-stopped containers in the refrigerator no change in the polymer could be detected by intrinsic viscosity determinations, even after several months.

*Viscosity Determinations*

The solution containing the fraction was diluted with benzene to obtain at least three and usually four solutions ranging in concentration from 0.35 to 0.05 gm./100 ml. of solution. The flow time, $t_s$, of each of these solutions was measured with the usual care (7), and values of reduced flow time $(t_r - 1)/c$, and inherent flow time, $(\ln t_r)/c$, calculated (2). The intrinsic flow time $[t]$ was obtained by plotting both of these against concentration and extrapolating to a common point at $c = 0$. Kinetic energy corrections were not applied, but because the flow times for benzene, $t_0$, in the three viscometers were 187.4, 166.2, and 162.5 sec. the difference between values of $[t]$ and of intrinsic viscosity $[\eta]$ will be very small. (Because the fractions were never dried, a small amount of methanol was present in these solutions, even in the solutions obtained by diluting the liquid fractions to 100 ml. The concentration of methanol was, however, never higher than 1.8%—as determined refractometrically—and was usually much lower. Because of this low concentration and because the later dilutions were made with pure benzene, the effect on the intrinsic viscosity would be negligible.)

## RESULTS

After three preliminary fractionations were performed to determine the most suitable procedures, to develop technique, and to acquire experience, careful fractional precipitation was begun from solutions of different concentrations. The first of these fractionations, run 4, was from a solution whose original concentration was 1.92 gm. whole polymer per 100 ml. solution. Fourteen fractions were obtained comprising 97% of the copolymer originally present. Then fractionations from solutions with concentrations of 1.00, 2.03, and 3.66% respectively (runs 5, 6, and 7) were begun. The second of these

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was terminated by accident after four fractions had been obtained and another fractionation (run 8), starting with a concentration of 2.10%, was begun. Because of the pressure of time, none of these fractionations were completed, but they were carried far enough for our purpose since improvements in the efficiency of fractional precipitation will affect principally the first (highest-molecular-weight) fractions.

Table I is a summary of further details regarding these fractionations. The weight of copolymer was calculated from that of the GR-S (whole polymer)

TABLE I

DETAILS OF FRACTIONATIONS

| Run | Concentration of soln. (gm./100 ml. soln.) | | Weight (gm.) | | Proportion ppted. (wt. %) | Number of fractions |
|---|---|---|---|---|---|---|
| | Original | At initial pptn. | GR-S (whole sample) | Copolymer | | |
| 4 | 1.92 | 1.61 | 7.68 | 7.12 | 97.0 | 14 |
| 5 | 1.00 | 0.84 | 3.97 | 3.68 | 73.1 | 15 |
| 6 | 2.03 | 1.71 | 8.04 | 7.45 | 22.1 | 4 |
| 7 | 3.66 | 3.10 | $14.4_4$ | $13.4_3$ | 68.3 | 14 |
| 8 | 2.10 | 1.76 | 8.32 | 7.71 | 42.5 | 8 |

by subtracting 7.34%, the portion soluble in the ethanol–toluene azeotrope. $Q$, the cumulative proportion (% by weight) of copolymer precipitated, is based on this weight. Table II is a materials balance for the completed fraction-

TABLE II

MATERIALS BALANCE—RUN 4

| | Starting material | | | Products | |
|---|---|---|---|---|---|
| | Wt. (gm.) | % (by weight) | | Wt. (gm.) | % (by weight) |
| ETA extractables | 0.56 | 7.34 | Copolymer in fractions | 6.91 | 90.1 |
| Copolymer | 7.12 | 92.66 | Residue | 0.75 | 9.8 |
| | 7.68 | 100.00 | | 7.66 | 99.9 |
| | | | Unaccounted for | 0.02 | 0.1 |
| | | | | 7.68 | 100.00 |

ation. The residue, the portion that could not be precipitated from solution but was recovered on drying, probably consists of the portion extractable with the ETA and copolymer species of very low molecular weight. The remainder of the original sample, a very small proportion, may be attributed to losses in handling fractions or to errors in concentration determinations.

In Table III are recorded data concerning the individual fractions. For each the viscosity-average molecular weight $\bar{M}_v$ was calculated from the intrinsic flow time $[t]$ assuming it to be equal to the intrinsic viscosity $[\eta]$ and using the equation of Scott, Carter, and Magat (18). $Q$ is again the cumulative percentage of copolymer precipitated and $S$ is a corrected $Q$ obtained for each

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TABLE III

EXPERIMENTAL DATA FOR THE FRACTIONS OBTAINED IN FRACTIONAL PRECIPITATIONS FROM SOLUTIONS OF THREE DIFFERENT CONCENTRATIONS

| Run | Original concentration (gm./100 ml.) | Fraction | $[\eta]$ | $\bar{M}_v$ ($\times 10^{-4}$) | $Q$ (%) | $S$ (%) |
|---|---|---|---|---|---|---|
| 4 | 1.92 | 1 | 4.06 | 63.5 | 8.82 | 4.41 |
| | | 2 | 3.74 | 56.0 | 17.26 | 13.04 |
| | | 3 | 3.53 | 51.5 | 20.86 | 19.06 |
| | | 4 | 3.32 | 46.9 | 25.66 | 23.26 |
| | | 5 | 2.98 | 39.9 | 28.99 | 27.33 |
| | | 6 | 2.61 | 32.8 | 33.79 | 31.39 |
| | | 7 | 2.31 | 27.4 | 41.15 | 37.47 |
| | | 8 | 1.94 | 21.1 | 47.11 | 44.13 |
| | | 9 | 1.70 | 17.3 | 54.40 | 50.76 |
| | | 10 | 1.36 | 12.4 | 63.99 | 59.20 |
| | | 11 | 1.07 | 8.7 | 74.00 | 69.00 |
| | | 12 | 0.82 | 5.8 | 83.34 | 78.67 |
| | | 13 | 0.63 | 4.0 | 89.83 | 86.59 |
| | | 14 | 0.42 | 2.1 | 97.02 | 93.43 |
| 5 | 1.00 | 1 | 4.91 | 84.1 | 3.55 | 1.78 |
| | | 2 | 4.83 | 82.0 | 8.53 | 5.99 |
| | | 3 | 4.36 | 70.1 | 12.99 | 10.76 |
| | | 4 | 3.78 | 57.0 | 17.23 | 15.11 |
| | | 5 | 3.72 | 53.8 | 20.74 | 18.98 |
| | | 6 | 3.23 | 45.1 | 24.06 | 22.40 |
| | | 7 | 3.12 | 42.8 | 28.63 | 26.34 |
| | | 8 | 2.86 | 37.5 | 33.64 | 31.14 |
| | | 9 | 2.36 | 27.0 | 39.81 | 36.73 |
| | | 10 | 2.02 | 22.4 | 45.98 | 42.90 |
| | | 11 | 1.68 | 17.0 | 52.15 | 49.07 |
| | | 12 | 1.52 | 14.7 | 57.15 | 54.65 |
| | | 13 | 1.33 | 12.0 | 63.42 | 60.29 |
| | | 14 | 1.13 | 9.4 | 68.75 | 66.09 |
| | | 15 | 0.94 | 7.1 | 73.13 | 70.94 |
| 6 | 2.03 | 1 | 4.24 | 67.6 | 6.70 | 3.35 |
| | | 2 | 4.08 | 64.0 | 12.70 | 9.70 |
| | | 3 | 3.86 | 58.8 | 16.48 | 14.59 |
| | | 4 | 3.42 | 49.1 | 22.07 | 19.28 |
| 7 | 3.66 | 3 | 3.07 | 41.8 | 8.79 | 4.40 |
| | | 2 | 2.97 | 39.8 | 15.21 | 12.00 |
| | | 5 | 2.93 | 39.0 | 21.39 | 18.30 |
| | | 1 | 2.87 | 37.8 | 28.84 | 25.12 |
| | | 4 | 2.81 | 36.7 | 31.83 | 30.34 |
| | | 6 | 2.73 | 35.1 | 36.79 | 34.31 |
| | | 7 | 2.68 | 34.1 | 41.86 | 39.33 |
| | | 8 | 2.48 | 30.5 | 46.00 | 43.93 |
| | | 9 | 2.33 | 27.7 | 50.29 | 48.15 |
| | | 10 | 2.15 | 24.5 | 54.08 | 52.19 |
| | | 11 | 2.08 | 23.4 | 57.99 | 56.04 |
| | | 12 | 1.95 | 21.2 | 62.38 | 60.19 |
| | | 13 | 1.71 | 17.5 | 65.56 | 63.97 |
| | | 14 | 1.61 | 16.0 | 68.33 | 66.95 |
| 8 | 2.10 | 1 | 4.18 | 66.1 | 7.97 | 3.99 |
| | | 2 | 4.03 | 62.5 | 14.99 | 11.48 |
| | | 3 | 3.82 | 57.8 | 21.28 | 18.14 |
| | | 4 | 3.52 | 51.3 | 26.23 | 23.76 |
| | | 5 | 3.18 | 44.0 | 30.37 | 28.30 |
| | | 6 | 3.00 | 40.4 | 34.19 | 32.28 |
| | | 7 | 2.72 | 35.0 | 38.93 | 36.56 |
| | | 8 | 2.47 | 30.3 | 42.46 | 40.70 |
| Whole polymer | | | 2.15 | 24.5 | | |

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fraction by adding half the percentage of copolymer in that fraction to the $Q$ for the preceding fraction. (This procedure is based on the assumptions that the molecular-weight distribution in each fraction is symmetrical and that in any fraction none of the polymer species are of molecular weight greater than the average molecular weight of the fraction next below—or above—it.) It should be noted that the values of $Q$, and therefore of $S$, are calculated in the

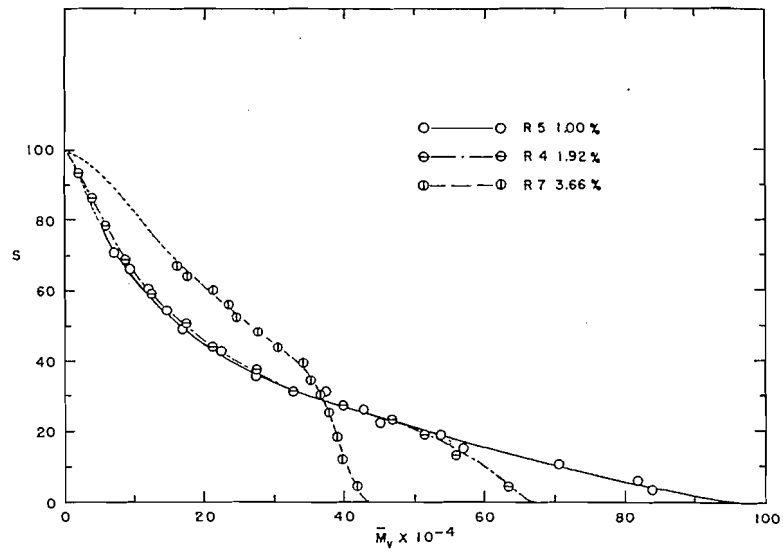



FIG. 1. Integral molecular-weight distributions obtained in fractionations from solutions of three different concentrations. System: GR-S–benzene–methanol.

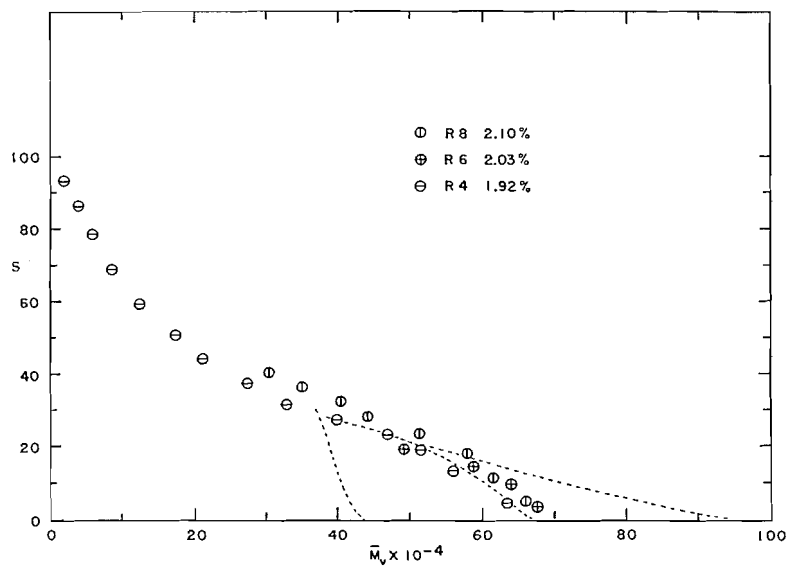



FIG. 2. Integral molecular-weight distributions obtained in three fractionations (two of them incomplete) from 2% solution.

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order of decreasing average molecular weight of the fractions rather than in the order of precipitation of the fraction.

The data of Table III for runs 4, 5, and 7 are plotted in Fig. 1 to give integral molecular-weight distribution curves for the three different concentrations. In Fig. 2 are plotted the data for runs 4, 6, and 8 to show the degree of reproducibility of results attained at one concentration. In Fig. 3 are the

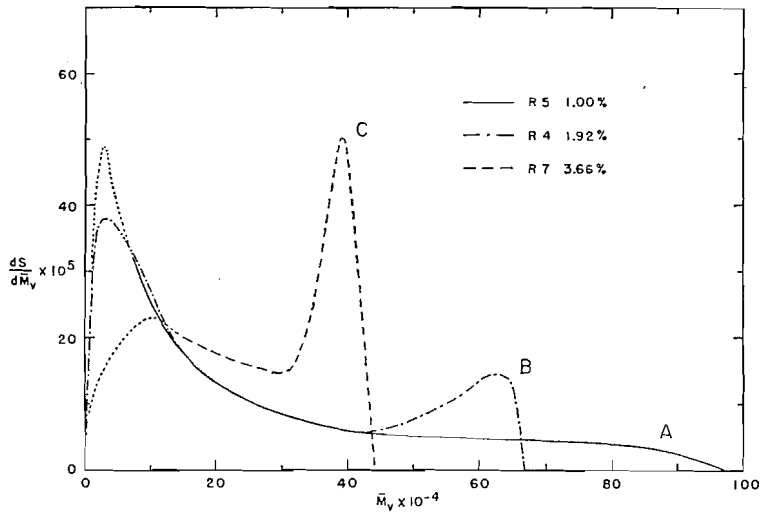



FIG. 3. Differential molecular-weight distribution curves obtained when fractionating at three different initial solution-concentrations.

three differential distribution curves corresponding to the three curves of Fig. 1 and obtained from them by drawing tangents and plotting their slopes, $dS/d\bar{M}_v$. Since only run 4 was completed, each of the other curves in Fig. 1 has been extrapolated, as indicated by the dotted portion in the low-molecular-weight region, to $S = 100\%$. The corresponding portions of the differential curves in Fig. 3 are similarly indicated. (The extrapolations in Figs. 1 and 3 were made having due regard to the usual shape of such curves and to the requirement that the total area under each of the differential distribution curves should be the same. The higher-molecular-weight regions of these curves are the most significant for our purposes; differences in those regions will, of course, be reflected by differences in the remainder of the curves, for low-molecular-weight species that come down in the first fractions cannot come down when they should in the later fractions.)

## DISCUSSION

It is evident from Figs. 1 and 3 that the efficiency of fractionation is considerably affected by the concentration of the solution. The effect is particularly noticeable in the high-molecular-weight range, as would be expected. Fractionation from 1% solution reveals species of molecular weight over 900,000 whereas at 2% and $3\frac{2}{3}\%$ the apparent upper limit of molecular weight is 700,000 and 450,000 respectively.

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*The differences between the distribution curves* in Fig. 1 are much too marked to be attributed to experimental error. As is indicated in Fig. 2 by the scatter of the points (for three runs at about the same concentration) the experimental error is by no means insignificant. But particularly in the high-molecular-weight region where the effects of poor separation will be most evident, these points are much less separated than are the curves of Fig. 1 (reproduced here as dotted lines) for the 1%, 2%, and $3\frac{2}{3}$% runs.

The effect of concentration on efficiency is even more noticeable in the differential distribution curves of Fig. 3. These are, of course, derived from the integral curves of Fig. 1 and therefore their shape depends on the choice of lines drawn through the experimental points of Fig. 1. Nevertheless, the differences between the three curves are too great to be dismissed. The shape of curve A is much as would be expected from theory and very similar to that of distribution curves obtained in careful fractionations of another sample of GR-S (Polymer, lot S-2834) by fractional precipitation (14) and by the so-called "coacervate method" (13). By contrast, there is an unmistakable second peak in curve B (2%) at $\bar{M}_v = 650{,}000$ and a very pronounced one in curve C ($3\frac{2}{3}$%) at $\bar{M}_v = 400{,}000$. These peaks are certainly spurious; they are due to low-molecular-weight species which, precipitating with the high-molecular-weight species, both increase the weight of the top fractions and decrease their viscosity-average molecular weight. As the efficiency of fractionation increases, this peak decreases in height and moves to higher molecular weights. Its near absence in curve A indicates that fractionation from 1% concentration (performed as described above) is efficient enough for all but the most precise work.

*The order of precipitation of the fractions* provides additional evidence of decreased efficiency of fractionation at higher concentrations. From the 1% and 2% solutions the fractions come down in the order of decreasing intrinsic viscosity, as they are supposed to do. But from the $3\frac{2}{3}$% solution the first fraction was third in (decreasing) order of intrinsic viscosity and the subsequent ones were, by this arrangement, numbers 2, 5, 1, and 4. Only with fraction 6 was the normal order attained. (See Table III.)

*The viscosity behavior of the fractions*, too, indicates differences in efficiency. In Fig. 4 are plotted, side by side for purposes of comparison, the inherent viscosity vs. concentration curves for the three fractionations of Fig. 1, i.e., runs 5, 4, and 7. Two different effects are noticeable. One is the increase in intrinsic viscosity for the corresponding top fractions and the resulting widening in the spread of intrinsic viscosities. This is the effect already discussed above, as revealed in distribution curves. The second is almost equally obvious but more difficult to describe. Ordinarily, that is with fractions obtained from a polymer comprised of linear species, the slopes of the lines in such a figure would all conform to the expression $-\beta[\eta]^2$, where $\beta$ is a "slope constant" having the same value over a wide range of molecular weights.*

* *The equation that fits all such lines is that of Mead and Fuoss (15)*

$$(\ln \eta_r)/c = [\eta] - \beta[\eta]^2 c.$$

*This may be compared to the Huggins equation (11)*

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c.$$

*The parameters $\beta$ and $k'$ are related by the equation $k' = 0.50 - \beta$ (8).*

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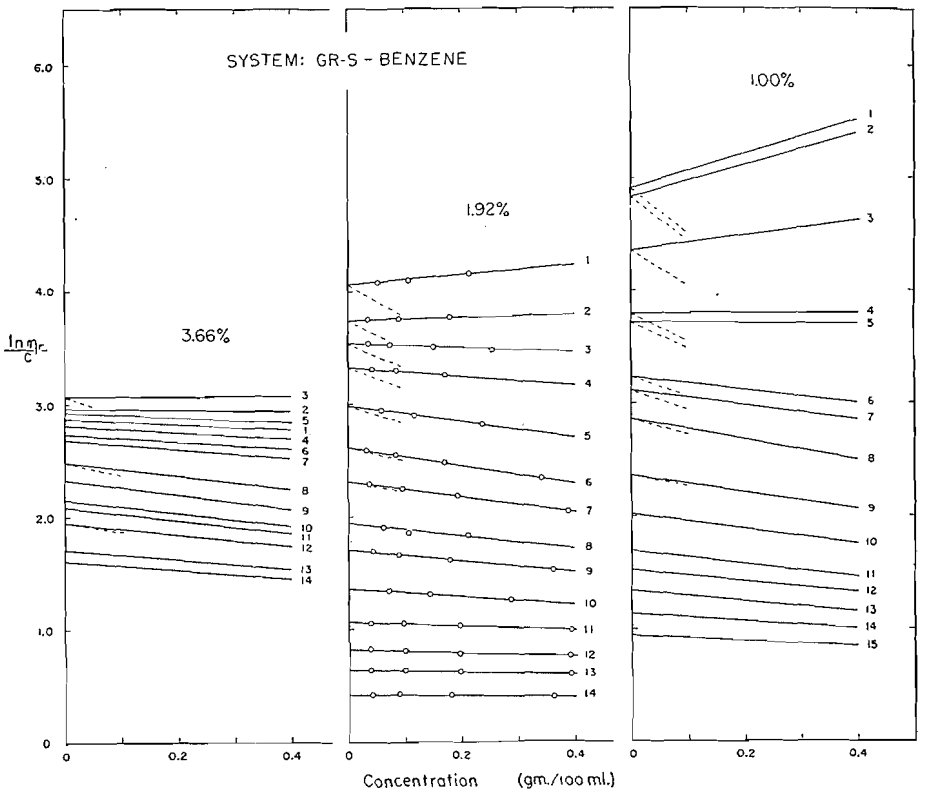



FIG. 4. Inherent viscosity vs. concentration curves for the fractions obtained in the three fractionations at different concentrations. (Actual points are plotted for the 1.92% fractionation to indicate the precision of measurements. Dotted lines indicate the slope corresponding to a constant value of $\beta$ equal to that for the lower fractions.)

This means that at higher and higher intrinsic viscosities the slopes should be more and more negative, as indicated by the dotted lines in Fig. 4. With this polymer, however, the slope becomes more negative, then less and less negative and, finally, positive. This change corresponds to a progressive decrease in $\beta$ (or increase in $k'$). It can be satisfactorily accounted for in terms of branching in the molecules, the degree of branching increasing with molecular weight (for further discussion of this effect, see References 6, 3, 4). The top fraction from the most concentrated solution has both a lower intrinsic viscosity and a less positive slope than the top fraction from the least concentrated solution. This suggests again that in fractionating at higher concentrations the species that are of highest molecular weight—and that are most branched—become more contaminated with species of lower molecular weight and lesser branching. If one compares fractions of approximately equal intrinsic viscosity (#5 at $3\frac{2}{3}$%, #5 at 2%, #8 at 1%), the fraction obtained at the lowest concentration appears to contain the least branching, but this is because here the species that are most highly branched have come down where they should, in the highest fractions. In other words, fractionation is most efficient at the lowest concentration.

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The increased efficiency of fractionation at lower concentrations may be attributed to at least two factors. The first is entanglement. Long randomly-kinked molecules in precipitating are bound to carry shorter molecules down with them. The fractionation procedure is designed to minimize this effect, through redissolving, slow uniform reprecipitating, and long equilibrating, but it cannot be wholly avoided. The effect should be greater with the large molecules (the first fractions), with the more highly branched molecules (the first fractions again), and in higher concentrations.

The second factor is the distribution of polymer species between the two liquid phases. According to theory, low-molecular-weight species will be present in both phases, the highest-molecular-weight species chiefly in the coacervate, and this contamination of the high with the lower will be minimized by making the volume ratio (supernatant liquid to coacervate) as high as practicable. This can be accomplished either by increasing relatively the volume of the supernatant liquid (precipitating the same proportion of polymer from a more dilute solution) or by decreasing relatively the volume of the coacervate (precipitating a smaller proportion of polymer from a solution of the same concentration). In order to obtain the same number of (equal) fractions from a 2% solution as from an equal volume of 1% solution one would have to precipitate coacervates twice as voluminous.* In order to keep the volume ratio the same it would, therefore, be necessary to take twice as many fractions from 2% as from 1% solution. This is all very well in theory; in practice, doubling the concentration makes it much more difficult even to obtain the same number of fractions as before. (For example, in these experiments our aim was to make all fractions about the same weight fraction of the original sample, namely, about 0.04 or 0.05. The data of Table IV indicate that we were successful at 1% and, except for the first two fractions, at 2%; at $3\frac{2}{3}$% the variation in size is much greater. This control of fraction size was

TABLE IV

SIZE OF FRACTIONS OBTAINED (CALCULATED AS WEIGHT FRACTION OF RUBBER IN THE ORIGINAL POLYMER SAMPLE)

| Fraction | $w_x$ | | |
|---|---|---|---|
| | Run 5 (1.00%) | Run 4 (1.92%) | Run 7 (3.66%) |
| 1 | 3.55 | 8.82 | 8.79 |
| 2 | 4.98 | 8.44 | 6.42 |
| 3 | 4.46 | 3.60 | 6.18 |
| 4 | 4.24 | 4.80 | 7.45 |
| 5 | 3.51 | 3.33 | 2.99 |
| 6 | 3.32 | 4.80 | 4.96 |
| 7 | 4.57 | 7.26 | 5.07 |

* *The assumption is made that the concentration of polymer in the coacervate is the same, or very nearly so, in two experiments. Actually, the concentration in the first coacervate from our run 5 ($c$ = 1.00) was 3.9 gm./100 ml. and in the first coacervate of run 4 ($c$ = 1.92) it was 4.1 gm./100 ml.*

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achieved fairly readily at 1%, with difficulty at 2%, and only by exercise of considerable effort, time, and patience at the highest concentration.) Hence, although maintaining the same volume ratio at different concentrations might have revealed less ambiguously the effect of concentration alone, the experiment as we performed it—i.e., taking off equal numbers* of fractions at different concentrations—was better designed to answer the practical question: what is the optimum concentration for convenient and efficient fractionation.

Our conclusions differ markedly from those of Morey and Tamblyn (16). But we believe their conclusions are not justified by their data. In both their fractionations and especially in that of the copolymer, there was noticeably better separation at high molecular weights from the more dilute solution (see Figs. 1 and 2, Reference 16). And this in spite of the fact that in both fractionations they took fewer fractions from the more dilute solution. With the copolymer, 14 fractions were taken from the more concentrated (1.0%) solution and only six from the more dilute one (0.2%), seven fractions being required to precipitate half the polymer from the 1.0% solution but only two fractions to precipitate that proportion of the polymer from the 0.2% solution. Had they taken the same number of fractions at the two concentrations—particularly in the high-molecular-weight region—their distribution curves would probably have indicated an even greater difference in the efficiency of fractionation at the two concentrations.

ACKNOWLEDGMENTS

We wish to express our thanks to Mr. T. H. Murray and Mr. J. A. Manson for their assistance in some of the experimental work and to Mr. G. R. H. Fern for the data of Table V. We are also grateful to Polymer Corporation for providing materials, to the Research Council of Ontario for financial assistance (in the form of a scholarship for D.F.S.), and to the Associate Committee on Synthetic Rubber Research of the National Research Council of Canada for a grant in aid of the research.

* *It may be objected that the decreased efficiency of separation of the two top fractions of run 4 ($c$ = 1.92%) as compared with run 5 ($c$ = 1.00%) may be due in large part to the fact that in run 4 the first two fractions are much larger. However, in runs 4 and 7 ($c$ = 1.92 and 3.66%) the first two fractions are of comparable size and yet the efficiency of separation is still quite different. Moreover, in parallel fractionations of another sample of GR-S from two solutions of concentrations 1% and 2% respectively the difference in the efficiency of separation of the top fractions was about the same as here, even though the relative size (weight fraction) of the fractions was kept the same. See Table V.*

TABLE V

PARTIAL FRACTIONATION OF ANOTHER GR-S SAMPLE FROM 1% AND FROM 2% SOLUTION TAKING FRACTIONS OF (APPROXIMATELY) EQUAL WEIGHT FRACTION

| Fraction | 1% | | 2% | |
|---|---|---|---|---|
| | $w_x$ | $[\eta]$ | $w_x$ | $[\eta]$ |
| 1 | 3.96 | 5.44 | 3.36 | 4.47 |
| 2 | 4.12 | 5.17 | 4.08 | 4.15 |
| 3 | 3.48 | 4.54 | 5.80 | 4.13 |
| 4 | 3.75 | 4.44 | 4.00 | 3.23 |

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## NOTE

### THE OXIDATION OF FERROUS SULPHATE BY $\gamma$-RAYS— THE TEMPERATURE COEFFICIENT OF AIR-SATURATED SOLUTIONS*

By T. J. Hardwick

The effect of temperature on the yield of ferric ion in the radiation-induced oxidation of ferrous sulphate in air-saturated 0.8 *N* sulphuric acid has been neglected by most radiation chemists, although the temperatures at which irradiations have been made range from 12° C. (4) to 25° C. (2). In view of the widespread use of this system in radiation actinometry, it is important to ascertain whether this neglect of temperature corrections is justified.

Previous experimental work on this matter was done by Minder (3), who reported no temperature coefficient, and by Dewhurst (1) who found an activation energy of 900 cal. Minder does not report the lower limits for his experimental results, while Dewhurst used apparatus which gave him considerable deviation from mean values. In view of this disagreement, it was considered worth while to reinvestigate the effect of temperature on the $\gamma$-ray oxidation of ferrous ion in 0.8 *N* sulphuric acid.

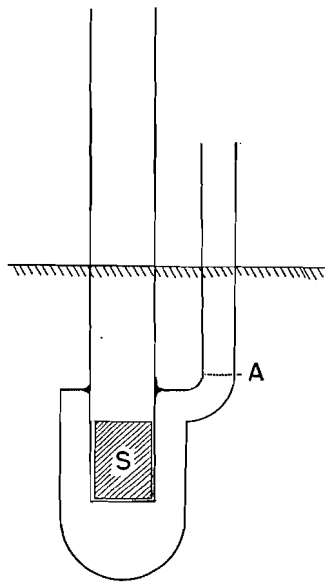



Fig. 1. Irradiation cell.

The apparatus in which the solution was irradiated was a well-type cell shown in Fig. 1. Ferrous sulphate ($10^{-3}$ *M*) in 0.8 *N* sulphuric acid was added to the cell up to the indicated mark *A* (volume = 21 ml.). The cell was then

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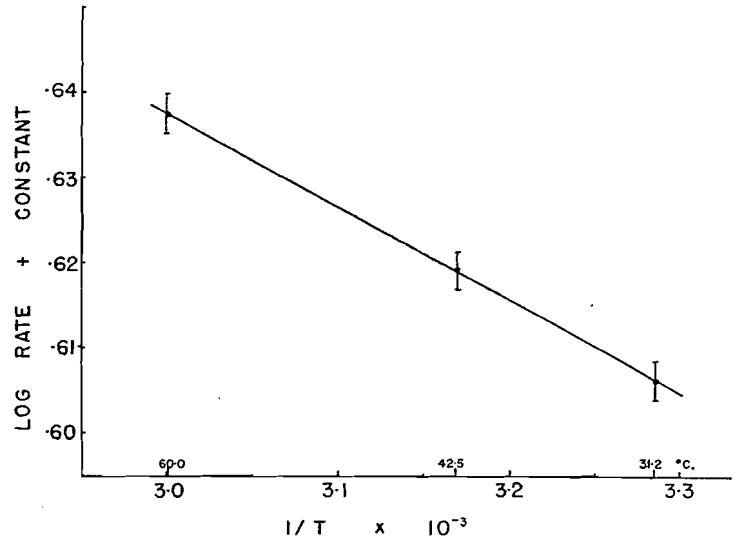



FIG. 2. Plot of log rate of reaction against the reciprocal of the absolute temperature.

immersed in a constant temperature bath to the level shown. When the sample reached bath temperature a 500 mc. $Co^{60}$ source in the form of a right cylinder was dropped into the well. At the end of the irradiation (usually overnight) the source was removed and the solution allowed to come to room temperature before analysis. The amount of oxidation was determined by analysis for ferrous ion, using the *o*-phenanthroline method. At least six runs were made at each temperature.

Unirradiated samples were maintained at each temperature for corresponding periods. Corrections for the thermal reaction (small in all cases) were made to the rates of radiation-induced oxidation. As the $\gamma$-ray absorption per unit volume of 0.8 *N* sulphuric acid decreases with increase in temperature, suitable corrections were applied to the measured rates of oxidation.

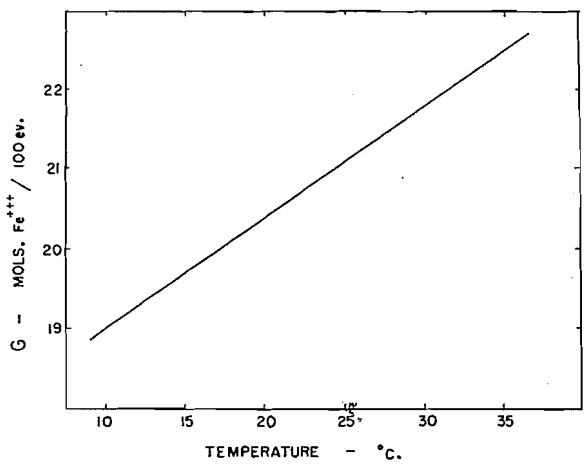



FIG. 3. Values of $G_{Fe^{+++}}$ at various temperatures. ($G$ = 20.4 at 20° C.)

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The results at three temperatures (31.2, 42.5, and 60.0° C.) are shown in Fig. 2. The length of the vertical lines at each temperature indicates the standard deviation. The temperature coefficient calculated from these data is $550 \pm 50$ cal., a value intermediate between that of Dewhurst and that of Minder.

Although small, this temperature coefficient must be considered if this system is used as a radiation actinometer; a difference of 5° C. will result in a 2% change in rate. In Fig. 3 the yield of ferric ions is plotted as a function of temperature, assuming $G = 20.4$ mols./100 ev. at 20° C. On the other hand, the magnitude of this temperature coefficient is such that it is difficult to assign it to any of the processes which occur during the $\gamma$-ray-induced oxidation of ferrous ion.

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# THE NITRATION OF 2-NITRAMINOTHIAZOLES AND 2-ACETAMIDOTHIAZOLES[1]

BY SILVIO J. VIRON[2] AND ALFRED TAURINS

## ABSTRACT

It has been shown by nitration with a mixture of 99–100% nitric acid and acetic anhydride that 2-nitraminothiazoles, such as 2-nitramino-5-nitrothiazole and 4-methyl-2-nitramino-5-nitrothiazole, can react in the tautomeric nitrimino form. The nitration occurs in the three position of the thiazole ring. Compounds with an acetamido group in the two position of the thiazole ring, such as 2-acetamido-5-bromo-2-thiazole and 2-acetamido-5-methylthiazole, can also be nitrated in the three position indicating the tautomeric change from the acetamido to the acetimido group.

## INTRODUCTION

Studies on nitration of 2-amino- and 2-acetamidothiazoles have been reported by several authors. Babo and Prijs (1) investigated the nitration of 2-aminothiazole. If the reaction is allowed to proceed for 12 hr., the nitration occurs in the amino group as well as in the five position, giving 2-nitramino-5-nitrothiazole (I).

Ochiai and Nagasawa (10) reported the nitration of 2-amino-4-methylthiazole which was prepared by the method of Dodson and King (3) to 4-methyl-2-nitramino-5-nitrothiazole (II). Nagasawa (9) prepared 2-amino-5-methylthiazole from 2-bromopropionaldehyde diethyl acetal and thiourea. An attempted nitration of this compound was unsuccessful. The nitration of 2-acetamido-5-methylthiazole (IV) gave a small yield of 2-acetamido-5-methyl-4-nitrothiazole.

The nitration of 2-acetamidothiazole was described by Ganapathi and Venkantaraman (5) who used a mixture of sulphuric and nitric acid at 10° to obtain 2-acetamido-5-nitrothiazole (V). The hydrolysis of (V) gave 2-amino-5-nitrothiazole, which could be also obtained by the nitration of 2-aminothiazole at low temperature.

Bellavita (2) showed that ethyl nitrate could be used as a nitrating agent for these compounds. Both 2-aminothiazole and 2-amino-4-methylthiazole

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*Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Que., with the financial assistance of the National Research Council of Canada, Ottawa.*
*Presented before the 36th Annual Conference of the Chemical Institute of Canada, June 5, 1953, Windsor, Ont.*
[2] *Holder of a National Research Council Studentship 1951—1952.*

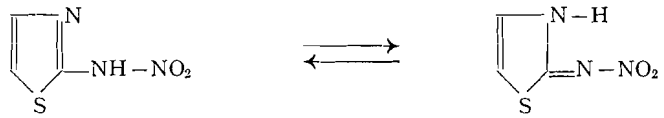
were nitrated in the five position to give 2-amino-5-nitrothiazole and 2-amino-4-methyl-5-nitrothiazole.

The same author found that nitration of 2-acetamidothiazole and 2-acetamido-4-methylthiazole with ethyl nitrate gave 2-acetamido-5-nitro derivatives. The nitration of 2-acetamido-5-bromothiazole (III) resulted in the replacement of halogen by a nitro group as it was observed by Hurd and Wehrmeister (7) who obtained 2-acetamido-5-nitrothiazole. Similar replacement of bromine atoms by nitro groups has been observed in thiophene series (6).

The objective of this work was to study the further nitration of 2-nitramino-5-nitrothiazoles to obtain evidence of the existence of the tautomeric nitrimino forms of these compounds. Similarly, the nitration of 2-acetamidothiazoles was studied to prove the existence of the tautomeric acetimido forms.

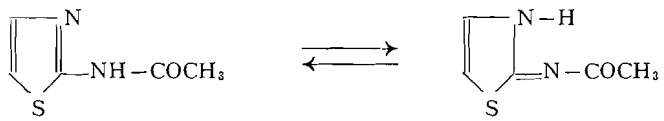
## DISCUSSION

The structure of 2-nitraminothiazole can be visualized in two tautomeric nitramino (A) and nitrimino (B) forms.




(A) (B)

Similarly, 2-acetamidothiazole can undergo the tautomeric change between acetamido (C) and acetimido (D) structures.




(C) (D)

The nitration of these compounds can occur in the position three only if the entering nitro group replaces the hydrogen atom which is attached to the ring nitrogen atom in the indicated position, in other words, if these compounds react in their nitrimino or acetimido forms.

*Nitration of 2-Nitraminothiazoles*

The nitration was carried out with a mixture of 99–100% nitric acid and acetic anhydride at temperatures between 0 and 5°. The original compounds (I) and (II) dissolved in the nitration mixture and new compounds precipitated after a short time.

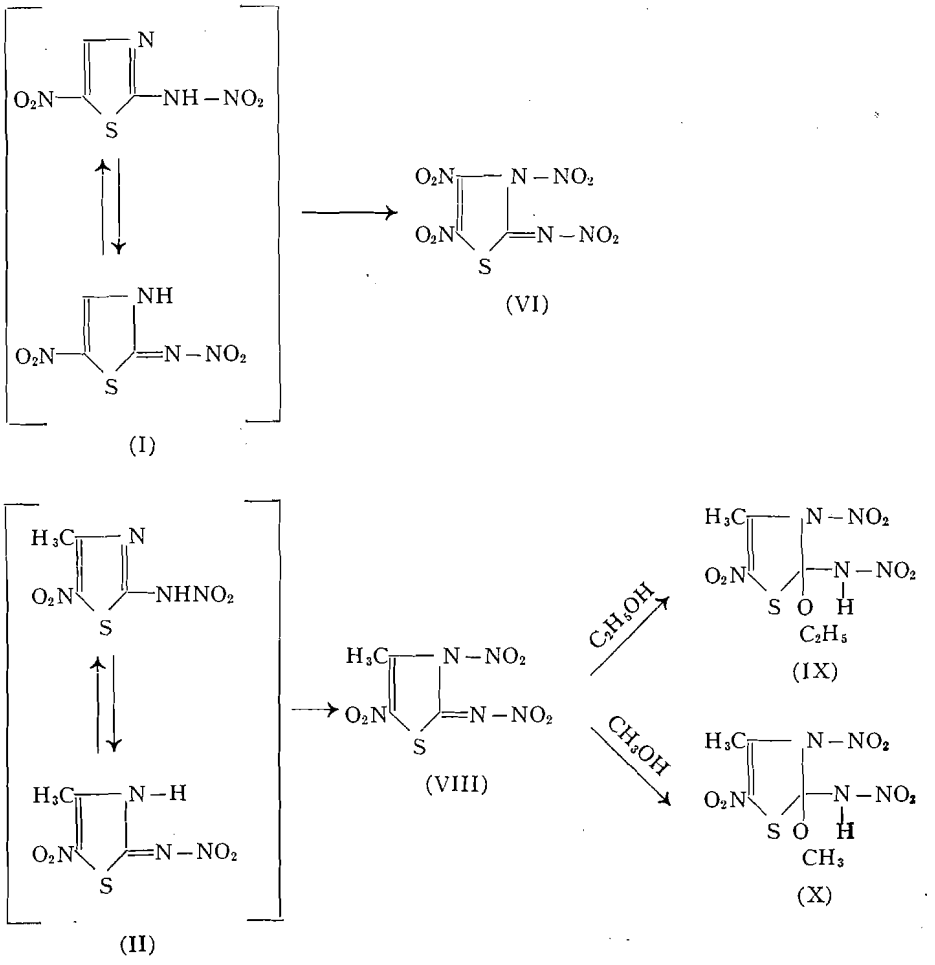
The isolation of the reaction product met with some difficulties. If the nitration product from (I) was allowed to stand after filtration without removal of the acid by washing it turned rather gummy in approximately fifteen minutes and then exploded. The best results were obtained if the product was washed well with glacial acetic acid. The recrystallization from benzene gave white crystals melting at 121–123°. Analysis of the nitration product

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indicated that it contained three nitro groups in the thiazole ring, and could be named as 2-nitramino-3,4,5-trinitro-2-thiazolone (VI). It seems that the unusually high accumulation of nitro groups in (VI) is responsible for its unstability. Attempts to prepare derivative with alcohol failed, because the product was an oil which decomposed readily. The compound (VI) was obtained by another method, namely, the nitration of 3,4-dinitro-2-thiazolimine, which will be discussed later.

The nitration product from (II) had better properties. After filtration, washing with glacial acetic acid, and drying, the new product melted at 89° with decomposition. Attempts to recrystallize this compound from benzene, ethyl acetate, or nitromethane failed owing to the decomposition. When the product was added to ethyl alcohol, it went into solution immediately. The addition of water precipitated a compound melting at 136° with decomposition. This product could be recrystallized from benzene or by solution in ethyl

CHART I




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alcohol, filtration, and precipitation by the addition of water. The analysis of this compound conformed to the structure for 3,5-dinitro-2-ethoxy-4-methyl-2-nitramino-$\Delta^4$-thiazoline (IX). It has been concluded that the original nitrated compound was 3,5-dinitro-4-methyl-2-nitrimino-2-thiazolone (VIII), which has added a molecule of ethanol to form (IX). The similar addition was found to occur when methanol was used in place of ethanol. The methanol derivative had a melting point 132°. It could be recrystallized from benzene or by solution in methanol followed by reprecipitation with water. The analytical data fitted the structure for 3,5-dinitro-2-methoxy-4-methyl-2-nitramino-$\Delta^4$-thiazoline (X).

The foregoing results are similar to those obtained by McKay and Wright (8) for the reaction of alcohols on 1-nitro-2-nitramino-$\Delta^2$-imidazoline to form 2-alkoxy-2-nitramino-1-nitro-$\Delta^2$-imidazoline.

The procedure of Babo and Prijs (1) for nitration of 2-aminothiazole to 2-nitramino-5-nitrothiazole was found unsatisfactory, since the step involving the pouring of the reaction mixture onto ice causes partial decomposition. The yield of (I) was greatly improved and a purer product obtained if the excess nitric acid was decomposed by the careful addition of absolute ethanol until gassing had ceased. Extreme caution must be observed in the addition of alcohol. If the alcohol is added too quickly or the temperature is allowed to rise above 40°, the mixture may froth over. After the excess acid had been decomposed, the mixture was poured onto crushed ice with the separation of a good yield of almost pure 2-nitramino-5-nitrothiazole.

*Nitration of 2-Acetamidothiazoles*

We nitrated 2-acetamido-5-bromothiazole with a mixture of 99–100% nitric acid and acetic anhydride.

2-Acetamido-5-bromothiazole (III) was prepared by first brominating 2-aminothiazole in glacial acetic acid followed by the acetylation of acetic anhydride of the compound obtained as described by Erlenmeyer and Kiefer (4). The nitration of (III) with 99–100% nitric acid in acetic anhydride yielded a compound which after the filtration must be washed well with glacial acetic acid to prevent the decomposition. After isolation the product was dried in a vacuum desiccator. Recrystallization of this compound from benzene yielded white needle-like crystals, which melted at 119–120°. The analysis of the substance conformed to the structure of 2-acetamido-5-bromo-3,4-dinitro-2-hydroxy-$\Delta^4$-thiazoline (XII) which was preceded by the intermediate 2-acetimido-5-bromo-3, 4-dinitro-2-thiazoline (XI). In this nitration reaction the bromine atom was not replaced as has been observed in other similar cases. Thus Hurd and Priestley (6) reported that red fuming nitric acid and acetic anhydride replaced the bromine atoms in 2-acetamido-3,5-dibromothiophene.

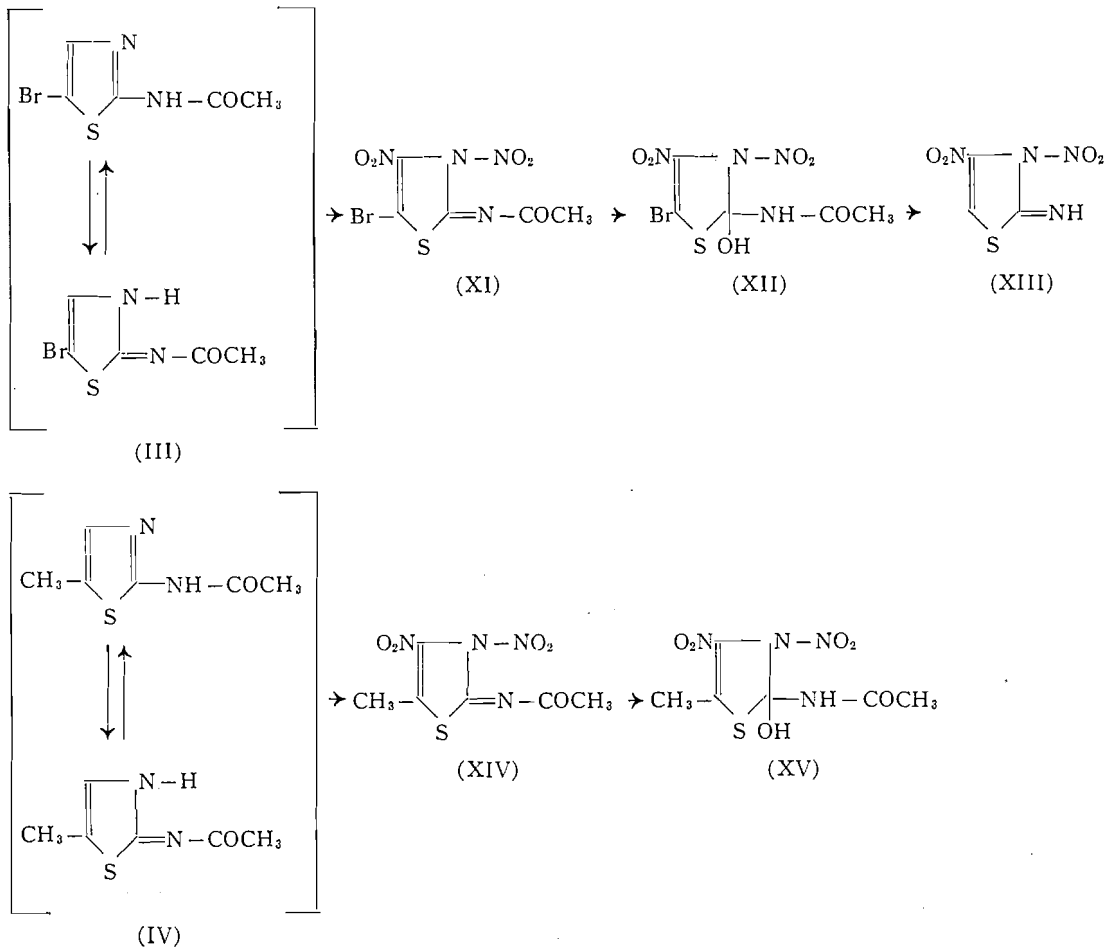
(XII) was easily hydrolyzed by boiling water. It was refluxed with water until complete solution, filtered hot, and then allowed to cool. As the solution cooled it deposited long yellow needles. This compound after recrystallization from water had a melting point of 172° (exploded), showed a negative test for bromine, and analyzed for 3,4-dinitro-2-thiazolinimine (XIII).

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CHART II



The nitration of 3,4-dinitro-2-thiazolinimine in 99–100% nitric acid and acetic anhydride yielded (VI), m.p. 121–122°, recrystallized from benzene. A mixed melting point with a sample of (VI) obtained by nitration of 2-nitramino-5-nitrothiazole showed no depression. The compound was easily decomposed by water and alcohol.

2-Amino-5-methylthiazole was prepared according to Nagasawa (9) and acetylated with acetic anhydride to obtain 2-acetamido-5-methylthiazole (IV). The reaction of (IV) with 99–100% nitric acid and acetic anhydride was allowed to proceed for 20 hr. at room temperature. The mixture was then poured onto crushed ice with the separation of a viscous substance. After decantation of the solution followed by trituration of the viscous produce with ethanol, a crystalline compound was obtained. It was recrystallized from ethyl acetate and benzene, and obtained in white crystals, m.p. 151.5–152°. The analysis conformed to the structure for 2-acetamido-3,4-dinitro-2-hydroxy-5-methyl-$\Delta^4$-thiazoline (XV). It is very probable that it was formed by the addition of a molecule of water to the nitration product (XIV).

The nitration of 2-acetamidothiazole with 99–100% nitric acid and acetic anhydride under the conditions described for (III) gave the same product 2-acetamido-5-nitrothiazole, m.p. 264–265°, as obtained by nitration of 2-acetamidothiazole with a nitric–sulphuric acid mixture (5).

## EXPERIMENTAL

*Preparation of 2-Nitramino-5-nitrothiazole* (I)

A solution of 10 gm. of 2-aminothiazole in 7 ml. of concentrated sulphuric acid was added to a mixture of 14 ml. of 90–95% nitric acid and 7 ml. of concentrated sulphuric acid with stirring at the temperature of 0–5°. The reaction mixture was stirred for two hours at this temperature range. Absolute alcohol was added drop by drop to decompose the excess nitric acid. Extreme care must be taken during this addition. The temperature must not be allowed to rise above 20 and the ethyl alcohol must not be added too quickly, otherwise the mixture may froth over. The ethanol was added until no further gassing was observed and then the mixture was poured onto 25 gm. of crushed ice. In this manner 9.1 gm. of almost pure 2-nitramino-5-nitrothiazole was obtained, melting at 167° (exploded).

*Nitration of 2-Nitramino-5-nitrothiazole* (I)

The following procedure was used for nitration of 2-nitraminothiazoles and 2-acetamidothiazoles.

Seven milliliters of acetic anhydride were added dropwise with stirring at 5° to 3 ml. of 99–100% nitric acid contained in a 125 ml. three-necked flask provided with a thermometer, mechanical stirrer, and dropping funnel. To this nitration mixture 5 gm. of (I) were added portionwise with stirring at such a rate that the temperature remained below 5°. The solid dissolved in approximately five minutes and after 30 min. the mixture started to become turbid. In a few minutes the mixture became semisolid.

Five milliliters of glacial acetic acid was added to make the mixture more

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fluid and stirring continued for an additional two hours. The mixture was then filtered and the product washed well with glacial acetic acid. The white crude product after drying weighed 5.45 gm. It could be recrystallized from either glacial acetic acid or benzene to obtain white crystals of (VI) melting at 121–123° (decomp.). The crystals decomposed slightly on longer standing with evolution of brown nitrogen dioxide.

Anal. calc. for $C_3N_6O_8S$: C, 12.87%.

Found: C, 12.68%.

*Preparation of 4-Methyl-2-nitramino-5-nitrothiazole* (II)

Five grams of 2-amino-4-methylthiazole was dissolved in 7 ml. of concentrated sulphuric acid, with cooling, and this solution added slowly to the nitrating mixture (at 5°) consisting of 7 ml. of fuming nitric acid and 7 ml. of concentrated sulphuric acid. Stirring was continued for an additional four hours after complete addition. The excess nitric acid was decomposed by slow addition of absolute alcohol below 20° and the mixture was poured onto 20 gm. of crushed ice; 4.8 gm. (69.0%) of 4-methyl-2-nitramino-5-nitrothiazole was obtained. The substance was recrystallized from glacial acetic acid and obtained in the form of yellow plates; m.p. 184–185° (decomposition). The reported melting point of (II) is 185° (10).

*Nitration of 4-Methyl-2-nitramino-5-nitrothiazole* (II)

To a nitrating mixture consisting of 1.5 ml. of 99–100% nitric acid and 3.5 ml. of acetic anhydride, 5 gm. of (II) was added portionwise with stirring at 5°. The mixture was stirred for two hours at this temperature. During this time the original had dissolved and a new product precipitated. Three milliliters of glacial acetic acid was added to facilitate stirring and the temperature was allowed to rise to 20°. The reaction mixture was allowed to stand without stirring for 10 hr. at room temperature. The white solid product (VIII) was collected on a filter, dried, and weighed (2.1 gm.); m.p. 98° (exploded). Many attempts to purify this substance were unsuccessful. When the nitrocompound was warmed with solvents such as benzene, ethyl acetate, or glacial acetic acid, brown fumes of nitrogen dioxide were liberated.

(*a*) *Ethanol Derivative of the Nitration Product*:

*3,5-Dinitro-2-ethoxy-4-methyl-2-nitramino-$\Delta^4$-thiazoline* (IX)

A portion of the nitration product (VIII) was dissolved in ethanol. Water was added to the solution to precipitate a white solid. After two recrystallizations from ethanol and the addition of water, it melted at 141–142° with gassing.

Anal. calc. for $C_6H_9N_5O_7S$: C, 24.39; H, 3.05%.

Found: C, 24.52; H, 3.11%.

(*b*) *Methanol Derivative of the Nitration Product*:

*3,5-Dinitro-2-methoxy-4-methyl-2-nitramino-$\Delta^4$-thiazoline* (X)

In a similar manner a new product was obtained by dissolving (VIII) in methanol and precipitating with water. Two recrystallizations from methanol

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by addition of water gave a product melting at 133–134°, with gassing.

Anal. calc. for $C_5H_7N_5O_7S$: C, 21.36; H, 2.84%.

Found: C, 21.50; H, 3.03%.

*Preparation of 2-Acetamido-5-methylthiazole* (IV)

Four grams of 2-amino-5-methylthiazole (9) was dissolved in 25 ml. of glacial acetic acid and 10 ml. of acetic anhydride. After the mixture had stood for two hours crystals started to separate. The mixture was allowed to stand for five hours, and then diluted with 50 ml. of water with the separation of 5.2 gm. (94%) of 2-acetamido-5-methylthiazole, m.p. 225°.

*Nitration of 2-Acetamido-5-methylthiazole* (IV)

Five grams of (IV) were nitrated with a mixture of 5.3 ml. of 99–100% nitric acid and 13 ml. of acetic anhydride at 0–5°. The mixture was allowed to stand at room temperature for 20 hr., and then poured onto 10 gm. of crushed ice with a separation of viscous substance. After trituration of the gummy mass with 2 ml. of ethanol a crystalline product was formed (1.4 gm.; 13%). Recrystallization was effected by dissolving the product in warm ethyl acetate, filtering it, and adding benzene. The substance (XV) melted at 151.5–152°.

Anal. calc. for $C_6H_8N_4O_6S$: C, 27.27; H, 3.03; N, 21.21%.

Found: C, 27.59; H, 2.99; N, 21.03%.

*Nitration of 2-Acetamido-5-bromothiazole* (III)

Five grams of (III) were nitrated with a mixture of 5.5 ml. of 99–100% nitric acid and 13.2 ml. of acetic anhydride at 0–5°. The solid dissolved in a few minutes and after 10 min. a new product precipitated. Five milliliters of glacial acetic acid was added to make the mixture more fluid. It was allowed to stand for two hours at 20°. The product was filtered, washed with glacial acetic acid, and pressed as dry as possible. The yield was 3.7 gm. Two recrystallizations from benzene yielded white needlelike crystals (XII), m.p. 119–120°.

Anal. calc. for $C_5H_5N_4O_6BrS$: H, 1.22; N, 17.02%.

Found: H, 1.58; N, 16.58%.

*3,5-Dinitro-2-thiazolinimine* (XIII)

One gram of (XII) was added to 5 ml. of water and the mixture refluxed for 30 min. During this period the solid dissolved and the solution took on a distinct yellow color. The solution was filtered hot and allowed to cool. While cooling, the solution deposited long needlelike crystals weighing 0.6 gm. Some of these crystals were as long as 2 cm. in length. The product melted at 172° (exploded) and the melting point did not change after one recrystallization. The same compound could be obtained by refluxing the original nitrated product with either ethanol or *n*-propanol.

Anal. calc. for $C_3H_2N_4O_4S$: C, 18.95; H, 1.05; N, 29.46%.

Found: C, 19.20; H, 1.69; N, 29.46%.

*Nitration of 3,5-Dinitro-2-thiazolinimine* (XIII)

To 0.6 ml. of nitric acid (99–100%) contained in a test tube, cooled to 0°, was added dropwise 1.5 ml. of acetic anhydride. To the nitrating mixture,

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1.0 gm. of (XIII) was added at such a rate that the temperature did not rise above 5° while the mixture was being cooled in an ice–salt bath. On being shaken, the solid dissolved slowly. The mixture was then allowed to stand for two hours at 0° with occasional shaking. After this time crystals had separated which after filtration and drying weighed 0.6 gm. After two recrystallizations from benzene, the substance melted at 123° (decomposition).

The product appeared to be the same as the compound (VI) obtained from the nitration of 2-nitramino-5-nitrothiazole (I). The compound was decomposed by water and alcohols, and produced a deep red coloration with alkalies. A mixed melting point with a sample of (VI) obtained by nitration of (I) showed no depression.

*2-Acetamido-5-nitrothiazole*

Four grams of 2-acetamidothiazole was nitrated with a mixture of 2.2 ml. nitric acid (99–100%) and 5.3 ml. acetic anhydride with constant stirring at 0–5°. After complete addition, the mixture was allowed to stand for five hours at 20°, during which time the product had separated. The product was collected on a filter and dried. The weight of crude 2-acetamido-5-nitrothiazole was 1.6 gm., melting at 264–265°. The filtrate was poured onto 10 gm. of crushed ice with the separation of more of the nitration product, weighing 0.8 gm. The over-all yield of it was 2.4 gm. (45.5%).

ACKNOWLEDGMENT

The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

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# THE ALKALOIDS OF *LYCOPODIUM* SPECIES

## XIII. *LYCOPODIUM DENSUM* LABILL.[1]

By R. H. F. Manske

ABSTRACT

*Lycopodium densum* has yielded lycopodine and two apparently new alkaloids, L34, $C_{16}H_{25}O_2N$, and L35, $C_{14}H_{21}ON$. The total alkaloid content of the plant was less than 0.1%.

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The alkaloid lycopodine has always been observed as one of the constituents of *Lycopodium* from the northern hemisphere but thus far it has not been isolated from a *Lycopodium* of southern origin (2). It is of course unlikely that the geographic distribution of these plants is a major factor in determining their alkaloid content. An examination of *Lycopodium densum* Labill. of New Zealand origin has now disclosed the presence of lycopodine and two other alkaloids, L34, $C_{16}H_{25}O_2N$, and L35, $C_{14}H_{21}ON$. Undoubtedly other alkaloids are elaborated by this plant but since the total alkaloid content was only 0.07% there was inadequate material for a more complete examination. Nicotine was not detected.

## EXPERIMENTAL

The dried plant material which weighed 2365 gm. was received from Dr. L. B. Moore, Botany Division, Department of Scientific and Industrial Research, Wellington, New Zealand.

### *Alkaloid L34*

The crude alkaloid (1) was subjected to slow distillation from a bulb tube in an air oven. Only two distinct fractions were obtained,—120–135° at 0.3 mm. and 165–170° at 0.3 mm.

The second fraction crystallized with great facility. It was washed with ether, dissolved in a large volume of boiling acetone, the solution concentrated to a small volume, and then treated with ether. The stout, well developed prisms of alkaloid L34 which then separated melted sharply at 236°*. Found: C, 72.62; H, 9.25; N, 4.99%. Calc. for $C_{16}H_{25}O_2N$: C, 73.00; H, 9.51; N, 5.32%.

### *Alkaloid L35*

The fraction of lower boiling point which was partly crystalline was washed with ether and recrystallized twice from the same solvent. Alkaloid L35 thus obtained consisted of stout, colorless polyhedra which melted at 133°. Found: C, 76.58, 76.46; H, 9.82, 9.84; N, 6.00, 5.74%. Calc. for $C_{14}H_{21}ON$: C, 76.71; H, 9.59; N, 6.39%.

[1] *Manuscript received May 22, 1953.*
*Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ont.*

**All melting points are corrected.*

*Lycopodine*

The solvent was removed from mother liquors resulting from the purification of alkaloid L35 and the residue extracted with several portions of boiling hexane. The somewhat concentrated extract, on being seeded with lycopodine, deposited this base in colorless crystals which melted at 116° either alone or in admixture with lycopodine.

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# ULTRAVIOLET ABSORPTION SPECTRA OF ARYL SUBSTITUTED UREAS[1]

By J. P. Picard[2] and A. F. McKay[3]

ABSTRACT

Absorption spectra of a number of substituted aryl- and *sym*-diarylureas have been determined in ethanol. As conjugation in the chromophores increased, a gradual displacement of the maxima of the conjugative absorption band towards the visible occurred. This displacement was accompanied by a progressive increase in intensity of absorption. The effect on the absorption spectra of replacing hydrogen of the aryl substituents by alkoxy, methyl, or halogeno groups is discussed. A relationship between the inductive effect of these groups and their influence on the absorption spectra is indicated.

## INTRODUCTION

The ultraviolet absorption spectra of a small number of arylureas have been reported (4, 6, 14, 15) in the literature. Schroeder *et al.* (14) have measured the ultraviolet absorption spectra of 26 arylureas. They were interested in the use of these spectra for the identification of stabilizers as well as the identification of their transformation products formed during the aging of propellants. Their data on the two arylureas, *sym*-diphenylurea and 1-ethyl-3-phenylurea, which are reported also in this paper, are in good agreement with the present studies.

Grammaticakis (4, 6) has reported the ultraviolet absorption spectra of a few arylureas in his investigation of the effect of ortho substituents on the absorption of N-alkyl, N-acyl, and N-carbamyl derivatives of arylamines and Stuckey (15) has reported the ultraviolet absorption spectrum for cinnamylurea. These investigations have been extended to include a large number of arylureas in an attempt to correlate their ultraviolet absorption spectra with structural changes.

## GENERAL DISCUSSION OF ULTRAVIOLET ABSORPTION SPECTRA OF ARYLUREAS

The arylureas in ethanol exhibit two absorption maxima in the middle ultraviolet region (220–400 m$\mu$). Maximum I of low intensity (benzenoid absorption) is closer to the visible end of the spectrum than maximum II (conjugative absorption) of high intensity. A third maximum would be expected below 220 m$\mu$ owing to ethylenic absorption but this region of the spectrum was not investigated in the present studies.

Benzene possesses absorption maxima of low intensities (7) (cf. Fig. 1) and




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the canonical structures I and II are considered contributing forms to this absorption. When one of the hydrogens of benzene is replaced by $NH_2$ to give aniline, conjugation of the free electron pair of the nitrogen with the benzene

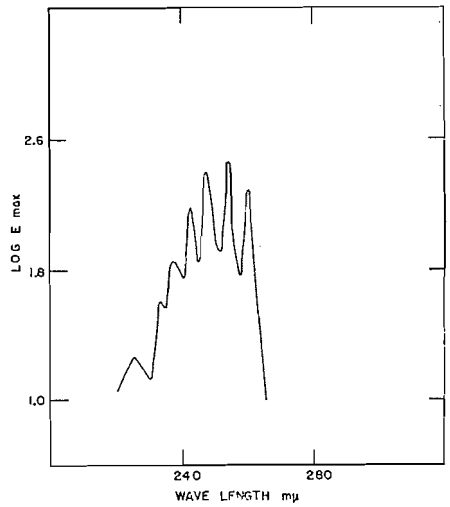
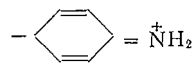
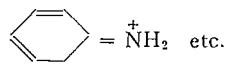



FIG. 1. Benzene.

nucleus can occur. This conjugation causes an appearance of a new absorption maximum at 232 m$\mu$ ($E_{max}$ 8300) along with an increase in intensity of absorption in the vicinity of the other maxima (benzenoid absorption). The latter absorption has a maximum at 280 m$\mu$ with a molar extinction coefficient of 1570 (8) (Curve *A*, Fig. 2). Contributing forms to this absorption are III and IV etc.

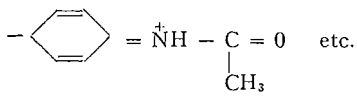


III



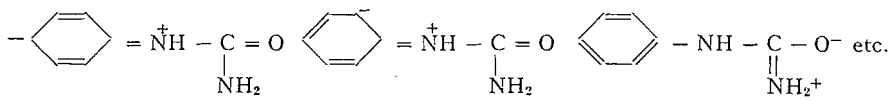
IV

A further extension of the conjugative systems occurs in acetanilide (5) as shown in electronic structures V etc.



V

Acetanilide has absorption maxima at 277 (shoulder) and 240 m$\mu$ (Curve *B*, Fig. 2). Thus maximum II has increased in intensity and undergone a batho-



VI VII VIII

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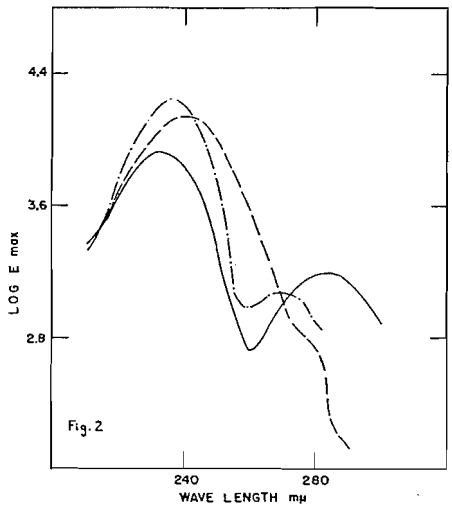



FIG. 2. Curve *A* —— Aniline.
Curve *B* – – Acetanilide.
Curve *C* – · – Phenylurea.

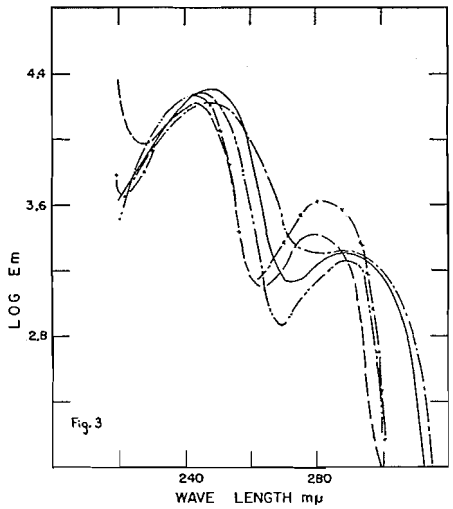



FIG. 3. Curve *A* —— 1-*p*-Phenetyl-2-imidazolidone.
Curve *B* – · – 2-*p*-Phenetylamino-2-oxazoline
Curve *C* – ·· – 2-*p*-Phenetyl-3-ethylurea.
Curve *D* – – 1-*m*-Phenetyl-3-ethylurea.
Curve *E* – x – 1-*o*-Phenetyl-3-ethylurea.

chromic shift of 8 m$\mu$. If the methyl group of acetanilide is replaced by an amino group to give an arylurea, a slight hypsochromic shift in the wave lengths of the absorption maxima (cf. phenylurea, Ref. 14 and Curve *C*, Fig. 2) occur. There is also a small increase in $E_{\max II}$. It is apparent from the canonical forms VI, VII, VIII etc., which would be considered as participating in the absorption, that there is little or no extension of conjugation over that existent in acetanilide. It is considered that the effect of structure VIII and similar struc-

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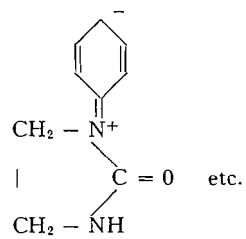
tures on absorption is unimportant relative to forms VI and VII. Table I shows that the monoarylureas have maxima at 240–249 mμ and 270–292 mμ. If cyclic ureas, e.g., ethyleneurea, are substituted on one of the nitrogens with an aryl group then the ultraviolet absorption maxima of these derivatives occur at

TABLE I

ABSORPTION SPECTRA OF ARYLUREAS
WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

| Compound | $\lambda_{max\ I}$, mμ | log $E_{max\ I}$ | $\lambda_{max\ II}$, mμ | log $E_{max\ II}$ |
|---|---|---|---|---|
| 1-Phenyl-3-ethylurea | 275 | 3.02 | 240 | 4.30 |
| 1-*p*-Tolyl-3-ethylurea | 281 | 3.11 | 243 | 4.37 |
| 1-*m*-Tolyl-3-ethylurea | 275 | 3.03 | 240 | 4.24 |
| 1-*o*-Tolyl-3-ethylurea | 270 | 2.90 | 240 | 4.08 |
| 1-*p*-Chlorophenyl-3-ethylurea | 284 | 3.12 | 248 | 4.40 |
| 1-*m*-Chlorophenyl-3-ethylurea | 282 | 3.09 | 246 | 4.25 |
| 1-*o*-Chlorophenyl-3-ethylurea | 280 | 3.12 | 242 | 4.30 |
| 1-*p*-Bromophenyl-3-ethylurea | | Inflection | 249 | 4.42 |
| 1-*p*-Anisyl-3-ethylurea | 292 | 3.23 | 244 | 4.25 |
| 1-*o*-Anisyl-3-ethylurea | 282 | 3.64 | 242 | 4.25 |
| 1-*p*-Phenetyl-3-ethylurea | 291 | 3.27 | 245 | 4.30 |
| 1-*m*-Phenetyl-3-ethylurea | 280 | 3.44 | 242 | 4.22 |
| 1-*o*-Phenetyl-3-ethylurea | 282 | 3.63 | 242 | 4.27 |
| 1-*p*-Tolyl-3-β-chloroethylurea | 280 | 2.98 | 243 | 4.26 |
| 1-*p*-Anisyl-3-β-chloroethylurea | 288 | 3.24 | 243–245 | 4.24 |
| 1-*p*-Phenetyl-3-β-chloroethylurea | 285 | 3.22 | 245 | 4.27 |
| 1-*p*-Tolylurea | 280 | 2.97 | 240 | 4.22 |
| 1-*p*-Anisylurea | 289 | 3.23 | 243 | 4.21 |
| 1-*p*-Phenetylurea | 289 | 3.21 | 241–243 | 4.23 |

about the same wave lengths as the corresponding monoarylureas. This is to be expected because the electronic structures (IX) contributing to absorption in the cyclic aryl substituted areas possess the same conjugative




IX

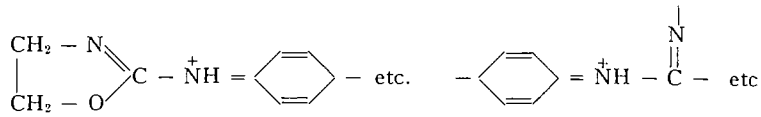
system (X) (chromophore) as the arylureas and as acetanilide. Furthermore




X

examination of the 2-arylamino-2-oxazolines (XI) discloses the participation of chromophores (XII) similar to XI in the absorption of these compounds.

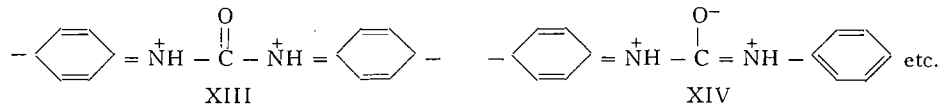
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XI XII

The exchange of O in chromophore X for N in chromophore XII has little if any effect on the observed ultraviolet absorption spectra of these compounds. An examination of the data in Tables I and III and Curves *A*, *B*, and *C* of Fig. 3 indicate that the corresponding monoarylureas, 1-aryl-2-imidazolidones and 2-arylamino-2-oxazolines possess similar absorption characteristics as well as molar extinction coefficients of the same order.

Finally the symmetrical substitution of urea with two aryl groups gives new chromophores with extended conjugative systems.



XIII XIV

This in accord with expectation causes bathochromic and hyperchromic shifts in maximum II. The effect on maximum I is discussed below in detail. Thus a gradual extension of the conjugative system from benzene through aniline to diarylureas effects a progressive bathochromic shift in maximum II and a progressive increase in its molar extinction coefficient. On the other hand the wave lengths of maximum I (benzenoid absorption) change with substitution on the benzene ring. The molar extinction coefficients of maximum I are much higher in the *sym*-diarylureas than the monoarylureas (cf. Tables I and IV).

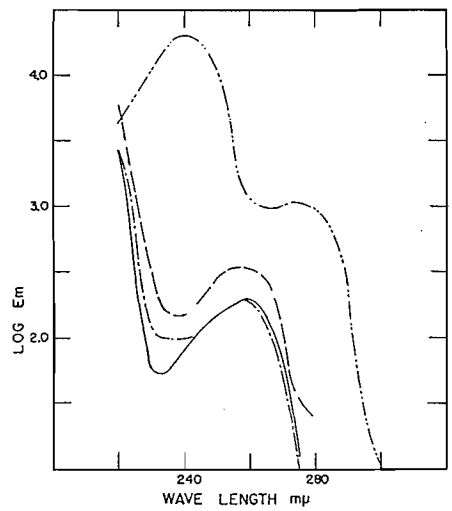



FIG. 4. Curve *A* —— 1-β-Phenylethyl-3-ethylurea.
Curve *B* – · – 1-Benzyl-3-ethylurea.
Curve *C* – – *sym*-Di-benzylurea.
Curve *D* – · · · – 1-Phenyl-3-ethylurea.

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## MONOARYLUREAS

The corresponding arylureas, 1-aryl-3-alkylureas and 1-benzyl-3-arylureas have similar maxima. Maximum II lies between 240 and 249 mμ while maximum I occurs between 270 and 292 mμ. If a methylene group is placed between the phenyl and urea group as in 1-benzyl-3-ethylurea, the maximum at 240 mμ disappears leaving only the maximum at 260 mμ (cf. Fig. 4) owing to the benzenoid absorption. This absorption maximum occurs at the same wave length as the absorption maximum of toluene. Thus the conjugation between the phenyl and urea has been eliminated by insertion of the methylene group. The molar extinction coefficient of $\lambda_{max}$ of *sym*-dibenzylurea (382) is just about twice that of 1-benzyl-3-ethylurea.

The effect of substitution in the benzene ring on the absorption of arylureas is quite uniform. In general the wave lengths of maxima I and II for para and meta substituted arylureas increase in the following order

$$H < CH_3 < RO < \text{halogen}.$$

With ortho substitution the wave length of maximum I increases in the order

$$CH_3 < H < RO < Cl,$$

while the increase of wave length of maximum II is

$$H, CH_3 < RO, Cl.$$

Also the wave lengths of maxima I and II of substituted arylureas generally decrease in the order $p > m > o$. However the wave length of the $\lambda_{max}$ of the meta substituted compound may be the same as either the *p*- or *o*-substituted compound. This order does not hold for the intensities of absorption. When an alkoxy group is substituted for a hydrogen on the benzene ring, the intensities of absorption of maximum I decrease in the order $o > m > p$ while there is very little change in the intensities of maximum II (cf. Curves *C*, *D*, and *E* (Fig. 3)). This order of decrease of maximum I is just reversed in the case of tolylureas and halogenophenylureas, viz $p > m > o$ (cf. Curves *A*, *B*, and *C* (Fig. 5)). Also with the methyl and halogen substituted arylureas the intensities of maximum II in general decrease in the order $p > m > o$ (cf.

TABLE II

ABSORPTION SPECTRA OF 1-BENZYL-3-ARYLUREAS
WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

| Compound | $\lambda_{max\ I}$, mμ | log $E_{max\ I}$ | $\lambda_{max\ II}$, mμ | log $E_{max\ II}$ |
|---|---|---|---|---|
| 1-Benzyl-3-*p*-tolylurea | 280 | 3.06 | 245 | 4.34 |
| 1-Benzyl-3-*m*-tolylurea | | Inflection | 245 | 4.29 |
| 1-Benzyl-3-*o*-tolylurea | | Inflection | 240 | 4.18 |
| 1-Benzyl-3-*p*-anisylurea | 290 | 3.22 | 245 | 4.30 |
| 1-Benzyl-3-*m*-anisylurea | 280 | 3.47 | 245 | 4.24 |
| 1-Benzyl-3-*p*-phenetylurea | 290 | 3.22 | 245 | 4.31 |
| 1-Benzyl-3-*p*-chlorophenylurea | 280 | 3.13 | 248 | 4.46 |
| 1-Benzyl-3-*p*-bromophenylurea | | Inflection | 250 | 4.42 |
| 1-Benzyl-3-*o*-bromophenylurea | 280 | 3.09 | 245 | 4.22 |

Tables I and II). These effects of substitution on maxima I and II also hold for the diarylureas.

If it is considered that substituents in the benzene ring of arylureas influence the ease of formation of electronic structures having the N conjugated with the benzene ring, there should be some consistency in behavior with respect to their electromeric or inductive effects. If the effect of the alkoxy groups is assumed to be due to an electromeric effect then the decrease in order of intensities of maximum I would be expected to follow the order $o > p > m$ or $o, p > m$. On the other hand an inductive effect would be expected to affect the order of decrease in intensities in such a manner that $o > m > p$ for

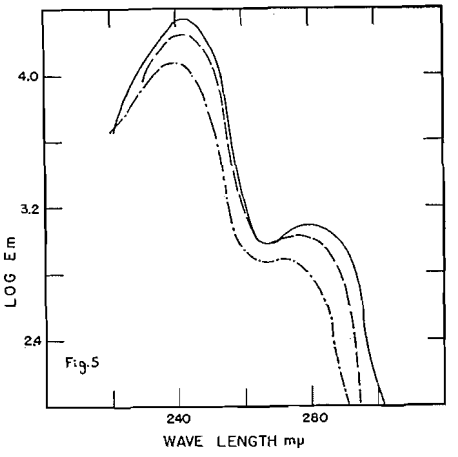



FIG. 5. Curve *A* —— 1-*p*-Tolyl-3-ethylurea.
Curve *B* – – 1-*m*-Tolyl-3-ethylurea.
Curve *C* – · – 1-*o*-Tolyl-3-ethylurea.

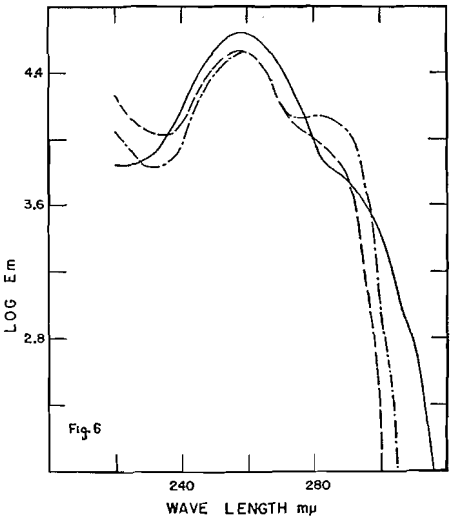



FIG. 6. Curve *A* —— 1-*p*-Anisyl-3-p-tolylurea.
Curve *B* – – 1-*m*-Anisyl-3-p-tolylurea.
Curve *C* – · – 1-*o*-Anisyl-3-p-tolylurea.

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alkoxy groups, while methyl groups would be expected to have the opposite effect on order, viz $p > m > o$. An examination of Figs. 3 and 5 and Tables I and II will indicate that substituents of arylureas affect the order of intensity variation in exactly the manner predicted on the basis of the inductive effect.[4] Table IV and Figs. 4 and 5 also show that the effect of substituents in diphenylurea is the same as in monophenylureas. Fig. 6 shows that the curve for 1-*p*-anisyl-3-*p*-tolylurea possesses an inflection at the wave length where maximum I would be expected to appear. As the methoxy substituent is moved from the *p*- to the *m*-position, this inflection acquires a higher intensity of absorption and finally in the *o*-isomer two distinct maxima appear. The final absorption of this maximum has a higher intensity of absorption than the inflections of the other two curves. It can be seen also in Fig. 5 that the one maximum and inflection of the curve of di-*p*-anisylurea is resolved into two maxima in di-*m*-anisylurea and di-*o*-anisylurea. Moreover in agreement with the monoarylureas, the intensity of absorption of maximum I decreases in the order $o > m > p$.

The inclusion of the arylurea group in a ring structure as in 1-*p*-phenetyl-2-imidazolidone and 2-*p*-phenetylamino-2-oxazoline causes a slight displacement of the whole absorption curve towards the visible end of the spectrum (compare Curves *A*, *B*, and *C* of Fig. 3). However, cyclization has very little effect on the position of the maxima. There occurs a slight increase in the intensity of absorption but it is not pronounced. The absorption maxima of

TABLE III

ABSORPTION SPECTRA OF 1-ARYL-2-IMIDAZOLIDONES
WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

| Compound | $\lambda_{max\ I}$, mμ | log $E_{max\ I}$ | $\lambda_{max\ II}$, mμ | log $E_{max\ II}$ |
|---|---|---|---|---|
| 1-Phenyl-2-imidazolidone | | Inflection | 245 | 4.28 |
| 1-*p*-Tolyl-2-imidazolidone | 280 | 3.11 | 247 | 4.29 |
| 1-*p*-Anisyl-2-imidazolidone | 290 | 3.42 | 247 | 4.32 |
| 1-*p*-Phenetyl-2-imidazolidone | 290 | 3.30 | 247 | 4.31 |

1-aryl-2-imidazolidones (Table III) should be compared with the absorption maxima of 1-aryl-3-ethylureas (Table I).

## DIARYLUREAS

The majority of the diarylureas studied displayed only one absorption maximum. This has not been due to a disappearance of the band characteristic of benzenoid absorption but rather to a coalescence of this band with the conjugative absorption band. This has resulted in the formation of a rather broad and unsymmetrical absorption band (cf. Figs. 8 and 9). In other cases (cf. Curve *A*, Fig. 7) an inflection appears on the shoulder of maximum II, while in the case of *sym*-di-*m*-alkoxyphenylureas and *sym*–di-*o*-alkoxyphenyl-

[4] *This apparent relationship of the inductive effect to absorption intensities will be investigated further.*

ureas the absorption bands are sufficiently separated to give two distinct maxima (cf. Curves *B* and *C* (Fig. 7)). When maximum I appears in the

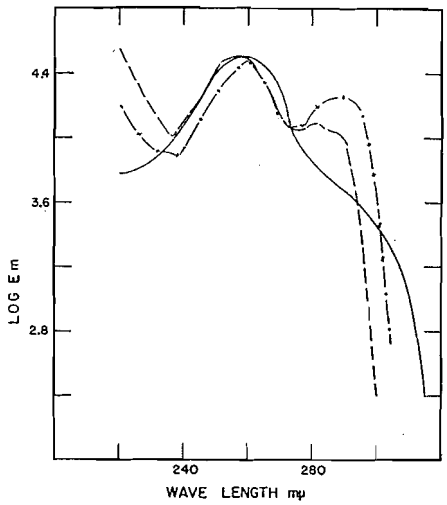



FIG. 7. Curve *A* —— 1,3-Di-*p*-anisylurea.
Curve *B* – – 1,3-Di-*m*-anisylurea.
Curve *C* –x– 1,3-Di-*o*-anisylurea.

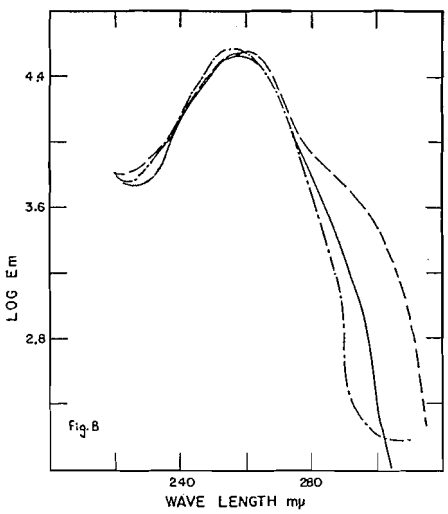



FIG. 8. Curve *A* —— 1,3-Di-*p*-tolylurea.
Curve *B* – – 1,3-Di-*p*-phenetylurea.
Curve *C* – · – 1,3-Diphenylurea.

diarylureas it has a much larger molar extinction coefficient (ca. 12,000–15,000) than the corresponding maximum in monoarylureas ($E_{max}$ 1000–3000). Maximum I appears to be pushed up by the large conjugative absorption. This separation of maximum I and II in the *sym*-di-*m*- and di-*o*-alkoxyphenylureas is not due to steric hindrance. Similarly substituted ureas having the

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alkoxy groups replaced by the larger halogeno group do not have this same degree of resolution of the two maxima (cf. Fig. 9 and Table IV). The inductive

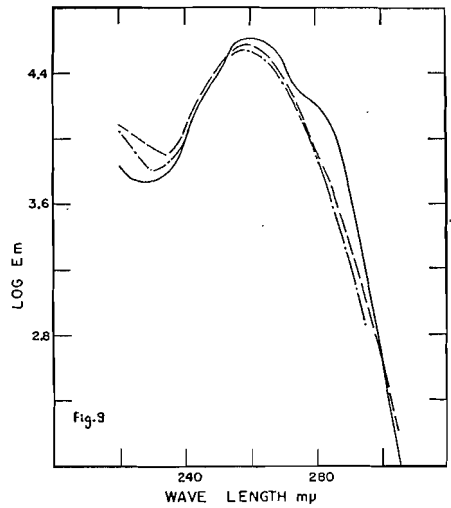



FIG. 9. Curve *A* —— 1-*p*-Chlorophenyl-3-*p*-tolylurea.
Curve *B* – – 1-*m*-Chlorophenyl-3-*p*-tolylurea.
Curve *C* –x– 1-*o*-Chlorophenyl-3-*p*-tolylurea.

effect of substituents in relation to their influence on maximum I was discussed above.

It is not easy to summarize the effects of *unsym*-substitution in *sym*-diphenylurea. However, the data in Table IV indicate that there is a definite adherence to the above discussed generalities.

The molar extinction coefficients of the monoarylurea including the 1-aryl-2-imidazolidones and 2-arylamino-2-oxazolines vary in general from 16,500–25,000. These values are approximately doubled in the correspondingly substituted *sym*-diarylureas.

It will be noted from curves of Figs. 3 and 7 that maxima I and II are sometimes broad and unsymmetrical. These maxima are quite likely the result of coalescence of two or more bands. An attempt will be made to further resolve these absorption bands by measuring the absorption spectra of some of these arylureas at lower temperatures.

## EXPERIMENTAL[5]

### *Arylureas*

The arylureas used in the ultraviolet absorption studies were analytically pure samples. The method of preparation of the majority of these compounds and their melting points have been published (11). The other known arylureas were prepared in the same manner.

### *1-Aryl-3-β-chloroethylureas*

A benzene solution of β-chloroethylamine was prepared as previously (9)

[5] *All melting points are uncorrected. Microanalyses by Mr. C. W. Beazley, Skokie, Ill.*

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TABLE IV

ABSORPTION SPECTRA OF 1,3-DIARYLUREAS
WAVE LENGTHS AND INTENSITIES OF THE MAXIMA

| Compound | $\lambda_{max\ I}$, mμ | log $E_{max\ I}$ | $\lambda_{max\ II}$, mμ | log $E_{max\ II}$ |
|---|---|---|---|---|
| 1,3-Diphenylurea | | | 255 | 4.57 |
| 1,3-Di-*p*-tolylurea | | | 257 | 4.52 |
| 1-*m*-Tolyl-3-*p*-tolylurea | | | 258 | 4.52 |
| 1-*o*-Tolyl-3-*p*-tolylurea | | | 255 | 4.47 |
| 1,3-Di-*m*-tolylurea | | | 258 | 4.72 |
| 1,3-Di-*o*-tolylurea | | | 252 | 4.32 |
| 1-*p*-Anisyl-3-*p*-tolylurea | | Inflection* | 258 | 4.63 |
| 1-*m*-Anisyl-3-*p*-tolylurea | | Inflection | 258 | 4.53 |
| 1-*o*-Anisyl-3-*p*-tolylurea | 282 | 4.15 | 260 | 4.52 |
| 1-*p*-Phenetyl-3-*p*-tolylurea | | | 259 | 4.55 |
| 1-*m*-Phenetyl-3-*p*-tolylurea | | Inflection | 259 | 4.54 |
| 1-*o*-Phenetyl-3-*p*-tolylurea | 282 | 4.13 | 260 | 4.52 |
| 1-*p*-Chlorophenyl-3-*p*-tolylurea | | Inflection | 262 | 4.61 |
| 1-*m*-Chlorophenyl-3-*p*-tolylurea | | | 260 | 4.57 |
| 1-*o*-Chlorophenyl-3-*p*-tolylurea | | | 258 | 4.54 |
| 1-*p*-Bromophenyl-3-*p*-tolylurea | | | 263 | 4.61 |
| 1-*m*-Bromophenyl-3-*p*-tolylurea | | | 260 | 4.57 |
| 1-*o*-Bromophenyl-3-*p*-tolylurea | | | 260 | 4.51 |
| 1-*m*-Tolyl-3-*p*-anisylurea | | | 258–260 | 4.49 |
| 1-*o*-Tolyl-3-*p*-anisylurea | | | 255 | 4.41 |
| 1,3-Di-*p*-anisylurea | | Inflection | 258–260 | 4.51 |
| 1-*m*-Anisyl-3-*p*-anisylurea | | Inflection | 258 | 4.49 |
| 1-*o*-Anisyl-3-*p*-anisylurea | 283 | 4.18 | 260 | 4.52 |
| 1-*p*-Phenetyl-3-*p*-anisylurea | | Inflection | 260 | 4.54 |
| 1-*m*-Phenetyl-3-*p*-anisylurea | | Inflection | 258 | 4.49 |
| 1-*o*-Phenetyl-3-*p*-anisylurea | 283 | 4.09 | 258–260 | 4.43 |
| 1-*p*-Chlorophenyl-3-*p*-anisylurea | | | 263 | 4.56 |
| 1-*m*-Chlorophenyl-3-*p*-anisylurea | | | 260 | 4.51 |
| 1-*o*-Chlorophenyl-3-*p*-anisylurea | | | 258–260 | 4.47 |
| 1-*p*-Bromophenyl-3-*p*-anisylurea | | | 262–264 | 4.59 |
| 1-*m*-Bromophenyl-3-*p*-anisylurea | | | 260 | 4.50 |
| 1-*o*-Bromophenyl-3-*p*-anisylurea | | | 258–260 | 4.44 |
| 1,3-Di-*m*-anisylurea | 282 | 4.10 | 257 | 4.51 |
| 1,3-Di-*o*-anisylurea | 288 | 4.25 | 260 | 4.49 |
| 1-*m*-Tolyl-3-*p*-phenetylurea | | | 260 | 4.53 |
| 1-*o*-Tolyl-3-*p*-phenetylurea | | | 255 | 4.46 |
| 1-*m*-Anisyl-3-*p*-phenetylurea | 283 | 4.19 | 260 | 4.51 |
| 1-*o*-Anisyl-3-*p*-phenetylurea | 282 | 4.18 | 260 | 4.52 |
| 1,3-Di-*p*-phenetylurea | | Inflection | 260 | 4.54 |
| 1-*m*-Phenetyl-3-*p*-phenetylurea | | Inflection | 260 | 4.55 |
| 1-*o*-Phenetyl-3-*p*-phenetylurea | 283 | 4.15 | 260 | 4.49 |
| 1-*p*-Chlorophenyl-3-*p*-phenetylurea | | | 262 | 4.62 |
| 1-*m*-Chlorophenyl-3-*p*-phenetylurea | | | 260 | 4.56 |
| 1-*o*-Chlorophenyl-3-*p*-phenetylurea | | | 258–260 | 4.45 |
| 1-*p*-Bromophenyl-3-*p*-phenetylurea | | | 263–265 | 4.58 |
| 1-*m*-Bromophenyl-3-*p*-phenetylurea | | | 260–263 | 4.53 |
| 1-*o*-Bromophenyl-3-*p*-phenetylurea | | | 258–260 | 4.46 |
| 1,3-Di-*m*-phenetylurea | 282 | 4.11 | 257 | 4.52 |
| 1-*p*-Tolyl-3-phenylurea | | | 258–260 | 4.56 |
| 1-*p*-Anisyl-3-phenylurea | | | 258–260 | 4.53 |
| 1-*p*-Phenetyl-3-phenylurea | | | 258 | 4.51 |
| 1-*p*-Chlorophenyl-3-phenylurea | | | 260 | 4.55 |

* *These inflections appear in the wave length region of maximum I but no attempt has been made to assign wave lengths to them.*

described. To this solution 0.0647 mole of an arylisocyanate was added. Almost immediately white precipitates of the products were obtained in good yields (95–98%). Purification was effected by one crystallization from 95%

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ethanol. In this way the following 1-aryl-3 β-chloroethylureas were prepared. *1-p-Tolyl-3 β-chloroethylurea* (m.p. 178–179° C.). Calc. for $C_{10}H_{13}ClN_2O$: C, 56.60; H, 6.13; Cl, 16.70%. Found: C, 56.46; H, 6.27; Cl 17.02%. *1-p-Anisyl-3 β-chloroethylurea* (m.p. 160–160.3° C.). Calc. for $C_{10}H_{13}ClN_2O_2$: C, 52.60; H, 5.69; Cl, 15.54%. Found: C, 52.75; H, 5.71; Cl, 15.55%. *1-p-Phenetyl-3 β-chloroethylurea* (m.p. 149–151° C.). Calc. for $C_{11}H_{15}ClN_2O_2$: C, 54.43; H, 6.19; Cl, 14.64%. Found: C, 54.65; H, 6.32; Cl, 14.65%.

*1-Aryl-2-imidazolidones*

The preparation of 1-phenyl-2-imidazolidone (2, 10) and 1-*p*-anisyl-2-imidazolidone (12) by the respective cyclizations in alkaline solutions of 1-phenyl-3 β-chloroethylurea and 1-*p*-anisyl-3 β-chloroethylurea have been described. In a similar manner 1-*p*-tolyl-2-imidazolidone (13) (m.p. 196.5–197° C.) and 1-*p*-phenetyl-2-imidazolidone (13) (m.p. 211.5–212° C.) were prepared in yields of 85.9 and 86.5% respectively.

*2-Arylamino-2-oxazolines*

2-*p*-Phenetylamino-2-oxazoline (m.p. 152.5–153° C.) was prepared from 1-*p*-phenetyl-3 β-bromoethylurea (m.p. 132° C.) in 72% yield by the method of Englemann (1). Englemann reports a melting point of 151° C. while Gebauer (3) gives a melting point of 153° C. Calc. for $C_{11}H_{14}N_2O_2$: N, 13.59%. Found: N, 13.70%.

2-*p*-Tolylamino-2-oxazoline (m.p. 165.2–166° C.) was prepared similarly from 1-*p*-tolyl-3 β-bromoethylurea (160–161° C.) in 62.6% yield. Calc. for $C_{10}H_{12}N_2O$: C, 68.18; H, 6.82; N, 15.91%. Found: C, 68.32; H, 6.82; N, 16.18%.

## DETERMINATION OF SPECTRA

The ultraviolet absorption spectra were measured in 95% ethanol with a Beckman Quartz Spectrophotometer, Model DU.

The concentrations of the solutions ranged from $2 \times 10^{-4}$ to $3.00 \times 10^{-5}$ mole/liter. In the majority of cases only one determination was made for each urea. However, several determinations at different concentrations were performed on about eight of the urea derivatives and the reproducibility of spectral measurements ascertained. Thus slight variations in absorption maxima and molecular extinction coefficients ($E_m$) are neglected in the above discussion. $E_{max}$ refers to the molecular extinction coefficient at the wave length of maximum absorption.

## ACKNOWLEDGMENTS

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# THE USE OF ISOTOPE DILUTION IN DETERMINATION OF GEOLOGIC AGE OF MINERALS[1]

By R. H. Tomlinson and A. K. Das Gupta[2]

ABSTRACT

The mass spectrometer has been used for the estimation of trace quantities of rubidium and strontium. The isotope dilution technique developed by Aldrich has been extended so that 0.01% of rubidium and 0.0001% strontium have been analyzed with 100 mgm. of mineral. The use of small quantities for mass spectrometric determination allows the use of easily available fission strontium and rubidium. The radioactivity of the fission strontium also simplifies the chemical manipulation. No chemical separation from the mineral was required for the rubidium but the strontium was concentrated by ion exchange methods. Ages are presented for one lepidolite and two biotite minerals and their ages compared to those found by other methods. With one of the biotites the effect of weathering on the fractionation of rubidium from strontium has been studied.

## INTRODUCTION

The possibility of measuring age of minerals by using the decay of naturally occurring rubidium has been under investigation since 1937. Naturally occurring rubidium consists of the isotopes 85 and 87, of which $Rb^{87}$ is radioactive and forms $Sr^{87}$ by beta decay. Since the half life of $Rb^{87}$ is of the order of $10^{10}$ years, which is very long compared to the age of the minerals under investigation, the age can be obtained from the following expression:

$$T(\text{age}) = \frac{\%\ Sr^{87}\ (\text{radiogenic})}{\%\ Rb^{87}} \cdot \frac{1}{\text{Decay const. of } Rb^{87}}. \qquad [1]$$

The accuracy of the determination of age will depend on the accuracy of determining the three factors involved: (i) % of radiogenic $Sr^{87}$, (ii) % of rubidium in the mineral, and (iii) the decay constant of $Rb^{87}$. It is imperative that weathering has not washed out either rubidium or radiogenic $Sr^{87}$.

Rubidium though present in traces in many minerals does not form any minerals of its own. The highest content of rubidium is found in the lepidolites in which the $Rb_2O$ content varies from 0.3 to 3.0%. The accurate determination of rubidium content by purely chemical methods, particularly in samples where the percentage may be only of the order of $10^{-2}$, is bound to be unreliable. Spectrographic methods have been found more suitable (1).

The determination of $Sr^{87}$ has presented great difficulties. Even in the older minerals the content of radiogenic $Sr^{87}$ would be about 1/100 that of $Rb^{87}$ which itself is 27.2% of the total rubidium. In minerals where the percentage of rubidium is only in the region of 0.01%, as in many of the biotites, the percentage of radiogenic $Sr^{87}$ would be expected to be about 0.0001 at best and is liable to be mixed with normal strontium. Under these conditions, accurate determination of radiogenic $Sr^{87}$ has not been reported.

This paper presents a method of estimating both $Rb^{87}$ and $Sr^{87}$ (radiogenic) even when they are present in very small quantities mixed with normal

[1] *Manuscript received June 22, 1953.*
*Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario.*
[2] *UNESCO Fellow, on deputation from the National Chemical Laboratory, Poona, India.*



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strontium, by using the technique of isotopic dilution along with the mass spectrometer (6). The mass spectrometer gives the ratio of the isotopes of an element, but it does not give any direct information as to the actual amount of a particular isotope. By addition to the sample to be analyzed of a known quantity of a single isotope of the element, the mass spectrometric ratio of the resultant mixture of isotopes can then be utilized to obtain the amount of each isotope. Since the isotopic ratios remain essentially constant through all chemical procedures, losses during manipulation do not affect the result. Whereas it is simplest to use a single separated isotope, any isotopic mixture whose isotopic abundance is different from that in nature may be used.

Aldrich *et al.* (2, 4) have reported a method for determination of the ages by the strontium method using the isotope dilution technique. Working only with lepidolites, in which the rubidium content is high, analyses were accomplished with 3-gm. samples. In this work 100-mgm. samples were found adequate even when the rubidium content was of the order of $10^{-2}\%$. This makes possible age determination of minerals hitherto beyond reach of any of the methods in use.

## EXPERIMENTAL

### *Mass Spectrometry*

The mass spectrometer used was a conventional 90° sector instrument with magnetic scanning and a hot filament ion source (5). For strontium analysis it was found that a platinum plated tungsten filament was most efficient. Suitable mass spectrograms were obtained with 0.5 μgm. of strontium and 0.01 μgm. of rubidium, although considerably smaller quantities could be used.

### *Preparation and Standardization of $Sr^{90}$ and Fission Rb Solutions*

Radioactive $Sr^{90}$ obtained from the commercial products division of Atomic Energy of Canada Limited was diluted so that 100 ml. of the solution contained about two millicuries of activity. The ratio of $Sr^{90}/Sr^{88}$ was measured both for this solution, and for a mixture of 10 ml. of the same solution with 0.673 μgm. of natural strontium added. The results are shown in Table I

TABLE I
STANDARDIZATION OF $Sr^{90}$ AND OF FISSION Rb SOLUTIONS

| $Sr^{90}$ solution | | Fission Rb solution | |
|---|---|---|---|
| Sample | $Sr^{90}/Sr^{88}$ | Sample | $Rb^{85}/Rb^{87}$ |
| Fission strontium | 1.255 ± .008 | Fission rubidium | 0.423 ± .003 |
| 10 ml. fission strontium + normal strontium containing 0.556 μgm. $Sr^{88}$ | 0.817 ± .007 | Natural rubidium | 2.68 ± .01 |
| | | 1 ml. fission Rb and 0.0142 μgm. natural Rb | 0.963 ± .003 |

from which it can be calculated that 5 ml. of fission strontium solution contained 0.650 μgm. $Sr^{90}$.

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Fission rubidium, which is rich in $Rb^{87}$, was separated from the divalent and trivalent fission product ions by preferential elution from Dowex 50 ion exchange column using 0.3 *N* hydrochloric acid. The concentration of a stock solution of this was determined by a method similar to that used for $Sr^{90}$. From the data shown in Table I the concentrations of $Rb^{87}$ and $Rb^{85}$ in the stock solution are found to be 0.0123 μgm./ml. and 0.00520 μgm. per ml. respectively.

*Separation and Estimation of Strontium*

The weight of the sample required for an age determination will depend on the Rb content and on the age of the mineral. Ten milligrams of the lepidolite and 100 mgm. of the biotites were used for analysis. The minerals after repeated hydrofluoric acid treatment were taken into solution with hydrochloric acid and diluted to 50 ml. Separations of strontium were carried out on a 8 cm. column of Dowex-50 ion exchange resin in the $NH_4^+$ form. The general principles of ion exchange separation of inorganic cations are very well known, and have been summarized by Schubert (9). The solutions of the minerals are relatively rich in cations such as $Fe^{+++}$, $Al^{+++}$, $K^+$, and $Na^+$. The aim of the separations was to obtain strontium sufficiently free from these elements to give strontium spectrograms with the mass spectrometer. Five milliliters of the $Sr^{90}$ solution was added to aliquots of every sample. Since it is desirable to have approximately the same amounts of $Sr^{90}$ and radiogenic $Sr^{87}$ in the mixture, the aliquot of the sample solution may have to be determined by a trial experiment. The mixture, after evaporation, is taken up in 5 ml. of 5% citric acid solution and transferred to the column. Two hundred milliliters of 5% citric acid adjusted to pH 3.6 with ammonium hydroxide was used to elute out all the trivalent ions along with $Y^{90}$, the radioactive daughter isotope of $Sr^{90}$. It was observed, by adding radioactive cesium, that the $NH_4^+$ concentration in the citric acid elutant was sufficient to move the monovalent ions. As an added precaution, however, 100 ml. of 0.6 *N* hydrochloric acid was run through the column to remove the last traces of the monovalent ions and to wash out the citric acid. Separating out the calcium, though possible at this stage, was not found necessary as the strontium obtained by eluting with 6 *N* hydrochloric acid was quite suitable for mass spectrometry.

To obtain the quantity of radiogenic $Sr^{87}$ it is only necessary to determine the ratio radiogenic $Sr^{87}/Sr^{90}$. The mass 87 peak on the spectrogram may in addition to radiogenic $Sr^{87}$ consist of a contribution from normal strontium together with any rubidium contamination. It was found possible to burn off rubidium at a somewhat lower temperature than is necessary to emit strontium ions. For this procedure to be effective it was required that all the sample to be analyzed be placed near the center of the filament. Even if the rubidium was not completely removed, a correction for the rubidium contamination could have been applied since the ratio of $Rb^{85}/Rb^{87}$ is known and since all the peak at mass 85 on the spectrogram is due to $Rb^{85}$. The presence of mass 86 is indicative of normal strontium in the sample. The

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TABLE II

SUMMARY OF DATA FOR AGE DETERMINATIONS OF MINERALS

| Sample No. | Mineral | Geologic location | Pretreatment | Weight of treated sample, gm. | % Radiogenic $Sr^{87}$ | % $Rb^{87}$ | Age in $10^9$ years |
|---|---|---|---|---|---|---|---|
| 1 | Lepidolite | Bob Ingersol Mine, S. Dakota | Washed with hot aqua regia | 0.00971 | $7.35 \pm .59 \times 10^{-3}$ | $4.49 \times 10^{-1}$ | 1.39 |
| 2 | Biotite magnetically separated from uraninite | Sickle Lake, N.E. Saskatchewan | Unwashed | 0.0709 | $6.95 \pm .12 \times 10^{-4}$ | $1.80 \pm .01 \times 10^{-2}$ | 3.23 |
| 3 | Uraninite containing biotite | " | Washed with hot aqua regia | 0.9595 | $2.13 \pm .10 \times 10^{-4}$ | $5.00 \pm .04 \times 10^{-3}$ | 3.56 |
| 4 | Biotite magnetically separated from uraninite | " | Washed with cold HCl | 0.0196 | $8.90 \pm .42 \times 10^{-4}$ | $2.22 \pm .03 \times 10^{-3}$ | 3.36 |
| 5 | Biotite | Mt. Monadnock New Hampshire | Unwashed | 0.1068 | $1.81 \pm .20 \times 10^{-4}$ | $2.64 \pm .03 \times 10^{-2}$ | 0.57 |

ratio $Sr^{86}/Sr^{87}$ in normal strontium being known, the contribution of normal strontium to mass 87 is easily corrected for.

*Determination of Rubidium*

The phenomenon of "saturation of ion source" mentioned by Aldrich (3) was not observed. Even a sample containing 15% potassium, 4.6% sodium, and $1.84 \times 10^{-2}$% rubidium gave the ratio $2.68 \pm .01$ for $Rb^{85}/Rb^{87}$. Nier (7) has reported the ratio $2.68 \pm .02$ for the rubidium isotopes. Therefore it was considered unnecessary to isolate the rubidium for mass spectrometry. An aliquot of the mineral solution was diluted so as to give a rubidium concentration of about 0.01 μgm. per ml. The $Rb^{85}/Rb^{87}$ ratio obtained from a mixture of 1 ml. of this solution with 1 ml. of the standardized fission rubidium solution was used to calculate the percentage of rubidium in the sample.

## RESULTS AND DISCUSSION

The percentages of $Rb^{87}$ and $Sr^{87}$ in the minerals analyzed, together with their ages calculated from equation [1] are presented in Table II. The value of the decay constant used was $1.195 \times 10^{-11}$ as suggested by Ahrens (1), although slightly different values have been reported since. Ahrens by spectrometric determination of Sr/Rb ratios has reported 0.9 to 1.5 billion years as the ages of lepidolites obtained from the same area as sample 1 in Table II. The age of the uraninite has been found by the lead isotope method to be $1.9 \times 10^9$ years (Department of Geophysics, University of Toronto). The age obtained for the biotite separated from the uraninite being much older (Sample 2, Table II), it was necessary to find the effect of weathering. Two age determinations were carried out, one on a sample of the uraninite washed with boiling aqua regia, and the other on the separated biotite washed with cold 12 *N* hydrochloric acid. The ages (Samples 3 and 4, Table II) were not found to have altered appreciably even with these treatments which were considerably more drastic than is likely to have occurred in nature. The percentages of strontium and rubidium for the Samples 2, 3, and 4 cannot be directly compared since Sample 3 contained a large quantity of silica while Sample 4 was merely depleted of iron and other soluble constituents. The age of the biotite obtained from Mt. Monadnock (Sample 5, Table II) is also found to be high when compared to the age limits 0.25 to 0.40 billion years given for ores from this area by the lead isotope method (8).

It is noted that although the age determined for the lepidolite is in general agreement with that obtained from the spectrographic Sr/Rb ratio, the other ages are considerably greater than those obtained from the lead isotope method. Since it has been shown that weathering did not appreciably affect the strontium method, it can be concluded that apart from possible error in the $Rb^{87}$ half life, the ages found are essentially correct.

For accurate analyses by the isotope dilution method, it is desirable to have about equal amounts of isotopic spike and the isotope to be estimated. Aldrich (2) for each age determination has used 50 μgm. of strontium containing 65% $Sr^{84}$ and 180 μgm. of rubidium containing 89% $Rb^{87}$. These

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quantities of isotopes are sufficient for 100 strontium and $10^4$ rubidium analyses by the method described in this work. The use of small quantities has greatly simplified chemical separation of strontium and has made separation unnecessary for rubidium. A further advantage of using less than microgram quantities of spiking isotope is the possibility of using $Sr^{90}$, which because of its radioactivity, would necessitate special precautions if it were required in much greater quantities. $Sr^{90}$ is a readily available, inexpensive fission product, which, being entirely absent in nature, makes the interpretation of the mass spectrograms simpler than those obtained with the use of enriched isotopic mixtures. Furthermore, in less than microgram quantities, the $Sr^{90}$, together with its daughter isotope $Y^{90}$, acts as a convenient tracer which greatly facilitates the handling of the sample.

ACKNOWLEDGMENTS

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# A NEW MECHANISM FOR PERSULPHATE OXIDATIONS[1]

By Leonard S. Levitt[2]

ABSTRACT

A new mechanism for oxidations by persulphate is presented, wherein it is postulated that the persulphate ion dissociates reversibly, by means of a heterolytic cleavage, into a sulphate ion and a molecule of sulphur tetroxide. Sulphur tetroxide is considered to be the active oxidizing species, combining reversibly with the substrate to form a complex whose subsequent decomposition gives the principal reaction products. The very small equilibrium concentration of sulphur tetroxide becomes the limiting factor in the rate of oxidation when a readily oxidizable substrate is present in relatively high concentration. The mechanism is applied to the data of Eager and Winkler for the oxidation of mercaptans, in which a limiting rate was attained above a certain mercaptan concentration. An empirical equation relating the rate constant to the mercaptan concentration is developed to fit the experimental data. Rate equations showing the rate dependence on mercaptan concentration are derived from the proposed mechanism and are found to be of the same form as the empirical equation. The mechanism is applied also to the persulphate oxidation of water.

## INTRODUCTION

In the paper by Eager and Winkler entitled "The oxidation of mercaptans by potassium persulphate in homogeneous solution" (3), it was shown that a maximum or limiting rate was attained at a certain low mercaptan concentration, above which no further increase in mercaptan concentration resulted in an increased rate. The reaction was always first order, however, with respect to the measured persulphate concentration. A mechanism was proposed in which it was assumed that the first and rate-controlling step was the reversible dissociation, $S_2O_8^= \rightleftharpoons 2\ SO_4^-$. No rate equations showing the rate dependence on mercaptan concentration were derived, however.

Quite similar results have also been observed in the persulphate oxidation of organic sulphides (7) and sulphoxides (9), in both cases a limiting rate being attained.

In the present article is proposed a new mechanism for persulphate oxidations, the application of which leads to the development of rate equations of the required form, showing the rate dependence on the concentration of the sulphur compound oxidized. The new mechanism will be applied to the data of Eager and Winkler.

## AN EMPIRICAL RATE EQUATION

Since a limiting value of the rate constant is attained at higher mercaptan concentrations, an equation of the following form is applicable:

$$-dP/dt = kP = [aS/(b + S)]P \qquad [1]$$

where $a$ and $b$ are empirical constants, $S$ is the mercaptan concentration,

[1] *Manuscript received May 25, 1953.*
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$P$ is the persulphate concentration, and $k$ is the observed rate constant. From Eq. 1, $k$ is seen to be given by

$$k = aS/(b + S). \quad [2]$$

It is obvious from Eq. 2 that at very low mercaptan concentrations $S \ll b$ and

$$k = (a/b)S \quad [3]$$

the rate being proportional to the mercaptan concentration. On the other hand, at high mercaptan concentrations $S \gg b$, and

$$k = a. \quad [4]$$

In this case, then, the rate is independent of the mercaptan concentration.

The constants $a$ and $b$ may be evaluated from the experimental data in a number of ways. From Eq. 4, $a$ is evidently equal to the experimentally

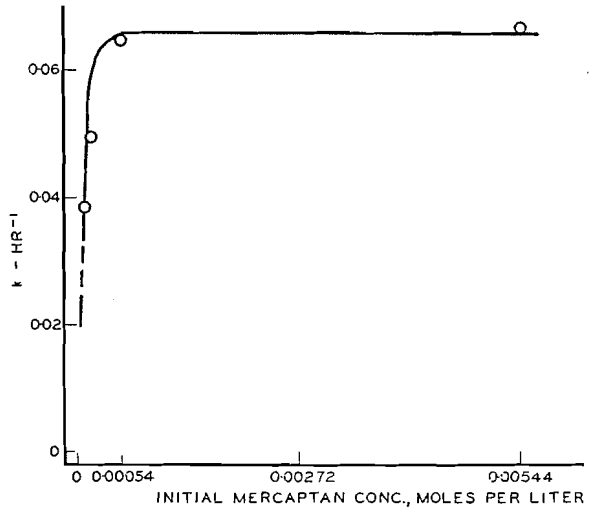



FIG. 1. Variation of $k$ with $n$-dodecyl mercaptan concentration. Initial potassium persulphate concentration, 0.00153 mole per liter; temperature, 25.00 ± 0.01°C.

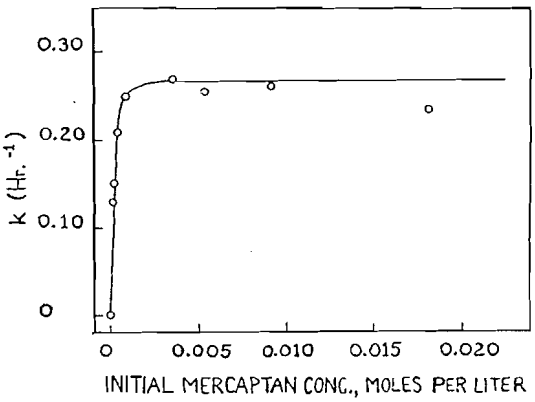



FIG. 2. Variation of $k$ with $n$-dodecyl mercaptan concentration. Initial potassium persulphate concentration, 0.00153 mole per liter; temperature, 35.00 ± 0.01°C.

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determined maximum rate constant. The ratio $a/b$ is seen from Eq. 3 to be the slope of the initial straight line portion of the plot of $k$ vs. $S$ (Figs. 1 and 2). In addition, it may be noted from Eq. 1 that $b$ is equal to the mercaptan concentration at which the velocity of the reaction has attained one-half its limiting value.

An alternate and more accurate method of evaluating the empirical constants is as follows. Equation 2 may be rearranged to give

$$S/k = (b/a) + (S/a). \qquad [5]$$

Thus, a plot of $S/k$ vs. $S$ should be a straight line with slope $1/a$ and intercept $b/a$. That a straight line does, indeed, result is evident from Figs. 3 and 4

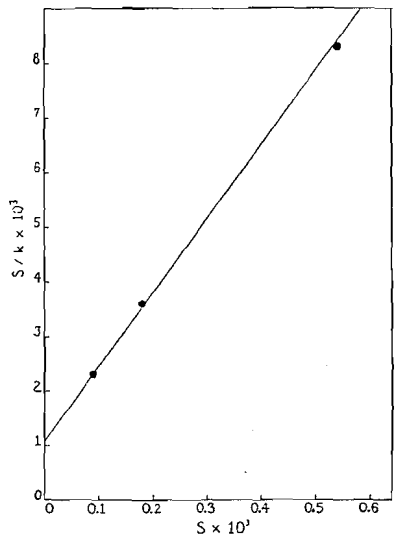



FIG. 3. Test of Equation 5 (at 25°).

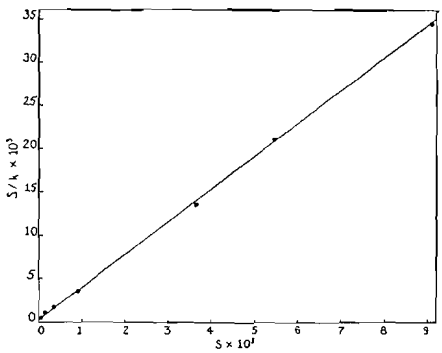



FIG. 4. Test of Equation 5 (at 35°).

in which such a plot has been made using the data for *n*-dodecyl mercaptan at 25°C. and at 35°C.

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At 25°, the slope is equal to 14.3 and hence $a = 0.070$; the intercept is equal to $1.04 \times 10^{-3}$ and thus $b = 7.3 \times 10^{-5}$. At 35°, the slope is 3.76 and the intercept 0.38, whence $a = 0.27$, and $b = 1.0 \times 10^{-4}$.

Substituting the numerical values for the constants $a$ and $b$ in Eq. 2, we have, at 25°

$$k = 0.070\ S/(0.000073 + S) \qquad [6]$$

and at 35°

$$k = 0.27\ S/(0.00010 + S). \qquad [6a]$$

The observed rate constants can thus be calculated from Equations 6 and 6$a$. Tables I and II give a comparison of the observed values of $k$ at different mercaptan concentrations with the values calculated from Equations 6 and 6$a$. The agreement is seen to be satisfactory.

TABLE I

OBSERVED RATE CONSTANTS FOR THE OXIDATION OF *n*-DODECYL MERCAPTAN AT 25°, AND THOSE CALCULATED USING EQ. 6.

| Mercaptan conc. ($M$) | $k$ (hr.$^{-1}$) | |
|---|---|---|
| | Obs. | Calc. |
| 0.00009 | 0.0388 | 0.039 |
| 0.00018 | 0.0494 | 0.050 |
| 0.00054 | 0.0649 | 0.062 |
| 0.00544 | 0.0668 | 0.069 |

TABLE II

OBSERVED RATE CONSTANTS FOR THE OXIDATION OF *n*-DODECYL MERCAPTAN AT 35°, AND THOSE CALCULATED USING EQ. 6$a$.

| Mercaptan conc. ($M$) | $k$ (hr.$^{-1}$) | |
|---|---|---|
| | Obs. | Calc. |
| 0.00004 | 0.131 | 0.08 |
| 0.00018 | 0.154 | 0.17 |
| 0.00036 | 0.208 | 0.21 |
| 0.00091 | 0.246 | 0.24 |
| 0.00363 | 0.267 | 0.26 |
| 0.00544 | 0.255 | 0.26 |
| 0.00907 | 0.262 | 0.27 |
| 0.01815 | 0.233 | 0.27 |

## THE NEW MECHANISM

The nature of the rate dependence upon mercaptan concentration suggests a mechanism involving one or more reversible steps, one of which is rate-determining. The mechanism should account also for the retarding effect of sulphate ion on the rate.*

**Although its effect in the acetic acid solvent used by Eager and Winkler is not clear, the retardation of the rate brought about by sulphate in aqueous solution is well known (6).*

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A mechanism in agreement with these requirements is as follows:

$$S_2O_8^{=} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_4^{=} + SO_4 \qquad [7]$$

$$R{:}\ddot{S}{:}H + \ddot{O}{:}SO_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R{:}\overset{\dot{+}}{\ddot{S}}{:}\ddot{O}{:}SO_3 \quad (H) \qquad [8]$$

$$R{:}\overset{\dot{+}}{\ddot{S}}{:}\ddot{O}{:}SO_3 \quad (H) \xrightarrow{k_3} R{:}\ddot{S}^{+} + H^{+} + SO_4^{=}. \qquad [9]$$

Only the final step is considered to be irreversible. Sulphate ion, if present initially, would retard the first step. The complex formed in Equation 8 may undergo the two reactions indicated. The ion $RS^+$ is here postulated to be the primary oxidation product of the mercaptan, and it might, in addition to being further oxidized, undergo such reactions as:

$$RS^+ + RSH \longrightarrow RSSR + H^+ \qquad [10]$$

and

$$RS^+ + HOH \longrightarrow RSOH + H^+. \qquad [11]$$

These reactions could be followed by further oxidation of the disulphide and of RSOH, which is not stable.

The molecule $SO_4$, sulphur tetroxide, has been prepared (12). It is considered to be the anhydride of $H_2SO_5$, Caro's acid, but reacts only slowly with water (4, p. 349). Sulphur tetroxide is a powerful oxidizing agent but is unstable toward heat, decomposing into sulphur trioxide and oxygen (4, p. 297). The intermediate formation of sulphur tetroxide would also explain the thermal decomposition of potassium persulphate in the absence of a solvent:

$$K_2S_2O_8 \longrightarrow K_2SO_4 + SO_4 \longrightarrow SO_3 + O. \qquad [12]$$

Also, it is quite possible that polymerizations catalyzed by persulphate may in reality be the result of initiation by oxygen atoms or sulphur tetroxide molecules, rather than by sulphate ion radicals ($SO_4^-$), as has been previously assumed (2, 5).

The reverse of Equations 7 and 12, the reaction of sulphur tetroxide with sulphate ion, may well constitute a new method for preparing persulphates (9, p. 108).

## DERIVATION OF THE RATE EQUATION

A rate equation of the required form (cf. Eq. 1) may be derived from the proposed mechanism in the following manner.

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In addition to the symbols $P$ and $S$ (defined above), let $A$ represent the concentration of sulphate ion; $B$, that of the sulphur tetroxide; and $X$, that of the complex.

Applying the steady-state treatment to both $B$ and $X$, one obtains

$$dB/dt = k_1P - k_2BS - k_{-1}AB + k_{-2}X = 0 \qquad [13]$$

and

$$dX/dt = k_2BS - k_{-2}X - k_3X = 0. \qquad [14]$$

Eliminating $B$ from Equations 13 and 14, solving for $X$, and setting the over-all rate equal to $k_3X$, one obtains the final rate expression

$$-\frac{dP}{dt} = \frac{k_1SP}{S + Ak_{-1}\left(\frac{k_{-2} + k_3}{k_2k_3}\right)}. \qquad [15]$$

Using the original chemical notation this becomes

$$-\frac{d[S_2O_8^{=}]}{dt} = \frac{k_1[RSH][S_2O_8^{=}]}{[RSH] + [SO_4^{=}]k_{-1}\left(\frac{k_{-2} + k_3}{k_2k_3}\right)}. \qquad [15a]$$

Hence, the observed rate constant, $k$, is evidently given by

$$k = \frac{k_1[RSH]}{[RSH] + [SO_4^{=}]k_{-1}\left(\frac{k_{-2} + k_3}{k_2k_3}\right)}. \qquad [16]$$

Comparing Equation 16 with the empirical expression (Eq. 2), it is seen that

$$a = k_1 \qquad [17]$$

and

$$b = [SO_4^{=}]k_{-1}\left(\frac{k_{-2} + k_3}{k_2k_3}\right). \qquad [18]$$

The rate constant $k_1$ for the dissociation of persulphate ion into sulphur tetroxide and sulphate ion has, therefore, been determined in these experiments; and the activation energy (26 kcal. per mole) calculated from the value of the maximum rate constant ($k_1$) at different temperatures, does, indeed, appear to be the value to be associated with that reaction (3). Unfortunately, there are not sufficient data to allow an evaluation of any of the four other rate constants.

## THE PERSULPHATE OXIDATION OF WATER

The molecular-ionic mechanism offered above can be applied with equal advantage to the decomposition of potassium persulphate in water, or, more exactly, the oxidation of water by persulphate. This reaction has been studied extensively (6, 8, 10). It may be represented by the over-all equation:

$$S_2O_8^{=} + H_2O \longrightarrow 2H^+ + 2\,SO_4^{=} + \tfrac{1}{2}\,O_2. \qquad [19]$$

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Previous mechanisms for this reaction have assumed either the intermediate formation of Caro's acid and hydrogen peroxide (10), or of sulphate ion radicals and hydroxyl radicals ($HO^{\bullet}$) (1).

The present mechanism includes none of these entities as necessary intermediates, though it allows for their possible formation in subsequent reactions. The new mechanism is:

$$S_2O_8^{=} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_4^{=} + SO_4 \qquad [20]$$

$$\cdot\cdot O{:}SO_3 + H{:}\ddot{O}{:}H \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H{:}\overset{+}{\ddot{O}}{:}\ddot{O}{:}SO_3^{-} \qquad [21]$$

$$H{:}\overset{+}{\ddot{O}}{:}\ddot{O}{:}SO_3^{-} \xrightarrow{k_3} H{:}\ddot{O}^{+} + H^{+} + SO_4^{=}. \qquad [22]$$

The ion $HO^{+}$, whose presence has been postulated in acidic aqueous hydrogen peroxide solutions (11), could then react in a number of ways, among which the most likely is probably:

$$HO^{+} + H_2O \longrightarrow H_3O^{+} + O. \qquad [23]$$

If the complex formed in Equation 21 were to lose a proton, Caro's acid ($HSO_5^{-}$) would result.

The rate equation developed from Equations 20–22 in a manner quite analagous to the derivation presented for the oxidation of mercaptans is identical with Equation 15*a*, except that $[H_2O]$ replaces [RSH]. Thus:

$$-\frac{dP}{dt} = \frac{k_1[H_2O][S_2O_8^{=}]}{[H_2O] + [SO_4^{=}]k_{-1}\left(\frac{k_{-2} + k_3}{k_2k_3}\right)}. \qquad [24]$$

The oxidation of water, however, proceeds much more slowly at a given temperature than the oxidation of mercaptans (3). The reaction of sulphur tetroxide with water is known to be slow (4, p. 349), and it is logical, therefore, to suppose that it is this reaction which retards the entire process. Equation 24 may be rearranged to:

$$-\frac{dP}{dt} = \frac{k_1k_2k_3[H_2O][S_2O_8^{=}]}{k_2k_3[H_2O] + [SO_4^{=}]k_{-1}(k_{-2} + k_3)}. \qquad [25]$$

In this form it is more easily seen that if $k_2$ is very small, the first term in the denominator is small by comparison with the second term, and the retarding effect of sulphate is accentuated. Furthermore, the value of the numerator is lessened considerably by a small value for $k_2$, and thus the rate of disappearance of persulphate is greatly diminished.

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# REACTIONS OF CYANOGEN IODIDE[1]

By L. E. Bodnar[2] and A. B. Van Cleave

ABSTRACT

A series of hydrogen chloride catalyzed reactions involving cyanogen iodide as the starting material have been investigated in dioxane and in aqueous solution at 30° and 45° C. The course of the reaction was followed by determining the decrease in the number of oxidation equivalents present. Reaction products identified were: iodine monochloride, iodine, ammonium chloride, and carbon dioxide. A possible reaction mechanism has been suggested.

## INTRODUCTION

A previous study (18) of the reaction between cyanogen chloride and water and between cyanogen bromide and water, catalyzed by hydrogen chloride or hydrogen bromide in dioxane solution, has established that the over-all reaction is represented by

$$XCN + 2H_2O \rightarrow CO_2 + NH_4X,$$

where X represents chlorine or bromine. In both cases the catalyst was indicated to be molecular hydrogen chloride or hydrogen bromide rather than hydronium ions. It is of interest to study the hydrolysis of cyanogen iodide under conditions similar to those employed for the other cyanogen halides. The present work indicates that the reactions undergone by cyanogen iodide are quite different from those of either cyanogen chloride or cyanogen bromide.

## EXPERIMENTAL

### 1. *Chemicals*

(*a*) Cyanogen idodide was prepared from potassium cyanide and iodine according to the method of Comastri (3). A yield of about 66% was obtained by thoroughly cooling vessels and reagents before use. Two purifications by sublimation were necessary to remove traces of iodine.

(*b*) Dioxane (Eastman Kodak) was purified by the method of Fieser (4) and was distilled from metallic sodium just before use.

(*c*) Alcohols: methanol and ethanol were dried by refluxing with magnesium turnings.

(*d*) Ammonium iodide (Merck) was dried over phosphorus pentoxide and stored in the dark.

(*e*) Solutions of hydrogen chloride in dioxane were prepared either by adding appropriate amounts of concentrated C.P. hydrochloric acid or by bubbling pure dry hydrogen chloride into anhydrous dioxane. Solutions prepared by the latter method were analyzed over a period of time to determine whether there were any reactions corresponding to that observed for

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*Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. Presented at the Annual Conference of the Chemical Institute of Canada, Windsor, June 1953.*

[2] *Graduate student, present address, Department of Chemistry, McMaster University, Hamilton, Ontario.*

solutions of hydrogen bromide in dioxane (17). Over a period of three weeks at 45° C., no detectable decrease in the concentration of hydrogen chloride in a 0.425 *M* solution was observed.

(*f*) Iodine monochloride was prepared by passing chlorine into solid iodine until the mass became liquid and then fractionating twice to remove idodine and iodine trichloride (2).

2. *Procedure*

A definite amount of solid cyanogen iodide was weighed into a 100 ml. volumetric flask, the desired amount of distilled water added, and the volume made up to 100 ml. with anhydrous dioxane containing known amounts of dry hydrogen chloride. After mixing, 10 ml. aliquots of the solution were transferred to glass reaction tubes which were cooled in ice water. The tubes were then quickly sealed with a torch and placed in a constant temperature bath. Individual tubes were opened for analysis at appropriate times using a hot wire glass cutter. The same general procedure was used in experiments with solvents other than dioxane.

3. *Analytical Methods*

In studying the reaction between cyanogen chloride or cyanogen bromide and water in dioxane solution, it was established that the solubility of the ammonium halide formed was low enough to permit rate studies by determining the amount of precipitated ammonium halide (18). Preliminary experiments on the solubility of ammonium iodide in dioxane–water solution at 25° C. indicated, however, that its solubility was too high for this method to be applicable to cyanogen iodide reactions. Consequently, a method based on the determination of the concentration of oxidizing agents in the solution was adopted.

A. *Determination of Cyanogen Iodide*

(1) Cyanogen iodide in dioxane or other solvent was added to 150 ml. of water containing 10 ml. of 6 *N* hydrochloric acid and titrated with standard sodium thiosulphate solution using starch as an indicator.* According to Meineke (9), the sequence of reactions is as follows:

$$ICN + 2Na_2S_2O_3 + 2HCl \rightarrow Na_2S_4O_6 + 2NaCl + HI + HCN$$
$$ICN + HI \rightarrow I_2 + HCN$$
$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI.$$

to give $2ICN + 4Na_2S_2O_3 + 2HCl \rightarrow 2Na_2S_4O_6 + 2NaCl + 2NaI + 2HCN.$

(2) The above method was modified by the addition of an excess of potassium iodide just before the titration. This resulted in the immediate liberation of iodine which was titrated with standard thiosulphate solution. With weighed samples of cyanogen iodide, quantitative recovery and good agreement

* *The blue color formed by starch and iodine does not appear in aqueous solutions which contain more than about 27% by volume of dioxane. In the region of 27% by volume of dioxane, the complex is brown and in solutions more concentrated in dioxane there is no color at all. A sufficiently large concentration of alcohol also prevents the formation of the blue starch–iodine color.*

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was obtained by either A(1) or A(2). In agreement with the results of Meineke (9) the reaction between cyanogen iodide and sodium thiosulphate in neutral solution was found to be incomplete.

B. *Determination of Iodine Monochloride*

(1) Since iodine monochloride was identified as a reaction product (Section 4), it was necessary to study its reaction with sodium thiosulphate. A direct titration in hydrochloric acid solution indicated that the reaction was incomplete and variable as reported by Lang (8).

(2) Following the method of Lang (8), iodine monochloride in dilute hydrochloric acid was added to 150 ml. of water containing 10 ml. of 6 *N* hydrochloric acid. Five grams of sodium acetate was added, followed by sufficient potassium cyanide to decolorize the solution. The reactions,

$$ICl + CN^- \rightarrow ICN + Cl^-$$
$$ICN + 2S_2O_3^= + H^+ \rightarrow I^- + HCN + S_4O_6^=$$

were found to be quantitative.

(3) Instead of adding sodium acetate and potassium cyanide as in (2) above, an excess of potassium iodide was added just before titration with thiosulphate solution. Iodine was liberated immediately by the reaction, $ICl + KI \rightarrow KCl + I_2$. Quantitative agreement was obtained between methods B (2) and B (3).

C. *Determination of Cyanogen Iodide, Iodine Monochloride, and Iodine*

No successful method was devised for determining both cyanogen iodide and iodine monochloride in the same solution. The total concentration of oxidation equivalents due to both was, however, determined by using the procedure outlined in A(2) or B(3) above. Furthermore, it was not found feasible to test for the presence or absence of iodine in iodine monochloride solutions. A solution of iodine monochloride in dilute hydrochloric acid gives a brown color with starch as does a solution of iodine and iodine monochloride. Although iodine monochloride is insoluble in chloroform, the chloroform test for iodine also fails, as the addition of iodine monochloride solution to a solution of iodine in chloroform results in the chloroform layer becoming colorless with no apparent change in the yellow hydrochloric acid layer.

It is possible to determine iodine in the presence of cyanogen iodide by precipitation of the former with silver nitrate. However, in the present experiments the situation was complicated by the presence of a relatively large amount of hydrochloric acid, which precipitated silver chloride along with any silver iodide that might form. When known amounts of cyanogen iodide containing hydrochloric acid were treated with varying amounts of silver nitrate solution and then titrated with sodium thiosulphate solution, it was observed that the apparent number of oxidation equivalents present decreased as the amount of silver nitrate present increased. This was probably due to some of the iodine, formed in the titration reaction, exchanging with chlorine in the silver chloride precipitate. It was concluded that it was not possible to analyze mixtures of cyanogen iodide and iodine quantitatively in the presence of hydrochloric acid by this method.

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A preliminary attempt was made to determine whether cyanogen iodide, iodine monochloride, and iodine could be distinguished in solution with a Beckman Model DU spectrophotometer. It was found that the solutions used in this work would have to be diluted many times to give readings on the instrument and that the results might not, therefore, be reliable. Furthermore, there appears to be considerable disagreement in the literature as to the positions of the absorption maxima for iodine. Also, the absorption maximum for iodine monochloride in solvents giving yellow solutions is reported (5) to coincide with an absorption maximum for iodine solutions. In view of these difficulties the search for a spectrophotometric method was abandoned.

Since no simple method of distinguishing between cyanogen iodide, iodine monochloride, and iodine was apparent, a method, A(2) or B(3), above, which determined only the total number of oxidation equivalents present was adopted.

4. *Identification of Reaction Products*

A. *Ammonium Chloride*

What appeared to be a mixture of crystals eventually appeared in most of the experiments conducted in dioxane solution. The bulk of these crystals had a yellow color but, mixed with this, there was always a smaller amount of a white crystalline material. In experiments where the initial molar ratio of water to cyanogen iodide was greater than 2: 1, only the white crystals formed. A quantity of these crystals, recovered after six weeks from an experiment in which the initial molar ratio of water to cyanogen iodide was 4: 1 and the initial hydrogen chloride concentration, 2.61 *M* gave a positive test for chloride and, on Kjeldahl analysis, 96.52% of the theoretical ammonia for ammonium chloride. (This compares with a 98.07% recovery of ammonia from a sample of pure ammonium chloride by the same procedure.) In another experiment, when the initial water to cyanogen iodide ratio was 10: 1, and the initial hydrogen chloride concentration 1.302 *M*, the white crystals were quantitatively recovered after one month. Their dry weight was 0.0810 gm., while the theoretical amount of ammonium chloride corresponding to complete conversion of the nitrogen in the cyanogen iodide was 0.0805 gm. The solubility of ammonium chloride in a dioxane–water solution of the concentration involved in this experiment was negligible (18). On the basis of these experiments it was concluded that ammonium chloride was quantitatively produced when more than the stoichiometric amount of water was present in the reaction mixture. Ammonium chloride was also positively identified in experiments where butanol was used as a solvent in place of dioxane.

The yellow crystalline material produced in all experiments in dioxane where the initial hydrogen chloride concentration was from 0.12 to 1.647 *M* and where the initial molar ratio of water to cyanogen iodide was not greater than 2: 1, was not definitely identified. This material was not very stable on exposure to the atmosphere and was believed to be a molecular compound of dioxane and ammonium iodide or iodine or iodine monochloride (15, 16).

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B. *Iodine Monochloride and Iodine*

It was observed that a brown coloration invariably appeared after a time in the reaction tubes. This coloration was first established as being due to iodine monochloride in an experiment with methanol as the solvent. In this particular case, a bright yellow color was produced immediately on adding 25 ml. of methanol, which was 7.71 *M* in hydrogen chloride, to 0.625 gm. of cyanogen iodide and 0.147 ml. of water. The solution darkened with time to a reddish color. A portion of this solution, after dilution with dilute hydrochloric acid and the addition of starch solution showed the brown color characteristic of iodine monochloride (8). This brown color changed to blue when potassium iodide was added, presumably owing to the reaction, $ICl + KI \rightarrow KCl + I_2$. Also, when a second portion of this reddish colored methanol solution was treated with sodium acetate followed by potassium cyanide, it was completely decolorized. The reaction would be (6), $ICl + KCN \rightarrow ICN + KCl$.

As an additional test, two equal portions of the methanol solution were diluted to five times their original volume, one with water and the other with dilute hydrochloric acid. The color darkened and iodine crystals separated from the water diluted solution in a few hours, owing to the reaction (12), $5ICl + 3H_2O \rightarrow HIO_3 + 5HCl + 2I_2$. There was no apparent change in the solution diluted with hydrochloric acid on standing over night. All of the above results are in accord with the known reactions of iodine monochloride.

Numerous similar tests were carried out for experiments in which dioxane was the solvent and, in all except one case, the brownish coloration appeared to be due to iodine monochloride. In the one exception, a positive test for iodine rather than iodine monochloride was obtained, but this was in an experiment that had been allowed to run to completion (about two weeks) and in which the iodine from the cyanogen iodide (or iodine monochloride) had been reduced to elementary iodine.

The appearance of iodine crystals was also noted in experiments conducted in aqueous solution after they had been in progress for a considerable time. This would be expected from the reaction between iodine monochloride and water indicated above.

C. *Carbon Dioxide*

Carbon dioxide was identified as a reaction product in cases where cyanogen iodide was allowed to react with hydrogen chloride in aqueous solution. However, no positive test for carbon dioxide was obtained for reactions in dioxane, although considerable gas pressure was noted in some tubes in which the reaction had proceeded for several days. Unfortunately, the literature does not appear to contain any information on the solubility of carbon dioxide in dioxane.

5. *Results*

A. *The Rate of the Reaction between Cyanogen Iodide, Water, and Hydrogen Chloride in Various Solvents*

Rate studies on the reaction between cyanogen iodide, water, and hydrogen chloride in aqueous solution and also in methanol, ethanol, and dioxane solutions at 45° C. were carried out by determining the change in the number

of equivalents of oxidizing agent present with time. As indicated above, the analytical method (Section 3 A(2)) adopted, did not distinguish between cyanogen iodide, iodine monochloride, or iodine. Typical results for these experiments are shown in Fig. 1. Except for the experiments in aqueous

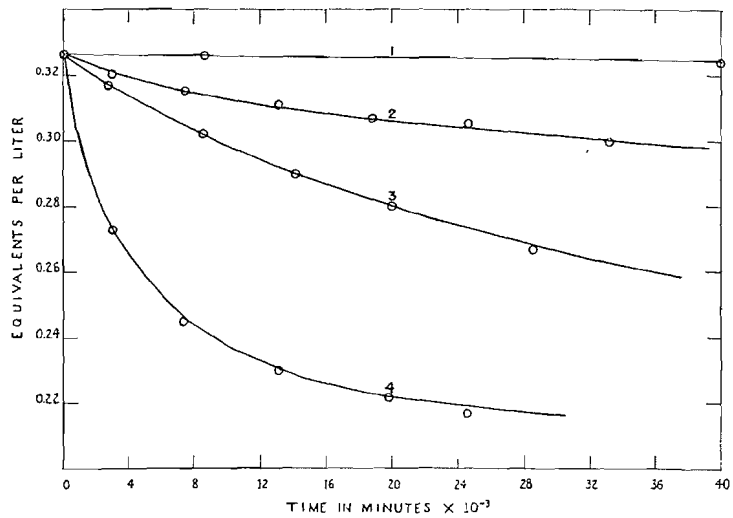



FIG. 1. The effect of solvent on the rate of reaction between cyanogen iodide, water, and hydrogen chloride.
1. Solvent, water, initial concentration of hydrogen chloride 0.233 *M*.
2. Solvent, methanol, initial concentration of hydrogen chloride 0.0916 *M*.
3. Solvent, ethanol, initial concentration of hydrogen chloride 0.0916 *M*.
4. Solvent, dioxane, initial concentration of hydrogen chloride 0.0916 *M*.

solution the initial molar ratio of water to cyanogen iodide was 2: 1. It is to be noted that the rate of decrease of oxidation equivalents was much slower in water than in the other solvents, even though the initial concentration of hydrogen chloride was considerably greater. Since the polar nature of the solvents decreases in the order, water, methanol, ethanol, dioxane, it is to be expected that the degree of dissociation of the hydrogen chloride in these solvents will decrease in the same order. These experiments may, therefore, be taken as qualitative evidence that it is probably molecular hydrogen chloride that reacts with, or catalyses some reaction of, cyanogen iodide.

### B. *The Effect of Hydrogen Chloride Concentration on the Rate of Reaction between Cyanogen Iodide and Water in Dioxane Solution*

A series of experiments at 45° C. was carried out in dioxane solution with initial concentrations of water and cyanogen iodide in the molar ratio of 2: 1 and with initial hydrogen chloride concentrations varying from 0.125 *M* to 1.647 *M*. The results shown in Fig. 2 indicate that, although there was a relatively rapid initial decrease in oxidation equivalents at 45° C., the reaction eventually became very slow at a concentration level which was dependent on the initial concentration of hydrogen chloride. It is to be noted that the lower the initial hydrogen chloride concentration, the greater was the decrease in the number of oxidation equivalents per liter.

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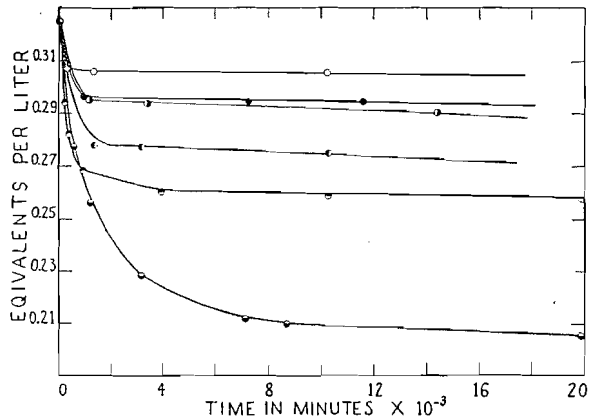



FIG. 2. The effect of hydrogen chloride concentration on the rate of reaction between cyanogen iodide and water in dioxane solution. Initial hydrogen chloride concentrations:
○ 1.647 *M* ◑ 0.991 *M* ◓ 0.491 *M*
● 1.302 *M* ◐ 0.656*M* ◒ 0.126 *M*

Since the curves shown in Fig. 2 do not fit any simple rate equation, very approximate relative rates of reaction for the initial stages of the reaction were determined by drawing tangents to the concentration vs. time curves. Relative reaction rates evaluated in this way are shown plotted against the initial

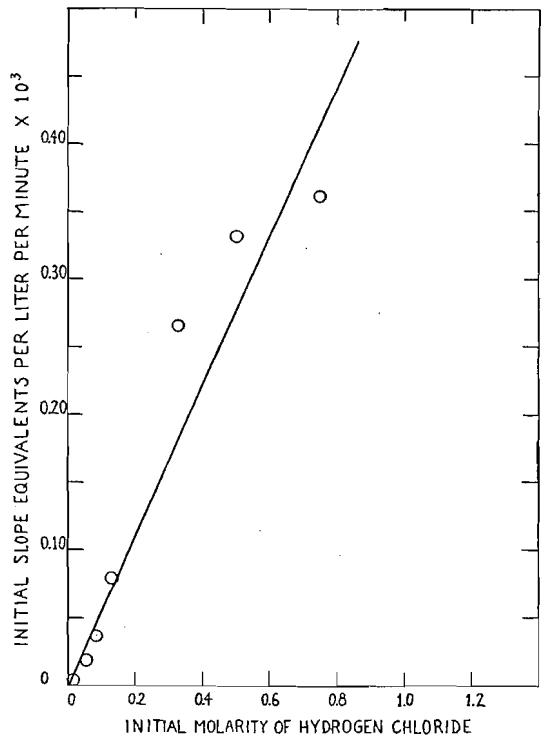



FIG. 3. The effect of hydrogen chloride concentration on the initial rate of reaction of cyanogen iodide with water in dioxane solution.

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molarity of hydrogen chloride in Fig. 3. In the presence of the relatively small concentration of water employed in these experiments (about 0.32 moles per liter), most of the hydrogen chloride may be assumed to be in the molecular condition and therefore the initial reaction rate is approximately proportional to the concentration of molecular hydrogen chloride in the dioxane.

C. *The Effect of Water Concentration on the Rate of the Reaction Between Cyanogen Iodide, Water, and Hydrogen Chloride in Dioxane Solution*

Experiments at 45° C. in dioxane which was 1.302 *M* with respect to hydrogen chloride and with initial ratios of cyanogen iodide to water of 1: 10, 1: 4, 1: 2, and 1: 0, respectively, gave results as indicated in Fig. 4. The decrease

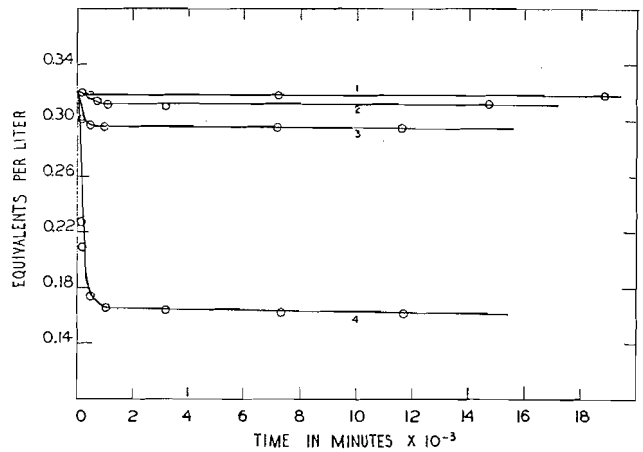



FIG. 4. The effect of water concentration on the rate of reaction between cyanogen iodide, water, and hydrogen chloride in dioxane solution. Initial concentrations of water: (1) 1.635 moles per liter; (2) 0.654 moles per liter; (3) 0.327 moles per liter; (4) 0.000.

in oxidation equivalents was most rapid in the case where no water was initially present and the higher the initial concentration of water the slower was the reaction and the smaller was the decrease in oxidation equivalents. The experiment with no water present was the only one in dioxane solution where the reaction apparently proceeded until all of the cyanogen iodide was converted to iodine, crystals of which were isolated. This result suggests that the cyanogen iodide was converted to iodine monochloride which, in turn, reacted with the dioxane with the eventual formation of iodine. Independent experiments established that solutions of cyanogen iodide in dioxane are reasonably stable and that iodine monochloride reacts with dioxane in the presence of hydrogen chloride.

D. *The Effect of Cyanogen Iodide Concentration on the Rate of the Reaction between Cyanogen Iodide, Water, and Hydrogen Chloride in Dioxane Solution*

In this series of experiments at 45° C. in dioxane, the initial concentrations of water and hydrogen chloride were kept constant at 0.327 and 0.324 moles per liter, respectively, while the initial concentration of cyanogen iodide was varied from 0.094 to 0.197 moles per liter. When the approximate initial slopes (as determined by drawing tangents) of the oxidation equivalents vs. time

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curves were plotted against the initial cyanogen iodide concentration, a straight line relationship was obtained, indicating that, at least in the initial stages, the reaction is of the first order with respect to cyanogen iodide.

E. *The Reaction Between Cyanogen Iodide, Water, and Hydrogen Chloride in Aqueous Solution*

To avoid some of the complications indicated in the experiments where dioxane was used as the solvent, a series of experiments was carried out in aqueous hydrochloric acid solution. As was indicated by the results shown in Fig. 1, it was necessary to use considerably higher hydrogen chloride concentrations than in dioxane solution to obtain appreciable reaction rates. The initial rate of decrease of oxidation equivalents was found, as in dioxane solution, to increase with increasing initial hydrogen chloride concentration. Also, in the later stages of the reaction an almost stationary level, depending on the initial hydrogen chloride concentration, was reached in all cases except those where the initial hydrogen chloride concentration was below about 6 *M*. The results of a typical series of such experiments at 45° C. are shown in Fig. 5.

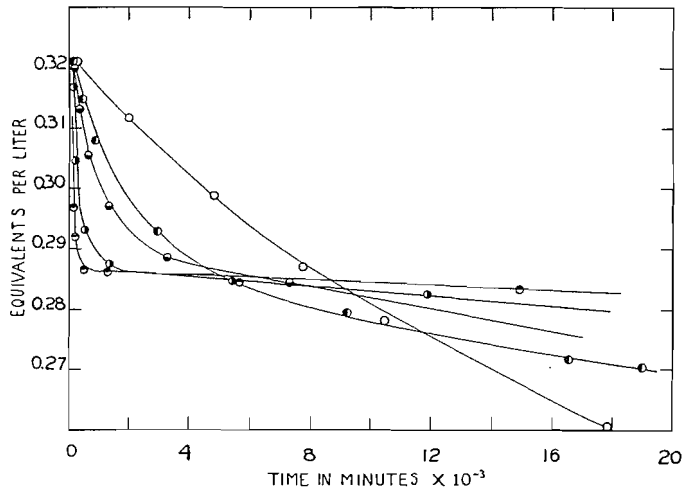



FIG. 5. The effect of hydrogen chloride concentration on the rate of reaction of cyanogen iodide with water in aqueous solution. Initial concentrations of hydrogen chloride:
○ 5.735 *M* ◑ 7.819 *M*
◐ 6.631 *M* ◓ 8.579 *M*
◒ 7.064 *M*

Approximate initial rates for the decrease of oxidation equivalents at 45° C. were determined by drawing tangents to the concentration vs. time curves. When these initial rates were plotted against the calculated activity of hydrogen chloride (1), a linear relationship was indicated as shown by Fig. 6. A similar relationship was indicated by a few results obtained at 30° C. These results suggest that the concentration of molecular hydrogen chloride controls the initial reaction rate.

Although the initial rates of reaction were greater at 45° C. than at 30° C. (for the same initial concentrations of hydrogen chloride and cyanogen iodide), it was observed that the reaction at 30° C. proceeded more nearly to completion

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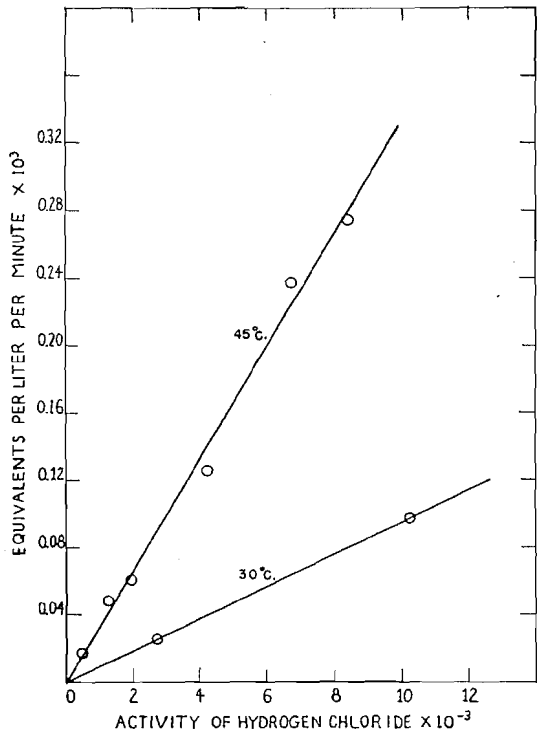



FIG. 6. Dependence of the initial rate of reaction between cyanogen iodide, water, and hydrogen chloride in aqueous solution on the activity of hydrogen chloride at 45° C. and 30° C.

before reaching the stage where the rate of decrease in oxidation equivalents became extremely slow. Assuming a first order reaction, the apparent activation energy for the initial reaction in 7 to 8 *M* hydrogen chloride was calculated to be about 8000 calories per mole.

F. *The Reaction of Formic Acid with Iodine Monochloride in the Presence of Hydrogen Chloride*

As shown above, iodine monochloride was produced in the reaction mixtures, probably by the reaction:

$$ICN + HCl \rightarrow ICl + HCN .$$

The hydrolysis of hydrogen cyanide in acid solutions has been studied (6, 7, 13, 14) and shown to proceed through the stages:

$$HCN \xrightarrow{H_2O} HCONH_2 \xrightarrow{H_2O} HCOOH .$$

Free energy calculations indicated that a reaction between iodine monochloride and formic acid was possible and consequently a few experiments were carried out to study this reaction.

The results of an experiment at 45° C. in 5.9 *M* hydrochloric acid with initial concentrations of formic acid and iodine monochloride, 2.210 and 0.446 moles per liter, respectively, are shown in Fig. 7. The analytical method employed was the same as that used in the cyanogen iodide experiments. In this

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case, however, iodine and iodine monochloride are the only oxidizing agents present that react with thiosulphate and the concentration of both could be calculated from one titration value. The reason for this is that, when the reaction of iodine monochloride and formic acid is complete, that is, all the iodine monochloride converted to iodine, one half of the original number of oxidation equivalents remain.

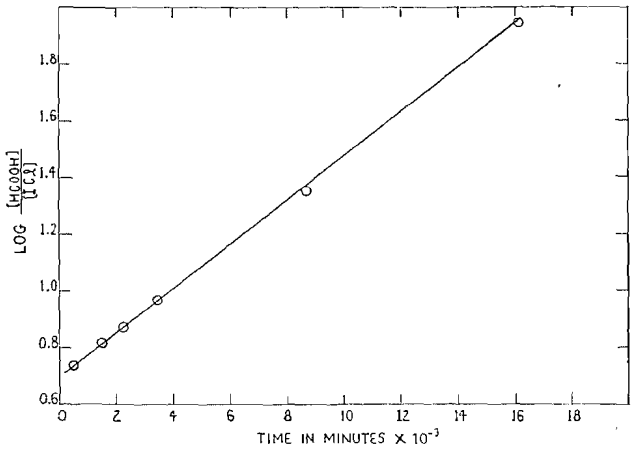



FIG. 7. Data for the reaction between formic acid and iodine monochloride, at 45° C., plotted on the basis of a bimolecular reaction.

Since no direct determination of the formic acid concentration was made, it was assumed that its rate of decrease was one half that shown by iodine monochloride, in accordance with the reactions:

$$\begin{aligned} &ICl + HCOOH \rightarrow HI + HCl + CO_2 \\ &ICl + HI \rightarrow I_2 + HCl \\ \hline &2ICl + HCOOH \rightarrow I_2 + 2HCl + CO_2 . \end{aligned}$$

Further, if it is assumed that the first of these reactions is rate determining and bimolecular (the second reaction is known to be very fast (10)), the plot of log [HCOOH]/[ICl] vs. time, should give a straight line relationship as observed in Fig. 7 to as high as 95% completion of the reaction. The average specific rate constant for this experiment was, $k = 4.7 \times 10^{-5}$ liters/mole/minute.

Some preliminary work was done on the effect of the hydrogen chloride concentration on the rate of the reaction between formic acid and iodine monochloride at 45° C. In these experiments the initial molar ratio of formic acid to iodine monochloride was approximately 1:1, with actual concentrations of the same order as would be produced in the cyanogen iodide experiments, that is, about 0.09 molar. Treating the data as indicated above, average specific rate constants of $k = 5.5 \times 10^{-5}$ liters/mole/minute, and $k = 1.4 \times 10^{-5}$ liters/mole/minute, were obtained for initial hydrochloric acid molarities of 5.86 and 7.87, respectively. That is, other factors being constant, the rate of reaction between formic acid and iodine monochloride decreases with

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increasing concentration of hydrogen chloride. This effect could possibly be due to a reversal of the suggested reactions but, since a constant rate was observed to 95% reaction of the iodine monochloride, this does not seem likely. It is more probable that the change in rate was a result of change in environment (11). In any case, these experiments indicated that the rate of reaction between formic acid and iodine monochloride was too slow to account for the observed rate of decrease in oxidation equivalents in the initial stages of the cyanogen iodide experiments.

## DISCUSSION

The formation of iodine monochloride indicates that the primary step in the reaction of cyanogen iodide with hydrogen chloride and water in either dioxane or aqueous solution is probably:

$$ICN + HCl = ICl + HCN . \qquad [1]$$

The hydrolysis of hydrogen cyanide in aqueous hydrochloric acid proceeds, according to Krieble and McNally (6), by the following steps:

$$HCN + HCl \rightleftarrows H-\overset{\displaystyle Cl}{\overset{|}{C}}=NH \qquad [2]$$

$$H-\overset{\displaystyle Cl}{\overset{|}{C}}=NH + H_2O \rightleftarrows H-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-NH_2 \qquad [3]$$

$$H-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-NH_2 \rightleftarrows H-\overset{\displaystyle O}{\overset{||}{C}}-NH_2 + HCl \qquad [4]$$

$$H-\overset{\displaystyle O}{\overset{||}{C}}-NH_2 + H_2O \rightleftarrows H-\overset{\displaystyle O}{\overset{||}{C}}-O-NH_4 . \qquad [5]$$

They suggested that reactions [5] and [4] were very fast compared to [2] and that the second hydrolysis, represented by [5] was faster than [3]. They also concluded that molecular hydrogen chloride was the effective catalyst. Krieble and Peiker (7) continued this study and concluded that the rate of hydrolysis of hydrogen cyanide was independent of its concentration.

Rabinovitch and Winkler (13, 14) have studied the hydrogen chloride catalyzed hydrolysis of formamide and hydrogen cyanide. They observed a maximum in the rate of hydrolysis of formamide in 4–6 *N* acid which they interpreted as being due to a maximum concentration of an amide cation. The relative rate ratios for the hydrolysis of the nitrile and amide were found to vary from 1: 12,000 in 1.00 *N* acid to 1: 3 in 8.47 *N* acid.

On the basis of these results obtained by previous authors and the information provided by the present work, it seems probable that the following series

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of reactions occur in aqueous hydrochloric acid solutions of cyanogen iodide: (reaction products definitely identified in this work are underlined).

$$ICN + HCl \rightleftarrows \underline{ICl} + HCN \quad [1]$$

$$HCN + H_2O \rightleftarrows H - \overset{\overset{O}{\|}}{C} - NH_2 \quad [2]^*$$

$$H - \overset{\overset{O}{\|}}{C} - NH_2 + H_2O \rightleftarrows H - \overset{\overset{O}{\|}}{C} - OH + NH_2 \quad [3]$$

$$NH_3 + HCl \rightleftarrows NH_4Cl \quad [4]$$

$$H - \overset{\overset{O}{\|}}{C} - NH_2 + 2ICl + H_2O \rightleftarrows \underline{CO_2} + I_2 + \underline{NH_4Cl} + HCl \quad [5]$$

$$H - \overset{\overset{O}{\|}}{C} - OH + 2ICl \rightleftarrows \underline{CO_2} + \underline{I_2} + 2HCl \quad [6]$$

To account for the reduction of the iodine in iodine monochloride, either the formamide and/or the formic acid, produced in reactions [2] and [3], must be oxidized. The preliminary study made of the oxidation of formic acid by iodine monochloride indicated that reaction [6] was not nearly rapid enough, under the conditions of these experiments, to account for the relatively rapid initial rate of reaction observed in both aqueous and dioxane solutions. It therefore appears necessary to postulate that the relatively rapid initial rate of decrease in oxidation equivalents is due to the oxidation of formamide by iodine monochloride as represented by equation [5]. Unfortunately, no information on this reaction is available. Since, at least in the initial stages, the rate of decrease of oxidation equivalents was found to be proportional to the activity of the undissociated hydrogen chloride (Fig. 6) it is suggested that reaction [1] is initially the rate controlling process.

Assuming that reaction [5] does occur at a more rapid rate than reaction [6], it is possible to account for the levelling off of the oxidation equivalent vs. time curves as shown in Figs. 2 and 5, as follows: The primary hydrolysis of hydrogen cyanide (reaction [2]) occurs at a rate which increases by a factor of 1000 on increasing the hydrogen chloride concentration from 1.95 *M* to 7.84 *M* (6), while the hydrolysis of formamide (reaction [3]) occurs at a rate which increases with increasing hydrogen chloride concentration, reaching a maximum in about 4 *M* acid, and then decreasing to one half the maximum value when the hydrogen chloride concentration is increased to about 8 *M* (13). In several of the present experiments the amount of ammonium chloride recovered corresponded to total conversion of the nitrogen in the cyanogen iodide, that is, to complete hydrolysis of the hydrogen cyanide formed in reaction (1).

* *Probably as a series of reactions as suggested by Krieble and McNally (6), whose results indicate that the rate of reaction [2] under comparable conditions, is considerably greater than the initial rate of decrease of oxidation equivalents observed in the present work.*

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At the same time, however, the reaction as measured by the decrease in oxidation equivalents was not nearly complete. If the formamide reacts both by hydrolysis (reaction [3]) and by oxidation (reaction [5]) and if the relative rates of these two reactions change with a change in the hydrogen chloride concentration, the initial relatively rapid rate of decrease of oxidation equivalents in solutions of high hydrogen chloride concentration could be accounted for in terms of higher iodine monochloride and formamide concentrations than are present in solutions of lower hydrogen chloride concentration. The greater degree of completion of the reaction (as measured by oxidation equivalents) in solutions of lower hydrogen chloride concentration may be explained by assuming that relatively more formamide is oxidized by iodine monochloride (reaction [5]) before complete hydrolysis of the formamide occurs (reaction [3]). As soon as all the formamide has been used up, both by hydrolysis and oxidation, the rate of decrease of oxidation equivalents becomes very small, as the oxidation of formic acid by iodine monochloride (reaction [6]) has been shown to be very slow under the experimental conditions. This could cause the virtual levelling off of the oxidation equivalent vs. time curves as observed.

When dioxane was used as the solvent it is probable that the same reactions occurred along with complications involving reactions of dioxane with cyanogen iodide, iodine monochloride, and iodine, to form molecular compounds.

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# THE THERMAL DECOMPOSITION OF *n*-BUTANE[1]

By V. A. Crawford[2] and E. W. R. Steacie

ABSTRACT

The thermal decomposition of *n*-butane at 442°C. has been investigated analytically in the pressure range 4–13 cm. Up to 9% decomposition, the rates of formation of $H_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ are independent of time; the dependence of the rates on butane pressure was approximately first order. The validity of the extrapolation procedure for obtaining the initial products was established, there being no significant variation in the composition of the products with extent of decomposition. In the nitric oxide fully inhibited reaction irreproducible rate data were obtained although the proportions in which the products are formed seemed to be roughly invariable. In view of this it is suggested that no very definite conclusions can be drawn from a comparison of the composition of the products of the normal and fully inhibited reactions. The heterogeneity of the fully inhibited reaction is stressed for the importance of this has not hitherto been sufficiently recognized. Attention is drawn to the apparent inefficiency of nitric oxide as an inhibitor.

The thermal decomposition of paraffin hydrocarbons has been abundantly studied in the past, resulting in the establishment of certain general characteristics of such reactions. Nevertheless, certain salient features of the pyrolysis of the paraffins still remain to be elucidated.

In order to identify the initial products, recourse is usually had to a procedure which involves extrapolation of the products formed at real conditions to their values at zero decomposition (9). Although it is possible in principle to decrease the extent of decomposition until primary products only are formed, excessive dilution of the products with undecomposed paraffin presents a formidable analytical problem. Because of this, pyrolyses at fairly high pressures were carried to extents of decomposition ranging from 20–50% and the results extrapolated to zero decomposition. In order to obtain the initial products, therefore, an unduly large extrapolation is involved and in order to test its validity the range 0–20% requires exploration. The less laborious and more exact methods of analysis which are now available enable this to be done with reasonable facility.

The decomposition of paraffin hydrocarbons with two to eight carbon atoms has been explained as being in part a chain reaction involving free radicals. Evidence for this comes not only from the sensitized decompositions (10, 3) but also from the nitric oxide inhibition from which mean chain lengths from 2 to 20 may be calculated. These latter values are calculated on the assumption that the fully inhibited reaction is a molecular rearrangement and not a free radical process. This hypothesis would seem to be reinforced by the fact that, although nitric oxide is much more efficient than propylene, both inhibitors reduce the rates to the same limiting value.

The reaction, however, is not stopped in the presence of nitric oxide but merely slowed down and after 20–25% decomposition the inhibited rate is

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identical with the uninhibited. Initial rates therefore provide the only reliable criterion of the extent of inhibition. Moreover, as was first shown by Dintzes and Frost (1) and more recently conclusively demonstrated by Stubbs and Hinshelwood (13) the sigmoid nature of the $\Delta p - t$ curves for the higher paraffins is due to self inhibition by the products of the reaction. When studied at large conversions, therefore, the artificial nitric oxide inhibition reaction is being investigated under conditions rendered complicated by the self inhibition of the products. The desirability of investigating the nitric oxide inhibited reaction at small conversions is evident.

That the minimal inhibited rate corresponds to a pure molecular rearrangement, that is to a complete suppression of chains, is doubted by Steacie and Folkins for two reasons. (1) From a study of the free radical induced decomposition of butane they concluded that there is a certain fraction of residual chain decomposition at all concentrations of nitric oxide. (2) The products of the inhibited reaction were found to be the same as those of the normal reaction. With regard to (2) it may be noted that whether the ratio of chain reaction to molecular rearrangement is 100 : 1 or 1 : 1 depends on the differences between the activation energies and entropies of the alternate reaction paths. On this basis Hinshelwood (4) has recently shown that it is quite possible for the products from the molecular process and chain reaction to be in the same proportions. Unfortunately, the results of Steacie and Folkins, and Hinshelwood *et al.*, are not as conclusive as they might be for the work was done at too high conversions.

In some studies it has been reported that nitric oxide is used up during the inhibition, whereas other workers maintain that the inhibitor is only gradually consumed, if at all.

There are still therefore several problems connected with the pyrolysis of paraffin hydrocarbons. In order to obtain unequivocal results which may be discussed with assurance, it is essential that both the normal and the inhibited reactions be studied at small extents of decomposition. The results of such an investigation are reported here, and because of its intermediate complexity butane was chosen for this work.

## MATERIALS

Butane which was obtained in cylinders from the Phillips Petroleum Company (Research grade) was stated to be 99.8% pure and was used without further purification except for bulb to bulb distillation and rigorous degassing.

Nitric oxide was obtained in cylinders from the Matheson Company. Its purity was stated to be not less than 98.7%, the balance being nitrogen and higher oxides of nitrogen. Consequently, the gas from the cylinder was passed through a trap at $-120°$C. to remove $NO_2$ and then into a storage bulb. It was condensed and distilled under vacuum in order further to ensure its purity.

## APPARATUS AND PROCEDURE

Since the pyrolysis was to be carried to only small extents of decomposition, the reaction was studied at temperatures where it proceeds slowly. Further-

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more, in order to ensure that sufficient products were available for accurate analysis, experiments were carried out in a static system using a large quartz reaction vessel which was about 12 in. long and 6 in. in diameter. It was contained in a furnace built of a steel tube 37 in. long, wound with 12 gauge Chromel A wire, and mounted vertically in a rectangular transite box lagged with asbestos fiber. Uniformity of temperature along the tube was achieved by winding the furnace in two sections. Three leads were brought out of the insulating box, one of which was a center tap common to each winding. Current for each winding was taken through a 20 amp. variac transformer from a 3 kva. Sorenson constant voltage regulator. The reaction vessel was mounted vertically in the center of the furnace and rested on a narrow transite ledge which was supported by a steel tube resting on the base of the furnace. The ends of the latter were closed by 5/16 in. boiler plate at the bottom and a tight fitting refractory plug at the top which contained holes for the reaction vessel outlet tube and thermocouples. By manual regulation it was possible to keep the temperature along the length of the vessel uniform to within 1–2°C. Temperatures were measured by using three chromel-alumel thermocouples. These were in contact with the outer surface of the reaction vessel and were situated at its base, center, and shoulder respectively. In addition, two variable thermocouples were available to explore the temperature variation along the whole length of the furnace. All thermocouples were calibrated in the temperature range to be used so the absolute values of the temperature should be accurate to $\pm 1$°C. The results reported have been obtained at 442°C.

The reaction system comprised the reaction vessel, mercury manometer, traps, and bulbs for the purification of gases and a 5-liter sharing bulb. The gas analysis system consisted of a sampling bulb, liquid nitrogen traps, mercury diffusion pump, a low temperature still similar to that described by LeRoy (5), a McLeod gauge, and combined Toepler pump and gas burette.

Each experiment was conducted by admitting a known pressure of butane to the sharing bulb and then expanding the gas for 10 sec. into the reaction vessel at which instant the sharing bulb was isolated. After the reaction had proceeded the desired length of time, samples of the reaction products for analysis were obtained by allowing the gases in the reaction vessel to expand for 10 sec. into an evacuated 1-liter sampling bulb at room temperature. Here the reaction products together with unchanged butane were frozen out in liquid nitrogen and the hydrogen and methane pumped off. Blank experiments showed that both these gases are removed quantitatively by repeated cycles of freezing, pumping, and evaporating. After removal of the noncondensables, the residue in the sampling bulb was condensed into the Ward still. Blank experiments showed a 100% recovery of small amounts of ethylene and ethane mixed with a large amount of butane (1 : 200). Unfortunately, however, it was not found possible to recover propylene quantitatively from a large excess of butane and hence propylene was not analyzed for. This is perhaps a disadvantage of the present work, but if it is agreed that it is important to study the initial stages of the reaction, then this is almost inevitable. Ward still analysis

separated the $C_2$ fraction from higher hydrocarbons and the former by mass spectrometer analysis was found to consist only of $C_2H_6$ and $C_2H_4$.

When the decomposition of butane in the presence of nitric oxide was studied, the nitric oxide was usually introduced into the reaction vessel just prior to the admission of butane. In some experiments, runs were made with mixtures of butane and nitric oxide which had been allowed to mix thoroughly before introduction to the reaction vessel. Within the rather large experimental error, no differences in the results were observed.

A sample for analysis was obtained in exactly the same manner as previously. The sampling bulb was cooled in liquid nitrogen and the noncondensables ($H_2$, $CH_4$, and NO) pumped off with the aid of the mercury diffusion pump and the pump down trap. By repeated cycles of freezing, pumping, and warming, it was possible to remove the NO completely from the sample. The residue in the sampling bulb was then condensed in the Ward still and the $C_2$ fraction obtained as before. Complete removal of NO from the $C_2$ fraction was always tested for by exposing it to an alkaline bead of sodium sulphite. The necessity for this procedure became apparent when it was found that nitric oxide on admission to the mass spectrometer gave the nitrogen *m/e* 28 peak the intensity of which was dependent on the pressure of nitric oxide. In the mass spectrometer, therefore, $N_2$ presumably arises from a bimolecular process involving nitric oxide. Furthermore, since NO and $C_2H_6$ have the same mass numbers there is perhaps some opportunity for confusion in their determination when they are present simultaneously. It was thought advisable, therefore, to separate the products not only from the large excess of unchanged butane but also from the nitric oxide. Indeed one of the distinguishing features of the present work is the very great care that has been taken to ensure that the $C_2$ fractions were uncontaminated with NO.

## RESULTS

Because of technical difficulties, only $H_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ were analyzed for quantitatively. The effect of time on the production of these gases at 442°C. in the absence of nitric oxide is shown in Figs. 1, 2, 3, and 4. It is evident that the formation of all four gases varies linearly with time up to a time of decomposition of 30 min., that is from 1.5 to 9% conversion. The initial rates of

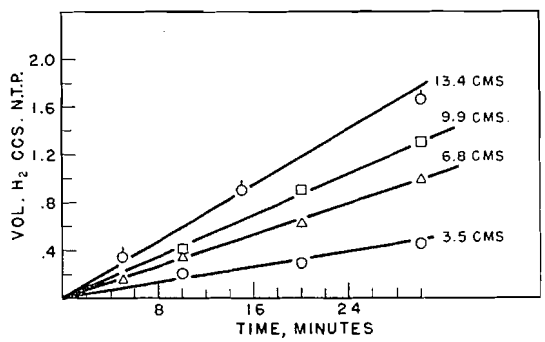



FIG. 1. Dependence of hydrogen formation on time and pressure of butane.

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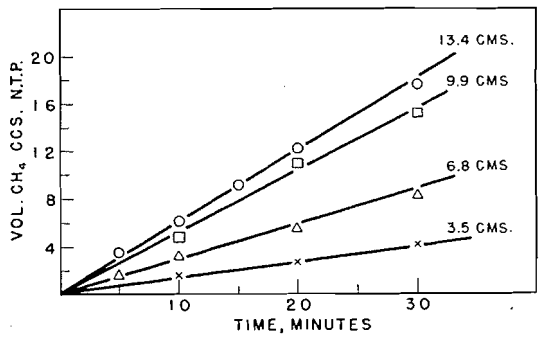



FIG. 2. Dependence of methane formation on time and pressure of butane.

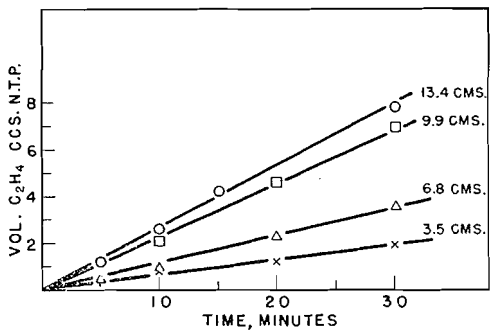



FIG. 3. Dependence of ethylene formation on time and pressure of butane.

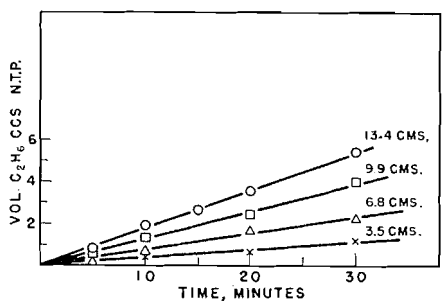



FIG. 4. Dependence of ethane formation on time and pressure of butane.

formation can therefore be determined unambiguously. It was found that at extents of decomposition greater than 10% there is a marked falling off from the linear relationship between formation of products and time. Stubbs and Hinshelwood (13) proved quite conclusively that the falling off in rate was due to inhibition by the products of the reaction. Since Rice and Polly (8) have shown that ethylene causes no detectable inhibition, the effect must be due largely to propylene.

A plot of the percentage products versus percentage decomposition was found to be linear up to 24% conversion. The extent of decomposition was computed from the pressure increase because technical difficulties made it impossible to determine the consumption of butane. This procedure is quite sound for whichever method is used it will correctly show the variation, if any,

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in the composition of the products with extent of decomposition. There was no significant variation in the products with changes in the initial pressure over the range 4–13 cm. This agrees with the earlier work of Steacie and Puddington (12) who found that varying the initial pressure of butane from 20–60 cm. produced no noticeable change in the relative proportions of the products.

*Inhibited Decompositions*

It is well known that the rate of decomposition of butane is reduced by small additions of nitric oxide while, in the presence of a sufficient quantity of the inhibitor, the rate is reduced to a well defined limiting minimum value. The inhibited decompositions were studied under conditions identical with that of the normal decomposition except that the butane was pyrolyzed in the presence of $\frac{1}{10}$th its pressure of nitric oxide, a value which is known to give maximum inhibition.

Unlike the normal decomposition where the rates of formation of the products were reproducible to within 2–5% it was now found impossible to obtain reproducible rate data. An example of this irreproducibility is shown in Table I which records the results of experiments carried out under identical conditions.

TABLE I

| Duration of run, min. | Volume of products generated in cc. N.T.P. | | | | $P_{Butane}$, cm. | $P_{NO}$, cm. |
|---|---|---|---|---|---|---|
| | $CH_4$ | $H_2$ | $C_2H_4$ | $C_2H_4$ | | |
| 5 | 0.91 | 0.055 | 0.16 | 0.066 | 13.24 | 1.50 |
| 5 | 0.93 | 0.072 | 0.20 | Absent | 13.19 | 1.41 |
| 5 | 0.88 | 0.076 | 0.40 | Absent | 13.14 | 1.43 |
| 5 | 1.69 | 0.103 | 0.44 | Absent | 13.60 | 2.08 |
| 5 | 0.62 | 0.048 | 0.30 | 0.022 | 13.84 | 1.33 |
| 30 min. | 2.705 | 0.173 | 0.98 | 0.074 | 13.64 | 2.03 |
| per 5 min. | 0.45 | 0.029 | 0.16 | 0.012 | | |

This may be accounted for in two ways. The mass spectrometer analyses of the very small quantities of products are not as accurate as may be desired. Secondly, and more important, the scatter in results may be a manifestation of the slight disturbance also noted by Stubbs and Hinshelwood (13) in the initial stages of the fully inhibited reaction.

TABLE II

| Extent of decomposition, % | % Composition of the products | | | | $P_{Butane}$, cm. | $P_{NO}$, cm. |
|---|---|---|---|---|---|---|
| | $CH_4$ | $H_2$ | $C_2H_4$ | $C_2H_6$ | | |
| 0.96 | 75.7 | 4.6 | 19.6 | Absent | 13.60 | 2.08 |
| 2.2 | 68.9 | 4.4 | 24.5 | 1.9 | 13.64 | 2.03 |
| 0.98 | 76.3 | 4.6 | 13.5 | 5.6 | 13.24 | 1.50 |
| 0.98 | 77.1 | 5.9 | 16.9 | Absent | 13.19 | 1.41 |
| 0.91 | 65.1 | 5.6 | 29.3 | Absent | 13.14 | 1.43 |
| 0.95 | 62.6 | 4.8 | 30.3 | 2.2 | 13.84 | 1.33 |
| | 58 | 5 | 24 | 12 | | |

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Table II gives the composition of the products resulting from the fully inhibited decomposition.

For comparison, the initial products of the normal decomposition are given in the bottom line of the table.

A few experiments were also made to determine the dependence of the rate of formation of $C_2H_4$ and $C_2H_6$ on the pressure of butane. The results obtained are given in Table III.

TABLE III

| Extent of decomposition, % | $P_{Butane}$, cm. | $P_{NO}$, cm. | cc. N.T.P. | | Duration of run, min. |
|---|---|---|---|---|---|
| | | | $C_2H_4$ | $C_2H_6$ | |
| 6.8 | 55.88 | 7.2 | 9.18 | 1.37 | 15 |
| 5.1 | 43.96 | 5.3 | 4.96 | 0.63 | 15 |
| 3.0 | 27.67 | 3.5 | 1.66 | 0.16 | 15 |

## DISCUSSION

### *Normal Decomposition*

There is no marked variation in the composition of the products from 2–24% decomposition, implying that in this range of decomposition no secondary changes are occurring. Since the conversion in the present work is small, the ethane may be considered to be practically unchanged. The olefins, however, have a greater reactivity than the paraffins from which they are formed, and may undergo polymerization and hydrogenation as well as decomposition. The relative rates of the different types of secondary reactions are dependent on the initial concentrations of the individual decomposition products, the total pressure in the system, the temperature, etc. But at the conversions of the present work, this is not likely to be serious. Indeed, experiments carried out by Marek and McCluer (6) with $N_2$–$C_2H_4$ mixtures to determine the extent of ethylene decomposition under their experimental conditions showed the loss of $C_2H_4$ from this source to be slight. There is a further loss of unsaturateds by the reversal of the decomposition reaction. But pyrolyzing the butane to small extents as in the present work to eliminate secondary changes will also largely eliminate this difficulty. In any case, approximate calculations have shown that loss of products by reversible reaction is only likely to be of significance at pressures greater than atmospheric.

The slight variation in composition of the products with extent of decomposition establishes the validity of the extrapolation procedure for obtaining the initial products, the composition of which is found to be $H_2$ 4.8%, $CH_4$ 58.0%, $C_2H_4$ 24.5%, and $C_2H_6$ 12.0%. Steacie and Puddington (12) studied the decomposition of butane at 552°C. at conversions ranging from 12 to 50%. Assuming for purposes of comparison that $H_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ are their only products, the results of Steacie and Puddington, when recalculated on this basis, give the initial composition of the products as $H_2$ 4.4%, $CH_4$ 51.3%, $C_2H_4$ 22.9%, and $C_2H_6$ 21.3%. It is noteworthy that, whereas Steacie and

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Puddington from 12 to 50% decomposition always found ethylene and ethane appearing in comparable quantities, in the present work the ratio of ethylene to ethane is approximately 2. This cannot be due to the difference in temperature of the two studies.

Within the temperature range of previous investigations (500–600°C.) it is usually stated that the products of the decomposition do not vary significantly with temperature. And such evidence as there is would seem to indicate that the relative probabilities of scission at the various bonds of a paraffin are only slightly affected by temperature. However, product paraffins higher than methane appear partly in the form of the corresponding olefins and hydrogen, and this effect while small at 440°C. might well be of significance at 600°C.

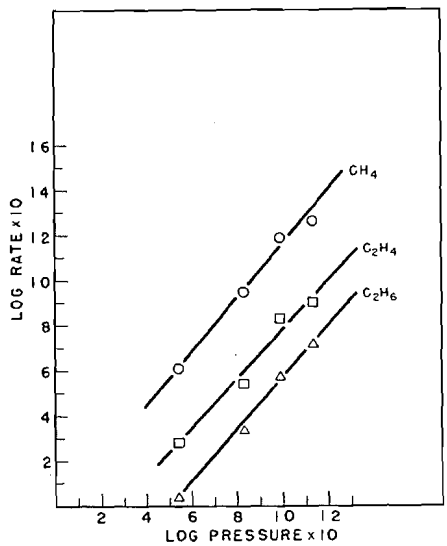



FIG. 5. Order determinations for the rates of formation of $CH_4$, $C_2H_4$, and $C_2H_6$ in the normal decomposition of butane.

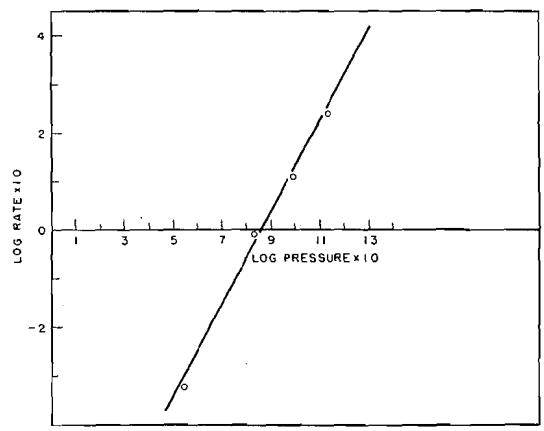



FIG. 6. Order determination for the rate of formation of hydrogen in the normal decomposition of butane.

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So, on this basis, temperature might be anticipated to affect the olefin paraffin ratio in the products. The effect observed here, however, is opposite to that which might have been expected from this reasoning.

The rates of formation of all four products decrease markedly with decreasing butane pressure. From a plot of log rate vs. log pressure, Figs. 5 and 6, orders of 0.9, 1.1, 1.0, and 1.1 were obtained for the rates of formation of $H_2$, $CH_4$, $C_2H_4$, and $C_2H_6$ respectively. Pease (7) investigated the decomposition of butane between 480 and 535°C. and from 10 to 60 cm. pressure. Comparison of times to 10% decomposition for different initial pressures indicated an order of 1.3, while if the initial portions of any curve were to be fitted, an order of as high as 5 or 6 was obtained.

Recently Stubbs and Hinshelwood (13) showed that for the normal decomposition, the variation of the initial rate (mm./min.) with initial pressure could be expressed by an empirical equation of the form

$$r_0 = Ap_0 + Bp_0^2$$

where $A/B = 2.45 \times 10^3$ for *n*-butane at 530°C.

An expression of this type does not correspond to any definite order for the slope of the log rate – log pressure plot would manifest a trend from the first order at low pressures to the second at infinite pressure. If, however, an expression such as the above applies not only to the over-all rate but also the rates of formation of the individual products, then at low pressures first order kinetics would be observed as found in the present work in the range 4–13 cm.

*Fully Inhibited Reaction*

Table II shows quite clearly that under the experimental conditions obtained in the present work, the composition of the products of the inhibited reaction is significantly different from that of the normal decomposition. In particular, the products of the inhibited decomposition contain proportionately more methane and less ethane than is found in the normal decomposition. This result is in striking contrast to all previous work which indicated that the composition of the products of the inhibited reaction was the same as that of the normal decomposition. Indeed, the identity of the composition of the products was regarded by Steacie and Folkins (11) as evidence for doubting the hypothesis of complete suppression of chains, for it meant that in the case of butane for example the three separate molecular splits

$$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$$
$$C_4H_{10} \rightarrow C_3H_6 + CH_4$$
$$C_4H_{10} \rightarrow H_2 + C_4H_8$$

would have to occur in just the right ratio to give the same composition of products as occurred in the normal decomposition.

In previous work, samples for analyses were obtained at too great extents of decomposition. This is a distinct disadvantage for it has been shown (10) that in the later stages of the decomposition there is little or no difference

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between the rate in the presence or absence of NO. This means that, as the butane decomposition progresses and the concentration of olefins increases, the inhibiting effect of the latter swamps that of the NO; as a result the rate of the NO-inhibited reaction approaches that of the normal rate in its later stages. In view of this, it is all the more surprising that the composition of the products of the inhibited reaction at large conversions should have been found to be the same as that of the normal decomposition.

Very recently Stubbs, Spall, Ingold, and Hinshelwood (14) found that at low pressures (8 mm.) the composition of the products of the inhibited reaction is indeed different from that of the normal, the former being proportionately richer in $H_2$ and $C_2H_4$, and poorer in ethane than the latter. They concluded that the fate of the ethane formed in

$$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$$

is pressure dependent, the fraction of the primary ethane which undergoes decomposition into hydrogen and ethylene increasing as the pressure diminishes. If this is indeed so, it will explain why earlier investigators whose experiments were conducted at high pressures found the composition of the products of the inhibited and normal decompositions to be identical.

Comparison of the composition of the products obtained in the present work with that found by Stubbs *et al.* (4) is shown in Table IV.

TABLE IV

COMPARISON OF COMPOSITION OF THE PRODUCTS OBTAINED IN PRESENT WORK WITH THAT FOUND BY STUBBS *et al.*

| Products | Present work | | Stubbs *et al.* | |
|---|---|---|---|---|
| | Normal decomposition, % | Fully inhibited decomposition sampled at 2% conversion, % | Normal decomposition, % | Fully inhibited decomposition sampled at 13% conversion, % |
| $H_2$ | 5 | 4.4 | 3.2 | 16.3 |
| $CH_4$ | 58 | 68.9 | 48.5 | 39.9 |
| $C_2H_4$ | 24 | 24.5 | 27.5 | 36.3 |
| $C_2H_6$ | 12 | 1.9 | 20.7 | 7.5 |

It is apparent that the only respect in which the present work agrees with that of Stubbs *et al.* is that the products of the inhibited reaction are poorer in ethane than the products of the normal decomposition. The genuineness of this result was recently confirmed by independent experiments carried out in collaboration with Dr. A. T. Blades in these laboratories. It should be noted, however, that there is no real reason why the two sets of results should be identical for they were obtained under different conditions. At small extents of decomposition, the manifestation of surface effects is more likely to be pronounced although this should have been reduced to a minimum in the present work in virtue of the large reaction vessel which was used.

The results of the present investigation have shown quite clearly that for the fully inhibited decomposition the rates of formation of the products are

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variable. This substantiates the findings of Stubbs and Hinshelwood, who noticed that for the nitric oxide fully inhibited reaction there is often an induction period and that this determines the initial rate. Furthermore, for *n*-butane the rate of the normal decomposition is unaffected by an increase of surface whereas that of the fully inhibited decomposition was markedly reduced. It was therefore concluded that the uncontrolled variations appearing with butane are of the same nature as those caused by an increase of surface.

It is to be emphasized, however, that although this disturbance gives rise to variable rate measurements, the present work shows that the proportions in which the products are formed seems to be roughly invariable. For this reason it is felt that no very definite pronouncements can be made from a comparison of the composition of the products resulting from the normal and fully inhibited decompositions.

It has been shown (14) that the decomposition of a paraffin reduced to its limiting rate has an unusual pressure dependence. Thus, the order of this reaction is of the second at low pressures, then decreases to the first order, increases again to the second, and finally at the highest pressures employed became first order once again.

The data given in Table III, when plotted in the conventional manner (Fig. 7) gave orders of 2.4 and 3.0 respectively for the rates of formation of $C_2H_4$ and $C_2H_6$. No significance is attached to these values for order only has

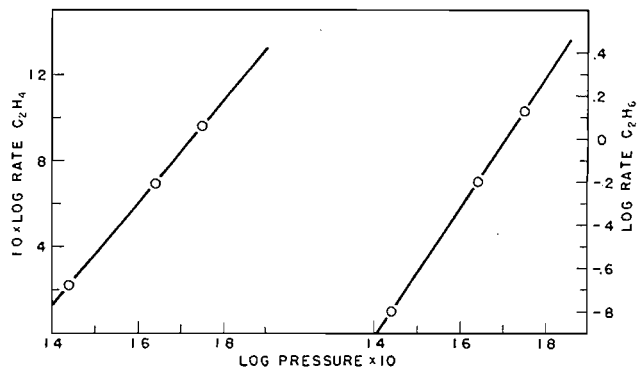



FIG. 7. Determination of "order" for the rates of formation of $C_2H_4$ and $C_2H_6$ in the nitric oxide inhibited decomposition of butane.

meaning when the dependence of the rate on pressure is restricted to a function of the form rate $\alpha\ p^n$. However, since the rates here were determined analytically, whereas those of Stubbs *et al.* refer to the over-all rates determined from pressure increases, the present result confirms that the dependence of the rate on pressure is complex.

The efficiencies of propylene and nitric oxide were recently compared (13) in the inhibition of *n*-pentane, when it was found that $C_3H_6$ is about 1/12 as efficient as nitric oxide. When propylene is used as an inhibitor, it is highly unlikely that radicals will be removed by the reaction

$$CH_3 + C_3H_6 \rightarrow C_4H_9$$

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for at the temperature of the experiment (530°C.) breakdown of $C_4H_9$ would be almost complete and radicals would therefore be regenerated. It seems more reasonable to assume the reaction

$$CH_3 + C_3H_6 \rightarrow CH_4 + C_3H_5.$$

The resulting allyl radical is known to be stable and will dimerize to form diallyl rather than continue the chain. On this basis it is possible to use information which is now available to compute the relative rates at 530°C. of the following two reactions

$$CH_3 + C_3H_6 \rightarrow CH_4 + C_3H_5 \quad [1]$$

$$CH_3 + NO \rightarrow \text{Products.} \quad [2]$$

With $E_1 = 7.7$ kcal. and $P_1 = 9 \times 10^{-4}$ (15) $k_1 = 7 \times 10^{-7}Z$, where $Z$ is the collision number.

For reaction [2] a collision yield of $1.5 \times 10^{-4}$ at room temperature was obtained (2). This may mean either $E_2 = 5.7$ kcal. and $P_2 = 1$ or $E_2 = 0$ and $P_2 = 1.5 \times 10^{-4}$ or some intermediate values. Considering the two extreme cases and assuming the collision numbers to be approximately the same

$$\frac{\text{Rate of 2}}{\text{Rate of 1}} \text{ at } 530°\text{C.} = \frac{5 \times 10^{-2}}{7 \times 10^{-7}} \text{ or } \frac{1.5 \times 10^{-4}}{7 \times 10^{-7}}$$

$$= 10^5 \text{ or } 2 \times 10^2.$$

The great discrepancy between the computed and observed relative rates may mean either that the mechanism of inhibition is incorrect or, if it is correct, that NO is very much less efficient as an inhibitor than might have been expected. A reason has already been given for regarding the association reaction $CH_3 + C_3H_6 \rightarrow C_4H_9$ as highly improbable at 530°C. The problem is therefore to explain the relative inefficiency of nitric oxide as an inhibitor compared with propylene. Lack of definite information, however, prevents further discussion of the problem at this stage.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to Dr. F. P. Lossing and Miss F. Gauthier for numerous mass spectrometric analyses. We are also indebted to Mr. R. Pilon for perfecting the technique for ensuring that the $C_2$ fractions were free from nitric oxide.

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# A CHEMICAL SYNTHESIS OF OCTA-*O*-ACETYL-β-D-MALTOSE[1]

By R. U. Lemieux

ABSTRACT

Reaction of tri-*O*-acetyl-D-glucosan ⟨1, 5⟩ α ⟨1, 2⟩ with 1,2,3,6-tetra-*O*-acetyl-β-D-glucose at 120°C. for 13 hr. followed by acetylation and then chromatographic separation of the products afforded octa-*O*-acetyl-β-D-maltose in about 8% yield.

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Brigl (2) found that tri-*O*-acetyl-D-glucosan ⟨1, 5⟩ α ⟨1, 2⟩ reacts readily with methanol to form methyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranoside in almost quantitative yield. Hickinbottom (8) and Hardegger and de Pascual ⟨5⟩ have applied the method for the preparation of a variety of alkyl-β-D-glucopyranosides. In 1943, Montgomery, Richtmyer, and Hudson (12) interpreted the reaction of Brigl's anhydride with methanol as proof for the configuration of the anomeric center in methyl-β-D-glucopyranoside.

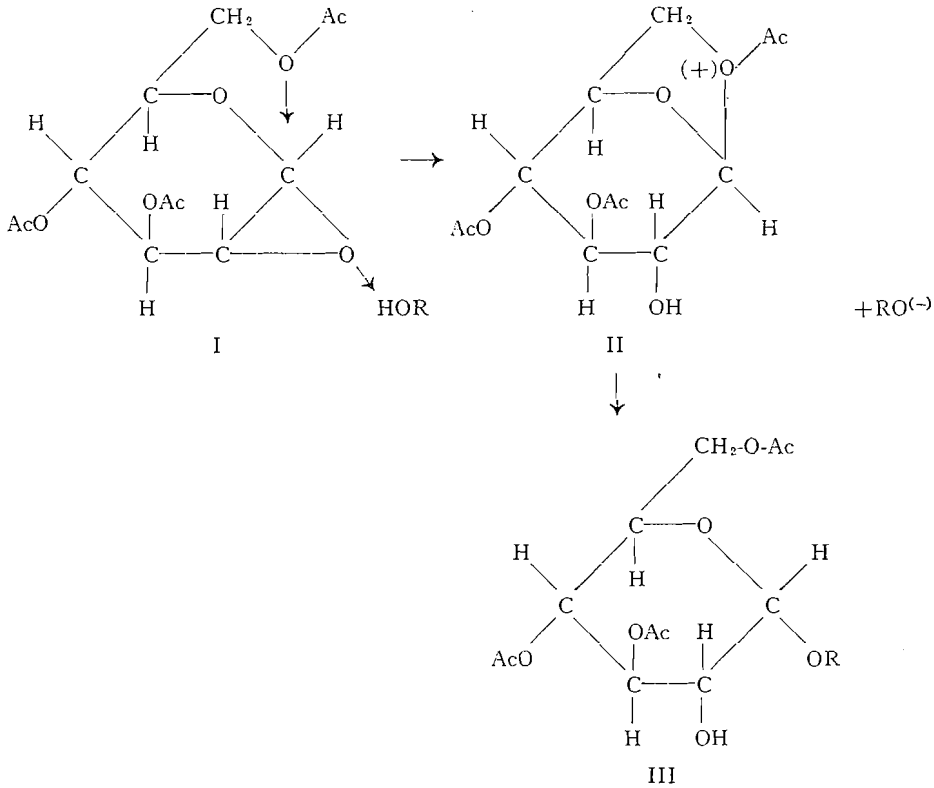
Although the Brigl anhydride yields β-D-glucopyranosides on reaction with alcohols at ordinary temperatures, evidence has long existed which indicates that α-D-glucopyranosides tend to be formed at elevated temperatures. In 1928, Hickinbottom (8) reported the preparation of phenyl-α-D-glucopyranoside by reaction of the anhydride with phenol at 100°C. for 20 hr. In 1931, Haworth and Hickinbottom (6) reacted the anhydride with 2,3,4,6-tetra-*O*-acetyl-β-D-glucose in benzene at 90°–100°C. for 37 hr. to form a hepta-*O*-acetyl derivative of a nonreducing disaccharide termed *neo*trehalose which appeared to be α-D-glucopyranosyl-β-D-glucopyranoside. In this case, the origin of the α-D-linkage could not be decided upon since it was possible that under the reaction conditions used the 2,3,4,6-tetra-*O*-acetyl-β-D-glucose underwent anomerization before reaction with the anhydride. More recently, Hardegger and de Pascual (5) have reacted the anhydride with cholestanol at 120°C. for 16 hr. to form the α-D-glucopyranoside.

The discovery first made by Bardolph and Coleman (1) that alkaline hydrolysis of Brigl's anhydride yields D-glucosan ⟨1, 5⟩ β ⟨1, 6⟩ (3, 10), and the observation (10) that dissociation of the C1 to acetoxy group bond of 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose with stannic chloride in chloroform yields tri-*O*-acetyl-D-glucosan ⟨1,5⟩ β ⟨1,6⟩, suggested to us (10) that the C6-oxygen atom of an α-D-glucopyranose derivative is capable of participation in replacement reactions at the anomeric center. Since direct replacements with retention of configuration are not known, the formation of α-glucosides from Brigl's anhydride requires the formation of an unstable intermediate from the anhydride. In the light of the above evidence for the ability of C6-substituents in glucose to participate in replacements at the lactol carbon atom, it seems probable that, at elevated temperatures and in the presence of an alcohol, the

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anhydride (I) is converted to the 1,6-β-D-cyclic ion (II) which is capable of interaction to yield an α-D-glucopyranoside (III).

Treatment of Brigl's anhydride with an equivalent amount of 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (7) at 120°C. for 13 hr. and acetylation of the product gave a sirup from which pure octa-*O*-acetyl-β-D-maltose was readily isolated in about 8% yield. The elegant procedure for the chromatographic separation of sugar acetates established by McNeely, Binkley, and Wolfrom (11) was used for the isolation. The substance was identified by mixed melting point determination and by comparison of its infrared absorption spectrum with that of a sample of octa-*O*-acetyl-β-D-maltose prepared by acetylation of maltose (9).




Although Pictet and Vogel (13) have reported the synthesis of maltose by heating β-glucose and α-glucose at 160°C. in a vacuum and by heating β-glucose and β-glucosan at 150°C. in vacuum with or without zinc chloride, Evans, Reynolds, and Talley (4, p. 35) have recently made the statement, "Of the common sugars, only those containing the sucrose and maltose type linkages still challenge the carbohydrate chemist to obtain them by a true chemical synthesis". Since octa-*O*-acetyl-β-D-maltose can be deacetylated readily to yield maltose (14), the present sequence of reactions make possible a true chemical synthesis of maltose.

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## EXPERIMENTAL

### *Octa-O-acetyl-β-D-maltose*

Pure tri-*O*-acetyl-D-glucosan ⟨1,5⟩ α ⟨1,2⟩ (2), m.p. 58–59°C., 55 mgm., and 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (7), m.p. 131–132°C., 60 mgm., were mixed in a tube and kept in a high vacuum at room temperature for 30 min. and then at 100°C. for 5 min. The tube was sealed and heated in an oil bath controlled at 120°C. for 13 hr. The hard, brown-colored reaction product was dissolved in 5 ml. of acetic anhydride and 100 mgm. of sodium acetate was added. After heating on the steam bath for one hour, the mixture was evaporated *in vacuo* to a salt cake. The residue was extracted with benzene to yield, on evaporation, a brown sirup.

The sirup was dissolved in about 2 ml. of benzene and added to the top of a 160 × 35 mm. column of a mixture, 50 gm., of five parts Magnesol and one part Celite (11) wetted with benzene. The chromatogram was developed with one liter of 250:1 benzene to ethanol mixture and the column extruded and streaked with a freshly prepared aqueous solution of 1% potassium permanganate in 2.5 *N* sodium hydroxide. Four distinct zones were observed and these were cut out and eluted with warm acetone. The first zone, 0–8 mm. from the top of the column, gave a dark brown sirup which was not investigated. The material from the second zone, 12–25 mm. from the top of the column, was crystallized from ethanol to yield 10.2 mgm. of a substance, m.p. 159–161°C., $[\alpha]_D^{20°}$ +63° (*c*, 0.36 in chloroform) which did not depress the melting point of an authentic sample of octa-*O*-acetyl-β-D-maltose, m.p. 161–162°C. The infrared spectrum of the substance, mulled with Nujol and measured with a Perkin-Elmer Model 21 double beam spectrometer, was identical with the spectrum obtained under the same conditions of the authentic sample of octa-*O*-acetyl-β-D-maltose. The third zone, 70–88 mm. from the top of the column, gave 2.4 mgm. of crystalline penta-*O*-acetyl-α-D-glucopyranose, m.p. 109–111°C. and the fourth zone, 110–128 mm. from the top of the column, gave 39.1 mgm. of penta-*O*-acetyl-β-D-glucopyranose, m.p. 131–132°C.

## ACKNOWLEDGMENT

The starting materials used in this work were prepared by Dr. H. F. Bauer and Dr. G. Huber.

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# α-OBSCURINE AND β-OBSCURINE: STRUCTURE STUDIES[1]

By Barry P. Moore[2] and Léo Marion

ABSTRACT

The alkaloid hitherto described as obscurine has been shown to consist of a mixture of two bases, α-obscurine ($C_{17}H_{26}ON_2$) and β-obscurine ($C_{17}H_{24}ON_2$). Dehydrogenation of α-obscurine by heating with palladium-charcoal gives rise to 7-methylquinoline and 6-methyl- α-pyridone. The infrared absorption spectrum of the base shows absorption bands indicative of a carbonyl and of a secondary amino group, possibly in a cyclic lactam, while absorption in the ultraviolet indicates the presence of a double bond conjugated with the carbonyl group. β-Obscurine on the other hand contains an α-pyridone ring as shown by its infrared absorption spectrum and also by the similarity of its ultraviolet absorption spectrum with that of 6-methyl- α-pyridone.

Obscurine (alkaloid L6) was first reported as occurring in *Lycopodium flabelliforme* L. (2) and later in *L. annotinum* L. (3) although it had first been isolated from *L. obscurum* L. var. *dendroideum* (Michx.) D. C. Eaton (4). It was described as a crystalline base melting at 282°, yielding analytical figures corresponding to the empirical formula $C_{18}H_{28}ON_2$, and forming a crystalline diperchlorate hydrate melting at 299°. On reanalysis of the base it was found difficult to obtain consistent results and an attempt was made to purify the base further. Repeated recrystallization of the base failed to effect a separation, but by chromatography on alumina it was possible to separate it into a main fraction and a small quantity of a second base. The main fraction which will be designated α-obscurine melted at 283–284° (dec.) and formed a monopicrate, m.p. 133–134°. The second base, which it is proposed to name β-obscurine, melted at 322–323° (dec.) and formed a monopicrate, m.p. 254°. From numerous analyses of the bases and their picrates it appeared that the most probable formulae were $C_{17}H_{26}ON_2$ for α-obscurine and $C_{17}H_{24}ON_2$ for β-obscurine. The perchlorates were prepared but they both absorbed water very readily and were not analyzed.

The infrared absorption spectrum of α-obscurine in chloroform solution showed a small absorption peak at 3411 cm.$^{-1}$ indicative of a secondary amino group and a broad band at 1667 cm.$^{-1}$ attributable to a carbonyl group. The infrared spectrum of β-obscurine contained an absorption peak indicative of a secondary amino group at 3385 cm.$^{-1}$, and a strong double peak at 1659 cm.$^{-1}$, 1651 cm.$^{-1}$ with smaller peaks at 1620 cm.$^{-1}$ and 1613 cm.$^{-1}$ suggestive of an α-pyridone (5) (Fig. 1).

On dehydrogenation by heating with palladium-charcoal, α-obscurine gave rise to 7-methylquinoline and to 6-methyl-α-pyridone, both identified by comparison with synthetic specimens. The infrared absorption spectrum of 6-methyl-α-pyridone in chloroform solution (Fig. 1) showed a small peak at 3387 cm.$^{-1}$ due to the imino group, a band at 1662 cm.$^{-1}$ (77%), and one at

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[2] *National Research Council of Canada Postdoctorate Fellow, 1950–1951.*



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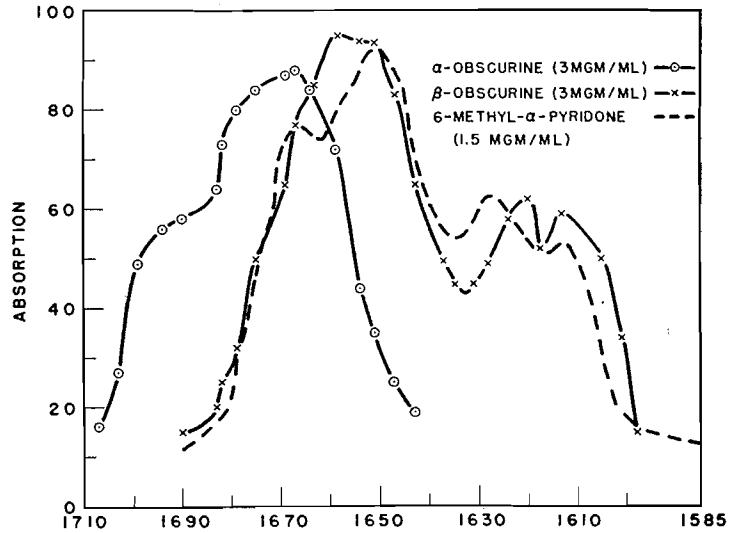



FIG. 1. Infrared spectra of chloroform solutions of α-obscurine, β-obscurine, and 6-methyl-α-pyridone, measured on Perkin-Elmer 12B single beam spectrometer with a calcium fluoride prism.

1651 cm.$^{-1}$ (92%) together with smaller peaks at 1628 cm.$^{-1}$ and 1613 cm.$^{-1}$ attributable to the α-pyridone structure. The similarity in position between these absorption bands and those appearing in the same region in the infrared spectrum of β-obscurine indicate that an α-pyridone ring must be present in β-obscurine. The infrared spectrum of α-obscurine shows that in that alkaloid the nitrogen is possibly part of a cyclic lactam which, however, is not a pyridone. In the infrared spectrum of a substituted dihydro-α-pyridone, the carbonyl band would be expected to occur either at the same place or at a lower wave number than it does in the spectrum of β-obscurine (5). In the spectrum of octahydrogelsemine, which contains a saturated five-membered lactam, the carbonyl band is observed at about 1690 cm$^{-1}$. It is therefore possible that the α-pyridone obtained by the degradation of α-obscurine is an artefact obtained by ring enlargement of a five-membered cyclic lactam. A comparison of the ultraviolet absorption spectra (Fig. 2) of β-obscurine (max. λ232 mμ, log ε, 3.98; λ315 mμ, log ε, 3.89) and 6-methyl-α-pyridone (max. λ229 mμ, log ε, 3.87; 304 mμ, log ε, 3.83) shows that they are almost identical and supports the conclusion drawn from the infrared evidence. On the other hand, the ultraviolet absorption spectrum of α-obscurine (Fig. 2) (max. λ255 mμ, log ε, 3.75) differs markedly and seems to indicate the presence of a cyclic lactam containing αβ-unsaturation. αβ-Unsaturated seven-membered cyclic lactams show a maximum at about 240 mμ in the ultraviolet (1,6). It has not been possible, however, to find in the literature ultraviolet absorption curves of αβ-unsaturated five- or six-membered cyclic lactams. Nevertheless, it has to be added that α-obscurine and β-obscurine are very similar not only in their empirical formulae but in their properties. 6-Methyl-α-pyridone and both α-obscurine and β-obscurine produce an orange-red color with aqueous

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ferric chloride and they couple with diazotized sulphanilic acid to produce a deep orange-red product.

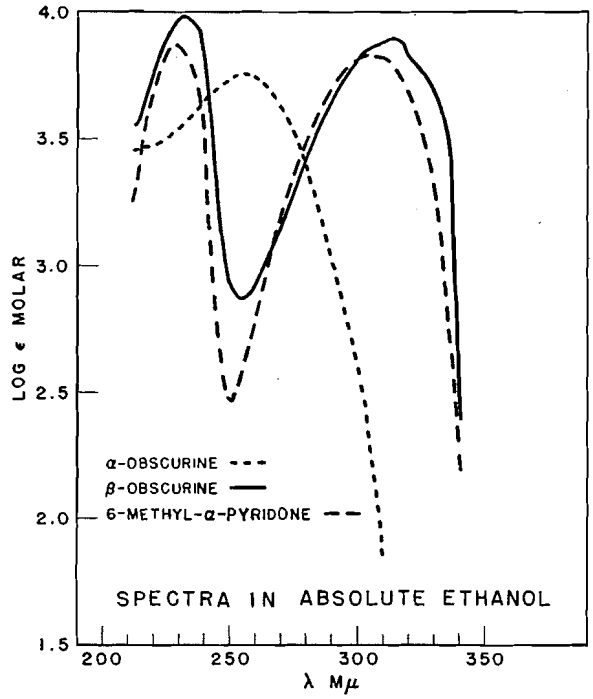



FIG. 2. Ultraviolet absorption spectra taken in absolute ethanol with a Beckman quartz spectrophotometer.

An attempt to dehydrogenate α-obscurine to β-obscurine by bromination followed by dehydrobromination altered the compound but did not give β-obscurine.

Both fragments obtained in the degradation of α-obscurine together provide 16 carbon atoms and therefore one carbon only is missing to complete the skeleton of the alkaloid. The empirical formulae of the bases require in each case a structure containing four rings. Since the degradation products account for three rings it may be assumed that the missing carbon is in a methylene group forming part of the fourth ring.

## EXPERIMENTAL[3]

### *Purification of Obscurine*

Obscurine, recrystallized twice from chloroform–methanol, consisted of colorless prisms, m.p. 281–282°. A quantity of recrystallized obscurine (500 mgm.) dissolved in a mixture of chloroform (25 ml.) and petroleum ether (75 ml. b.p. 30–60°) was chromatographed on alumina and eluted first with 1:1 chloroform – petroleum ether (140 ml.), 3:1 chloroform – petroleum ether (60 ml.), chloroform (30 ml.), 1:1 methanol – chloroform (40 ml.), and finally with

[3] *All melting points are corrected.*

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pure methanol. Two fractions, A (408 mgm.) and B (92 mgm.) were thus obtained from the chromatogram. Fraction A was practically all present in the 1:1 chloroform – petroleum ether eluate, while fraction B was all obtained from the 1:1 methanol–chloroform eluate.

*α-Obscurine*

Fraction A, which was crystalline, was recrystallized twice from methanol from which it separated as colorless prisms, m.p. 283–284°. Rechromatography of a sample of this base (now designated α-obscurine) showed that it was homogeneous. Calc. for $C_{17}H_{26}ON_2$: C, 74.41; H. 9.55; N, 10.21. Found: C, 74.80, 74.17; H, 9.80, 9.12; N, 10.45%. No imino-methyl group was present. A quantity of α-obscurine was dissolved in chloroform and to it was added an ethereal solution of picric acid. The picrate crystallized out and after recrystallization from methanol–ether it consisted of yellow needles, m.p. 135°. Drying at 100° at 0.1 mm., over phosphoric anhydride did not alter the melting point. Calc. for $C_{17}H_{26}ON_2.C_6H_3O_7N_3$: C, 54.86; H. 5.81; N, 13.91. Found: C, 54.39, 54.45; H, 6.10, 6.14; N, 14.19. 14.39%. In contact with aqueous ferric chloride it produced an orange-red coloration. On coupling with diazotized sulphanilic acid α-obscurine produced a deep orange-red color.

A small quantity of α-obscurine was dissolved in methanol, the solution neutralized with perchloric acid and diluted with ether. The precipitated perchlorate was recrystallized from ethyl acetate containing a drop of perchloric acid. It separated as colorless prisms, m.p. 255° (dec.), but was too soluble and deliquescent to constitute a characteristic derivative and was not analyzed.

*β-Obscurine*

Fraction B of the chromatogram was crystalline and after recrystallization from methanol consisted of colorless prismatic rods, m.p. 322–323° when immersed at 240°. Calc. for $C_{17}H_{24}ON_2$: C, 74.96; H, 8.88; N, 10.29. Found: C, 75.18, 74.67; H, 8.62, 8.47; N, 10.22%. The imino-methyl determination was negative. β-Obscurine with aqueous ferric chloride produced an orange-red color and on coupling with diazotized sulphanilic acid gave a lighter orange-red color. An ethereal solution of picric acid was added to a small quantity of this base (now designated β-obscurine) in chloroform. The crystalline precipitate was recrystallized twice from methanol from which it separated as yellow plates, m.p. 254° (dec.). Calc. for $C_{17}H_{24}ON_2.C_6H_3O_7N_3$: C, 55.08; H, 5.43; N, 13.97. Found: C, 54.89, 54.90; H, 5.60, 5.06; N, 13.85%.

The perchlorate prepared from β-obscurine in the usual way consisted of colorless needles, m.p. 322° (dec., with previous darkening). Like the perchlorate of α-obscurine it was very soluble in methanol and in water and was not analyzed.

*Dehydrogenation of α-Obscurine*

α-Obscurine (200 mgm.) and freshly prepared palladium-charcoal (50 mgm., 5% Pd) were thoroughly mixed and heated in a small bulb in a Wood's metal bath to 290° under a slow stream of dry oxygen-free nitrogen. The exit gas was washed in a trap containing *N*/1 aqueous hydrochloric acid. Sublimation of

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the α-obscurine occurred at first but when decomposition had started the refluxing product washed the crystals down again. After 30 min. the temperature of the bath was lowered to 280° and maintained at this temperature for 90 min. After cooling, the reaction mixture was extracted with chloroform and the extract filtered and evaporated to remove the solvent. There was left an oily residue which when distilled *in vacuo* yielded the following fractions: (I) colorless liquid, b.p. 95–105° at 0.5 mm., wt. 20 mgm. (II) a solid subliming at 115–125° at 0.5 mm., wt. 12 mgm. (III) a resin, b.p. 190–120° at 0.5 mm., wt. 20 mgm.

*7-Methylquinoline*

Fraction I (20 mgm.) was dissolved in ether and to the solution an ethereal solution of picric acid was added as long as a precipitate formed. The liquid was decanted and the precipitate washed with ether and dissolved in boiling methanol. The solution was evaporated down to a volume of 5 ml. which on cooling deposited a small quantity of yellow needles. After recrystallization from methanol the picrate melted at 235°. In admixture with an authentic specimen of 7-methylquinoline picrate (m.p. 241°) it melted at 238°. A small quantity of picrate was also obtained from fraction II.

*6-Methyl-α-pyridone*

Fraction II (12 mgm.) consisted of crystals contaminated with a small quantity of an oily base which was removed by washing with petroleum ether. This base was converted to a picrate which proved identical with 7-methylquinoline picrate. The solid which had been washed with petroleum ether was crystallized from acetone – petroleum ether from which it separated as cream-colored prisms. This crystalline product was sublimed at 115–120° at 0.1 mm. and the sublimate consisted of clusters of colorless prisms, m.p. 158.5°. Calc. for $C_6H_7ON$: C, 66.03; H, 6.47; N, 12.84. Found: C, 67.66; H, 7.23; N, 12.60%. The analysis, which is not too satisfactory, was performed on extremely small quantities and could not be repeated. The compound, however, gave an orange-red color with aqueous ferric chloride and a deep orange-red product on coupling with diazotized sulphanilic acid. The infrared absorption spectrum of the substance (Fig. 1) showed an absorption band at 3387 $cm.^{-1}$ indicative of an NH group, a double carbonyl band at 1662–1651 $cm.^{-1}$, and smaller bands at 1628 and 1613 $cm.^{-1}$ usually attributable to a pyridone structure. It was assumed that the compound was 6-methyl- α-pyridone and this substance was synthesized as described by Simonsen (7) by the diazotization of 2-amino-6-methylpyridine. The synthetic substance consisted of cream-colored prisms, m.p. 158-159°, and admixture with the degradation compound failed to depress the melting point. Both substances gave similar color tests with aqueous ferric chloride and reacted in an identical manner with diazotized sulphanilic acid. Synthetic 6-methyl-α-pyridone was sublimed *in vacuo* for use in the determination of the ultraviolet and infrared absorption spectra. Both these spectra were respectively superimposable on the corresponding spectra of the degradation product.

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ACKNOWLEDGMENT

The authors wish to thank Dr. R. N. Jones and Mr. R. Lauzon of these laboratories for determining the infrared absorption spectra.

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# THREE MINOR ALKALOIDS OF *GELSEMIUM SEMPERVIRENS* AIT.[1]

By H. Schwarz[2] and Léo Marion

ABSTRACT

After the removal of gelsemine and sempervirine from the extract of the root of *Gelsemium sempervirens* Ait. the residual alkaloids left in the mother liquors were benzoylated. It was thus possible to separate the tertiary bases from the secondary bases which were obtained as a mixture of the neutral benzoyl derivatives. Purification by chromatography yielded the benzoylated mixture in crystalline form. This was hydrolyzed and the recovered secondary bases were separated by fractional crystallization of the perchlorates into alkaloid A and alkaloid B. Alkaloid A was shown by direct comparison to be identical with the gelsemicine ($C_{20}H_{26}O_4N_2$) of Chou. Alkaloid B, now designated gelsedine, was shown to be distinct from either gelsemicine or gelsemine. It appears to be identical with the alkaloid $C_{19}H_{24}O_3N_2$ claimed by Janot and his co-workers to be gelsemicine. From the tertiary bases there was isolated an apparently new base, gelseverine, as its crystalline perchlorate. Whereas gelsemine is a 3,3-disubstituted oxindole, gelsedine appears to be a 1,3-disubstituted oxindole and gelseverine a 1,3,3-trisubstituted oxindole. Gelsemicine shows many of the characteristics of an indole alkaloid.

Besides the two previously known alkaloids, gelsemine and sempervirine, Chou (3) isolated from the root of *Gelsemium sempervirens* Ait. a third base, gelsemicine, m.p. 171°, $[\alpha]_D$ −140° to which he assigned the empirical formula $C_{20}H_{25}O_4N_2$ [*sic*]. Chou (3) also described the hydrochloride of the base, m.p. 140°.

From the same plant Forsyth, Marrian, and Stevens (4) also isolated gelsemicine. They reported m.p. 170°, $[\alpha]_D$ −140°, but corrected the formula to $C_{20}H_{24-26}O_4N_2$. According to those authors gelsemicine forms a picrate, m.p. 203°, yields a nonbasic monobenzoyl derivative, m.p. 232°, and behaves as a secondary base giving rise when treated with methyl iodide to N-methylgelsemicine hydriodide, m.p. 227°. It is inert towards the usual carbonyl reagents (4). Raymond-Hamet (7) compared the ultraviolet absorption spectrum of Chou's gelsemicine with the spectra of other alkaloids and concluded that gelsemicine contained an indole nucleus.

More recently, Janot, Goutarel, and Friedrich (5) isolated and described a base that they assumed to be the alkaloid gelsemicine although they reported m.p. 171°, $[\alpha]_D$ −160°, and they proposed the quite different empirical formula $C_{19}H_{24}O_3N_2$. They prepared the benzoyl derivative, m.p. 262°, $[\alpha]_D$ −117°, and the N-methyl base, m.p. 134°. According to them the basic nitrogen of their base is secondary and the base contains two active hydrogens. Furthermore, its ultraviolet absorption spectrum resembles that of gelsemine (oxindole). Their publication, however, contained no experimental section.

In the course of our work on gelsemine the isolation of the alkaloids of *G. sempervirens* has been reinvestigated as already reported in a preliminary

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note (9). By modifying the usual procedure (see experimental part) it was possible to increase the yield of gelsemine from 36 gm. to 58 gm., and the yield of sempervirine nitrate from 18 gm. to 42 gm. per 22.6 kgm. of dry ground root. The modification consisted in adsorbing on filtercel the tarry residue obtained after evaporation of the methanol percolate of the plant material. This supplies a large adsorption surface and can as in this case overcome the difficulties always arising in the process of working up plant extracts containing a large amount of water-insoluble tarry material. It has the advantage of not leaving the alkaloids in long contact with alkali, thus avoiding the loss of alkali-sensitive natural products. The method can be recommended especially for quaternary bases of which mostly all salts are only slightly soluble in water, e.g. sempervirine, serpentine, alstonine, berberine, etc. Gelsemine and sempervirine together constituted about 75% of the alkaloid content of the root while the remaining 25% was to be found in the mother liquors. The accumulation of relatively large quantities of alkaloid-rich mother liquors prompted us to attempt the isolation of the minor alkaloids present in the plant.

The basic residue obtained by evaporation of the mother liquors was separated into secondary and tertiary bases by benzoylation or acetylation. Benzoylation yielded a basic fraction containing the tertiary bases and a neutral fraction which represented the secondary bases. The latter was purified by chromatography and produced a crystalline benzoylated product, the melting point of which (233–240°) was not improved by recrystallization. A chromatogram of the crystalline substance furnished fractions differing in melting points, but infrared absorption spectra showed that none of these fractions consisted of a pure compound. This method of direct separation of the benzoylated bases was abandoned because the middle fractions were too large and the separation proved too laborious and unsatisfactory.

The benzoylated product was hydrolyzed and the free base crystallized from ethyl acetate. It melted at 136–139°, which was 32–35° lower than the reported melting point of gelsemicine and had $[\alpha]_D$ −150°, a value intermediate between the two figures previously reported (3, 4, 5). Fractional crystallization did not yield any higher melting crop, although some fractions contained two distinct forms of crystals, i.e., large stout rhombs and elongated rhombs. The alkaloids could not be chromatographed as they decomposed on the column.

Acetylation instead of benzoylation was not conducive to better results. Chromatography and fractional crystallization of the acetylated product both led in small yield to a fraction, m.p. 161°. On hydrolysis this fraction gave a base, m.p. 162–165°, which could not be purified further by recrystallization.

The crystalline base obtained by hydrolysis of the benzoylated product formed a picrate which could be separated into two fractions, each of which, however, still consisted of a mixture.

Finally, a successful method of separation was found in the fractional crystallization of the perchlorates. In the course of an attempt to prepare a perchlorate from the free base (obtained by hydrolysis of the crystalline benzoylated product), it was noted that the yield of crystalline salt was at best

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75%, and that on further recrystallization the yield decreased to about 40–50%. This perchlorate was almost insoluble in the cold solvent (methanol–water 1:1); it melted at 183° and yielded analytical figures in agreement with the formula $C_{19}H_{24}O_3N_2 \cdot HClO_4$. From the final mother liquors no more perchlorate could be induced to crystallize thus suggesting that separation had

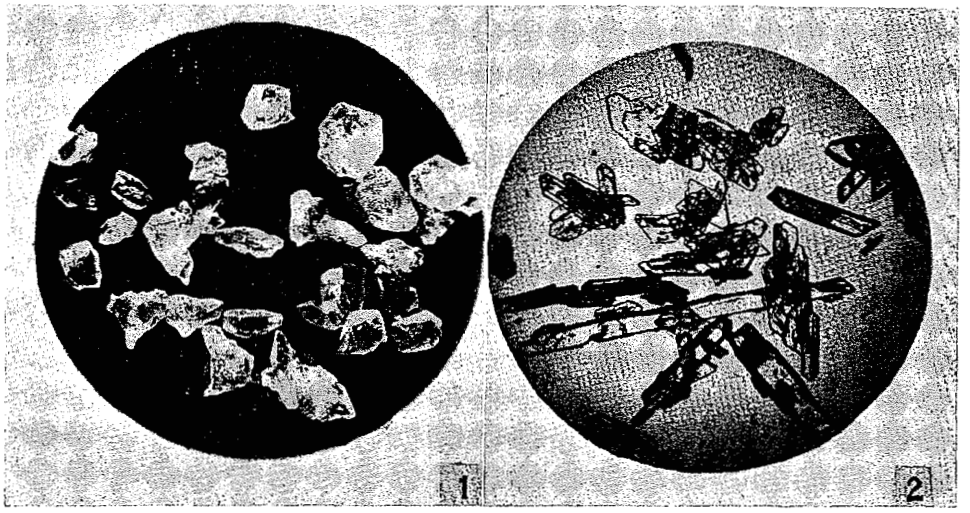



FIG. 1. Photomicrograph of gelsemicine crystals. ×5
FIG. 2. Photomicrograph of gelsedine crystals. ×20

been effected into a sparingly soluble crystalline perchlorate and a very soluble perchlorate. The latter when decomposed yielded alkaloid A while decomposition of the crystalline perchlorate gave alkaloid B. Both bases were obtained as prismatic crystals, but these were readily distinguishable as shown in Figs. 1 and 2.

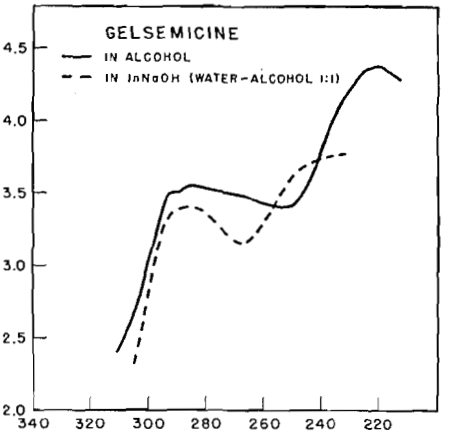



FIG. 3. Ultraviolet spectra of gelsemicine.

Alkaloid A, m.p. 171–172°, $[\alpha]_D$ −142°, yielded analytical figures corresponding to the empirical formula $C_{20}H_{26}O_4N_2$. It formed a picrate, m.p. 206–208°,

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a benzoyl derivative, m.p. 235–236°, $[\alpha]_D$ −106°, and an acetyl derivative, m.p. 174–175°. Alkaloid B, m.p. 172.5–174°, $[\alpha]_D$ −158°, gave analytical figures corresponding to the formula $C_{19}H_{24}O_3N_2$. It formed a picrate, m.p. 224–226°, a benzoyl derivative, m.p. 251–252°, and an acetyl derivative, m.p. 165–166°. Alkaloid A was quite distinct from alkaloid B, but it had the

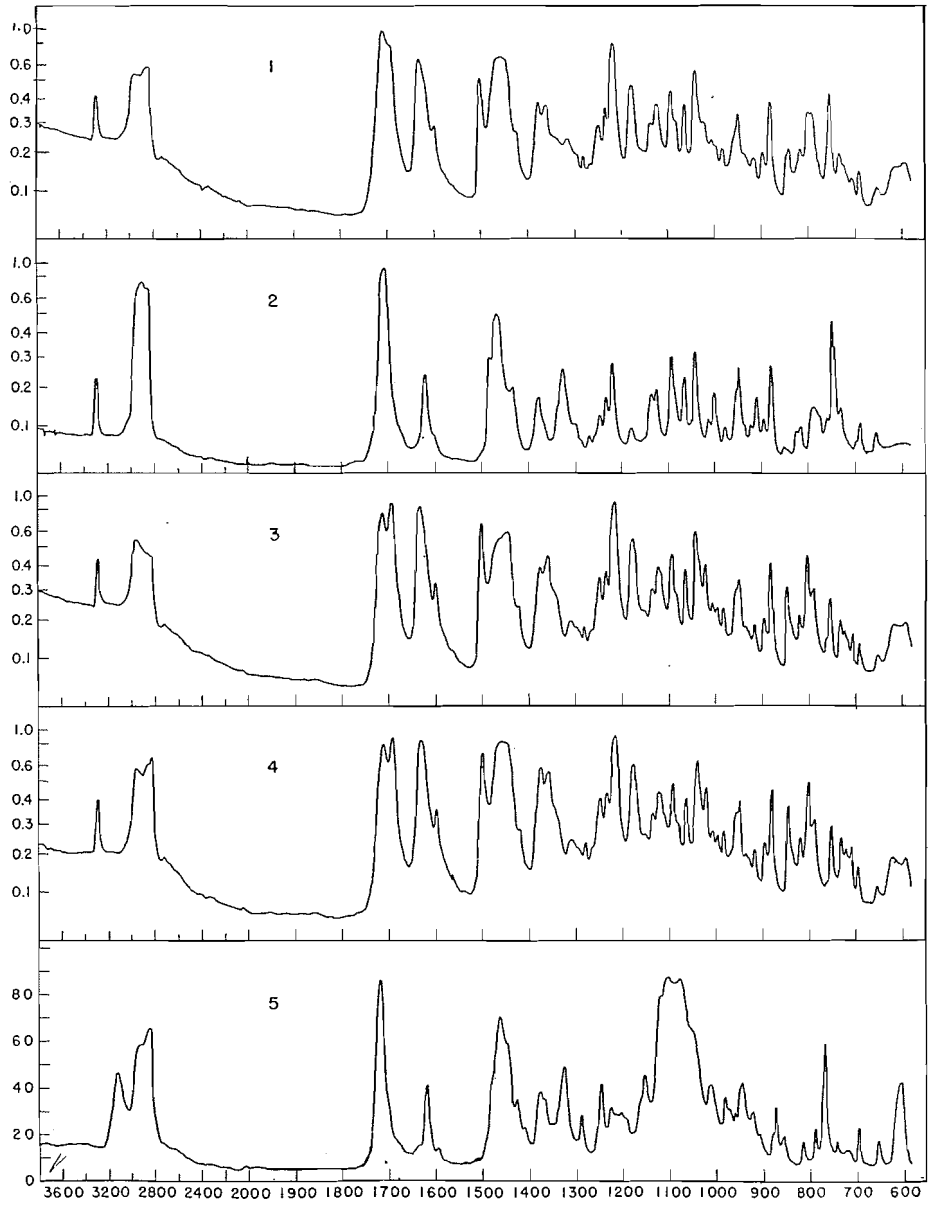



FIG. 4. Infrared absorption spectra in Nujol mull. curve 1, mixture of gelsemicine and gelsedine; curve 2, gelsedine; curve 3, gelsemicine; curve 4, Chou's gelsemicine; curve 5, gelsevirine perchlorate.

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same physical constants and so had its picrate and benzoyl derivative as those reported by Chou (3) for gelsemicine and by Forsyth, Marrian, and Stevens (4) for the corresponding derivatives. Both the ultraviolet (Fig. 3) and the infrared absorption spectra of alakloid A were superimposable on the corresponding spectra of a sample of Chou's gelsemicine which was kindly supplied to us by Dr. Raymond-Hamet (curves 3 and 4, Fig. 4). Furthermore, alkaloid A showed no depression in melting point in admixture with Chou's alkaloid. It is therefore identical with gelsemicine.

The physical constants of alkaloid B and its derivatives (except for the melting point of its benzoyl derivative) were very close to those described by Janot, Goutarel, and Friedrich (5) for the alkaloid, which they assumed to be gelsemicine, and its derivatives. The empirical formulae of the bases were identical and so was the maximum in their ultraviolet absorption spectra (Fig. 5). It seems, therefore, highly probable that alkaloid B is identical with

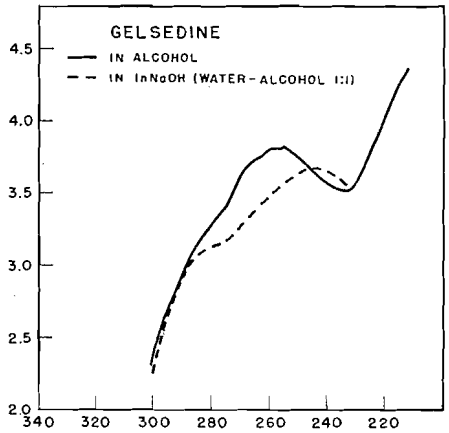



FIG. 5. Ultraviolet spectra of gelsedine.

Janot's "gelsemicine" and since it is quite different from Chou's gelsemicine, it is proposed to designate this new base as gelsedine.

Alkaloid A (gelsemicine) and alkaloid B (gelsedine) on admixture showed a melting point depression, the melting point of the mixture (136–139°) being the same as that observed for the original mixture before separation. The acetyl derivatives also showed a melting point depression on admixture. The mixed picrates melted in a range between the melting points of the pure picrates, but a definite depression could be observed after prolonged grinding of the mixture in a mortar. The benzoyl derivatives, however, did not show a melting point depression under any condition.

From the basic fraction separated from the benzoylation reaction mixture, alkaloid C was isolated as the perchlorate, m.p. 251–252°. The liberated base was a noncrystallizable oil and it formed an oily picrate. It, however, furnished a crystalline methiodide, m.p. 259–262° (dec.). The analytical figures of the perchlorate indicated for the base the empirical formula $C_{21}H_{24}O_3N_2$, although those obtained from the distilled base and from the methiodide agreed better

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with $C_{21}H_{26}O_3N_2$. The infrared absorption spectrum of the perchlorate (curve 5, Fig. 4) showed that alkaloid C was not identical with any so far identified from *G. sempervirens* and was therefore probably new. It is proposed to designate this alkaloid as gelsevirine. Forsyth, Marrian, and Stevens (4) reported the isolation of a methiodide, m.p. 261°, but the analytical figures of this salt did not agree with those found for gelsevirine.

The mother liquor from which gelsevirine perchlorate separated contained more alkaloidal material, but it has not yet been possible to identify any further bases (see experimental).

Gelsedine ($C_{19}H_{24}O_3N_2$) contained one methoxyl, one imino-methyl, one C-methyl, and one active hydrogen (Janot and his co-workers (5) report two active hydrogens for their base). Its infrared absorption spectrum (curve 2, Fig. 4) showed an NH band, a carbonyl band, and a band (1620 cm.$^{-1}$) characteristic of a benzene ring. The ultraviolet spectrum (Fig. 5) in alcohol showed a minimum at 235 m$\mu$, a maximum at 258 m$\mu$, and a shoulder at 280 m$\mu$. In acidic solution the absorption was about the same. In aqueous alkali gelsedine dissolved slowly with the development of a bright yellow color. In aqueous-alcoholic alkali, however, the color did not develop immediately and in such a solution the absorption in the ultraviolet was shifted giving a maximum at 244 m$\mu$ and a shoulder at 280 m$\mu$. However, if the spectrum of this solution was measured after some lapse of time, the maximum was shifted below 230 m$\mu$, the shoulder became a maximum and a new absorption band developed in the visible (405 m$\mu$). It is noteworthy that this spectrum is very similar to that of N-methyl-isatin.

Both acetyl and benzoyl gelsedine were neutral substances no longer containing active hydrogen. Acetyl gelsedine, which, as expected, contained two C-methyl groups, had the same ultraviolet absorption as gelsedine in alcohol. The infrared absorption spectrum of benzoylgelsedine in nujol mull or in chloroform solution (Fig. 6) showed no absorption in the NH, OH region, and contained the two expected bands in the carbonyl region.

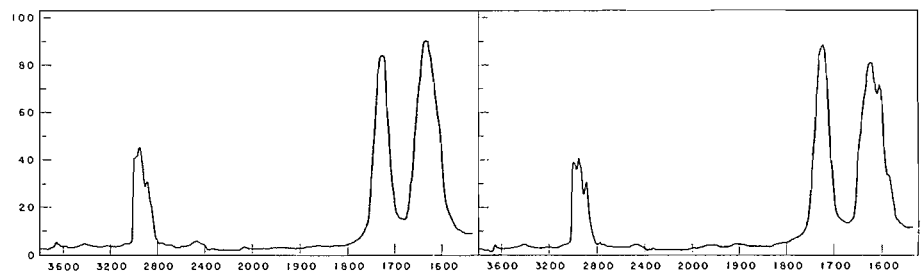



FIG. 6. Infrared spectra in chloroform solution. Left, acetylgelsemicine. Right, benzoylgelsedine.

In glacial acetic acid solution over Adams' catalyst at room temperature gelsedine was not hydrogenated but at 60–70° it took up hydrogen very slowly giving rise to hexahydrodesmethoxygelsedine, $C_{18}H_{28}O_2N_2$. The loss of the O-methyl was not a simple hydrolysis since the analysis indicated the loss of

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the oxygen as well. Hexahydrodesmethoxygelsedine showed no absorption above 240 mμ in the ultraviolet. Its infrared absorption spectrum contained only one peak in the NH,OH region due to the secondary nitrogen and one in the carbonyl region, but none corresponding to a benzene ring so it was this ring which was hydrogenated.

Reduction of gelsedine with lithium aluminum hydride furnished a mixture from which one product was separated by distillation *in vacuo*. This product of uncertain purity (see experimental part) had lost two oxygens, no longer contained a methoxyl, and its infrared spectrum showed no absorption in the carbonyl region, and only one peak in the OH, NH region. The ultraviolet spectrum of the product of this reduction (Fig. 7) had maxima at 243 mμ and

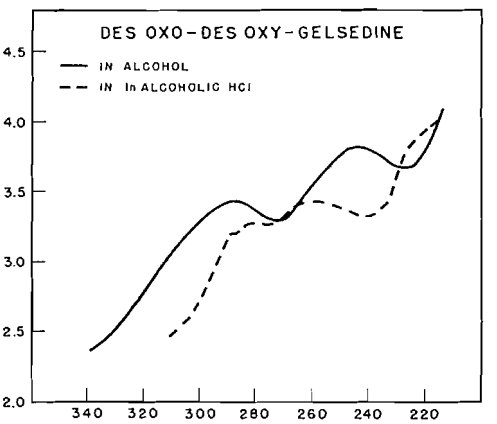



FIG. 7. Ultraviolet spectra of des-oxo-des-oxygelsedine.

289 mμ and minima at 226 mμ and 277 mμ. The hypsochromic displacement in acid medium (Fig. 7) is characteristic of compounds containing an imino group attached to a chromophoric system.

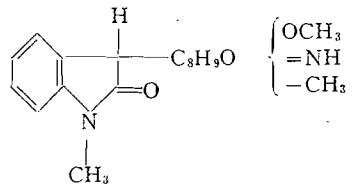
Of the two nitrogens in gelsedine, one, N(*b*) is basic (pK ∽ 9.3) and secondary while the other, N(*a*) is neutral and tertiary and likely carries the N-methyl group. The latter is contained in a lactam group and is attached to the aromatic ring as is shown by the ultraviolet spectrum of the lithium aluminum hydride reduction product. The carbonyl peak at 1720 cm.$^{-1}$ (see gelsevirine) in the infrared and the ultraviolet spectrum of gelsedine are characteristic of oxindoles. A comparative study of the ultraviolet spectra of variously substituted oxindoles (forthcoming publication) suggested that the changes in the ultraviolet absorption in alkaline solution as observed with gelsedine may be indicative of a 1,3-disubstituted oxindole.[3] The benzene ring in gelsedine seems to be ortho-disubstituted as indicated by a band at ca. 750 cm.$^{-1}$ in its infrared spectrum and in those of its derivatives. Such a band is also present in the infrared spectra of gelsemine and its corresponding derivatives. The

[3] *From the interpretation of the ultraviolet spectrum Janot, Goutarel, and Friedrich (5) had already proposed an oxindole structure for their base $C_{19}H_{24}O_3N_2$ which they had assumed to be gelsemicine.*

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catalytic hydrogenation confirms the presence of a benzene ring and shows the absence of other readily reducible double bonds. It is not likely that the methoxyl is attached to the benzene ring since it is lost during both types of reduction.

From the foregoing the following partial formula for gelsedine can therefore be suggested.




The methoxyl which is lost during the reduction of gelsedine with lithium aluminum hydride or with hydrogen over Adams' catalyst must be in an activated position. Since only one carbonyl appears to be present it is suggested that the methoxyl is in an $\alpha$- or $\beta$-position to the lactam carbonyl and to the benzene ring. That a methoxy group in a benzyl position is removed under the above mentioned conditions is a known fact. But there have been cases observed where a methoxyl in $\beta$-position to a carbonyl is lost on hydrogenation over Adams' catalyst[4]. The N-methyl-isatin-like ultraviolet spectrum of gelsedine under certain conditions might be explained by the formation of either a $\beta$-methylene oxindole system by base catalyzed elimination of methanol, or of N-methyl-isatin by oxidative cleavage of the $\beta$ C–C bond. The third oxygen is unaccounted for as yet and is probably present in an ether linkage since there are rather few C-atoms left to make up the other three rings which gelsedine must contain.

Gelsemicine ($C_{20}H_{26}O_4N_2$) contained two methoxyls, one N-methyl, one C-methyl, and one active hydrogen. Its infrared absorption spectrum (curve 3, Fig. 4) showed an NH band, a split band in the carbonyl region, and the usual absorption due to the presence of a benzene ring. The spectrum also contains a strong sharp band at 1500 cm.$^{-1}$ which is characteristic of gelsemicine and all its derivatives. This band is not present in the spectrum of gelsedine and therefore has some analytical value in handling mixtures of the two alkaloids. The ultraviolet spectrum of gelsemicine (Fig. 3) in alcohol showed the two maxima characteristic of 1,2,3-trisubstituted indoles (compare Raymond-Hamet (8)), although the general shape of the curve was not the same, the minimum being higher than usual, thus causing a flattening of the curve. The spectrum did not change in acidic solution, but in alkaline solution the minimum was displaced towards higher wave lengths (Fig. 3). The ultraviolet absorption spectrum of tetrahydrocarbazole measured under the same conditions does not show this shift. Nevertheless, the similarity of the ultraviolet spectrum of gelsemicine with that of indoles led Raymond-Hamet (7) to suggest an indole structure for the alkaloid.

[4] *Private communication from Dr. O. E. Edwards.*

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Both acetyl and benzoyl gelsemicine were neutral substances. The infrared absorption spectra of both derivatives showed no absorption in the NH, OH region but both contained one carbonyl band besides that attributable to the substituent (Fig. 6). Neither derivative contained active hydrogen. The ultraviolet spectrum of acetylgelsemicine was the same as that of the alkaloid.

Of the two nitrogens in gelsemicine one is secondary and basic while the other is tertiary and neutral and probably carries the N-methyl group. If the assumption of an indole nucleus be correct (and the evidence is strengthened by a positive Hopkins-Cole test) then the presence of another chromophoric group must be postulated to account for the additional absorption in the ultraviolet causing the flattening of the curve (1) and for the difference in absorption in alkaline solution. The infrared spectrum of the base contains a very intense second peak at 1632 cm.$^{-1}$ (curve 3, Fig. 4) similar to that present in the spectra of corynantheine and Py-tetrahydroalstonine (1) and hence the second chromophoric group is likely similar to that of the latter. It is not, however, identical since gelsemicine is not hydrolyzable by acids (94% of the base being recovered on acid hydrolysis of the benzoylated mixture).

Two of the four oxygen atoms in the molecule are present in methoxyl groups. The ultraviolet spectrum of the alkaloid is different from those of 4-, 5-, and 6-methoxyindoles but similar to that of 7-methoxy-2,3-disubstituted indole (actually 8-methoxy-2,3,4,5-tetrahydrocarbazole), although one of the maxima is at 270 m$\mu$ instead of 285 m$\mu$. The absence of an N-methyl substituent in the model compound might account for this difference. It is therefore possible that one of the methoxyl groups might be present in the benzene ring in the similar position.

The assignment of an empirical formula to the third alkaloid, gelsevirine, and the determination of its functional groups proved difficult. Whereas the perchlorate analyzed correctly for $C_{21}H_{24}O_3N_2$ containing two methoxyls, one N-methyl, but no C-methyl, the analytical figures obtained from the free base and the methiodide did not agree as well, the methoxyl values particularly being low. It appears that the base may have undergone partial decomposition or hydrolysis in the process of its liberation from its perchlorate. The ultraviolet spectrum of gelsevirine perchlorate was very similar to that of gelsedine ($\lambda_{max}$ 255 m$\mu$, $\lambda_{min}$ 231 m$\mu$) but did not change either in acidic or alkaline solution. This is characteristic for either 1,3,3-trisubstituted oxindoles (forthcoming communication) or N-acyl-indolines of the strychnine or aspidospermine type. The infrared spectrum of gelsevirine perchlorate (curve 5, Fig. 4) contained a carbonyl band at 1715 cm.$^{-1}$ which was in agreement with an oxindole structure since it was too high for a six-membered lactam (strychnine, 1665 cm.$^{-1}$ (6)) or an acyl amide (diaboline, 1660 cm.$^{-1}$ (2)). The infrared spectrum also contains a relatively strong band at 3120 cm$^{-1}$. Such a band is present neither in gelsemine perchlorate nor in gelsedine perchlorate and therefore it cannot be due to an NH in the oxindole or the other moiety of the molecule. Since further all three oxygens are accounted for in a carbonyl and two methoxyls, the absorption band cannot be attributed to a hydroxyl and it may be due to CH-stretching.

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## EXPERIMENTAL[5]

All infrared absorption spectra were taken in nujol mulls with a Perkin-Elmer double-beam spectrophotometer, model 21. All ultraviolet spectra were taken with a Beckman spectrophotometer model DU.

The finely powdered root of *Gelsemium sempervirens* Ait. (22.6 kgm.) was percolated with methanol until all the alkaloids had been removed (test with Mayer's reagent). The methanol was distilled off under reduced pressure at a water bath temperature of 40–50°. To the residual thick sirup, water was added and the distillation resumed in order to remove the methanol quantitatively. While still warm the tarry residue was poured into a large jar and the distillation flask rinsed with a suspension of filtercel in water. Filtercel (Johns-Manville Hyflo super-cel, 3.7 kgm.) and water (5 l.) were added to the tar and the resulting paste stirred for 24 hr. The contents of the jar was filtered onto a large Büchner funnel and the cake of filtercel and tar was stirred with water (5 l.) another 24 hr. and filtered. This procedure was carried out six more times with 10% acetic acid instead of water, which proved sufficient to complete the extraction of the alkaloids from the tar (test with Mayer's reagent). The filtrates were combined and worked up in suitable portions. It was first extracted three times with ether (extract A), then it was made alkaline with ammonia and extracted with 90: 10 ether–methanol until no more alkaloids were taken up by the organic phase (extract V) and finally concentrated aqueous sodium hydroxide was added and the liquor extracted exhaustively with chloroform (extract C).

Extract A did not contain any alkaloids and was discarded.

From the chloroform extract C, the alkaloids were removed by shaking with 10% acetic acid. The combined acid extract was heated to boiling and a concentrated aqueous solution of ammonium nitrate was added. Sempervirine nitrate precipitated as very fine yellow needles. The mixture was cooled, allowed to stand four hours at 0°, and filtered. Yield, 41 gm. The nonprecipitated alkaloids were recovered from the filtrate and combined with extract B.

Extract B in ether solution was shaken repeatedly with normal hydrochloric acid. The combined acid solution was made alkaline with ammonia and extracted with chloroform. The combined chloroform extract was dried over potassium carbonate and the solvent removed by distillation under reduced pressure. The residue was dissolved in acetone and the solution on standing deposited gelsemine in needles having a slight yellow cast. Yield, 58 gm. The acetone mother liquor was evaporated to dryness, the residue (ca. 30 gm.) dissolved in absolute ethanol, and the residual gelsemine removed quantitatively according to Chou's procedure (3).

The dark brown mother liquor from the gelsemine hydrobromide was evaporated to dryness, the residue taken up in water, and the solution filtered through filtercel to remove some insoluble material. The filtrate was made alkaline with ammonia and extracted exhaustively with ether. The combined ether extract was shaken with several portions of 2 *N* hydrochloric acid, the

[5] *All melting points are corrected.*

combined solution was made alkaline with ammonia, and the bases extracted with chloroform (the combined extract contained 200 ml. of chloroform).

For the separation of the minor alkaloids two methods were applied, i.e., benzoylation and acetylation. The former has the advantage of giving a product which crystallizes readily and can be purified more easily than the acetylation product. Both methods, however, give about the same yields.

*Benzoylation*[6]

The above chloroform extract (200 ml.) together with 10% aqueous sodium hydroxide (700 ml.) and benzoyl chloride (30 ml.) was shaken in a separatory funnel for 10 min. A further 20 ml. of benzoyl chloride was added and the shaking continued until the odor of benzoyl chloride had disappeared (20 min.). The chloroform layer was separated and washed twice with 10% aqueous sodium hydroxide (discarded), five times with 2 *N* sulphuric acid, and three times with water. The acid and water washings which contained the tertiary alkaloids were combined (solution T).

The chloroform solution was then dried and evaporated to dryness leaving a semisolid brown mass (56 gm.) which was dissolved in 250 ml. of benzene. This solution was chromatographed on aluminum oxide No. III (Brockmann scale). A volume of 90 ml. of the solution was poured onto a column containing 300 gm. of alumina. The product was eluted with: (1) benzene (250 ml.), discarded; (2) benzene (250 ml.) which yielded 3.2 gm. of oil; (3) benzene (250 ml.) which gave 0.745 gm. of foam; (4) benzene (250 ml.) which gave 0.482 gm. of foam; (5) benzene (500 ml.) which gave 0.436 gm. of foam; (6) benzene (1000 ml.) which gave 0.400 gm. of oil; (7) benzene–chloroform, 4:1 (500 ml.) which gave 0.139 gm. of oil; (8) benzene–chloroform, 1:1 (500 ml.) which gave 0.088 gm. of oil.

Fraction 2 was triturated with 1:1 ether–pentane in order to remove color and oily material. On filtration of the mixture there was obtained 1.2 gm. of crystalline benzoylated product. Fractions 2, 3 and 4 crystallized on addition of ethanol; 4, 5 and 6 crystallized after standing for several days in alcoholic solution, while 7 and 8 failed to furnish any crystalline material. After recrystallization the benzoylated product (2.40 gm.) melted at 233–240°. The remainder of the benzene solution of the benzoylated product was chromatographed in the same way and the over-all yield from both chromatograms was 8.06 gm. The mother liquor from the crystallizations was rechromatographed and it yielded a further 0.55 gm. of crystalline product. A small sample after three recrystallizations from ethanol still melted at 236–239°. It was dried for eight hours, over phosphorus pentoxide at 100° at 0.1 mm. Found: C, 71.95, 71.67, 71.86, 71.87; H, 6.44, 6.77, 6.37, 6.98; N, 6.31, 6.28. Calc. for $C_{27}H_{30}O_5N_2$: C, 70.11; H, 6.54; N, 6.06. Calc. for $C_{26}H_{28}O_4N_2$: C, 72.20; H, 6.53; N, 6.48%.

Rechromatography of 205 mgm. of the benzoylated product gave three fractions respectively melting at 243–246°, 237–239°, and 234–237°. The infra-

[6] *This method was not applied to the batch of alkaloids obtained by the above described method, but to one worked up by the method previously extant. The yields given here are therefore too low. Improved yields of minor alkaloids are given under "Acetylation Method".*

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red absorption spectra of these fractions, however, showed that all three were still mixtures of the same components, but in different ratios.

A quantity of the benzoyl compound was hydrolyzed and the resulting mixture of bases crystallized from ethyl acetate, m.p. 136–139°, $[\alpha]_D^{25}$ −150° (*c*, 1.29 in chloroform). Fractional crystallization did not raise the melting point although two forms of crystals were distinctly visible. A few crystals of one form picked out mechanically melted at 160–166°. Chromatography of the mixed bases on alumina did not prove satisfactory as some decomposition occurred.

A small quantity of the crystalline mixed bases was converted to the perchlorate. The crystalline salt was recrystallized three times from methanol–water (1:1). The yield of salt was low, but the mother liquor failed to yield more crystalline salt (see below).

*Hydrolysis of the Benzoyl Compound*

The benzoyl compound (3.5 gm.) was refluxed for four hours with ethanol containing sulphuric acid (5 *N* in alcohol–water, 7:3) (260 ml.). Water (400 ml.) was then added and after distillation of 300 ml. under reduced pressure, the resulting solution was cooled and extracted with ether (this extract yielded a small quantity of unchanged benzoyl compound). To the acid aqueous liquor ammonia was added to pH ~ 9, and the solution extracted with five portions of ether[7]. This procedure ensured quantitative removal of the bases. The combined ether extract was washed with water and without drying evaporated to dryness *in vacuo*. The residual amorphous bases weighed 2.46 gm. (92% yield).

*Separation of the Bases into Alkaloids A and B*

The base mixture (2.40 gm.) obtained on hydrolysis of the benzoyl compound was dissolved in 10% acetic acid (50 ml.), sodium acetate was added, and the solution was seeded with a trace of the crystalline perchlorate described above. Perchloric acid was then added slowly and the turbidity which appeared was cleared as crystals formed on shaking. When a further quantity of 1 ml. of acid failed to cause any turbidity, the mixture was slowly cooled to 0° and the oil which separated solidified on shaking. After 30 min. at 0° the semicrystalline mass was filtered, dried at room temperature, and weighed. It was heated with methanol (1 ml. for every 300 mgm. of perchlorate) until it had all dissolved and an equal volume of water was added. On cooling, crystals separated which were recrystallized from the same mixture to constant melting point. Each mother liquor was worked up as follows: it was distilled under reduced pressure in order to remove the methanol, the residual liquor diluted with water, made alkaline with ammonia, and extracted repeatedly with ether. The combined ether extract after being washed with water was evaporated to dryness without drying and the residual base crystallized from acetone.

All the fractions of base recovered from the perchlorate mother liquors melting above 160° were identical and will be referred to as alkaloid A. The

[7] *Neither ammonia nor sodium hydroxide caused the precipitation of a base. If the solution was made basic with sodium hydroxide, extraction of the base was extremely slow and still incomplete after 10 extractions.*

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lower melting fractions were still mixtures and were combined with the next lot of mixed bases to be separated. Table I shows the detail of one series of fractional recrystallizations.

A quantity of crystalline perchlorate (1.175 gm.) was decomposed by shaking with ammonia and ether. The ether solution was washed with water, evaporated to dryness, and the residual base crystallized from ethyl acetate, wt. 0.797 gm., m.p. 171–173°.

TABLE I

FRACTIONAL RECRYSTALLIZATION OF THE PERCHLORATES

| Times recryst. | Base $HClO_4$ cryst. | | Base $HClO_4$ in solution*, | Free base from soluble perchlorate | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Theoretical yield, | Yield, first crop | | Yield, second crop | |
| | Gm. | M.p. | gm. | gm. | Gm. | M.p. | Gm. | M.p. |
| 0 | — | — | | 2.46 | — | 136–39° | — | — |
| 1 | 2.828 | 151° | 0.502 | 0.350 | 0.270 | 168–70° | 0.039 | 164–7° |
| 2 | 1.976 | 165° | 0.852 | 0.664 | 0.449 | 168.5–70° | 0.051 | 163–6° |
| 3 | 1.557 | 172° | 0.419 | 0.340 | 0.227 | 167–70° | 0.064 | 165–8° |
| 4 | 1.376 | 176° | 0.181 | 0.141 | 0.068 | 165–8° | 0.020 | 153–7° |
| 5 | 1.293 | 181° | 0.083 | 0.065 | 0.040 | 155–8° | — | — |
| 6 | 1.226 | 183° | 0.068 | 0.053 | 0.028 | 136–44° | — | — |

*Calculated as the difference.*

From 2.46 gm. of mixed bases the foregoing method of separation gave 1.193 gm. of alkaloid A (from the perchlorate mother liquors) and 0.797 gm. of alkaloid B (liberated from the crystalline perchlorate). Unseparated bases and amorphous material recovered from the final mother liquor amounted to 0.367 gm. Hence 81% of the mixture was separated into pure alkaloids.

*Identity of Alkaloid A with Gelsemicine*

The higher melting fraction of alkaloid A was recrystallized twice from acetone from which it separated in large stout rhombs (Fig. 1), without solvent of crystallization, m.p. 171–172°, $[\alpha]_D^{25}$ −142° (*c*, 0.945 in chloroform). A sample for analysis was dried three hours at 100° at 0.2 mm. Found: C, 66.84, 66.89, 67.27; H, 6.92, 7.00, 7.31; N, 7.78; $OCH_3$, 16.22, 16.47, 18.53; $N\cdot CH_3$, 2.47, 3.96; $C\cdot CH_3$, 3.34; act. hydrogen (Zerewitinow) 0.22%. Calc. for $C_{20}H_{26}O_4N_2$: C, 67.02; H, 7.31; N, 7.82; 2 $OCH_3$, 17.30; 1 $N\cdot CH_3$, 4.18; 1 $C\cdot CH_3$, 4.18; 1 act. hydrogen, 0.28%. Calc. for $C_{20}H_{24}O_4N_2$: C, 67.39; H, 6.79; N, 7.86%. In admixture with alkaloid B (m.p. 172.5–174°) it melted at 136–139° but in admixture with a sample of Chou's gelsemicine (m.p. 164–167°) supplied to us by Dr. Raymond-Hamet, it melted at 168–170°. Both the ultraviolet and infrared absorption spectra of alkaloid A (Fig. 3, and curves 3 and 4, Fig. 4) were identical with the corresponding spectra of Chou's gelsemicine.

*Gelsemicine Picrate*

Gelsemicine (60 mgm.) was dissolved in ethanol (2 ml.) and a slight excess of picric acid in ethanol was added. On scratching the picrate separated in scalelike square plates. It was recrystallized three times from ethanol and dried

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for fours hours at 100° at 0.2 mm., m.p. 206–208°[8]. Found: C, 53.49; H, 5.21; N,11.88. Calc. for $C_{20}H_{26}O_4N_2 \cdot C_6H_3O_7N_3$: C, 53.15; H, 4.98; N, 11.92%.

*Benzoyl Gelsemicine*

Gelsemicine (100 mgm.) was dissolved in chloroform (10 ml.) and to the solution benzoyl chloride (0.4 ml.) and 2 *N* aqueous sodium hydroxide (10 ml.) were added. After the mixture had been shaken for 10 min., benzoyl chloride (0.2 ml.) was added and the reaction mixture shaken for a further 20 min. after which the odor of benzoyl chloride had disappeared. The chloroform layer was separated, extracted twice with 2 *N* aqueous sodium hydroxide, three times with *N* hydrochloric acid, and three times with water. It was then dried over sodium sulphate and evaporated to dryness. The residue was washed with pentane to remove some remaining benzoyl chloride. Yield, 142 mgm. After three recrystallizations from ethanol, benzoyl gelsemicine melted at 235–236°. $[\alpha]_D^{25}$ −107° (*c*, 0.97 in chloroform). For analysis a sample was dried at 100° at 0.1 mm. for three hours. Found: C, 70.02; H, 6.50; N, 6.21. Calc. for $C_{27}H_{30}O_5N_2$: C, 70.11; H, 6.54; N, 6.06%.

*Acetyl Gelsemicine*

A solution of gelsemicine (272 mgm.) in benzene (1.5 ml.) and acetic anhydride (1.0 ml.) was refluxed for three hours. The solution was evaporated under reduced pressure, benzene added, and the solution evaporated again under reduced pressure. This process was repeated several times until the excess acetic anhydride had been removed. The residue was dissolved in ethyl acetate, the solution washed three times with *N* hydrochloric acid, three times with water, dried over sodium sulphate, and evaporated to dryness under reduced pressure. Acetyl gelsemicine thus obtained (wt. 286 mgm.) was still colored even after several recrystallizations from ethyl acetate or ethyl acetate – ether. A quantity (224 mgm.) in benzene solution was filtered through a column of 2.5 gm. of acid-washed alumina No. III (Brockmann scale) and the column eluted with alcohol-free chloroform (50 ml.). The colorless product obtained from the eluate (189 mgm.) after two recrystallizations from ethyl acetate – ether, melted at 174–175°. A sample was dried for analysis for three hours at 100° at 0.1 mm. $[\alpha]_D^{25}$ −126° (*c*, 0.95 in chloroform). Found: C, 65.66; H, 7.15; N, 6.80; C·$CH_3$, 6.74; no active hydrogen. Calc. for $C_{22}H_{28}O_5N_2$: C, 65.98; H, 7.05; N, 7.00; 2 C·$CH_3$, 7.48%.

*Alkaloid B (Gelsedine)*

Alkaloid B (170 mgm.) was recrystallized twice from ethyl acetate from which it separated as fine elongated rhombs (Fig. 2) without solvent of crystallization, m.p. 172.5–174°. For analysis a sample was dried for three hours at 100° at 0.1 mm. $[\alpha]_D^{25}$ −159° (*c*, 1.35 in chloroform). Found: C, 69.77, 69.81; 69.69; H, 7.52, 7.36, 7.30; N, 8.57; $OCH_3$, 8.73, 9.18; N·$CH_3$, 4.22; C·$CH_3$, 3.04, act. hydrogen (Zerewitinow) 0.32. Calc. for $C_{19}H_{24}O_5N_2$: C, 69.49; H, 7.37; N, 8.53; 1 $OCH_3$, 9.43; 1 N·$CH_3$, 4.57; 1 C·$CH_3$, 4.57, act. hydrogen, 0.304%. The ultraviolet and infrared absorption spectra of this base (Fig. 5.

[8] *On slow heating decomposition begins at about 200°.*

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and curve 2, Fig. 4) were both different from the corresponding spectra of gelsemicine and of gelsemine. Alkaloid B is therefore distinct from gelsemicine and it is suggested to designate it as gelsedine.

Gelsedine is not soluble in alkali at first but during a few hours it slowly dissolves under development of a bright yellow color. After several days a flocculent precipitate appears and the color starts to fade. This behavior has been studied by taking the ultraviolet spectrum of a solution of gelsedine in 1 *N* sodium hydroxide (alcohol–water 1: 1) in intervals. The maxima observed were the following:

| | | | | |
|---|---|---|---|---|
| ½ hr. | 244 | [282] | — | mμ |
| 1½ hr. | 242 | 283 | — | mμ |
| 6 hr. | 240 | 284 | — | mμ |
| 2 days | 240 | 282 | 408 | mμ |
| 2 weeks | below 230 | 285 | 405 | mμ |

[ ] = inflexion point

*Alkaloid B (Gelsedine) Perchlorate*

The crystalline perchlorate (50 mgm.) obtained in the separation of the alkaloids was recrystallized from water–methanol (1: 1) m.p. 183°[9]. It was kept overnight over calcium chloride in an evacuated desiccator. $[\alpha]_D^{25}$ −96° (*c*, 0.73 in chloroform). Found: C, 50.98, 51.29, 51.23; H, 6.01, 6.30, 6.27; N, 6.57, 6.14; Cl, 8.10. Calc. for $C_{19}H_{24}O_3N_2 \cdot HClO_4 \cdot H_2O$: C, 51.06; H, 6.06; N, 6.27; Cl, 7.93%; $H_2O$: 4.03%. For reanalysis a sample of the salt was dried *in vacuo* at 120° to constant weight. Loss on weight: 3.78%. Found C, 53.41; H, 5.78; N, 6.43. Calc. for $C_{19}H_{24}O_3N_2 \cdot HClO_4$: C, 53.21; H, 5.88; N, 6.53%.

*Gelsedine Picrate*

This was prepared like gelsemicine picrate and recrystallized three times from ethanol, m.p. 224–226° (dec.)[10]. For analysis it was dried at 100° at 0.1 mm. for four hours. Found: C, 54.03; H, 4.84; N, 12.37. Calc. for $C_{19}H_{24}O_3N_2 \cdot C_6H_3O_7N_3$: C, 53.86; H, 4.88; N, 12.56%. In order to observe a melting point depression on admixture with gelsemicine picrate, unusually long grinding in a mortar was necessary (m.p. 191–195°). Ordinary mixing gave m.p. 198–207°.

*Benzoyl Gelsedine*

This was prepared as described for the similar derivative of gelsemicine. After three recrystallizations from ethanol it melted at 251–252°. In admixture with benzoyl gelsemicine, m.p. 235–236°. A sample for analysis was dried at 100° at 0.2 mm. for four hours. $[\alpha]_D^{25}$ −116° (*c*, 0.99 in chloroform). Found: C, 72.23; H, 6.55; N, 6.54; act. hydrogen (Zerewitinow) nil. Calc. for $C_{26}H_{28}O_4N_2$: C, 72.20; H, 6.53; N, 6.48%.

*Acetyl Gelsedine*

The method described for the preparation of acetyl gelsemicine gave with gelsedine an impure product which did not crystallize well. The required derivative was prepared as follows. A mixture of gelsedine (75 mgm.), pyridine

[9] *With very slow heating water is given off between 150°–160° and at 183°, and the partially melted substance melts completely at 204°.*

[10] *On slow heating decomposition starts at ca. 218°.*

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(1 ml.), and acetic anhydride (0.5 ml.) was allowed to stand at room temperature for 24 hr. Pyridine and acetic anhydride were removed by evaporating the mixture several times with benzene. The residue was dissolved in ethyl acetate, the solution washed six times with water, dried over sodium sulphate, and evaporated to dryness. The residue was crystallized twice from ethyl acetate, m.p. 165–166°. In admixture with acetyl gelsemicine, m.p. 148–152°. For analysis the product was dried at 100° at 0.1 mm. for three hours. $[\alpha]_D^{25}$ −139° (*c*, 0.72 in chloroform). Found: C, 67.99; H, 7.43; N, 7.42. Calc. for $C_{21}H_{26}O_4N_2$: C, 68.09; H, 7.07; N, 7.56%.

*Hydrogenation of Gelsedine*

Gelsedine (100 mgm.) in glacial acetic acid and 30 mgm. of Adams' catalyst were shaken in a hydrogen atmosphere. The hydrogen uptake stopped as soon as all the platinum oxide had been reduced. No hydrogen was taken up during the next three hours. The hydrogenation, therefore, was continued at 60–70°. The hydrogen absorption was very slow. After eight hours another 20 mgm. of Adams' catalyst was added and the hydrogenation continued for another eight hours. After cooling the solution was filtered and the acetic acid removed under reduced pressure. The residue was taken up in water, made alkaline with ammonia, and extracted with ether. Large quantities of ether were necessary because the base was only sparingly soluble in this solvent. The combined ether extract was dried over potassium carbonate. During the evaporation of the solvent silky white needles separated. They were very soluble in methanol and ethanol and almost insoluble in ether, ethyl acetate, and acetone. For analysis they were recrystallized twice from ethanol–acetone and dried for three hours at 0.05 mm. and 100°, m.p. 277°. Found: C, 71.15, 71.24; H, 9.13, 9.00; $OCH_3$, 0.0. Calc. for $C_{18}H_{28}O_2N_2$: C, 71.01; H, 9.27%.

The ultraviolet spectrum of this hexahydrodesmethoxygelsedine did not show any absorption above 240 mμ.

*Reduction of Gelsedine with Lithium Aluminum Hydride*

A solution of 150 mgm. of gelsedine in 20 ml. of dry ether was slowly added to an emulsion of 300 mgm. of lithium aluminum hydride in 10 ml. of dry ether. The mixture was refluxed for three hours, and the excess lithium aluminum hydride destroyed by addition of 6 ml. of methanol. After boiling for another hour the mixture was filtered through filtercel. The filtered precipitate was washed with chloroform, and the combined filtrates washed with water (four times), dried over potassium carbonate, and evaporated to dryness. Yield: 138 mgm. The oily material could not be obtained crystalline from any of the usual solvents. Therefore, it was distilled at $2 \times 10^{-4}$ mm. and 130–150° in a metal block. The oil crystallized partly after standing at room temperature for several weeks. It was analyzed in this state. Found: C, 76.55; H, 8.93; N, 9.21; $OCH_3$, 0.0. $C_{19}H_{26}ON_2$: C, 76.47; H, 8.78; N, 9.39. The infrared spectrum showed no band in the carbonyl region.

*The Acetylation Method*

The crude basic mixture from 22.6 kgm. of root obtained before benzoylation (see above) was added to dry benzene (100 ml.) containing acetic anhydride

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(70 ml.) and the solution refluxed for 3.5 hr. The excess acetic anhydride was removed by evaporating several times with benzene and the final dry residue (30 gm.) was dissolved in ethyl acetate. The solution was washed three times with 2 *N* sodium carbonate (discarded), four times with 2 *N* hydrochloric acid, and three times with water. The acid and aqueous washings which contained the tertiary bases were combined (solution T). The washed ethyl acetate solution was dried over sodium sulphate and evaporated to dryness under reduced pressure. The residue (wt. 20 gm.) was dissolved in benzene (250 ml.) and worked up in two batches.

The first batch (150 ml. of the solution) was chromatographed on a column containing 150 gm. of acid washed alumina No. III (Brockmann scale). The elution gave the following fractions: (1) trace from 100 ml. of benzene; (2) dark red, 9.061 gm. from 150 ml. benzene; (3) orange, 0.917 gm. from 250 ml. benzene; (4) yellow, 0.480 gm. from 375 ml. chloroform; (5) yellow, 1.050 gm. from 250 ml. chloroform; (6) brown, 1.088 gm. from 250 ml. chloroform containing 0.75% ethanol. Fractions 1 and 6 were discarded. Fractions 3, 4, and 5 when combined and crystallized from ethyl acetate – ether yielded 1.855 gm. of acetyl product. Fraction 2 contained several red pigments which were very difficult to remove. When dissolved in ethyl acetate – ether, the solution on standing 24 hr. deposited 2.861 gm. of dark brown crystalline material. This was rechromatographed on 60 gm. of alumina. The pigments were eluted first by benzene while the middle fractions (benzene, benzene–chloroform, chloroform containing 0.75% ethanol) gave 1.959 gm. of almost colorless crystals.

All the mother liquors from the crystallizations were combined, evaporated, and the residue rechromatographed in benzene solution on alumina. Most of the pigments were eluted first while the subsequent fractions of the eluate yielded 2.45 gm. of crystalline acetyl product. The over-all yield from 22.6 kgm. of bark was 9.3 gm. (corresponds to ca. 12 gm. of benzoyl product).

*Alkaloid C (Gelsevirine)*

Solution T (see above) contained the nonacetylated (or nonbenzoylated bases) as sulphates. Addition of perchloric acid to the solution caused the gradual separation of an oil. After standing for three months the oil was covered with a crystalline perchlorate which was loosened with a spatula and separated from the very viscous oil and the aqueous liquor by decantation. The crystals (wt. 1.9 gm.) were dissolved in methanol and the solution allowed to stand at room temperature for two months. After that time a rather pure perchlorate (alkaloid C perchlorate) had separated which was filtered. After standing another month the mother liquor deposited a second crop. Several crops of crystals were thus slowly obtained. The oil from which the perchlorate had first been separated was dissolved in methanol and the solution after standing three months at room temperature had deposited 200 mgm. of the same perchlorate. So far, about 1 gm. of this perchlorate has been isolated.

A quantity of the perchlorate (200 mgm.) was recrystallized three times from methanol. It then melted at 250–252°. It did not contain solvent of

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crystallization. For analysis a sample was dried at 100° at 0.05 mm. for three hours. Found: C, 55.75; 55.90; H, 5.66, 5.69; N, 6.34; Cl, 8.15; $OCH_3$, 13.95; $NCH_3$, 3.10; $C \cdot CH_3$, 0.0. Calc. for $C_{21}H_{24}O_3N_2 \cdot HClO_4$: C, 55.69; H, 5.56; N, 6.19; Cl, 7.83; $2OCH_3$, 13.72; $N \cdot CH_3$, 3.32. Calc. for $C_{21}H_{26}O_3N_2 \cdot HClO_4$: C, 55.44; H, 5.96; N, 6.16; $2OCH_3$, 13.62; $NCH_3$, 3.30%.

*Gelsevirine*

The base liberated from the perchlorate could not be crystallized. It was distilled at 130–150° at $10^{-4}$ mm., and the colorless oil thus obtained analyzed. Found: C, 71.18; H, 7.00. Calc. for $C_{21}H_{24}O_3N_2$: C, 71.57; H, 6.87. Calc. for $C_{21}H_{26}O_3N_2$: C, 71.16; H, 7.39%. The picrate of the base was also an oil.

*Gelsevirine Methiodide*

The methiodide obtained by adding excess methyl iodide to a solution of the base in acetone was recrystallized three times from ethanol from which it separated as colorless needles, m.p. 259–261°. After drying for three hours at 100° at 0.05 mm. it yielded the following analytical figures. Found: C, 52.08, 52.09, 52.58; H, 5.95, 5.77, 6.05; N, 5.48, 5.43; $OCH_3$, 7.69, 8.40; $N \cdot CH_3$, 6.28. Calc. for $C_{21}H_{24}O_3N_2 \cdot CH_3I \cdot \frac{3}{4}H_2O$: C, 52.02; H, 5.65; N, 5.52; $H_2O$, 2.6. Calc. for $C_{21}H_{26}O_3N_2 \cdot CH_3I \cdot \frac{1}{2}H_2O$: C, 52.28; H, 5.98; N, 5.54; $H_2O$, 1.8; $OCH_3$, 6.13; $NCH_3$, 2.96%. Dried at 140° and 0.05 mm. overnight. Loss 1.6%. Found: C, 53.02, 52.87, 52.69; H, 6.07, 6.09, 5.74; N, 5.75. Calc. for $C_{21}H_{24}O_3N_2 \cdot CH_3I$: C, 53.44; H, 5.48; N, 5.67. $C_{21}H_{26}O_3N_2 \cdot CH_3I$: C, 53.22; H, 5.89; N, 5.64%.

To the solution T from which the crystalline and the oily perchlorates had been separated more perchloric acid was added. After standing for about two months a second crystalline perchlorate (about 1.5 gm.) had separated. It was filtered off and dissolved in methanol in which it turned to an oil before going into solution. Crystals have not been obtained from this solution as yet, even after seeding with some crystals of the perchlorate of gelsevirine.

The filtered solution T still contained alkaloids as a heavy precipitate with Mayer's reagent indicated. These alkaloids presumably form very soluble perchlorates.

ACKNOWLEDGMENT

The authors express their gratitude to Dr. Raymond-Hamet, Paris, for the gift of a sample of gelsemicine, to Mr. R. Lauzon and Dr. R. Norman Jones of these laboratories for taking the infrared absorption spectra, to Dr. N. F. H. Bright who made the photomicrographs, and finally to Mr. M. Lesage for technical aid in working up the alkaloid extracts.

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# ORGANIC PHOSPHORUS COMPOUNDS

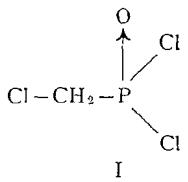
## II. PREPARATION OF CHLOROMETHANEPHOSPHONYL DICHLORIDE[1]

By R. A. B. Bannard, J. R. Gilpin, G. R. Vavasour, and A. F. McKay

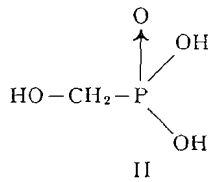
ABSTRACT

Hydroxymethanephosphonic acid was prepared by treating paraformaldehyde with phosphorus trichloride at atmospheric pressure and subsequent hydrolysis of the resultant complex. Chloromethanephosphonyl dichloride was obtained by chlorination of hydroxymethanephosphonic acid with thionyl chloride in the presence of pyridine. On the other hand hydroxymethanephosphonic acid combined slowly with phosphorus pentachloride to give the hitherto unknown dichlorophosphorylmethanephosphonyl dichloride, $Cl_2P(O)OCH_2P(O)Cl_2$, together with chloromethanephosphonyl dichloride. The structure of dichlorophosphorylmethanephosphonyl dichloride was confirmed by its conversion with phosphorus pentachloride at 78°C. into chloromethanephosphonyl dichloride and phosphorus oxychloride. The preparation of chloromethanephosphonyl dichloride by interaction of paraformaldehyde and phosphorus trichloride in an autoclave at 250°C. was studied in reference to the influence of heating time on the yield.

Prat, Bourgeois, and Ragon (9) first prepared chloromethanephosphonyl dichloride (I) in 1948 from phosphorus pentachloride and hydroxymethanephosphonic acid (II). Later Yakubovitch, Ginsburg, and Makarov (11) obtained the same compound by the reaction of phosphorus pentachloride with diazomethane, followed by oxidation of the resultant chloromethanedichlorophosphine. More recently, Kabachnik and co-workers (3, 4, 5) have prepared this compound by heating a mixture of phosphorus trichloride and paraformaldehyde in an autoclave at 250°C. Prat, Bourgeois, and Ragon (9)




I




II

could not obtain chloromethanephosphonyl dichloride by the action of thionyl chloride on hydroxymethanephosphonic acid nor by reaction of phosphorus pentachloride with the hydroxy acid in carbon tetrachloride suspension. The chlorination of hydroxymethanephosphonic acid was reinvestigated using phosphorus pentachloride and thionyl chloride to establish whether yields superior to those (60–65%) reported by Kabachnik and Shepeleva (5) could be obtained.

Hydroxymethanephosphonic acid (II) was obtained as a liquid when Page's (8) procedure was followed. However, the modifications described in the Experimental section gave good yields of crystalline acid II. Crude hydroxymethanephosphonic acid has a melting point of 84–86°C. in a closed

[1] *Manuscript received July, 2, 1953.*
*Contribution from Defence Research Chemical Laboratories, Ottawa, Canada. Issued as D.R.C.L. Report No. 123.*

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tube and it is not contaminated with nonionizable chlorine as Prat and co-workers (9) claimed. Recrystallization of this crude acid from ethanol – ethyl acetate raised the melting point to 98.5–100.5°C. as reported previously by Kabachnik and Shepeleva (5). Hydroxymethanephosphonic acid melting at 98.5–100.5°C. appears to be much less hydroscopic than the material melting at 88–90°C., which suggests that the acid having the lower melting point contains a small proportion of a very hydroscopic impurity. Microanalysis of both samples, however, gave no indication of the presence of an impurity.

Chlorination of hydroxymethanephosphonic acid with thionyl chloride gave a 56.6% yield of chloromethanephosphonyl dichloride (I).

A mixture of phosphorus trichloride and paraformaldehyde heated in a stainless-steel autoclave at 250°C., yielded chloromethanephosphonyl dichloride as previously reported by Kabachnik and co-workers (3, 4, 5). Kabachnik and Shepeleva (5) established that maximum yields of 60–65% were obtained with a molar ratio of phosphorus trichloride to formaldehyde of 1.5:1 and with heating periods of 5 to 10 hr. at 235–250°C. The present studies (cf. Table I) of the effect of heating time on the yield of chloromethanephosphonyl dichloride (I) indicate that maximum yields of 53% are obtained with heating periods of five to six hours. Longer or shorter heating periods cause a marked decrease in yield. Run 2, in which the mixture of phosphorus trichloride and formaldehyde was allowed to stand at room temperature for 17 hr. in the sealed autoclave prior to heating at 250°C., shows that prolonged standing at room temperature has no influence on the yield. However in run 3, where phosphorus pentachloride (0.385 mole) was added to the reaction mixture at room temperature prior to heating, a very marked decrease in yield occurred. In runs 6 and 7, the phosphorus trichloride and paraformaldehyde were combined at atmospheric pressure according to the method of Page (8) for the preparation of hydroxymethanephosphonic acid. The resultant turbid sirup was transferred to the autoclave and heated under the conditions specified in Table I. The abrupt decrease in yield from those obtained in runs 4 and 5, which were performed under otherwise identical conditions, suggests that the hydrogen chloride which is evolved during formation of the phosphorus trichloride – formaldehyde complex is beneficial in the interaction of these substances at

TABLE I
EFFECT OF HEATING TIME ON YIELD OF $ClCH_2POCl_2$

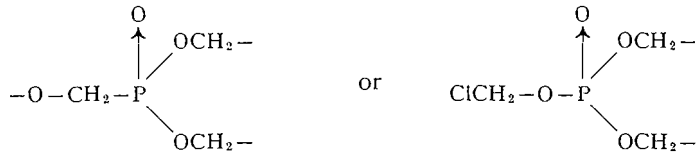
| Run No. | $(CH_2O)n$, moles | $PCl_3$, moles | Temp., °C. | Gauge pressure, p.s.i. | Heating time, hr. | Yield $ClCH_2POCl_2$, moles | % Yield |
|---|---|---|---|---|---|---|---|
| 1 | 0.500 | 0.750 | 245–249 | 330–340 | 1.0 | 0.195 | 39.0 |
| 2 | 0.500 | 0.750 | 250–252 | 335–350 | 1.0 | 0.200 | 40.0 |
| 3 | 0.500 | 0.750 | 249–250 | 400–410 | 1.0 | 0.026 | 5.2 |
| 4 | 0.500 | 0.750 | 249–250 | 330–350 | 3.0 | 0.226 | 45.2 |
| 5 | 1.00 | 1.50 | 249–250 | 365–380 | 3.0 | 0.467 | 46.7 |
| 6 | 1.00 | 1.50 | 247–250 | | 3.0 | 0.328 | 32.8 |
| 7 | 1.00 | 1.50 | 243–250 | 310 | 3.0 | 0.327 | 32.7 |
| 8 | 0.500 | 0.750 | 246–251 | 390–400 | 5.0 | 0.264 | 52.8 |
| 9 | 0.500 | 0.750 | 246–255 | 380–410 | 6.0 | 0.265 | 53.0 |
| 10 | 0.500 | 0.750 | 247–251 | 390–410 | 7.0 | 0.242 | 48.4 |

elevated temperatures and pressures. Kabachnik and Shepeleva (5) infer that there is no difference whether the substances are heated directly in the autoclave or converted to the phosphorus trichloride – formaldehyde complex at atmospheric pressure before heating in the autoclave. However, the low yields in runs 6 and 7 are contrary to this inference.

These authors (5) have discussed the mechanism of this reaction and they have concluded that the tarry residues which remain after removal of the chloromethanephosphonyl dichloride are formed by an intermolecular Arbuzov (1; 6, p. 121) rearrangement of tri(chloromethyl)phosphite (III).

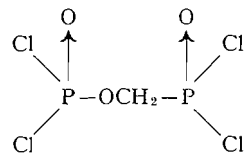
$$P(OCH_2Cl)_3$$
III

It was assumed (5) that the residue contained the structural elements



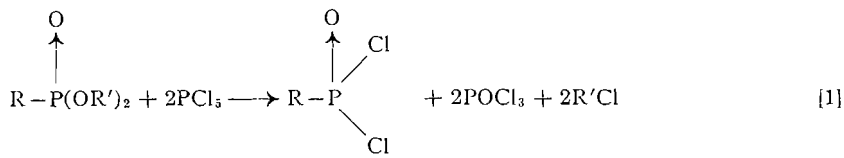

since the residue on heating with phosphorus pentachloride yielded additional chloromethanephosphonyl dichloride by the cleavage of P–O–C bonds. This result agrees with the postulated mechanism for formation of the residue. However, numerous attempts to confirm the production of chloromethanephosphonyl dichloride by heating the residue with phosphorus pentachloride under the conditions given (5) were unsuccessful. It is concluded that either the experimental conditions are not sufficiently specific to follow or the proposed mechanism of formation of the nondistillable residue is inadequate.

Hydroxymethanephosphonic acid in methylene chloride on treatment with phosphorus pentachloride gave the hitherto unknown dichlorophosphorylmethanephosphonyl dichloride (IV) along with the expected chloromethane-



IV

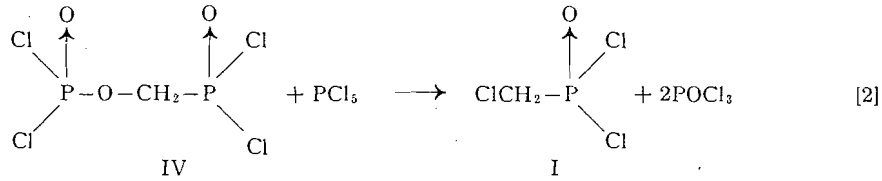
phosphonyl dichloride. The structure of dichlorophosphorylmethanephosphonyl dichloride (IV) was inferred by its percentage composition and molecular refractivity. This was confirmed by the behavior of the compound on treatment with phosphorus pentachloride. Esters of phosphonic acids, on heating with phosphorus pentachloride, undergo cleavage according to equation [1] (2; 6, p. 62; 10).



[1]

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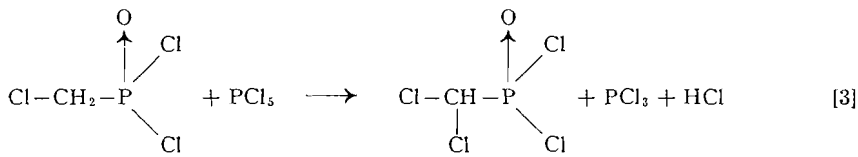
On the basis of reaction [1] dichlorophosphorylmethanephosphonyl dichloride (IV) should be converted to chloromethanephosphonyl dichloride (I) and phosphorus oxychloride as in equation [2].



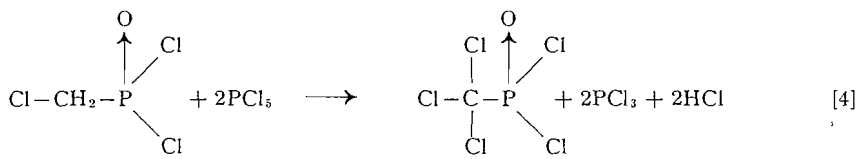

[2]

In agreement with this equation dichlorophosphorylmethanephosphonyl dichloride (IV) heated with an equimolar quantity of phosphorus pentachloride gave a 61% yield of chloromethanephosphonyl dichloride (I) and a 104% yield of phosphorus oxychloride based on unrecovered IV. Hydrogen chloride, phosphorus trichloride, and an unknown crystalline substance (m.p. 175–177°C. with decomposition), which contains phosphorus and chlorine, were obtained as by-products of this reaction (cf. Table II). It is obvious from these results that one or more side-reactions are occurring. The small discrepancy between the quantity of phosphorus oxychloride isolated and that theoretically obtainable via reaction (2) can be explained by the unavoidable partial oxidation of by-product phosphorus trichloride to phosphorus oxychloride (7).

Since a large portion of the dichlorophosphorylmethanephosphonyl dichloride (IV) was recovered unchanged (cf. Table II), it is considered probable that the side-reaction is substitutive chlorination of chloromethanephosphonyl dichloride (I) by phosphorus pentachloride as shown in equations [3] and [4].




[3]




[4]

Reactions [3] and/or [4] would explain the low yield of the dichloride (I).

Qualitative confirmation of this hypothesis has been obtained by heating chloromethanephosphonyl dichloride (I) with phosphorus pentachloride under the same conditions as used for the cleavage of dichlorophosphorylmethanephosphonyl dichloride (IV). The substances react with evolution of hydrogen chloride producing a solution which contains a large proportion of phosphorus trichloride, a trace of phosphorus oxychloride, unreacted I, and the colorless crystalline substance of m.p. 175–177°C. (with decomposition). All of these

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products were isolated from the previously described experiment on the cleavage of IV.

## EXPERIMENTAL[2]

### *Hydroxymethanephosphonic Acid*

One hundred and thirty-seven grams (1.00 mole) of phosphorus trichloride was placed in a 200-ml., four-neck, round-bottom flask equipped with a "trubore" stirrer, thermometer, addition tube, and reflux condenser protected with a calcium chloride tube. Ninety grams (3.00 mole) of paraformaldehyde were added in small portions over a period of 45 min. Each addition was made at 40 to 45°C. and the mixture heated to 60–65°C., at which temperature an exothermic reaction occurred with evolution of hydrogen chloride causing the temperature to rise to 75–78°C. As soon as the temperature began to fall, the solution was cooled to the starting temperature by means of an ice-bath and the cycle repeated. After all the formaldehyde had been added, the opalescent solution was stirred at 80°C. until a colorless solution was obtained (one to two hours). The solution was allowed to stand overnight and the phosphorus trichloride – formaldehyde complex hydrolyzed by pouring the solution into 2 liters of water stirred mechanically at 25°C. At first the oily complex remained immiscible although the temperature rose to 43°C. and formaldehyde was evolved. After the mixture was stirred for 30 min. a clear solution resulted but stirring was continued for a further 30 min. The solution was filtered and concentrated to a volume of about 250 ml. by distillation *in vacuo*. Treatment of the residue as in either Method A or B below produced colorless crystalline hydroxymethanephosphonic acid in 87–92% yield (97.5–102 gm.) m.p. 84–86°C. (closed tube).

*Method A.*—The pale yellow solution was diluted with 300 ml. of absolute ethanol and about 250 ml. of the ethanol removed by slow distillation at atmospheric pressure, to remove any trace of residual formaldehyde as the diethyl acetal. The residue was concentrated to constant bulk at 0.1 mm. pressure at 80°C. and allowed to cool to room temperature while evacuation was continued. The substance crystallized completely to a very hard colorless solid after one to two hours.

*Method B.*—The pale yellow solution was concentrated to constant bulk at 0.1 mm. pressure at 80°C. and allowed to cool to room temperature while evacuation was continued. The substance crystallized completely after two hours to two days.

The crude acid (100 gm. )was recrystallized by dissolving it in absolute ethanol (65 ml.) followed by filtration in a dry-box and addition of purified ethyl acetate in 200-ml. portions followed by cooling in the refrigerator to obtain successive crops of crystals, yield 52 gm. (52%). Most of the recrystallized acid had a melting point of 88–90°C. but one crop had a melting point of 98.5–100.5°C. Calc. for $CH_5O_4P$: C, 10.73; H, 4.50; P, 27.67%. Found for acid m.p. 88–90°C.: C, 10.72; H, 4.53; P, 28.15%. Found for acid m.p. 98.5–100.5°C.: C, 11.09; H, 4.88; P, 27.44%.

[2] *All melting points and boiling points are uncorrected. Microanalyses by C. W. Beazley, Skokie, Ill.*

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*Chlorination of Hydroxymethanephosphonic Acid with Thionyl Chloride in the Presence of Pyridine*

Hydroxymethanephosphonic acid (22.4 gm.; 0.200 mole) was suspended in 150 ml. of anhydrous benzene in a 500-ml., three-neck, round-bottom flask equipped with a "trubore" stirrer, thermometer, dropping funnel, and reflux condenser protected with a calcium chloride tube. Pyridine, 47.5 gm. (0.600 mole), was added in one portion to the stirred suspension at room temperature, causing the phosphonic acid to change to a sirup which settled to the bottom of the flask. The stirred mixture was heated to 55°C. and purified thionyl chloride (71.4 gm.; 0.600 mole) was added at 55–65°C. over a period of 30 min. Vigorous evolution of sulphur dioxide occurred during the addition and a homogeneous solution resulted. The solution was allowed to cool to 30°C. over a period of two hours while stirring was continued. Pyridine hydrochloride began to separate and the mixture was stirred in an ice-bath for 30 min. to complete precipitation. The crystalline material was collected by suction filtration and washed with 5 × 60 ml. of anhydrous benzene. The filtrate and washings were combined and concentrated by distillation at atmospheric pressure in an apparatus protected from entry of moisture. The residue was fractionated *in vacuo* yielding 18.9 gm. (56.6%) of chloromethanephosphonyl dichloride, b.p. 90–93°C. (18 mm.), $n_D^{24.8}$1.4976.

In another experiment using the same quantities of reactants as above and the same procedure, except that the thionyl chloride and pyridine were mixed before addition to the benzene suspension of hydroxy acid, 12.4 gm. (37.1%) of chloromethanephosphonyl dichloride b.p. 77–78°C. (10 mm.), $n_D^{24.8}$1.4970, $d_4^{25.0}$1.650 were obtained. Kabachnik and Shepeleva (5) report b.p. 77–79°C. (10 mm.), $n_D^{20}$1.4978–1.4990, $d_4^{20}$1.6361.

*Chlorination of Hydroxymethanephosphonic Acid with Phosphorus Pentachloride in Methylene Chloride*

Phosphorus pentachloride (187 gm.; 0.900 mole) was suspended in 150 ml. of anhydrous methylene chloride in a 500-ml. three-neck, round-bottom flask equipped with a "trubore" stirrer, addition tube, thermometer, and reflux condenser protected with a calcium chloride tube. Hydroxymethanephosphonic acid, 33.6 gm. (0.300 mole) was placed in a 250 ml. Erlenmeyer flask and attached to the addition tube by means of wide diameter rubber tubing. The hydroxymethanephosphonic acid was added to the stirred suspension of phosphorus pentachloride at 23–26°C. over a period of 30 min., during which vigorous evolution of hydrogen chloride occurred. This mixture was heated under reflux for 18 hr. while slow evolution of hydrogen chloride continued. After heating had been in progress for two hours a homogeneous pale yellow solution resulted. This solution was concentrated by heating at 40 to 60°C. under pressure of 40–60 mm. It was necessary to complete the concentration in three stages to ensure a reasonable recovery of liquid from the unreacted phosphorus pentachloride which separated on cooling the solution. The phosphorus pentachloride was collected by suction filtrations in the dry-box. The final filtrate was transferred to a 50 ml. modified Claisen flask and traces

of volatiles removed by heating to 50°C. in a water bath at 20 mm. pressure. The residue was fractionated *in vacuo* yielding 10.6 gm. (21.1%) of chloromethanephosphonyl dichloride, b.p. 78–81°C. (10 mm.), $n_D^{24.8}$ 1.4978 and 26.7 gm. (33.5%) of dichlorophosphorylmethanephosphonyl dichloride, b.p. 94–95°C. (0.2 mm.), $n_D^{24.8}$ 1.4990, $d_4^{25.5}$ 1.750. Calc. for $CH_2P_2O_3Cl_4$: C, 4.52; H, 0.76; P, 23.30; Cl, 53.32%. Found: C, 4.78; H, 0.88; P, 22.97; Cl, 52.90%. Molecular refractivity calc.: 44.05. Found: 44.35.

*Reaction of Paraformaldehyde with Phosphorus Trichloride at 250°C.*

All runs were made in a 300 ml. stainless-steel autoclave equipped with a pressure gauge.

Fifteen gm. (0.500 mole) of paraformaldehyde and 103 gm. (0.750 mole) of phosphorus trichloride were placed in the autoclave which was sealed immediately and shaken thoroughly to ensure mixing. An exothermic reaction occurred. The autoclave was heated to 250°C. over a period of two and one quarter hours and the temperature was held at 246–255°C. for six hours. The pressure rose to 380 p.s.i. during heating to 250°C. and remained at 380–410 p.s.i. during the remainder of the heating period. The autoclave was removed from the bath, allowed to stand for one hour, then immersed in an ice bath for 20 min. There was no residual pressure when the autoclave was opened. The dark mobile solution was filtered to remove a small quantity of gray residue, and transferred to a modified Claisen flask. The excess phosphorus trichloride was removed by distillation at 40–60 mm. pressure, after which the residue was fractionated *in vacuo* yielding 44.2 gm. (52.0%) of crude chloromethanephosphonyl dichloride as a colorless mobile liquid of piercing odor; b.p. 77–95°C. (9 mm.); $n_D^{24.8}$ 1.4953 to 1.4944. During the latter stages of the distillation the residue became very dark and viscous. Refractionation of the crude product gave 39.0 gm. (46.7%) of pure material b.p. 79–81°C. (10 mm.), $n_D^{24.8}$ 1.4954 to 1.4959, $d_4^{25.5}$ 1.655.

*Action of Phosphorus Pentachloride on Dichlorophosphorylmethanephosphonyl Dichloride*

Dichlorophosphorylmethanephosphonyl dichloride 38.9 gm. (0.146 mole) and 30.4 gm. (0.146 mole) of phosphorus pentachloride were placed in a 125 ml. two-neck, round-bottom flask equipped with a "trubore" stirrer and reflux condenser protected with a calcium chloride tube. The mixture was heated slowly in a mechanically stirred oil bath to 77°C. over a period of 50 min., at which temperature a slow evolution of hydrogen chloride was observed. Heating was continued with mechanical stirring at 74–78°C. for a further two and one-quarter hours, during which slow evolution of hydrogen chloride continued. The phosphorus pentachloride had dissolved after heating at 74–78°C. for one hour. This solution was allowed to stand overnight at room temperature, during which a small quantity of phosphorus pentachloride separated. The solution was fractionated yielding the fractions given in Table II.

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TABLE II

PRODUCTS FROM REACTION OF DICHLOROPHOSPHORYLMETHANEPHOSPHONYL DICHLORIDE WITH PHOSPHORUS PENTACHLORIDE

| Fraction No. | B.p., °C. | Pressure, mm. | Refractive index, $n_D^{24.8}$ | Density, $d_4^t$ | Wt., gm. | Identity | Moles | % Yield based on equation [2] |
|---|---|---|---|---|---|---|---|---|
| 1 | 74 | 745 | 1.5023 | 1.554(25.0) | 3.8 | $PCl_3$ | 0.0277 | By-product |
| 2 | 105–106 | 745 | 1.4578 | 1.660(27.0) | 28.4 | $POCl_3$ | 0.186 | 104 |
| 3 | 62 | 9 | | | 0.3 | Unknown | | By-product |
| 4 | 71 | 8 | 1.4970 | 1.653(27.5) | 9.1 | $ClCH_2P(O)Cl_2$ | 0.0545 | 61.0 |
| 5 | 103 | 1 | 1.4982 | 1.755(26.5) | 15.1 | $Cl_2(O)POCH_2P(O)Cl_2$ | 0.0367 | Starting material |
| 6* | | | | | 2.0 | | | |
| 7** | | | | | 2.9 | | | |

**Distillation residues.*
***Transfer losses.*

ACKNOWLEDGMENT

The authors thank Messrs. R. L. Benness and R. O. Braun for assistance with the preparations of hydroxymethanephosphonic acid and its chlorination with phosphorus pentachloride.

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# ELECTROPHORESIS OF RESIN EMULSIONS

## II. THE EFFECT OF ELECTROLYTE CONCENTRATION ON THE MOBILITIES AND ZETA POTENTIALS[1]

BY L. A. MUNRO AND F. H. SEXSMITH

ABSTRACT

Electrolyte concentration, rather than pH, concentration of resin particles, or dispersity, is the most significant variable affecting the mobility of polyvinyl acetate emulsions. The mobility–electrolyte concentration curves for latices prepared with nonionic and mixed nonionic and anionic emulsifiers, indicate micelle formation at low electrolyte concentrations. Zeta potentials calculated for a typical latex show the potential drop in the double layer to be of the order of $10^{-7}$ volts for a variation of thickness of the ionic atmosphere from $10^{-5}$ to $10^{-6}$ cm. over the range of salt concentration used.

## INTRODUCTION

In a previous paper the effect of the chemical nature of the emulsifying agent on the mobility and sign of polyvinyl acetate emulsions was reported. It was noted that electrolyte concentration, rather than pH, concentration of resin particles, or dispersity, was the most significant variable affecting the mobility of any one emulsion.

The present paper describes the divergent effects of increasing electrolyte content on the mobilities of various emulsions and the zeta potential curve calculated for a very uniform latex.

## EXPERIMENTAL

### *Incremental Salt Addition*

A 3 liter stock suspension was prepared by diluting the given latex to an appropriate total solids content. Fifty-milliliter samples of each stock solution were then mixed with exactly equivalent volumes of pure, rigorously standardized solutions of sodium chloride. For each study at least 12 samples varying in salt concentration from 0 to 0.01 $M$ were used. For salt concentrations below $2.57 \times 10^{-4}$ $M$ the electrolyte concentration of the samples was checked conductimetrically. It is in this low range that the effect of the salt on mobility is most significant.

The samples of latex with added electrolyte, after vigorous shaking, were allowed to stand for approximately twelve hours before the mobilities were

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*Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.*



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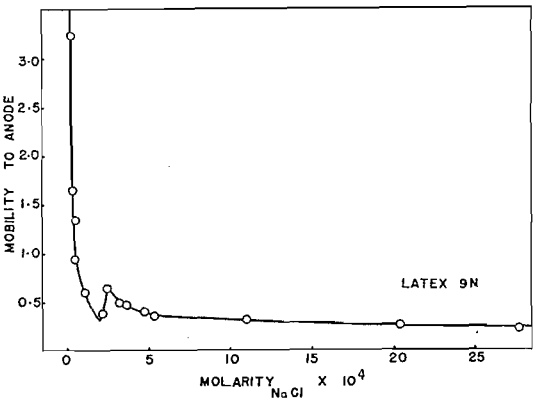



FIG. 1. Mobility curve for latex prepared with nonionic emulsifier.

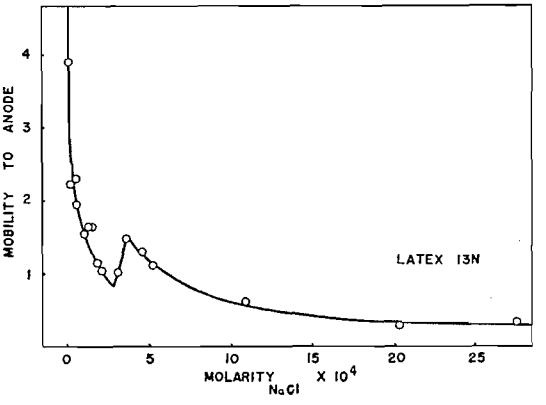



FIG. 2. Mobility curve for a very uniform latex prepared with a nonionic emulsifier.

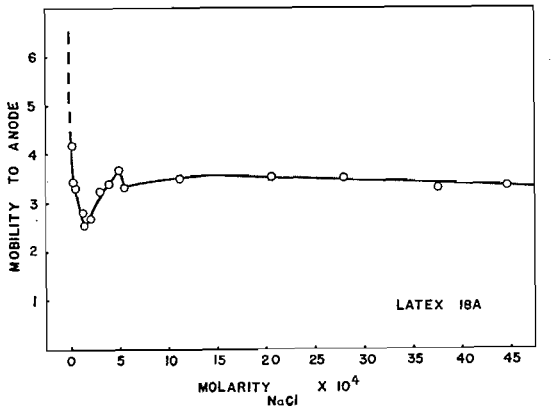



FIG. 3. Mobility curve of typical anionic latex.

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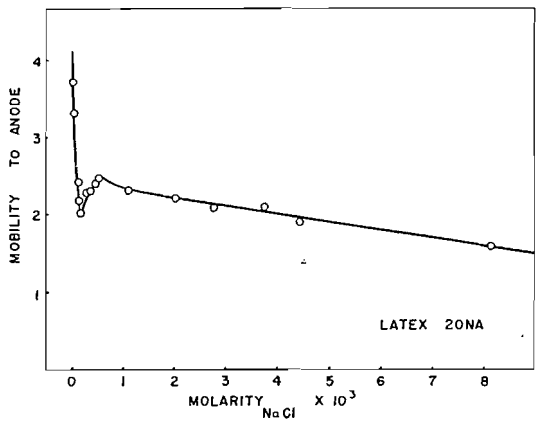



FIG. 4. Mobility curve for a latex prepared with mixed nonionic and anionic emulsifiers.

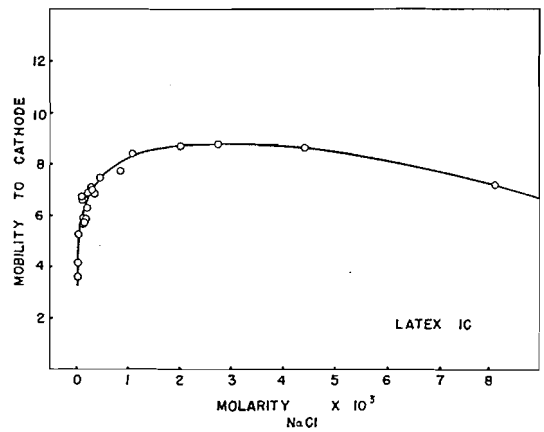



FIG. 5. Mobility curve for a latex prepared with a cationic emulsifier.

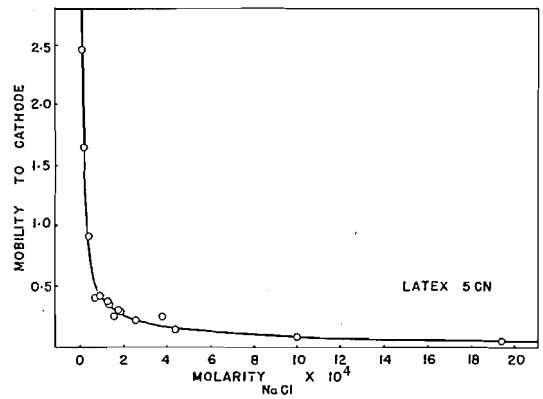



FIG. 6. Mobility curve for a latex prepared with mixed cationic and nonionic emulsifiers.

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measured. The apparatus and technique were the same as previously described (12).

## EXPERIMENTAL RESULTS

The experimental results for the emulsions described are shown graphically in Figs. 1–6. Figs. 1 and 2 are for two specimens prepared with nonionic emulsifying agents (9N213N), Fig. 3 represents the results using a latex prepared with an anionic agent (18A), Fig. 4 mixed nonionic and anionic emulsifiers (20NA) while Figs. 5 and 6 refer to emulsions prepared with cationic (1C) and mixed cationic and nonionic agents (5CN) respectively.

## DISCUSSION

The most striking results of the electrophoretic investigations lie in the irregularities in the curves of mobility vs. concentration of sodium chloride. Similar irregularities in surface tension, interfacial tension, viscosity, light scattering, foaming characteristics with increasing concentration of surfactant or emulsifying agent have been reported in the literature (3, 18). The concentration at which such changes in direction of the curve take place has been termed the "critical concentration for the formation of micelles" or C.M.C.

The critical micelle concentration is an important factor in the mechanism of emulsion polymerization (6, 21). It is believed the C.M.C. represents the limit where solubilized colloidal salt or emulsifying agent begins to form a new phase of minute spherical droplets or micelles. Hartley (7) visualized these globules as being two ion lengths in diameter with polar heads outward in water and the long chains forming a hydrophobic interior. McBain (11) has postulated a lamellar micelle consisting of two layers of surface active molecules arranged side by side, the adjacent long chains forming a hydrophobic layer. The electron micrograph of a resin emulsion in which micelles of emulsifier are probably present (Fig. 7) would seem to confirm the postulated spherical shape.

The minima and maxima in our experimental curves are attributed respectively to the critical micelle concentration and to an increasing rate of removal of charge by added sodium chloride. The minima represent alterations in the distribution of soluble capillary-active substance between the bulk of the sol and the surface of the polyvinyl acetate particles. The total amount of emulsifying agent is constant in each latex system. In the absence of salt no micelles are present. When the proper amount of salt is added micelles begin to form and the mobility of the latex increases. This is effectively a lowering of the C.M.C. by added salt. The same situation could be promoted by adding additional quantities of the emulsifying agent used in the emulsion formulation as evidenced by the experiments of Powney and Wood (16, 17).

It is possible that the emulsifying layer increased in size by adsorption to a maximum, and being itself charged contributed a finite amount to the electrical density of each particle, increasing the mobility. Thereupon discrete

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micelles began to form in the aqueous media. Although increasing concentration of salt steadily diminished the amount of solubilized colloid, it also had the effect of enhancing the retarding force of the Gouy ionic atmosphere around the particle. This explains the ultimate falling off in electrophoretic mobility. The "nonionic" emulsions which displayed C.M.C. may be assumed to be partially anionic.

Neither of the positively charged latices evidenced C.M.C. irregularities comparable with the mobility curves for nonionic and anionic emulsions. Latex 1C (Fig. 5) is known to have been made with an excess of cationic material. It is quite possible that the amount of detergent inherently present in the diluted samples was alone sufficient to exceed the C.M.C. Addition of salt immediately promoted micellar migration to the resin particle interfaces with attendant increase in positive electrophoretic mobility up to relatively high concentration of sodium chloride.

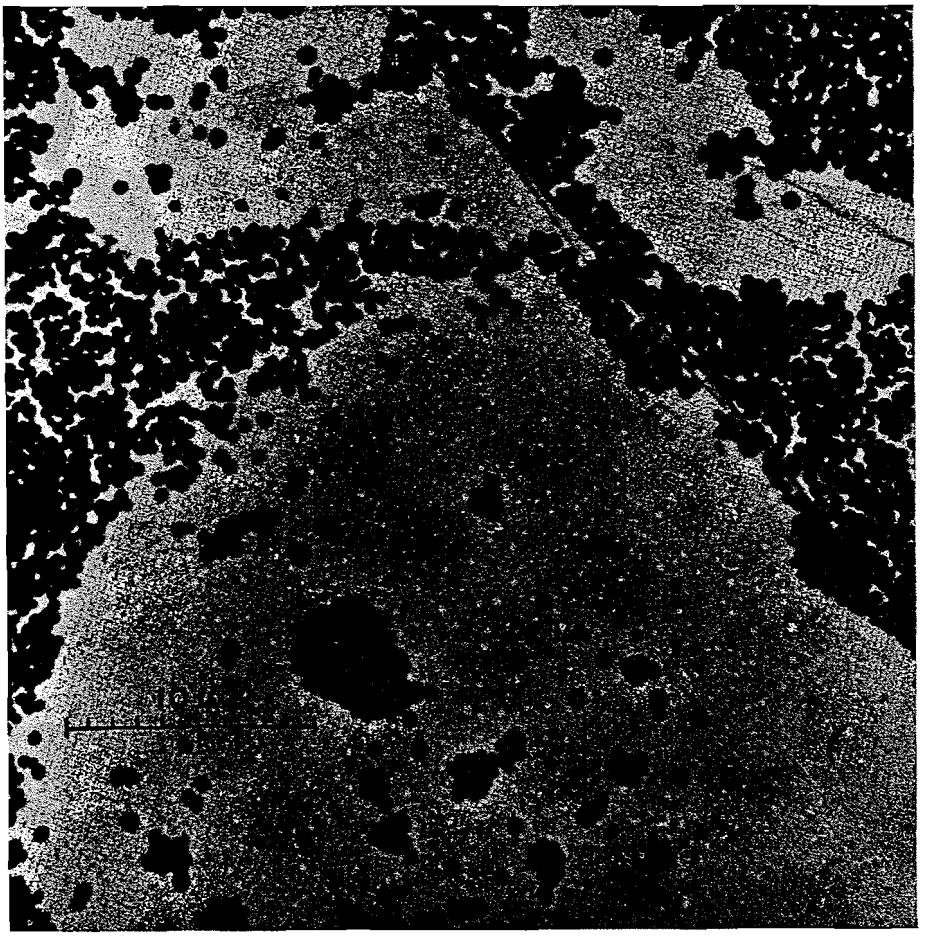


FIG. 7. Electron-micrograph of latex 13N.

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Doscher has stated (4) that cationic materials above the critical concentration in general exhibit a strong tendency to be sorbed on surfaces as charged aggregates or micelles rather than as simple ions. This characteristic was used to explain the inability of cationic agents to effect suspension and their inefficiency as detergents (4). The sorption of these aggregates evidently results in a hydrophobic exterior regardless of the substrate to which they are attached. From this point of view the behavior of Latex 1C under salt addition is more easily explained.

On the other hand, emulsion 5CN was formulated using a minimum of emulsifying agent, a large percentage of which was nonionic material. The salt addition graph (Fig. 6) executed almost an exponential drop. Possibly any micellar phenomena were not revealed in electrophoresis owing to the combined effect of different protective colloids. This is proposed in view of the possible anionic character of the 'nonionic' agent used for emulsification. Another possibility is that dilution of the latex resulted in a low concentration of solubilized colloidal electrolyte. Hence, upon addition of salt, the micellar aggregation was of insufficient magnitude to affect the electrophoretic mobility.

It has already been shown by previous investigators that the mechanism of micelle formation from anionic colloids differs from anything observed with invert soaps or cationic materials. Schulman and Cocbain stated in contrast with the views of Doscher (4) that long chain quaternary ammonium compounds are too soluble in water and too highly ionized to form other than highly expanded vaprous films at oil–water interfaces (19). While investigating the electrophoretic mobility of oil drops in detergent solutions, Powney and Wood observed no C.M.C. irregularity when the colloidal addend was dodecylpyridinium chloride. Cassie and Palmer noted that their theories relating to the C.M.C. did not appear to apply even qualitatively for cationic surfactants (2).

It will be noted that the difference between the maximum and minimum mobilities near the critical micelle concentration increases as the character of the protective colloid becomes more anionic. The limiting mobility value follows the same trend.

The concept of a limiting mobility value has been suggested by Ham and Dean (5), who studied the effect of added salts on the mobility of octadecane dispersions. The mobility did not fall to zero, but decreased logarithmically, tending toward limiting values dependent on the valency of the added salt. The results of Ham and Dean inferred strongly that there was a limit beyond which salt addition could have no further electrokinetic effect.

## ZETA POTENTIAL

The zeta potential of a typical latex was calculated by use of the Henry modification of the Smoluchowski equation (20). Henry's (8) equation also affords an estimate of the dimensions of the ionic layer of the latex particles. Various slight improvements have been suggested (1, 9, 10, 13, 14, 15) but none of the modifications gives corrections of more than negligible magnitude.

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The Henry equation is: $U = \epsilon E \zeta F(b)/4\pi\eta$

where $U$ = mobility

$\epsilon$ = dielectric constant

$E$ = field strength

$\eta$ = viscosity

The quantity ($b$) is directly related to the thickness of the ionic atmosphere. It has been equated to $\kappa(a)$ where $\kappa(a)$ is the radius of the colloidal particle independent of the double layer, and $\kappa$ is the Debye-Huckel factor for the reciprocal of the ionic atmosphere thickness.

Table I gives the values for the quantities in the Henry–Smoluchowski equation for emulsion 13N at different concentrations of salt. $\kappa(a)$ values were derived from the experimental data. The large original electron micrograph from which Fig. 7 is reproduced served for determining particle size of latex 13N. This uniform latex had an average particle radius of $2.40 \times 10^{-5}$ cm.

The $F(b)$ values were obtained from Henry's graph, except in three cases where $b > 25$. The latter were calculated from the appropriate equation (9). By these methods each correction was determined to three significant figures.

TABLE I

QUANTITIES IN HENRY–SMOLUCHOWSKI EQUATION FOR DIFFERENT CONCENTRATION OF SALT (Emulsion 13N)

| Salt conc., $M \times 10^{-6}$ | Mobility, $\mu$/sec./volt/cm. | $\kappa$, cm.$^{-1} \times 10^{-5}$ | $\kappa(a)$ | $F(b)$ | $\zeta$, volts $\times 10^{7}$ | $Q$, coulombs $\times 10^{9}$ |
|---|---|---|---|---|---|---|
| 0.838 | 3.90 | 0.951 | 2.28 | 0.708 | 8.73 | 5.50 |
| 1.59 | 2.23 | 1.31 | 3.15 | 0.727 | 4.87 | 3.86 |
| 5.00 | 2.30 | 2.33 | 5.58 | 0.764 | 4.77 | 6.04 |
| 5.13 | 1.95 | 2.36 | 5.65 | 0.767 | 4.02 | 5.13 |
| 10.6 | 1.55 | 3.39 | 8.13 | 0.800 | 3.08 | 5.32 |
| 13.0 | 1.63 | 3.76 | 9.01 | 0.813 | 3.19 | 6.14 |
| 15.5 | 1.64 | 4.09 | 9.83 | 0.828 | 3.14 | 6.52 |
| 18.3 | 1.15 | 4.45 | 10.67 | 0.838 | 2.17 | 4.85 |
| 20.5 | 1.05 | 4.71 | 11.29 | 0.844 | 1.97 | 4.66 |
| 30.8 | 1.02 | 5.77 | 13.83 | 0.865 | 1.88 | 5.35 |
| 36.1 | 1.47 | 6.25 | 14.98 | 0.875 | 2.66 | 8.17 |
| 46.3 | 1.31 | 7.07 | 16.95 | 0.886 | 2.34 | 8.07 |
| 52.2 | 1.12 | 7.51 | 18.00 | 0.891 | 1.99 | 7.26 |
| 109 | 0.622 | 10.9 | 26.02 | 0.919 | 1.09 | 5.68 |
| 203 | 0.275 | 14.8 | 35.58 | 0.931 | 0.49 | 3.50 |
| 276 | 0.339 | 17.3 | 41.40 | 0.939 | 0.57 | 4.68 |

*Note*: *Viscosity measurements showed that the electroviscous effect was of no significance with the above samples.*

Table I lists the mobility in cm. per sec. per volt per $\times 10^{4}$, molarity of sodium chloride $\times 10^{5}$, $\kappa$ in cm. $^{-1} \times 10^{-5}$, $\zeta$ in volts $\times 10^{7}$, $Q$ the particle charge in coulombs $\times 10^{9}$.

There is no regular trend in charge variation with electrolyte concentration. This is not unexpected particularly with nonionogenic emulsifiers.

Fig. 8 is a plot of the zeta potential versus salt concentration for emulsion 13N. This curve is very similar to the mobility curve, Fig. 2, showing the same minimum and maximum.

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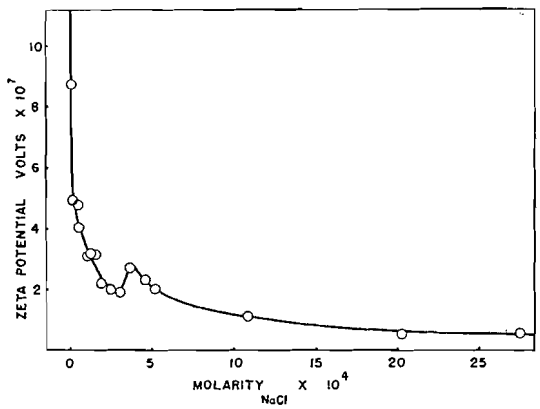



FIG. 8. The zeta potential for latex 13N at increasing concentration of salt.

In view of the opposing ideas as to whether there is any relation between the zeta potential and stability, a study of the stability of an emulsion with such a characteristic potential curve would be of interest.

## ACKNOWLEDGMENTS

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# A NOTE ON THE VALIDITY OF THE GIBBS-DALTON LAW AS APPLIED TO DILUTE MIXTURES OF WATER VAPOR WITH HYDROGEN, HELIUM, AND ARGON AT ROOM TEMPERATURES[1]

By E. A. Flood

ABSTRACT

Water vapor at room temperature and at pressures in the neighborhood of 10 mm. Hg behaves as a vacuum to each of the three gases hydrogen, helium, and argon, at pressures up to about 100 mm. Hg. The thermodynamic potentials of constituent gases in such mixtures of water vapor and hydrogen, water vapor and helium, etc. probably do not differ from those of the pure components, at equal volume concentrations, by more than 0.3%. Thus these gas mixtures obey the Gibbs–Dalton Law very closely and accordingly must also obey Dalton's Law. Velocity distribution functions of these gases under our experimental conditions are essentially Maxwellian.

## INTRODUCTION

Gases which obey the ideal gas laws quite closely and whose mixtures obey Dalton's Law may interact with one another in a variety of ways and the gas mixtures thus deviate considerably from the Gibbs–Dalton Law (1). However, when the Gibbs–Dalton Law is obeyed Dalton's Law is necessarily obeyed, the former being a special case of the latter.

While the range of validity of Dalton's Law, as applied to mixtures of the more common gases and vapors, is fairly well known, there are comparatively few data available concerning the validity of the Gibbs–Dalton Law. McHaffie (3) has shown that air at 25 atmospheres exerts a very considerable positive solvent action on water vapor while exerting both a negative and positive solvent action at still higher pressures. Gillespie (2) has shown that both hydrogen and nitrogen at higher pressures exert a considerable solvent action of ammonia. In view of these data, it is hardly permissible to assume that such effects vanish entirely at pressures below one atmosphere. It may be remarked that there are a good many standard methods of measurement dependent on the assumption that the hydrogen, nitrogen, etc. behave as perfect vacua to various vapors. Thus the determination of the density of adsorbates by helium displacement and many dynamic methods of determining vapor pressure are entirely dependent on the assumption that the Gibbs–Dalton Law holds accurately as applied to the systems concerned.

From a purely theoretical point of view, the validity of the Gibbs–Dalton Law is of interest as providing a fairly sensitive test of the validity of the Maxwellian distribution. It is easily shown that kinetic theory model gases having velocity distribution functions only slightly different from the Maxwellian cannot behave as thermodynamically independent of one another, cannot have equal mean translational kinetic energies, and cannot obey the Gibbs–Dalton Law if their molecular weights differ appreciably.

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Accordingly it seemed worth while to ascertain whether any departures from the Gibbs–Dalton Law could be detected in the case of mixtures of water vapor with such inert gases as helium, hydrogen, and argon in pressure regions where Dalton's Law might be expected to hold fairly accurately.

## EXPERIMENTAL

When the Gibbs–Dalton Law holds for a gas mixture, the thermodynamic potentials of constituent gases are mutually independent. Thus, if water vapor and helium obey this law, the potential of the water in a given volume is not altered by the addition of helium. Since the interiors of simple ionic crystals such as NaBr and $NaBr.2H_2O$ will not be appreciably influenced by helium at lower hydrostatic pressures, the potential of water vapor in equilibrium with these salts will be constant at constant temperature. Accordingly, if helium influences the potential of water vapor, the concentration of water vapor in a mixture of helium and water vapor in equilibrium with these salts will depend on the helium concentration. The salt system thus behaves like a volume of pure water vapor at constant pressure separated from the gas mixture by a semipermeable membrane. Accordingly the experimental method used was to provide a large volume that could be opened to, or closed from, a small volume containing $NaBr–NaBr.2H_2O$, and to determine weights of water vapor contained within the large volume when equilibria had been established with the salt system, the equilibrations being carried out both in the presence and absence of diluent gases.

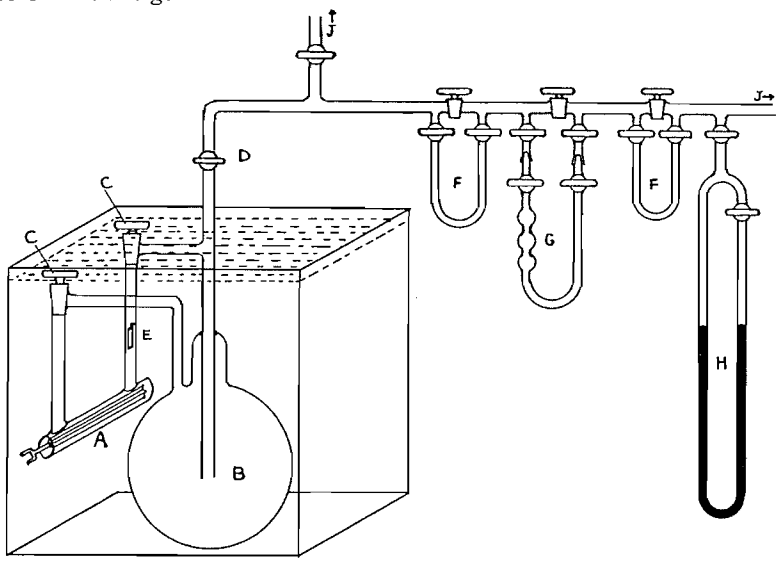



FIG. 1. A. Tube containing $NaBr–NaBr.2H_2O$ mixture and mechanical stirring device.
B. 13 liter flask (13,060 ml. collection volume).
C, C, D. Stopcocks.
E. Vibratory circulator operated by electromagnet (not shown).
F. Collecting traps containing brass wire to remove mercury.
G. Weighing trap.
H. Manometer.
J. To pumping system, flowmeter, etc.
N.B. The drawing is not to scale.

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The apparatus used is indicated diagrammatically in Fig. 1 and described in the legend.

The small salt-containing vessel (A) as well as the 13 liter flask (B) were immersed in a water thermostat whose temperature was maintained constant to within about ±0.005°C. During most of the experiments the temperatures were constant to within ±0.002°C. and were probably within ±0.01 of the mean temperature of all experiments, namely 26.2°C.

The procedures used were as follows: With the 13 liter flask (B) evacuated and cock (D) closed, cocks (C) were opened very slowly allowing water vapor to flow into the empty flask. The stirring device in (A) was then set in operation (the stirring device turned over about one-half of the total salt mixture once in every one or two seconds). After 48 hr. the stirring was discontinued, the systems allowed to stand for about one hour and the cocks (C) closed. The vapor contained in the 13 liter flask between cocks (C) and (D) was then removed by evacuation through liquid air traps, the traps containing brass wire coils to remove mercury. (Brass wire was found to be somewhat better than gold foil under our experimental conditions.) The water collected in the traps was distilled into a small weighing tube and finally the weight of water was obtained by comparison with the weight of duplicate counterpoise tube. The weights of water collected in this way, after a standardized procedure was adopted, are shown in the upper part of Table I following the legend "equilibria approached from zero water pressure".

TABLE I

WEIGHTS (GM.) OF WATER COLLECTED

| | | | |
|---|---|---|---|
| Equilibria approached from zero $H_2O$ pressure | 0.1170<br>0.1173<br>0.1170 | 0.1167<br>0.1172<br>0.1167 | 0.1171<br>0.1168<br>0.1169<br>Mean 0.1170 |
| Equilibria approached from $H_2O$ pressure in mm. Hg as shown in parenthesis | 0.1168 (12)<br>0.1173 (12)<br>0.1168 (13) | 0.1171 (15)<br>0.1170 (15)<br>0.1178 (16) | 0.1183 (18)<br>0.1181 (22)<br>Mean 0.1174 |

A second series of experiments was carried out in which water vapor was introduced into the 13 liter (B) flask at pressures greater than the equilibrium pressure. The results are recorded in the lower part of Table I. Possibly, the values at higher initial water vapor pressure 18 and 22 mm. are significantly higher than the mean. Of course, higher values are to be expected, in general, when equilibria are approached from higher values and in this case appreciable adsorption effects are also to be expected at vapor pressures above 50% of saturation.

In order to determine what effect a diluent gas would have on the collection procedure and on introducing errors due to adsorption or desorption from the glass walls, etc., a series of experiments were carried out in which the equilibration procedures were essentially the same as in the first series, but where hydrogen at various pressures was introduced into the 13 liter flask (B) after

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equilibrium concentration of water vapor had been attained therein, and the cocks (C) closed. The hydrogen pressures were calculated from Dalton's Law. (It may be remarked that previous experiments had shown that within our experimental error, Dalton's Law was obeyed for mixtures of water vapor at about 10 mm. and various pressures of hydrogen, helium, and argon. The experimental error in pressure readings was probably not more than 8%.) The mixture of water vapor and hydrogen was then removed from the 13 liter flask and the water collected as in the previous experiments. The weights of water so obtained are recorded in Table II. The data in Tables I and II thus

TABLE II

WEIGHTS OF $H_2O$ COLLECTED (GM.). HYDROGEN AT PRESSURES (MM. Hg) SHOWN ADDED AFTER EQUILIBRATION. EQUILIBRATIONS APPROACHED FROM ZERO WATER PRESSURES EXCEPT WHERE SHOWN

| | | |
|---|---|---|
| 0.1175 ( 8.0) | 0.1169 (21.7) | 0.1165 (44.5) |
| 0.1171 (17.7) | 0.1170 (28.5) | 0.1169 (46.6) |
| 0.1163 (17.7) | 0.1172 (29.9) | 0.1170 (50.0) |
| | | Mean 0.1169 |
| 0.1184* (20.3) | | |
| 0.1168* (21.0) | | |
| 0.1187**(32.0) | | |
| | | Mean 0.1180 |

*Equilibrations approached from 11 mm.*
***Equilibrations approached from 14 mm.*

establish the weight of water vapor contained within the flask under equilibrium conditions as well as establishing some measure of the experimental error involved. The mean of all the control experiments is $0.1172 \pm 0.0004$. The exceptionally high figures are probably due to desorption errors. If these are excluded, the mean value is close to $0.1170 \pm 0.0001$.

In the final series of experiments, diluent gases were present in both the salt containing tube and the 13 liter flask during the equilibration period. The approach to equilibrium could be observed by cathetometer readings of the pressure changes involved. When the diluent gas pressures were less than 10 mm., equilibrium was attained quite rapidly. However, in all of these experiments equilibrations were carried out over periods from one to two weeks. It may be remarked that in the case of argon at pressures of 100 mm. or greater, equilibrium was not attained even after three weeks. While it was hoped that reliable results with diluent gas pressures up to one atmosphere could be obtained with this equipment (a vibrating 'reed' gas circulator (E) was provided with this end in view) it soon became apparent that in the presence of diluent gases at pressures near atmospheric, the times required for attainment of equilibria would be entirely impracticable. It may be remarked that the vibrating 'reed' type circulating pump that was installed in the equilibration system had been previously tested in a similar apparatus and was found to be capable of pumping air at atmospheric pressure at the rate of almost 4 liters per minute. Possibly the presence of diluent gas at higher pressures interferes with the dynamic equilibrium existing between interfaces of salt and its hydrate.

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The weights of water collected when equilibrations were carried out in the presence of hydrogen, helium, and argon are recorded in Table III. Evidently the diluent gases do not change the thermodynamic potential of the water vapors. Some casual experiments were carried out using nitrogen and methane

TABLE III

WEIGHTS OF WATER COLLECTED (GM.)

*Equilibration in Presence of Gases.*—Weights of water collected. Equilibrium values approached from zero water pressures except where indicated. Initial diluent gas pressures in mm. Hg given in parentheses. V.P. $H_2O$ 9.27 mm. Hg

| | | | |
|---|---|---|---|
| Hydrogen | 0.1172 ( 0.9) | 0.1171 ( 3.0) | 0.1168 (34.1) |
| | 0.1168 ( 1.3) | 0.1178* (12.7) | 0.1171 (82.6) |
| | 0.1169 ( 4.9) | 0.1168 (13.4) | 0.1170 (83.1) |
| | | | Mean 0.1171 |
| Argon | 0.1178 ( 3.1) | 0.1181 (10.0) | 0.1168 (22.0) |
| | 0.1168 ( 4.9) | 0.1167 (10.3) | 0.1168 (56.4) |
| | 0.1168 ( 6.1) | 0.1169 (21.8) | 0.1168**(56.8) |
| | | | Mean 0.1171 |
| Helium | 0.1170 (10.6) | 0.1165 (113.6) | |
| | 0.1168 (10.6) | 0.1173 (229.8) | |
| | 0.1170 (20.3) | | |
| | | | Mean 0.1169 |

**Equilibrium approached from 11 mm. $H_2O$ pressure.*
***Equilibrium approached from 9.5 mm. $H_2O$ pressure.*

at pressures of about 2 cm. The weights of water collected were essentially the same. The equilibrium pressure of water vapor over NaBr–NaBr.$2H_2O$ was found to be 9.27 mm. $\pm$0.05 mm. at 26.2°C.

## CONCLUSION

Water vapor at room temperature and at pressures in the neighborhood of 10 mm. Hg behaves as a vacuum to each of the three gases hydrogen, helium, and argon, at pressures up to about 100 mm. Hg. The thermodynamic potentials of constituent gases in such mixtures of water vapor and hydrogen, water vapor and helium, etc., probably do not differ from those of the pure components, at equal volume concentrations, by more than 0.3%. Thus these gas mixtures obey the Gibbs–Dalton Law very closely and accordingly must also obey Dalton's Law. Velocity distribution functions of these gases under our experimental conditions are essentially Maxwellian.

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# NOTE ON THE DIELECTRIC CONSTANTS OF ETHYL CHLORIDE AND *n*-BUTANE ADSORBED ON NONPOROUS $TiO_2$[1]

By M. H. Waldman,[2] J. A. Snelgrove,[3] and R. McIntosh[4]

ABSTRACT

The dielectric constants of ethyl chloride and *n*-butane adsorbed on nonporous $TiO_2$ were measured. The plot of capacity change versus volume adsorbed was found to reveal two linear sections in the case of ethyl chloride with an abrupt change in the slope of the plot occurring at the $V_m$ value calculated using the B.E.T. or Hüttig adsorption equations. With *n*-butane the plot was linear beyond $V_m$. For ethyl chloride on rutile a slight temperature dependence in the polarization was observed for the volume of gas adsorbed above $V_m$, while a negligible temperature dependence was noted for the portion below $V_m$. It is postulated that the observations with the polar gas on the nonporous rutile can be explained by a change from oscillatory to rotational motion of the adsorbed molecule after the monolayer is complete. It was noted that gases adsorbed on nonporous $TiO_2$ behaved differently from gases adsorbed on porous silica gel. This appears to lead to the necessity of postulating changes of density for the adsorbed phase on silica gel.

## INTRODUCTION

In earlier work the dielectric properties of gases adsorbed on porous gels have been examined. Because of the relatively large quantities which can be adsorbed on porous adsorbents, the measurements are more readily carried out, but the porous structure of the adsorbent complicates the adsorption process and renders any correlation of the electrical data with adsorption theories very difficult to make. Thus it has not yet been established whether the discontinuities of the slopes of the plots of capacity change of test cell versus volume of gas adsorbed, observed by Higuti (3), Kurbatov (5), and in this laboratory (6, 8), are associated with the completion of the unimolecular layer, variations of the density of the adsorbate, or interactions which influence the rotational or oscillatory motions of the adsorbed molecules. In an attempt to distinguish among these possibilities, the dielectric properties of ethyl chloride and *n*-butane, adsorbed on $TiO_2$ (rutile) of specific surface to nitrogen equal to 85 sq. meters, have been determined. The adsorbent is believed to be nonporous. Owing to the comparatively small specific surface, the electrical data are less precisely defined than when activated silica gel was employed. Nevertheless, typical data given below indicate that:

(1) On a nonporous adsorbent a polar adsorbate may exhibit a sudden change of electrical properties at some critical quantity of adsorbed matter.

(2) This change was not observed using the nonpolar adsorbate.

(3) The critical quantity of the polar adsorbate agrees remarkably well with the volume required to complete the unimolecular layer ($V_m$) when this volume is computed by either the B.E.T. (1) or Hüttig adsorption equations (4).

[1] *Manuscript received June 16, 1953.*
*Contribution from the Chemistry Department, University of Toronto, Toronto, Canada.*
[2] *Graduate Student, Department of Chemistry, University of Toronto.*
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[4] *Associate Professor of Chemistry.*



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(4) Certain distinctions between the behavior of adsorbates on porous and nonporous adsorbents are clear, and presumably may be accounted for on the basis of the structures of the adsorbents.

In this preliminary report no attempt will be made to discuss all the observed phenomena. The difference of behavior of the polar and nonpolar adsorbates on the nonporous adsorbent is of fundamental importance, however, as it seems to show that the type of discontinuity to be described below is attributable to the polar character of the adsorbate, and not to the density of the adsorbed film.

## EXPERIMENTAL

The experimental procedures were essentially those previously described (6, 8). Mercury cutoffs were used instead of stopcocks in order to prevent

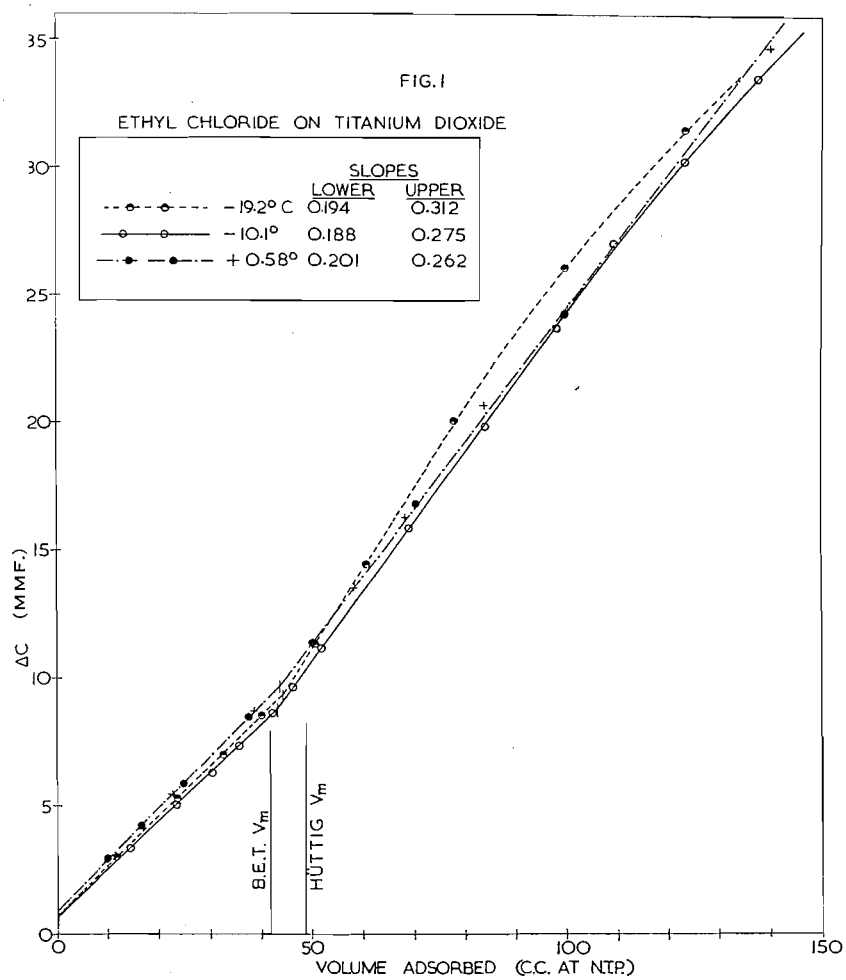



FIG. 1. Plots of capacitance change versus volume adsorbed for ethyl chloride on rutile at various temperatures.

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errors in the quantity adsorbed due to the solubility of the gases in the stopcock grease. All electrical measurements were made at the single frequency of 3.70 mc. per sec. since no Debye type dispersion was apparent up to that frequency.

The solid adsorbent was obtained from Dr. J. A. Morrison, of the National Research Council. Its preparation and some of its properties have been reported by Morrison, Los, and Drain (7).

## RESULTS

Typical results using ethyl chloride are shown in Fig. 1. The sudden change of slope, which occurs at the computed $V_m$* value, should be noted. Fig. 2

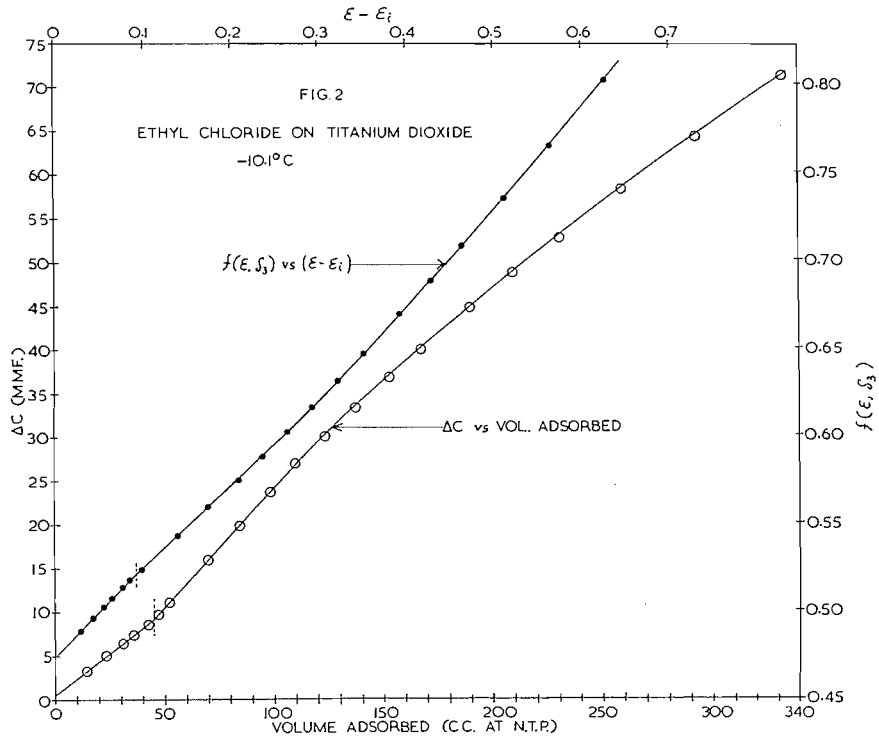



FIG. 2. (*a*) Plot of capacitance change versus volume adsorbed for ethyl chloride on rutile at − 10.1°C. (*b*) Plot of $f(\epsilon, \delta_3)$ versus $(\epsilon - \epsilon_i)$ for ethyl chloride on rutile at − 10.1°C.

shows results at − 10.1°C. in greater detail to emphasize the sharpness of the discontinuities of the slopes in both the plot of the primary data and in that of the functional plot from which the polarization is calculated (6). It should also be noted that the material adsorbed beyond $V_m$ has a higher polarizability than that adsorbed before $V_m$. This is in contrast with results obtained when the adsorbent was activated silica gel (6).

As shown in Table I, the polarization of the material adsorbed is approximately the same as that of bulk liquid for the first material adsorbed on silica

*B.E.T. $V_m$ = 41.9 cc.; Hüttig $V_m$ = 47.8 cc.

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TABLE I

DIELECTRIC CONSTANTS AND POLARIZATIONS FOR ETHYL CHLORIDE AND *n*-BUTANE ADSORBED ON $TiO_2$ AND SILICA GEL

| | Dielectric constant | | | Polarization per cc. | | | |
|---|---|---|---|---|---|---|---|
| | Section 1 | Section 2 | By Onsager formula | Section 1 | Section 2 | By Onsager formula | Temp., °C. |
| Ethyl chloride on $TiO_2$ | 5.70 | 11.14 | 12.31 | 0.61 | 0.77 | 0.79 | −19.2 |
| | 5.84 | 8.65 | 11.68 | 0.62 | 0.72 | 0.78 | −10.1 |
| | 6.30 | 7.82 | 11.00 | 0.64 | 0.69 | 0.77 | 0.58 |
| | 6.16 | 7.77 | 11.00 | 0.63 | 0.69 | 0.77 | 0.60 |
| Ethyl chloride on silica gel | 8.66 | 4.36 | 10.9 | 0.72 | 0.53 | 0.77 | 0.1 |
| | 7.89 | 4.14 | 10.0 | 0.70 | 0.51 | 0.75 | 15.0 |
| | | | By R.I. | | | By R.I. | |
| Butane on $TiO_2$ | 2.05 | .. | 1.80 | 0.26 | .. | 0.21 | 5.3 |
| Butane on silica gel | 1.80 | 1.61 | 1.79 | 0.21 | 0.17 | 0.21 | 0.1 |
| | 1.78 | 1.58 | 1.79 | 0.21 | 0.16 | 0.21 | 15.0 |

*R.I.* = *Refractive Index.*

gel. In the case of ethyl chloride on rutile this is so for the adsorbate taken up after the unimolecular layer is completed. Thus the two cases are distinct in that the change of polarizability with amount adsorbed is from higher to lower values on silica, but from lower to higher values on rutile.

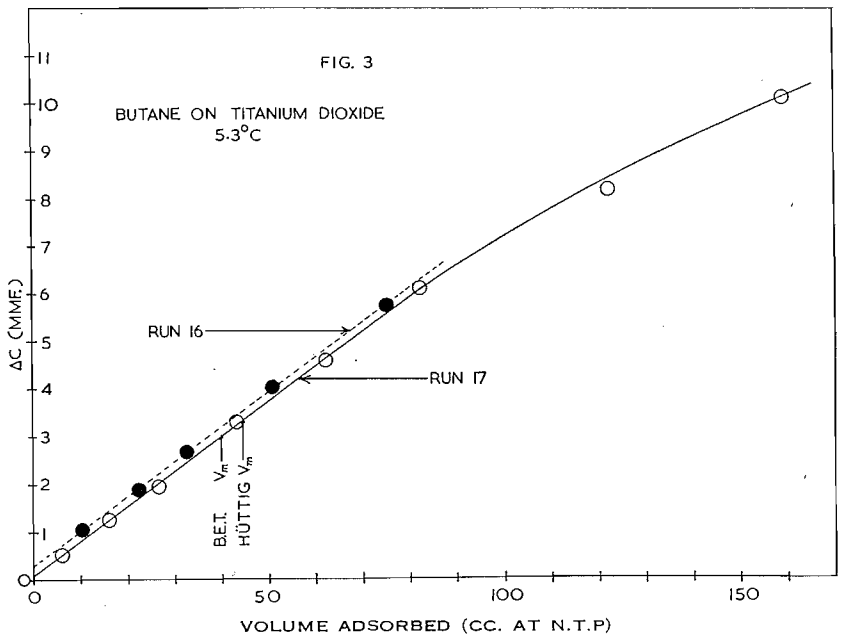



FIG. 3. Plot of capacitance change versus volume adsorbed for *n*-butane on rutile at 5.3°C.

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The existence of a temperature coefficient of polarizability for ethyl chloride beyond $V_m$ seems established, while a very small or possibly zero temperature coefficient is observed before the $V_m$ value. This is again opposite to the observations made when silica gel was used as the adsorbent.

In Fig. 3 are shown two experiments using butane. Within the limits of the reproducibility of the measurements the plots are linear to volumes adsorbed well above $V_m$, and thus no change of electrical properties is observed. A discontinuous change to a lower value was observed on silica gel, however. This result very strongly suggests that density variations associated with the porous structure of the silica gel are required to explain the results found using silica, and that the behavior found using ethyl chloride on rutile is not caused by such factors.

The values of polarization given in the table are based on the use of the density of the liquid state to evaluate the volume of the dielectric occupied by adsorbed matter. The somewhat greater value of the polarization of butane than is calculated using known refractive index data (2) suggests that the packing is somewhat closer than for the bulk liquid state. However, the increase of capacity of the test cell caused by the adsorption of butane is comparatively small, and until the value of the polarization reported here is thoroughly established, comment on this point is not warranted.

## CONCLUSIONS

Snelgrove and McIntosh (9) have shown that a negligible temperature coefficient would signify oscillatory motion while a negative temperature coefficient would suggest rotational motion of the adsorbed molecule. Therefore, since a negligible temperature coefficient below $V_m$ and a negative temperature coefficient above $V_m$ was observed, the data for ethyl chloride can apparently be accounted for by postulating that the molecules are oscillators when adsorbed into the first layer, and may rotate, showing the dielectric properties of the bulk liquid in higher layers. Since the isosteric heat of adsorption is high (9500–7000 cal. per mole) for quantities adsorbed less than $V_m$, it is to be expected that the first layer would be substantially complete before adsorption into higher layers is appreciable. Thus the agreement found between the $V_m$ values by adsorption and the $V_m$ values obtained from the position of the discontinuity seems reasonable, and for such systems the electrical data yield a value of $V_m$.

Since no changes of the properties of butane are observed as the amount adsorbed passes through $V_m$, there is no suggestion that variations of the density of the film occur. This must also mean that the results with butane and silica gel are explicable on the basis of the density of the adsorbate.

## ACKNOWLEDGMENT

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# THE INFRARED SPECTRA OF ALPHA AND BETA OXIMES[1]

By Ann Palm[2] and Harold Werbin[3]

ABSTRACT

The spectra of several isomeric oximes in the solid state were examined in the range 700–3600 $cm^{-1}$. The associated OH stretching frequency near 3250 $cm.^{-1}$ in the $\alpha$ oximes is displaced towards lower frequency in the $\beta$ oximes. The region of the OH stretching mode of several oximes was also studied in benzene and chloroform solutions. The frequencies near 1300 $cm.^{-1}$ and 920 $cm.^{-1}$ are tentatively assigned to the OH deformation and the N-OH stretching modes, respectively. No consistent differences are observed between the $\alpha$ and the $\beta$ oximes with respect to these vibrations. The band at approximately 1640 $cm.^{-1}$ ascribed to the C=N vibration remains essentially unchanged in the spectra of the two isomeric forms.

Although the infrared spectra of several oximes that are of value as analytical reagents have been reported (10, 23), a review of the literature indicates that no serious attempts have been made to compare the infrared spectra of the $\alpha$ and $\beta$ oximes. The 7000 $cm.^{-1}$ region (first overtone of the OH stretching frequency) of dilute carbon tetrachloride solutions of $\alpha$ and $\beta$ benzilmonoximes (16) were found to be identical while $\alpha$ benzoinoxime acetate showed two weak bands that did not appear in the $\beta$ form (24).

The spectra of $\alpha$ and $\beta$ oximes are not expected to be identical since the arrangement and bonding of the atoms in the molecule give rise to characteristic absorption bands. The present investigation was undertaken, therefore, in order to determine possible differences in the infrared spectra of the two isomeric forms. The data presented in this report on 15 oximes in the solid state, 10 of which are geometric isomers, demonstrate that one can distinguish between the $\alpha$ and $\beta$ compounds on the basis of the position of the OH stretching frequency.

## EXPERIMENTAL

### *Infrared Spectra*

The spectra were recorded in the region 700–3600 $cm.^{-1}$ with a Perkin-Elmer Model 21 double-beam spectrometer. The crystalline compounds were dried over phosphorus pentoxide, ground to a fine powder to reduce the scattering effect, and measured between two salt plates as Nujol mulls. The solutions (about 0.02 *M*) were examined in sodium chloride cells of 0.03 mm. thickness. The instrument was set at a slit schedule of 4 and speed 3 for each run. Duplicate spectra of the same compound did not differ by more than $\pm 10$ $cm.^{-1}$ at 3000 $cm.^{-1}$ and $\pm 5$ $cm.^{-1}$ at 1500 $cm^{-1}$.

### *Materials*

The following oximes were commercial samples and, with the exception of $\alpha$-benzaldoxime which was used directly, were recrystallized until the melting

[1] *Manuscript received June 8, 1953.*
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[2] *Present address: Spectroscopy Laboratory, Illinois Institute of Technology, Chicago, Ill.*
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points agreed with those reported in the literature: α-benzilmonoxime, benzophenone oxime, cyclohexanone oxime, acetophenone oxime, and N-benzylidineaniline. The α- and β-*p*-chloro- and α-*o*-chlorobenzaldoximes were prepared according to Erdmann and Schwechten (11). The β-benzilmonoxime, m.p. 112°C., was prepared by following the directions of Taylor and Marks (21), but it required repeated recrystallization from benzene to reach that melting point. β-Benzaldoxime melted at 128°C. after being recrystallized twice from petroleum ether (4). The α-nitrobenzaldoximes were prepared in the usual manner (13). The methods of Forster and Dunn (12) were employed in the preparation of β-*o*- and *p*-nitrobenzaldoximes which melted at 145° and 174°, respectively. They reported 154° and 184°, while others have found 143–145° for the *o*-nitro oxime and 177° for the *p*-nitro oxime (6, 17). An attempt was made to convert the α-*m*-nitrobenzaldoxime, m.p. 121°, into the β isomer by the above procedure (12). The resulting compound melting at 119° (Forster and Dunn obtained 123°) was believed to be the β oxime; however, the infrared spectrum was identical with that of the α oxime, indicating that the β oxime had not been made.

Analytical reagent grade benzene and chloroform were used for the solution studies. The solvents were dried and distilled before use.

## RESULTS AND DISCUSSION

In Fig. 1 is summarized an abbreviated form of the infrared spectra of the α and β oximes in the solid state. The 1700–2900 $cm.^{-1}$ region is omitted in the diagram. The absorption bands due to OH stretching, OH deformation, and

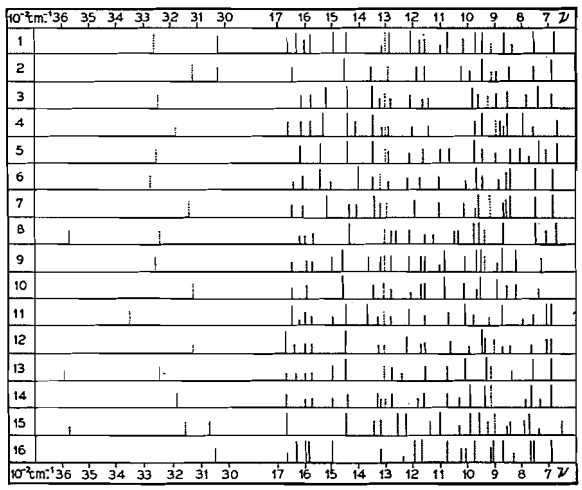



FIG. 1. Infrared spectra of:

1. α-Benzaldoxime
2. β-Benzaldoxime
3. α-*o*-Nitrobenzaldoxime
4. β-*o*-Nitrobenzaldoxime
5. α-*m*-Nitrobenzaldoxime
6. α-*p*-Nitrobenzaldoxime
7. β-*p*-Nitrobenzaldoxime
8. α-*o*-Chlorobenzaldoxime
9. α-*p*-Chlorobenzaldoxime
10. β-*p*-Chlorobenzaldoxime
11. α-Benzilmonoxime
12. β-Benzilmonoxime
13. Acetophenone oxime
14. Benzophenone oxime
15. Cyclohexanone oxime
16. N-Benzylideneaniline

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N–OH stretching vibrations occurring at about 3200, 1300, and 920 cm.$^{-1}$, respectively, which appear to differ the most, are represented by dotted lines. The height of the line gives an indication of the intensity of the band represented.

The OH stretching mode could be assigned unambiguously, while the C=N, the OH deformation, and the N–OH vibrations were located with less certainty because of interfering bands due to C–H vibrations.

In the spectra of the $\alpha$ oximes the OH absorption band is found at about 3250 cm.$^{-1}$, whereas it appears near 3115 cm.$^{-1}$ in the $\beta$ oximes. This frequency shift is noted in the spectra of each pair of isomeric oximes. It would indicate that the OH vibrations are more strongly bonded in the $\beta$ isomers (1, 2). This increase in the strength of the hydrogen bridge is in line with the higher melting points of the $\beta$ oximes (with the exception of $\beta$-benzilmonoxime), their larger conductivities (18) and previous studies on carboxylic acids which demonstrate that an increase in acidity is accompanied by a shift in the OH stretching vibration to lower frequency (9, 22).

Reference to Table I suggests that the oximes are associated both in the crystalline state and to a somewhat lesser extent in solution. The spectra of the

TABLE I
O–H ABSORPTION BANDS (FREQUENCIES IN CM.$^{-1}$)

| Compound | In Nujol | | In benzene | | In chloroform | |
|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\alpha$ | $\beta$ | $\alpha$ | $\beta$ |
| Benzilmonoxime | 3345(m) | 3110(w,bd) | 3250(w) | 3485(m) | 3520(w)<br>3250(w,bd) | 3570(w)<br>3200(w) |
| Benzaldoxime | 3260(s,bd) | 3115(m,bd) | *n.m.* | 3520(w)<br>3240(w,bd) | *n.m.* | 3570(w)<br>3270(m,bd) |
| *o*-Nitro-benzaldoxime | 3240(m) | 3175(w,bd) | 3515(s)<br>3300(w) | 3420(w) | 3560(w)<br>3260(w) | *n.m.* |
| *m*-Nitro-benzaldoxime | 3250(m,bd) | *a* | 3500(m) | *a* | 3560(m)<br>3280(w) | *a* |
| *p*-Nitro-benzaldoxime | 3270(m) | 3120(s) | 3500(m) | *n.m.* | 3550(m)<br>3280(w) | 3260(w) |
| *o*-Chloro-benzaldoxime | 3572(m)<br>3235(m,bd) | *b* | 3510(s)<br>3270(s) | *b* | 3555(m)<br>3280(w,bd) | *b* |
| *p*-Chloro-benzaldoxime | 3260(m,bd) | 3110(m,bd) | 3510(m) | 3495(m) | 3300(w) | 3280(w) |
| Acetophenone oxime | 3590(w)<br>3240(m,bd) | | 3520(w)<br>3250(w,bd) | | 3560(m)<br>3260(m,bd) | |
| Benzophenone oxime | 3170(m) | | | | | |
| Cyclohexanone oxime | 3570(w)<br>3140(m) | | | | | |

*a = An attempted synthesis was unsuccessful.*
*b = This compound was not prepared.*
*n.m. = Not measured.*
*Intensities: weak (w), medium(m), broad band (bd), and strong(s).*

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$\alpha$ oximes as solids or in solutions (benzene and chloroform) show the bonded OH at essentially the same position, around 3250 cm.$^{-1}$ However, the OH band of the $\beta$ oximes occurs near 3115 cm.$^{-1}$ in the solid spectra and at approximately 3250 cm.$^{-1}$ in the solution spectra. Thus it seems that one can distinguish the $\alpha$ from the corresponding $\beta$ compounds on the basis of the OH stretching frequency in the solid state only. The spectra of the benzene and chloroform solutions of some oximes (see Table I) have an unassociated OH valence vibration at 3500 cm.$^{-1}$ and 3550 cm.$^{-1}$, respectively. This difference of about 50 cm.$^{-1}$ is due to a slightly larger solvation effect in the former solvent.The 'free' OH absorption band is well defined in contrast to the hydrogen-bonded OH band which is broad and diffuse, as is commonly observed.

The association of oximes through hydrogen bonds has been observed by several groups (3, 7). From the present studies, as well as the previous ones, it cannot be determined whether the hydrogen bonds are of the N—H–O or O—H–O type. In the case of acetoxime, X-ray diffraction data have shown that the molecules form sheets of planar trimers held together by N—H–O bonds (5).

Benzophenone and cyclohexanone oximes which exist in one form only, have an OH stretching vibration in the region comparable to that of the $\beta$ oximes, around 3150 cm$^{-1}$. This is also true for acetoxime (8). The results of the Beckmann rearrangement of acetophenone oxime suggest that it exists as the $\alpha$ isomer (14). The present investigation also provides evidence for the $\alpha$ configuration because the OH stretching frequency appears at 3240 cm$^{-1}$.

It is known that the OH deformation mode occurs in the range 1274–1595 cm.$^{-1}$ (19). Since this vibration is at least as sensitive to neighboring atoms as the OH stretching mode (20), it would be expected to exist at different positions and with varying intensities in the spectra of the $\alpha$ and $\beta$ oximes. Most of the compounds studied show (see Fig. 1) a fairly intense band around 1300 cm.$^{-1}$ which may possibly be attributed to the OH deformation vibration since it is absent from the spectra of the corresponding aldehydes. However, no consistent shift is observed in the position of the OH bending mode as in the case of the OH stretching vibration.

Frequencies occurring near 900 cm.$^{-1}$ are ascribed to the N–OH stretching vibration (15). The fact that these maxima are not found in the spectra of the corresponding aldehydes lends support to the correctness of this assignment. Fig. 1 shows that each pair of isomeric oximes exhibits differences in the absorption bands in that region. As for the OH bending mode, no consistent distinguishing features are discernible for the N–OH frequencies.

Aliphatic oximes have an absorption band near 1670 cm.$^{-1}$ which is attributed to the C=N vibration (19). A displacement of 30–40 cm.$^{-1}$ towards lower frequency, the usual concomitant of conjugation with a phenyl group, is noticed in the present studies also. Since the spectra of some oximes revealed rather weak C=N maxima, only approximate band positions could be located. A possible explanation for the low intensities may be the existence of ionic resonating forms as suggested by Goubeau (15). As seen in Table II, the C=N frequencies are independent of ring substitution. Again, no consistent

TABLE II
C=N FREQUENCIES OF SOLID OXIMES

| Compound | Cm.$^{-1}$ | Compound | Cm.$^{-1}$ |
|---|---|---|---|
| α-Benzaldoxime | 1630(s) | β-Benzaldoxime | 1645(m) |
| α-*o*-Nitrobenzaldoxime | 1614(m) | β-*o*-Nitrobenzaldoxime | 1618(m) |
| α-*p*-Nitrobenzaldoxime | 1640(w) | β-*p*-Nitrobenzaldoxime | 1643(m) |
| α-*p*-Chlorobenzaldoxime | 1650(m) | β-*p*-Chlorobenzaldoxime | 1645(m) |
| α-Benzilmonoxime | 1620(w) | β-Benzilmonoxime | 1640(w) |
| α-*m*-Nitrobenzaldoxime | 1619(m) | Cyclohexanone oxime | 1662(s) |
| α-*o*-Chlorobenzaldoxime | 1618(w) | Acetophenone oxime | 1630(vw) |
| | | *N*-benzylideneaniline* | 1630(s) |

**Included for comparative purposes.*
*Intensities are represented by the same symbols as in Table I.*

differences are noted in the position and intensity of the C=N band between the α and β oximes examined in these studies.

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# THE ELECTRICAL CONDUCTIVITY OF MOLTEN OXIDES[1]

By A. E. van Arkel[2], E. A. Flood, and Norman F. H. Bright[3]

ABSTRACT

Electrical conductivities of some molten oxides have been determined. In order of decreasing equivalent conductances at their melting points the oxides investigated were: $Li_2O$, PbO, $TeO_2$, $MoO_3$, $Bi_2O_3$, $V_2O_5$, $Sb_2O_3$, and $CrO_3$. The variation of the observed values of the specific conductivities, $K$, with the absolute temperature, $T$, can be described by an equation of the form,

$$\log K = A + BT^{-1} + CT^{-2} \ldots,$$

where $A$, $B$, $C$, etc. are constants. While the experimental data are adequately described by an equation of this form containing only the constants $A$ and $B$, a slightly better fit is obtained using three constants. The conductivities of the molten oxides follow a pattern of variation from element to element which is substantially the same as that of the molten halides. For elements giving more than one oxide stable in the molten state, the oxide corresponding to the highest state of valency has the lowest conductivity.

## INTRODUCTION

A good deal of information is available in the scientific literature concerning the electrical conductivities of the molten halides of the various elements of the Periodic System. The following are some general trends:

(i) Compounds of the lighter halogens usually have better conductivities than the corresponding compounds of the heavier halogens.

(ii) In the alkali metal group the conductivities for each molten halide decrease with increasing size of the positive ion. (The liquid hydrogen halides are, of course, all poor conductors.)

(iii) In groups other than the alkali metal group the conductivities of the molten halides increase with increasing size of the positive ion; thus molten beryllium chloride is a poor conductor whereas magnesium, calcium, strontium, and barium chlorides are all good and increasingly so in that order.

(iv) As one goes across the Periodic System from Group I to Group VII, the further down each Group it is necessary to go before good conductors are reached; thus, in Group I the chloride of the lightest member, lithium chloride, conducts well whereas in Group VI, tungsten chloride is a poor conductor and it is only the heaviest member of the group, uranium, that yields a chloride having a good conductivity in the molten state.

(v) In the case of an element which forms more than one stable molten halide with any given halogen, the compound corresponding to the highest state of stoichiometric valency usually has the lowest conductivity. Tin and indium chlorides furnish good examples of this tendency.

While there are some striking contrasts between the trends of the conductivities of the molten halides and the trends of the conductivities of their aqueous solutions, in general, the former are qualitatively consistent with

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TABLE I

| Element | Oxide | Reference number | Information available |
|---|---|---|---|
| Hydrogen | $H_2O$ | 18 | Specific conductivity at O°C. = $1.5 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$; at 15°C. = $0.85 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$ |
| Beryllium | BeO | 19 | Can be fused and distilled in the electric arc furnace, so presumably the melt is conducting |
| Boron | $B_2O_3$ | (i) 27 | Stated to be a nonconductor |
| | | (ii) 1 | Specific conductivity varies from $7 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$ at 800°C. to $46 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$ at 1000°C. |
| Carbon | $CO_2$ | 7 | Stated by various workers to be a nonconductor |
| Nitrogen | $N_2O_3$ | 29 | Liquid will not conduct across a narrow gap |
| | $NO_2$ | (i) 11 | Stated to be a poor conductor in the liquid state |
| | | (ii) 15 | Specific conductivity varies from $1.16 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$ at −10°C. to $14.2 \times 10^{-8}$ ohm$^{-1}$cm.$^{-1}$ at 20°C. |
| Magnesium | MgO | 23 | Fusible in the electric arc furnace (Much information is available on the conductivity of the solid oxide under various conditions) |
| Aluminum | $Al_2O_3$ | 23 | As for magnesium oxide |
| Silicon | $SiO_2$ | 10 | Specific conductivity of liquid at melting point (*ca.* 1625°C.) = $10^{-5}$ ohm$^{-1}$ cm.$^{-1}$ |
| Phosphorus | $P_2O_3$ | 25 | Specific conductivity at 25°C., less than $1.2 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$ |
| Sulphur | $SO_2$ | (i) 4 | Stated to be a nonconductor |
| | | (ii) 9 | Specific conductivity at −15°C. = $0.85 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$ |
| | | (iii) 28 | Specific conductivity at O°C. = $0.90 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$ |
| | $SO_3$ | 21, 13 | Stated by various workers that the liquid was either a poor or a nonconductor |
| Potassium | $K_2O$(?) | 11 | Faraday stated that molten "potassa" conducted |
| Calcium | CaO | 23 | As for magnesium oxide |
| Titanium | $TiO_2$ | 23 | As for magnesium oxide |
| Vanadium | $V_2O_5$ | 6 | Stated to be a fairly good conductor |
| Chromium | $Cr_2O_3$ | 23 | As for magnesium oxide |
| | $CrO_3$ | (i) 23 | Stated by some workers to be a good conductor |
| | | (ii) 3 | Stated to be a nonconductor if pure, but to conduct well when it has absorbed water |
| Manganese | MnO | 23 | As for magnesium oxide |
| | $MnO_2$ | 22 | Fusible in the electric arc but decomposes |
| | $Mn_2O_7$ | 20 | Stated to have an immeasurably low conductivity |
| Iron | $Fe_2O_3$ | 22 | As for manganese dioxide |
| Cobalt | CoO | 23 | As for magnesium oxide |
| Nickel | NiO | 23 | As for magnesium oxide; gives a green crystalline material on cooling |
| Copper | CuO | 22 | As for manganese dioxide |
| Zinc | ZnO | 23 | Fusible in the electric arc but immediately volatilizes |
| Arsenic | $As_2O_3$ | 3 | Stated to be a good conductor, but volatile |
| Strontium | SrO | 23 | As for magnesium oxide |
| Zirconium | $ZrO_2$ | 23 | As for magnesium oxide |
| Molybdenum | $MoO_3$ | 14 | Stated to be a good conductor and could be electrolyzed |
| Ruthenium | $RuO_4$ | 20 | Stated to have immeasurably low conductivity at its melting point (25.5°C.) |
| Tin | $SnO_2$ | 23 | As for magnesium oxide but volatilizes in the arc |
| Antimony | $Sb_2O_3$ | (i) 11 | Stated by Faraday to conduct well when molten |
| | | (ii) 27 | Stated to be a nonconductor in the liquid condition when dry |
| | $Sb_2O_5$ | 11 | Stated by Faraday to conduct well, but this is doubtful owing to decomposition |
| Iodine | $I_2O_5$ | 8 | Stated to decompose no more when a potential is applied across the melt than it does thermally, and concluded from this that the liquid does not conduct |
| Barium | BaO | 23 | As for magnesium oxide |
| Cerium | $CeO_2$ | 23 | As for magnesium oxide |
| Osmium | $OsO_4$ | 4, 5 | Stated by various workers to be a very poor conductor in both solid and liquid states |
| Lead | PbO | 12 | Faraday stated it to be a good conductor |
| Bismuth | $Bi_2O_3$ | 11 | Stated to be a good conductor |

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what is known concerning the structures of these substances, the natures of the bonds involved, the ion sizes, and charge ratios, the ion coordination numbers in the various melts, the deformabilities of the ions, etc.

It was considered of interest to determine whether the molten oxides exhibited the same trends and pattern of variation of conductivity as do the molten halides. What little information is available in the literature concerning the conductivity of the fused oxides is summarized in Table I. The table gives the conductivity, in general terms, of the various oxides in the molten state, together with the sources of the information.

SPECIFIC AND EQUIVALENT CONDUCTANCES

| Substance | Melting point, °C. | Specific conductivity at melting point, $ohm^{-1}$ $cm.^{-1}$ | Density of solid, gm./cc. | Assumed density of liquid (75% of solid), gm./cc. | Equivalent conductance, $ohm^{-1}$ $cm.^{-2}$ |
|---|---|---|---|---|---|
| MgO | 2800 | 35 | 3.6 | 2.70 | 261 |
| CaO | 2580 | 40 | 3.3 | 2.48 | 453 |
| $TiO_2$* | 1650 | 10 | 4.2 | 3.15 | 63 |
| $ZrO_2$ | 2600 | 15 | 5.7 | 4.28 | 108 |
| $ThO_2$ | 3050 | 8 | 9.7 | 7.28 | 73 |
| $Cr_2O_3$ | 2275 | 65 | 5.2 | 3.90 | 844 |
| $Al_2O_3$ | 2050 | 15 | 3.9 | 2.93 | 175 |

**Titanium dioxide is generally assigned the formula $TiO_{1.90 \rightarrow 1.98}$ and might be expected to be a semiconductor.*

It will be seen from this table that there are only a very few oxides for which there are any quantitative data, and of these only four are applicable over a range of temperatures, viz., $H_2O$, $B_2O_3$, $NO_2$, and $SO_2$. These are all poor conductors and there would not appear to be any quantitative determinations of the conductivities of molten metallic oxides. There are a considerable number of qualitative observations concerning the possibility of striking and maintaining an electric arc under various molten metallic oxides, and it has been assumed that where this is possible the molten oxides concerned must be conducting.

Various oxides are handled commercially by the electric arc furnace technique. These include the following materials: MgO, CaO, $TiO_2$, $ThO_2$, $ZrO_2$, $Cr_2O_3$, $Al_2O_3$, $UO_2$, and $U_3O_8$. Semiquantitative figures for the conductivity of some of these oxides have been supplied to the authors in a private communication by the Norton Company, Chippawa, near Niagara Falls, Ont., to whom we are indebted for them. These figures are probably not reliable to better than $\pm 50\%$ owing to the indirect means necessary to obtain them.

In view of the scarcity of quantitative information it was felt desirable to augment the observations by direct experimental measurements of the electrical conductivity of some molten oxides over a range of temperatures. Consideration showed that the number of oxides available for convenient investigation is limited by several factors such as instability, volatility, and difficulty in finding suitable container and electrode materials.

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## EXPERIMENTAL

The oxides which have been studied in the molten state are lithium oxide, molybdenum trioxide, antimony trioxide, bismuth trioxide, vanadium pentoxide, tellurium dioxide, lead monoxide, and chromium trioxide ($CrO_3$).

In the case of lithium oxide a reasonably suitable material for the cell was found to be synthetic fused magnesia in the form of large single crystals* from which crucibles and lids could be conveniently, though laboriously, drilled. Molten lithium oxide has a quite remarkable solvent action on almost all the known refractory materials and, in addition, readily attacks most high-melting metals in both inert and active atmospheres; even platinum is readily attacked by it *in vacuo* with the probable production of an alloy of platinum and lithium. The alloy of 40% of rhodium with 60% of platinum, however, appears to be able to withstand the action of molten lithium oxide reasonably well and this was the material adopted for fabrication of the electrodes. The oxide was prepared by heating pure hydroxide, available commercially, to 1000°C. for several hours *in vacuo* in a platinum crucible. There is no appreciable attack on the platinum at this temperature. The oxide was subsequently handled in an atmosphere dried over phosphorus pentoxide. The cell, whose design is shown in Fig. 1, was loaded with finely ground lithium oxide and was heated inside a larger graphite crucible, placed in a surrounding quartz tube. Atmospheric pressure of argon gas was used in the heating tube. Induction heating was employed and the temperature estimated by means of an optical pyrometer sighted through the top window of the outer vessel. The lithium oxide was found to melt quite sharply at 1570°C. The resistance of the cell was measured on a simple a-c. bridge circuit at a frequency of 1000 c.p.s. The measured resistance dropped from a figure of over $10^5$ ohms while the oxide was still solid to about 30–40 ohms on melting corresponding, in this case, to a specific conductivity of 7 $ohm^{-1}$ $cm.^{-1}$. It was found by trial that, within the limits of measurement employed herein, it made no difference what frequency was used for the a-c. bridge circuit, within the range 2000 c.p.s. to the lowest audible limit; accordingly, 1000 c.p.s. was chosen as a convenient working frequency.

The cell was filled with just the required amount of material, previously determined by volume measurements, to ensure that the melt rose sufficiently far up the narrow holes in the lid that electrical contact was made with the platinum/rhodium electrodes.

The cell constant had previously been determined, using molten potassium chloride, whose conductivity is well established from the data of Jaeger and Kapma (17) and of Biltz and Klemm (2). It was found that the resistance of the cell, calculated from its dimensions and the known conductivity of molten potassium chloride, agreed well with the directly measured value.

The magnesium oxide of the crucible was attacked to a considerable extent by the lithium oxide (to about 20% of the lithium oxide weight). Accordingly an attempt was made to determine the conductivity as a function of concentration of magnesium oxide and thus determine by extrapolation the conduc-

*Supplied through the courtesy of the Norton Company, Chippawa, Ont.

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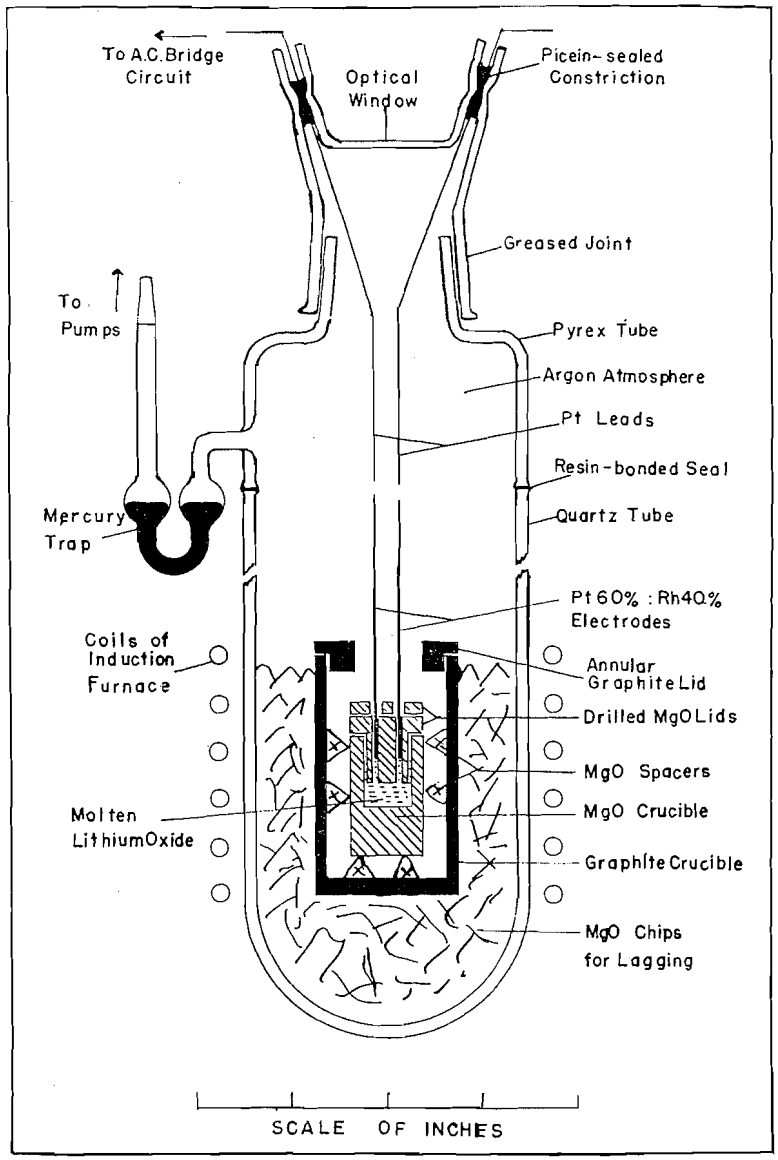



Fig. 1

tance of pure lithium oxide. To this end the conductivities of synthetic mixtures of magnesium and lithium oxides were determined and it was found that the conductivity was practically independent of magnesium oxide concentration from zero to 20% magnesium oxide by weight.

The equivalent conductance of fused lithium oxide at its melting point was found to be 108 $ohm^{-1}\ cm^{-2}$. It is considered that this figure may be taken as representing the conductivity of molten lithium oxide at its melting point to within $\pm 20\%$.

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TABLE II

DETAIL EXPERIMENTAL RESULTS

Temperatures ($t$) are given in degrees Centigrade. Specific conductivities ($K$) are given in ohm$^{-1}$ cm$^{-1}$. All the readings quoted below are given in the order in which they were obtained experimentally for each individual oxide.

| Bismuth trioxide ($Bi_2O_3$) | | | Tellurium dioxide ($TeO_2$) | | | Lead monoxide (PbO) | | | Molybdenum trioxide ($MoO_3$) | | | Vanadium pentoxide ($V_2O_5$) | | | Chromium trioxide ($CrO_3$) | | | Antimony trioxide ($Sb_2O_3$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cell | $t$ | $K$ | Cell | $t$ | $K$ | Cell | $t$ | $K$ | Cell | $t$ | $K$ | Cell | $t$ | $K$ | Cell | $t$ | $K$ | Cell | $t$ | $K$ |
| A | 933 | 1.416 | B | 911 | 2.330 | D | 891 | 1.030 | F | 858 | 1.50 | H | 867 | 0.0969 | I | 218 | $2.958\times10^{-5}$ | J | 842 | 0.1004 |
| | 929 | 1.217 | | 932 | 2.532 | | 914 | 1.523 | | 895 | 2.58 | | 884 | 0.1348 | | 228 | $1.479\times10^{-4}$ | | 828 | 0.0792 |
| | 880 | 0.716 | | 948 | 2.773 | | 939 | 1.843 | | 950 | 4.65 | | 888 | 0.1444 | | 235 | $3.697\times10^{-4}$ | | | |
| | 871 | 0.591 | | 952 | 2.841 | | 957 | 2.189 | | | | | 899 | 0.1590 | | 240 | $1.479\times10^{-3}$ | K | 854 | 0.1161 |
| | 860 | 0.495 | | 941 | 2.588 | | | | G | 847 | 0.99 | | 924 | 0.1993 | | 245 | $2.958\times10^{-3}$ | | 864 | 0.1231 |
| | 848 | 0.420 | | 873 | 2.080 | E | 897 | 1.251 | F | 840 (solid) | 0.141 | | 937 | 0.2359 | | 252 | $5.916\times10^{-3}$ | | 870 | 0.1286 |
| | 833 | 0.302 | | 843 | 1.879 | | 918 | 1.523 | | 809 " | 0.086 | | 949 | 0.2483 | | 262 | $8.964\times10^{-3}$ | | 888 | 0.1442 |
| | 829 | 0.292 | | 814 | 1.664 | | 941 | 1.751 | | 822 " | 0.105 | | 964 | 0.2888 | | | | | | |
| | 837 | 0.377 | | 789 | 1.493 | | 953 | 2.189 | | 841 " | 0.150 | | | | | | | | | |
| | 849 | 0.435 | | 773 | 1.420 | | 987 | 2.694 | | 857 | 1.41 | | | | | | | | | |
| | 872 | 0.609 | | 750 | 1.213 | | | | | 862 | 1.79 | | | | | | | | | |
| | 888 | 0.742 | | | | | | | | | | | | | | | | | | |
| | | | C | 812 | 1.713 | | | | | | | | | | | | | | | |
| | 904 | 0.846 | | | | | | | | | | | | | | | | | | |
| | | | | 840 | 1.879 | | | | | | | | | | | | | | | |
| | 908 | 0.937 | | | | | | | | | | | | | | | | | | |
| | | | | 868 | 2.080 | | | | | | | | | | | | | | | |
| | 911 | 1.068 | | | | | | | | | | | | | | | | | | |
| | | | | 908 | 2.377 | | | | | | | | | | | | | | | |
| | 920 | 1.269 | | | | | | | | | | | | | | | | | | |
| | | | | 930 | 2.532 | | | | | | | | | | | | | | | |
| | 930 | 1.353 | | | | | | | | | | | | | | | | | | |
| | | | | 941 | 2.647 | | | | | | | | | | | | | | | |
| | 955 | 1.450 | | | | | | | | | | | | | | | | | | |
| | | | | 960 | 2.841 | | | | | | | | | | | | | | | |

*Cell constants in cm.$^{-1}$*

| | | | | | |
|---|---|---|---|---|---|
| A | 609 | E | 35 | H | 1415 |
| B | 582 | F | 465 | I | 29.6 |
| C | 583 | G | 445 | J | 550 |
| D | 35 | | | K | 714 |

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It may be remarked that although nothing can be said of the nature of the carriers responsible for the conduction, such a high specific conductivity suggests the presence of a simple ionic melt, i.e., an arrangement of ions of small and comparable sizes, in an approximately close-packed configuration, analogous to that in the crystalline oxide.

The other oxides were all of much lower melting point and their conductivities were studied over a range of temperatures. In most cases the quartz capillary tube conductivity cell was heated by means of a bath of molten sodium chloride, and temperatures were measured by means of a Pt:Pt/Rh thermocouple. In the case of lead monoxide, which attacks quartz very readily, a platinum crucible containing a suitably drilled piece of polycrystalline magnesium oxide with a platinum electrode was used, the crucible itself acting as the other electrode. In all cases, care was taken to maintain the oxide under investigation free from any lower oxide whose presence might well lead to the intrusion of semiconductivity. In most cases conductivity measurements were made with both rising and falling temperatures, yielding concordant results; with vanadium pentoxide, however, the onset of decomposition at the highest temperatures investigated prohibited this procedure. In determining the cell constants for the quartz capillary cells, aqueous $N/1$ and $N/10$ potassium chloride solutions at a measured room temperature were used, employing the conductivity data of Parker and Parker (24), quoted by the International Critical Tables. Allowance was made for the temperature of the potassium chloride solution in determining the cell constant, but no account was taken of possible variation of the cell constant with temperature during the oxide conductivity determinations.

It is not considered that any variations of temperature within the oxide melts themselves, in either the lithium oxide experiments or those in the capillary U-tube cells, would have been sufficient to have caused variations in the measured conductivities which would have been significant in these comparatively crude experiments.

The results obtained with the various oxides other than lithium oxide, which has already been dealt with, are shown in Table II. The expression of the conductivity, $K$, as a function of absolute temperature, $T$, in the form,

$$\log K = A + B/T$$

will give a quantity, $B$, which when expressed in the proper units will be proportional to an 'activation energy'. However, when $\log K$ is plotted against $1/T$, it is apparent that in most cases there is an appreciable departure from linearity, and it would appear possible that it might be better to express $\log K$ as a quadratic function of $1/T$, thus,

$$\log K = A + B/T + C/T^2.$$

In this case, the 'activation energy' will itself be temperature dependent. An attempt has been made to determine by statistical means which is the more justifiable form to take as representing the experimental results. The best linear and quadratic equations connecting $\log K$ and $1/T$ were worked out by the usual least square methods, and from them the standard deviations of a single determination of $\log K$. In every case this quantity was less for the

quadratic plot than for the linear as, of course, it should be since an extra parameter, $C$, has been introduced. Often, however, the improvement obtained with the more complex form was slight.

As an additional test of the relative validity of the two forms of temperature dependence, correlation coefficients* were determined and appear together with other relevant data in Tables III and IV.

It will be noted that the correlation coefficients appearing in Tables III and IV show no significant difference as between the linear and the quadratic plots. However, it has recently been shown by Spooner and Wetmore (26) that the variation of the conductivity of molten silver nitrate with temperature is much better expressed by a quadratic plot than by a linear plot.

## DISCUSSION

In view of the double charge carried by the oxygen ion and the rather striking differences which exist as between the melting points of halides and of oxides, the molten oxides might be expected to exhibit marked and systematic differences in conductance behavior as compared with the corresponding halides. In the case of lithium oxide, it was thought that the strong fields about the oxygen and lithium ions might lead to a melt containing rather large ion clusters or to a melt having considerable covalent character, and thus be a poor conductor in comparison with fused lithium chloride or fluoride. However, the conductivity of fused lithium oxide, while somewhat lower than that of lithium fluoride, is quite comparable with the conductivity of the molten chloride, and is considerably greater than that of fused potassium chloride.

It may be pointed out that, in cases where the temperature coefficients of conductivity are comparatively large, the oxides were observed to form rather viscous liquids on melting, while where the temperature coefficients are small, it was noticed that the oxides melt sharply yielding comparatively mobile liquids. This suggests that in the former case, ion clusters of appreciable size having, perhaps, considerable covalent character are present in the melts, while in the latter case, the crystals melt to form liquids where the ion coordinations are essentially similar to those of simple ionic crystals. In Table V we present in diagrammatic form a summary of the information available to date concerning the conductivities of the fused oxides.

*This quantity is defined as follows:
Let log $K$ be denoted by $y$ and $1/T$ by $x$. Then the experimentally determined points will be $(x_1, y_1),(x_2, y_2), (x_3, y_3) \ldots (x_n, y_n)$. The correlation coefficient, $R$, is defined by the equation, $R^2 = 1 - U/n\sigma_y^2$
where $n$ = number of experimental observations.
$\sigma_y$ = standard deviation of $y$.
$U$ = sum of squares of residuals (differences between the observed values of $y$ and those calculated from the best linear or quadratic equation, as the case may be).
Thus for the linear equation

$$R^2 = 1 - \left(\sum_n(y_1^2) - A\sum_n(y_1) - B\sum_n(x_1y_1)\right) \Big/ \left(\sum_n(y_1^2) - \frac{1}{n}\left[\sum_n(y_1)\right]^2\right).$$

and for the quadratic equation

$$R^2 = 1 - \left(\sum_n(y_1^2) - A\sum_n(y_1) - B\sum_n(x_1y_1) - C\sum_n(x_1^2y_1)\right) \Big/ \left(\sum_n(y_1^2) - \frac{1}{n}\left[\sum_n(y_1)\right]^2\right).$$

cf. Udny Yule, G. and Kendall, M. G. An Introduction to the theory of statistics. C. Griffin and Co. Ltd., London. 1947. pp. 328–330.

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TABLE III
SUMMARY OF RESULTS CALCULATED ACCORDING TO LINEAR PLOT

| Oxide | Melting point, °C. | Range studied, °C. | $\log_{10} K = A + B/T$ A | B | Standard deviation of log $K$ | Correlation coefficient | Extrapolated $K$ at m.p., $ohm^{-1}$ $cm.^{-1}$ | Equivalent conductance at m.p. | Activation energy, kcal./mole |
|---|---|---|---|---|---|---|---|---|---|
| $Bi_2O_3$ | 828 | 829–955 | 7.057 | −8,354 | 0.0471 | 0.981 | 0.29 | 5.15 | 38.2 |
| $TeO_2$ | 730 | 750–960 | 2.162 | −2,109 | 0.0088 | 0.997 | 1.14 | 7.75 | 9.65 |
| PbO | 888 | 891–987 | 5.245 | −6,041 | 0.0237 | 0.983 | 1.10 | 12.89 | 27.6 |
| $MoO_3$ | 847 | 847–950 | 7.309 | −8,089 | 0.0552 | 0.973 | 1.22 | 6.51 | 37.0 |
| $V_2O_5$ | 690 | 867–964 | 4.670 | −6,427 | 0.0234 | 0.989 | 0.00988 | 0.107 | 29.4 |
| $CrO_3$ | 196 | 218–262 | 27.828 | −15,838 | 0.1821 | 0.980 | $1.16 \times 10^{-6}$ | $6.9 \times 10^{-6}$ | 72.5 |
| $Sb_2O_3$ | 656 | 828–888 | 3.800 | −5,364 | 0.0206 | 0.973 | 0.011 | 0.18 | 24.5 |

TABLE IV
SUMMARY OF RESULTS CALCULATED ACCORDING TO QUADRATIC PLOT

| Oxide | $\log_{10} K = A + B/T + C/T^2$ A | B | C | Standard deviation of log $K$ | Correlation coefficient | Extrapolated $K$ at m.p., $ohm^{-1}$ $cm.^{-1}$ | Equivalent conductance at m.p. | Activation energy, in kcal./mole $T_1$ | $T_2$ | $T_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $Bi_2O_3$ | −24.039 | 63,729 | $-41.729 \times 10^{-6}$ | 0.0380 | 0.988 | 0.26 | 4.57 | 55.2 | 33.9 | 20.6 |
| $TeO_2$ | 1.418 | −425 | $-0.950 \times 10^{-6}$ | 0.0085 | 0.997 | 1.12 | 7.60 | 10.6 | 9.69 | 9.05 |
| PbO | 5.499 | −6,646 | $+0.361 \times 10^{-6}$ | 0.0238 | 0.984 | 1.10 | 12.89 | 27.6 | 27.7 | 27.8 |
| $MoO_3$ | −5.476 | 21,898 | $-17.561 \times 10^{-6}$ | 0.0490 | 0.978 | 1.19 | 6.35 | 43.3 | 36.8 | 31.2 |
| $V_2O_5$ | −26.368 | 67,313 | $-43.767 \times 10^{-6}$ | 0.0164 | 0.996 | 0.000217 | 0.00235 | 107.9 | 33.4 | 19.5 |
| $CrO_3$ | −136.885 | 152,997 | $-43.234 \times 10^{-6}$ | 0.1231 | 0.991 | $6.2 \times 10^{-8}$ | $3.7 \times 10^{-7}$ | 143.3 | 86.3 | 35.2 |
| $Sb_2O_3$ | −59.006 | 136,614 | $-80.214 \times 10^{-6}$ | 0.0071 | 0.996 | $1.27 \times 10^{-5}$ | $2.17 \times 10^{-4}$ | 165.0 | 28.6 | 0.7 |

*N.B. $T_1$, $T_2$, $T_3$ in Table IV refer to the melting point, middle, and upper end respectively of the temperature range investigated.*

The interpretation of the behavior pattern in terms of the natures of the bonds involved, ion sizes, etc. is of course obscured by the large differences in temperature at which the various measurements were made. However, it is a rather striking fact that the molten oxides—like the halides—are usually either fairly good conductors or insulators. For example, molten $TiO_2$ is a fairly good conductor while molten $SiO_2$ is virtually an insulator, the melting points of the two oxides being not very different.

It is also observable that there is a tendency in the case of elements which give more than one oxide which is stable in the molten state for the oxide corresponding to the highest state of valency of the element to have the lowest conductivity; chromium and manganese furnish good examples of this tendency.

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TABLE V
SUMMARY OF INFORMATION ON CONDUCTIVITY OF MOLTEN OXIDES

| Group I | Group II | Group III | Group IV | Group V | Group VI | Group VII | Group VIII |
|---|---|---|---|---|---|---|---|
| *$H_2O$*** | — | — | — | — | — | — | — |
| $Li_2O$* | BeO | *$B_2O_3$*** | *$CO_2$* | *$N_2O_3$* *$NO_2$*** | *$O_2$* | | |
| | MgO* | $Al_2O_3$* | *$SiO_2$** | *$P_2O_3$** | *$SO_2$** *$SO_3$* | | |
| $K_2O$(?) | CaO* | | $TiO_2$* | $V_2O_5$** | *$CrO_3$*** | *$Mn_2O_7$* $MnO_2$ | $Fe_2O_3$ CoO |
| | | | | | $Cr_2O_3$* | MnO | NiO |
| CuO | ZnO | | | $As_2O_3$ | | | |
| | SrO | | $ZrO_2$* $SnO_2$ | $Sb_2O_3$** | $MoO_3$** $TeO_2$** | *$I_2O_5$* | *$RuO_4$* |
| | BaO | | $CeO_2$ PbO** | $Bi_2O_3$** | | | *$OsO_4$* |
| | | | $ThO_2$* | | $UO_2$ $U_3O_8$ | | |

*Data in italics: Nonconducting oxides.*
*Data in roman: Conducting oxides.*
**Isolated quantitative data available.*
***Data available over a range of temperature.*

While the picture is by no means as complete as that for the halides, it is evident that the conductivities of the molten oxides of the elements of the Periodic System exhibit essentially the same general pattern of behavior as do the molten halides.

ACKNOWLEDGMENTS

The authors wish to express their indebtedness to Dr. H. J. Bernstein and to Dr. M. Cohen for helpful discussions at various stages during this investigation.

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# PYRIDINE DERIVATIVES

## PART V.* ON FLUORO-NITROPYRIDINES[1]

By W. Gruber

ABSTRACT

2-Fluoro-5-nitropyridine has been synthesized and its properties compared with 2,4-dinitro-fluorobenzene. Absorption spectra are given. The highly reactive compound was used to prepare well defined derivatives from alcohols, amines, and amino acids.

In conjunction with other studies in the pyridine series we were interested in the synthesis and properties of some fluoro-nitropyridines, which are 'structurally analogous' to the well known dinitro-fluorobenzenes.

The preparation of the 2- and 3-fluoropyridines from the amines has been effected by: (*a*) diazotation in 60% hydrofluoric acid (4,2), (*b*) decomposition of the fluoborates (Schiemann reaction) (9), (*c*) decomposition of the fluosilicates (1). We have obtained 2-fluoro-5-nitropyridine from 2-amino-5-nitropyridine in 20–30% yield by method (*a*); methods (*b*) and (*c*) gave only traces. However, attempts to obtain other fluoro-nitropyridines by these methods were unsuccessful. From 2-amino-3-nitropyridine only the 2-hydroxy derivative was obtained by methods (*a*) or (*b*) and 4-fluoro-3-nitropyridine was not obtained from the 4-amino derivative. The failure of 4-aminopyridine to give 4-fluoropyridine has been reported (9).

As the fluorine in 2-fluoro-5-nitropyridine (NFP) shows the expected high reactivity, some precautions are necessary in its isolation. It gave 2-methoxy-5-nitropyridine (4) with sodium methoxide, or, more slowly with 10% aqueous methanol. From NFP and *o*-toluidine, glycine ethylester or phenylalanine, the corresponding N-substituted 2-amino-5-nitropyridines were obtained. Though NFP had advantages over 2-chloro-5-nitropyridine, which gave no such derivative with glycine ester, it is inferior to 2,4-dinitrofluobenzene for the characterization of phenols (12): with low melting xylenols, NFP gave only oily ethers.

*Ultraviolet Absorption Spectra*

The comparison of 2-fluoro-5-nitropyridine with the (corresponding) 1-fluo-2,4-dinitrobenzene could not be made, since the latter shows only end-absorption. However, it was interesting to compare the spectra of the fluoropyridines with the fluoro-nitrobenzenes.

It is known (8) that introduction of fluorine has very little effect on the general shape of the pyridine curve; it produces only a slight bathochromic and hyperchromic shift. These shifts fit very well in the pattern proposed by Spiers and Wibaut (11) for halopyridines.

[1] *Manuscript received June 29, 1953.*
*Contribution from the Division of Chemistry, British Columbia Research Council, Vancouver 8, B.C.*

**The paper "Synthesis of 3-hydroxy-2-alkylpyridines", Can. J. Chem. 31: 564. 1953, is regarded as Part IV of this series.*



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On the contrary, introduction of fluorine in nitrobenzene changes the shape of the absorption curve considerably (Fig. 1). Nitrobenzene shows one maximum at 255 mμ, which is also the sole maximum in the symmetrically substituted *p*-fluoro-nitrobenzene. In the ortho- and meta-compounds this maximum is shifted towards shorter wave lengths, and a second maximum occurs near 280 mμ.

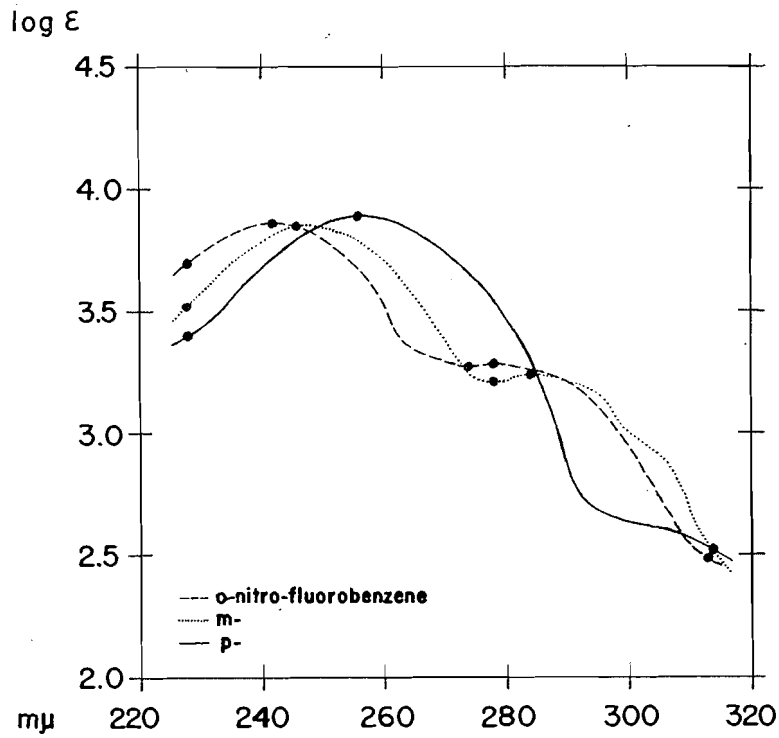



FIG. 1

2- and 4-Nitropyridines also show very distinctly a second maximum in the region of longer wave lengths, whereas this second maximum is absent in 3-nitropyridine (Fig. 2). However if the absorption spectra are measured in an unpolar solvent, e.g. trimethylpentane, instead of in alcohol, 3-nitropyridine also shows a second maximum.*

It is worth while noticing, that NFP shows nearly the same ultraviolet absorption curve as does 3-nitropyridine, the introduction of fluorine producing only a bathochromic effect (Fig. 3).

## EXPERIMENTAL**

### *5-Nitro-2-fluoropyridine (NFP)*

Of the several preparative methods tried, the following proved to be the most satisfactory. 2-Amino-5-nitropyridine (10.4 gm.) (3) was dissolved in

*The effect of the solvent on the absorption spectra of heterocyclic bases, e.g. pyridine, is discussed in (8).

**Melting points are corrected. Analyses are by A. Bernhardt, Mühlheim (Ruhr), Germany.

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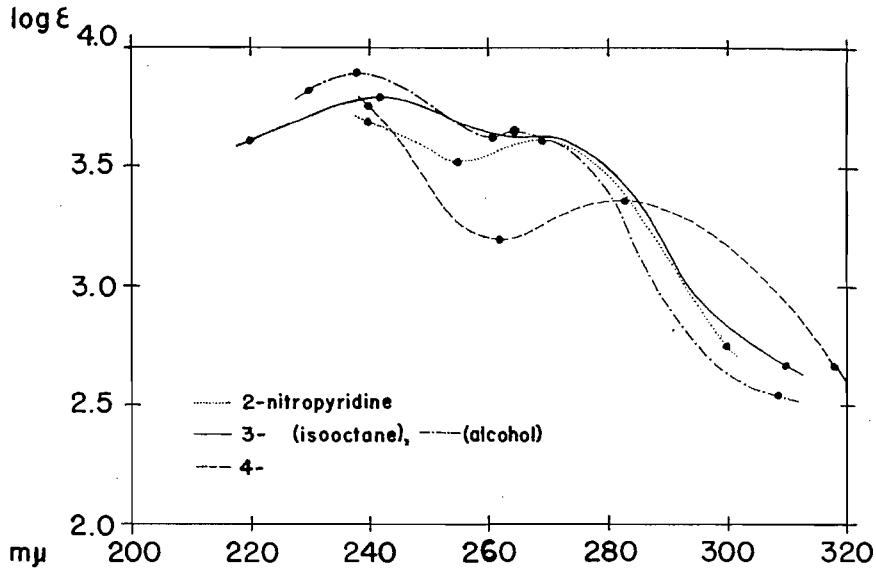



FIG. 2

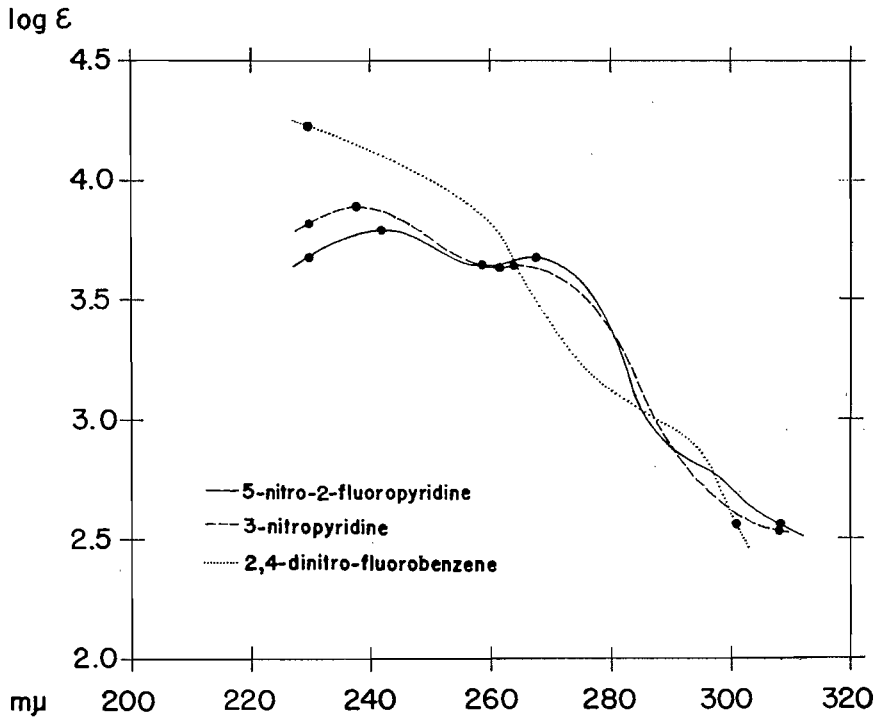



FIG. 3

100 ml. of 60% hydrofluoric acid, cooled to 0°C., and 6.3 gm. sodium nitrite added in small portions to the well stirred solution. After standing overnight

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at room temperature, the acid was neutralized with sodium bicarbonate, an excess of sodium bicarbonate added, and the mixture saturated with sodium chloride. The mixture was extracted continuously with ether for 12 hr., the solvent evaporated, and the residue, consisting of NFP and 2-hydroxy-5-nitropyridine, distilled *in vacuo*. The receiver was cooled with dry ice-acetone mixture. NFP is rather volatile, has a characteristic smell, and is a typical lachrymator, even in low concentrations; it also has an irritating action on the skin, like 2,4-dinitro-fluobenzene. Yield 2.3 gm. (i.e. 22%), m.p. 19–21°C.; white prisms; b.p. 79–81°C. at 5–6 mm. Hg. Calc. for $C_5H_3FN_2O_2$: C, 42.26; H, 2.13; N, 19.72%. Found: C, 42.52; H, 2.01; N, 19.60%. $n_D^{23°} = 1.5258$; sp. gr.$\frac{23°}{23°} = 1.410$; found: $R_D = 30.93$. Ultraviolet absorption in 2,2,4-trimethylpentane ($c = 0.00011$): $\lambda_{max}$ 242 mμ (log $\epsilon = 3.78$); 268 mμ (log $\epsilon = 3.67$) (Fig. 3).

Attempts to prepare NFP by heating 2-chloro-5-nitropyridine with potassium fluoride in a nonpolar solvent, corresponding to the convenient synthesis of 2,4-dinitro-fluorobenzene (5), were unsuccessful.

*5-Nitro-2-methoxypyridine*

Sodium, 200 mgm. was dissolved in absolute methanol, (5 ml.) the solution was cooled to 10°C. and added to a cooled solution of 420 mgm. NFP in 3 ml. of absolute methanol. A violent reaction set in and was completed by heating the mixture on the steam bath for 30 min. After cooling, the mixture was poured into water and the precipitate collected on a Büchner funnel. After sublimation *in vacuo* (39 mm.), the yield was 425 mgm. (94%); m.p. 104–108°C. After recrystallization from diluted methanol, the m.p. was 109–110°C. The mixed m.p. with an authentic sample was not depressed.

A solution of 300 mgm. NFP in 8 ml. of dilute methanol (15% v/v) was kept for 12 hr. at room temperature, after which no more crystals precipitated. Yield of 5-nitro-2-methoxypyridine 15 mgm., m.p. 109–110°. Calc. for $C_6H_6N_2O_3$: N, 18.18; $OCH_3$, 20.14%. Found: N, 18.05; $OCH_3$, 20.20%.

*N-(5-nitropyridyl-2)-o-toluidine*

A mixture of 600 mgm. NFP and 600 mgm. *o*-toluidine was heated on the steam bath for two hours; the solid content of the flask was recrystallized from 70 ml. 10% hydrochloric acid with a little charcoal, and then twice from dilute alcohol; m.p. 137–139°C., mixed melting point with a sample prepared from 2-chloro-5-nitropyridine was not depressed. Yield almost quantitative. Calc. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84%. Found: C, 63.12, 62.83; H, 4.74, 4.76%.

*Ethyl N-(5-nitropyridyl-2)-aminoacetate*

A solution of 250 mgm. of glycine ethyl ester hydrochloride and 336 mgm. of sodium bicarbonate in 5 ml. water was added to a solution of 284 mgm. of NFP in 10 ml. of ethanol. After standing at 5°C. for five hours the precipitation of white needles began. They were collected the next day and had a melting point of 140–145°C.; crude yield 425 mgm. After purification by recrystallization from dilute alcohol the melting point was 142–143°C. Calc. for $C_9H_{11}N_3O_4$: C, 48.00; H, 4.92; N, 18.66%. Found: C, 47.94; H, 5.00; N, 18.72%.

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*N-(5-nitropyridyl-2)-β-phenylalanine*

Phenylalanine (330 mgm.) and sodium bicarbonate (336 mgm.) were dissolved in 15 ml. water and mixed with a solution of 284 mgm. NFP in 5 ml. alcohol. After 15 hr. at room temperature the solvents were removed *in vacuo* at 30°C., and the residue recrystallized several times from absolute methanol. Brownish-yellow plates, yield 291 mgm. (52%), m.p. 183–185°C. Calc. for $C_{14}H_{13}N_3O_4$: C, 58.53; H, 4.56; N, 14.63%. Found: C, 58.42; H, 4.63; N, 14.47%.

*Ultraviolet Absorption Spectra*

The fluoro-nitrobenzenes and dinitrobenzenes were prepared from the nitroanilines in a Schiemann reaction according to Org. Synth., Coll. Vol. II, p. 225. The nitropyridines were prepared by oxidation of the aminopyridines with hydrogen peroxide in oleum (6, 7, 10). The spectra were measured in 2,2,4-trimethylpentane ('isooctane') unless otherwise stated.

*o*-Nitro-fluorobenzene b.p. 86–87°C. at 10–11 mm. Hg ($c$ = 0.00015);
$\lambda_{max}$: 242 mμ (log $\epsilon$ = 3.86), 278 mμ (log $\epsilon$ = 3.27).

*m*-Nitro-fluorobenzene b.p. 53–54°C. at 1–2 mm. Hg. ($c$ = 0.00021);
$\lambda_{max}$: 246 mμ (log $\epsilon$ = 3.87), 284 mμ (log $\epsilon$ = 3.23).

*p*-Nitro-fluorobenzene b.p. 86–88°C. at 12–14 mm. Hg ($c$ = 0.00021);
$\lambda_{max}$: 256 mμ (log $\epsilon$ = 3.88).

2-Nitropyridine m.p. 70–71°C., in 95% ethanol ($c$ = 0.00014);
$\lambda_{max}$: 269 mμ (log $\epsilon$ = 3.60).

3-Nitropyridine m.p. 35–36°C., ($c$ = 0.00014);
$\lambda_{max}$: 238 mμ (log $\epsilon$ = 3.88), 264 mμ (log $\epsilon$ = 3.64). In 95% ethanol ($c$ = 0.00016), $\lambda_{max}$: 242 mμ (log $\epsilon$ = 3.78).

4-Nitropyridine m.p. 49–51°C., in 95% ethanol ($c$ = 0.00013):
$\lambda_{max}$: 282 mμ (log $\epsilon$ = 3.35).

ACKNOWLEDGMENT

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# SYNTHESIS, POTENTIOMETRIC TITRATIONS, AND SPECTRA OF PYRAZOLONES[1]

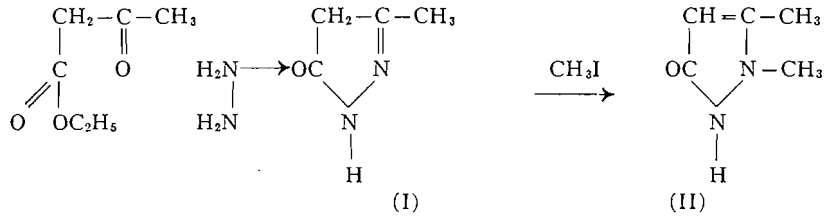
By Paul E. Gagnon, Jean L. Boivin[2], and René J. Paquin[3]

ABSTRACT

Monosubstituted benzoylacetic esters, obtained by condensation of *n*-alkyl halides with ethyl benzoylacetate, were reacted with hydrazine and phenylhydrazine to give 3-phenyl and 1,3-diphenyl 5-pyrazolones monosubstituted in position 4 by alkyl radicals R (R = H, $C_nH_{2n+1(n=1\text{ to }10)}$, and $C_6H_5CH_2$.). The dissociation constants of the pyrazolones were determined by potentiometric titrations. A study was made of the ultraviolet absorption spectra in both neutral and acid medium and of the infrared absorption spectra. X-ray powder diffraction patterns and data of the pyrazolones were obtained.

## INTRODUCTION

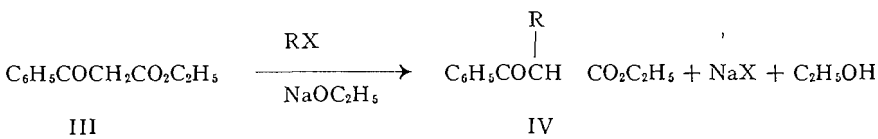
The condensation of hydrazine and its monosubstituted derivatives with β-keto esters gives the corresponding hydrazone which, by elimination of ethanol, cyclizes into pyrazolones. Antipyrin (II) was thus prepared by methylation of 3-methyl-4-pyrazolone (I) which was obtained from ethyl acetoacetate and hydrazine (12).



(I) (II)

The main object of the present work was to synthesize and study the properties of 4-monosubstituted-3-phenyl-5-pyrazolones and 4-monosubstituted-1,3-diphenyl-5-pyrazolones obtained by condensation of hydrazine and phenylhydrazine with a homologous series of β-keto esters.

The starting esters used in the present work, the ethyl α-monosubstituted α-benzoylacetates (IV), were prepared by alkylation of ethyl benzoylacetate (III) with the required alkyl halide.



III IV

$$R = C_nH_{2n+1\ (n=1\text{ to }10)} \text{ and } C_6H_5CH_2$$

[1] *Manuscript received June 16, 1953.*

*Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.*

[2] *Defence Research Board, C.A.R.D.E., Valcartier, Que.*

[3] *Graduate Student, holder of a Canadian Industries Limited Research Scholarship in 1950–51; of a National Research Council of Canada Studentship in 1951–52, and of a Shell Oil Company Research Fellowship in 1952–53.*

Several of these β-keto esters were reported previously (3, 15, 16). In the present investigation other esters of the homologous series were obtained in good yields, some dehydrobenzoyl acetic acid being isolated as a by-product in each case. The properties and analyses of the ethyl α-monosubstituted benzoylacetates prepared are given in Table I.

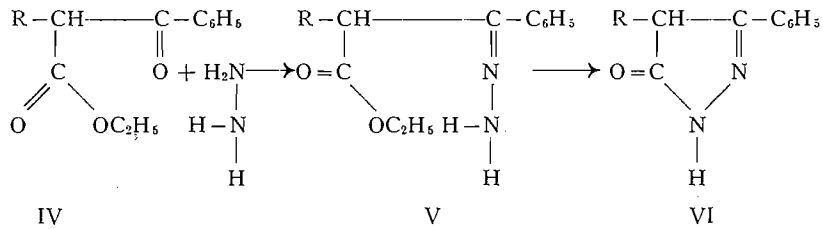
TABLE I
ETHYL α-SUBSTITUTED BENZOYLACETATES $C_6H_5COCH(R)CO_2C_2H_5$

| R | B.p., °C. | Yield, % | $d_{25°C}$ | Formula | Analysis | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Calculated | | Found | |
| | | | | | C | H | C | H |
| $C_5H_{11}$ | 149–153 (2 mm.) | 61 | 1.4980 | $C_{16}H_{22}O_3$ | 73.28 | 8.40 | 73.52 | 8.47 |
| $C_6H_{13}$ | 156–159 (2 mm.) | 68 | 1.4952 | $C_{17}H_{24}O_3$ | 73.91 | 8.69 | 74.33 | 9.00 |
| $C_7H_{15}$ | 170–173 (2 mm.) | 62 | 1.4939 | $C_{18}H_{26}O_3$ | 74.48 | 8.97 | 74.38 | 9.11 |
| $C_8H_{17}$ | 180–182 (2 mm.) | 80 | 1.4928 | $C_{19}H_{28}O_3$ | 75.00 | 9.21 | 74.93 | 9.32 |
| $C_9H_{19}$ | 158–160 (0.4 mm.) | 67 | 1.4909 | $C_{20}H_{30}O_3$ | 75.47 | 9.43 | 75.30 | 9.24 |
| $C_{10}H_{21}$ | 162–164 (0.2 mm.) | 66 | 1.4997 | $C_{21}H_{32}O_3$ | 75.89 | 9.63 | 75.57 | 9.58 |

The condensation of hydrazine with ethyl benzoylacetate (IV, R = H) to give 3-phenyl-5-pyrazolone (VI, R = H) was carried out by Curtius (4).

Similarly, 4-methyl-3-phenyl-5-pyrazolone (VI, $R = CH_3$) was prepared by Auwers and Mauss (2) from ethyl α-methyl benzoylacetate (IV, $R = CH_3$) and hydrazine hydrate.

Other 4-monosubstituted-3-phenyl-5-pyrazolones (VI) were prepared from the corresponding β-keto esters (IV) and hydrazine by modifying slightly the method used by Curtius, Auwers, and Mauss. The esters were refluxed with an excess of hydrazine hydrate and then heated under reduced pressure. The pyrazolones were isolated by dissolving the reaction product in alkali and precipitating with acetic acid. The hydrazones (V), presumably formed during the reaction, were not isolated.



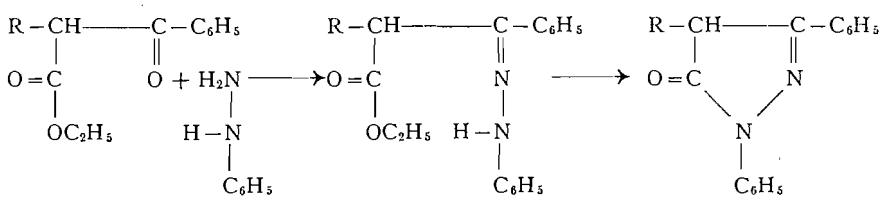
IV V VI

$R = C_nH_{2n+1}$ ($n$=1 to 10) and $C_6H_5CH_2$

1,3-Diphenyl-5-pyrazolone (VII, R = H) was prepared by Knorr and Klotz (13) by heating a mixture of ethyl benzoylacetate (IV, R = H) and phenylhydrazine in ethanol.

A series of 4-monosubstituted-1,3-diphenyl-5-pyrazolones (VIII) was thus prepared by heating mixtures of substituted ethyl benzoylacetates (IV) with phenylhydrazine.

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IV VII VIII

$R = C_nH_{2n+1}$ ($n$=1 to 10) and $C_6H_5CH_2$

The individual properties and analyses of all the pyrazolones prepared are given in Tables II and III.

TABLE II

4-MONOSUBSTITUTED-3-PHENYL-5-PYRAZOLONES

| R | M.p., °C. | Yield, % | Formula | Analysis | | | | | | Ultraviolet absorption maxima | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calculated | | | Found | | | Neutral | | Acid | |
| | | | | C | H | N | C | H | N | Å | log $E_m$ | Å | log $E_m$ |
| H* | | | | | | | | | | 2500 | 4.21 | 2500 | 4.28 |
| $CH_3$** | | | | | | | | | | 2540 | 4.21 | 2520 | 4.12 |
| $C_2H_5$ | 165–168 | 83 | $C_{11}H_{12}N_2O$ | 70.21 | 6.38 | 14.89 | 69.84 | 6.53 | 14.80 | 2500 | 4.14 | 2440 | 4.18 |
| $C_3H_7$ | 186–188 | 91 | $C_{12}H_{14}N_2O$ | 71.28 | 6.93 | 13.86 | 71.19 | 6.93 | 13.63 | 2500 | 4.10 | 2440 | 4.12 |
| $C_4H_9$ | 180–181 | 95 | $C_{13}H_{16}N_2O$ | 72.22 | 7.41 | 12.96 | 72.38 | 7.46 | 12.95 | 2500 | 4.10 | 2500 | 4.10 |
| $C_5H_{11}$ | 139–140 | 91 | $C_{14}H_{18}N_2O$ | 73.04 | 7.82 | 12.18 | 73.00 | 7.73 | 12.25 | 2500 | 4.15 | 2460 | 4.13 |
| $C_6H_{13}$ | 116–117 | 96 | $C_{15}H_{20}N_2O$ | 73.77 | 8.19 | 11.48 | 73.66 | 8.05 | 11.48 | 2500 | 4.12 | 2480 | 4.17 |
| $C_7H_{15}$ | 108–109 | 96 | $C_{16}H_{22}N_2O$ | 74.42 | 8.52 | 10.85 | 74.31 | 8.47 | 10.82 | 2500 | 4.10 | 2480 | 4.06 |
| $C_8H_{17}$ | 110–111 | 92 | $C_{17}H_{24}N_2O$ | 75.00 | 8.83 | 10.28 | 75.28 | 9.08 | 10.10 | 2520 | 4.11 | 2440 | 4.11 |
| $C_9H_{19}$ | 100–102 | 87 | $C_{18}H_{26}N_2O$ | 75.52 | 9.09 | 9.79 | 75.26 | 9.14 | 9.84 | 2500 | 4.17 | 2420 | 4.09 |
| $C_{10}H_{21}$ | 95–96 | 88 | $C_{19}H_{28}N_2O$ | 76.00 | 9.33 | 9.33 | 76.34 | 9.45 | 9.24 | 2500 | 4.21 | 2480 | 4.07 |
| $C_6H_5CH_2$ | 184–185 | 90 | $C_{16}H_{14}N_2O$ | 76.80 | 5.60 | 11.20 | 76.66 | 5.49 | 11.13 | 2520 | 4.17 | 2500 | 4.09 |

* *Curtius, T. J. prakt. Chem. 50: 515. 1894; Michaelis, A. and Rassmann, W. Ann. 352: 158. 1907.*

** *Auwers, K. and Mauss, H. J. prakt. Chem. 110: 206. 1925.*

TABLE III

4-MONOSUBSTITUTED-1,3-DIPHENYL-5-PYRAZOLONES

| R | M.p., °C. | Yield, % | Formula | Analysis | | | | | | Ultraviolet absorption maxima | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calculated | | | Found | | | Neutral | | Acid | |
| | | | | C | H | N | C | H | N | Å | log $E_m$ | Å | log $E_m$ |
| H* | | | | | | | | | | 2700 | 4.35 | 2700 | 4.35 |
| $CH_3$ | 204–205 | 81 | $C_{16}H_{14}N_2O$ | 76.80 | 5.59 | 11.20 | 77.02 | 5.33 | 11.22 | 3100 | 4.09 | 3100 | 3.78 |
| | | | | | | | | | | 2500 | 4.57 | 2500 | 4.29 |
| $C_2H_5$ | 213–214 | 77 | $C_{17}H_{16}N_2O$ | 77.28 | 6.06 | 10.60 | 77.95 | 5.57 | 10.64 | 3100 | 3.80 | 3100 | 3.81 |
| | | | | | | | | | | 2500 | 4.32 | 2520 | 4.30 |
| $C_3H_7$ | 198–199 | 71 | $C_{18}H_{18}N_2O$ | 77.70 | 6.47 | 10.07 | 77.77 | 6.16 | 9.93 | 3100 | 3.81 | 3100 | 3.76 |
| | | | | | | | | | | 2480 | 4.31 | 2520 | 4.24 |
| $C_4H_9$ | 192–193 | 70 | $C_{19}H_{20}N_2O$ | 78.09 | 6.89 | 9.59 | 78.77 | 6.89 | 9.60 | 3100 | 3.90 | 3100 | 3.73 |
| | | | | | | | | | | 2500 | 4.39 | 2520 | 4.19 |
| $C_5H_{11}$ | 174–175 | 60 | $C_{20}H_{22}N_2O$ | 78.43 | 7.19 | 9.15 | 78.83 | 7.12 | 9.26 | 3114 | 3.88 | 3120 | 3.87 |
| | | | | | | | | | | 2530 | 4.33 | 2520 | 4.32 |
| $C_6H_{13}$ | 158–159 | 60 | $C_{21}H_{24}N_2O$ | 78.75 | 7.50 | 8.75 | 79.16 | 7.18 | 8.92 | 3100 | 3.85 | 3200 | 3.81 |
| | | | | | | | | | | 2520 | 4.29 | 2520 | 4.30 |
| $C_7H_{15}$ | 134–135 | 55 | $C_{22}H_{26}N_2O$ | 79.04 | 7.78 | 8.38 | 79.20 | 7.60 | 8.52 | 3110 | 4.08 | 3100 | 4.15 |
| | | | | | | | | | | 2540 | 4.54 | 2510 | 4.61 |
| $C_8H_{17}$ | 144–145 | 53 | $C_{23}H_{28}N_2O$ | 79.31 | 8.05 | 8.05 | 79.48 | 7.95 | 8.02 | 3120 | 4.15 | 3150 | 4.13 |
| | | | | | | | | | | 2540 | 4.55 | 2520 | 4.56 |
| $C_9H_{19}$ | 133–134 | 50 | $C_{24}H_{30}N_2O$ | 79.56 | 8.29 | 7.74 | 79.23 | 8.02 | 7.84 | 3120 | 3.79 | 3100 | 3.79 |
| | | | | | | | | | | 2520 | 4.27 | 2520 | 4.25 |
| $C_{10}H_{21}$ | 116–117 | 51 | $C_{25}H_{32}N_2O$ | 79.80 | 8.51 | 7.44 | 80.26 | 8.33 | 7.32 | 3100 | 3.82 | 3100 | 3.77 |
| | | | | | | | | | | 2500 | 4.32 | 2500 | 4.27 |
| $C_6H_5CH_2$ | 178–179 | 73 | $C_{22}H_{18}N_2O$ | 80.98 | 5.52 | 8.59 | 80.81 | 5.41 | 8.75 | 2630 | 4.10 | 2630 | 4.13 |

* *Knorr, L. and Klotz, C. Ber. 20: 2546. 1887.*

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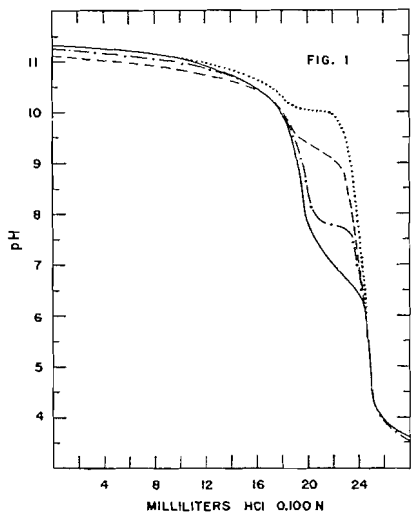
*Potentiometric Titrations*

Pyrazolones may be considered as weak acids PYRH which dissociate into pyrazolone ions $PYR^-$ (II) and protons $H^+$.

$$PYRH + H_2O \rightleftharpoons PYR^- + H_3O^+$$

As previously reported (5) their dissociation constants were determined, with a good approximation, from the pH values of the midpoint of the flat portion of their titration curves.

All the 3-phenyl and 1,3-diphenyl-4-monosubstituted-5-pyrazolones give titration curves of the same shape (Figs. 1 and 2) and are less acidic in character than carbon dioxide.



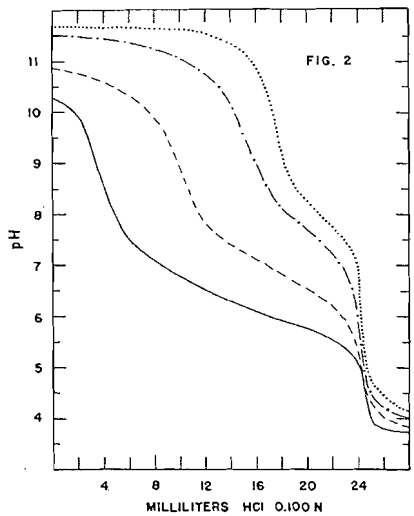




FIG. 1. Potentiometric titration curves of:
——— 3-Phenyl-5-pyrazolone. ..... 4-Octyl-3-phenyl-5-pyrazolone.
– – – – 4-Heptyl-3-phenyl-5-pyrazolone. –·–·–·– 4-Benzyl-3-phenyl-5-pyrazolone.

FIG. 2. Potentiometric titration curves of:
——— 1,3-Diphenyl-5-pyrazolone. ..... 4-Heptyl-1,3-diphenyl-5-pyrazolone.
– – – – 4-Propyl-1,3-diphenyl-5-pyrazolone. –·–·–·– 4-Benzyl-1,3-diphenyl-5-pyrazolone.

The value of the $pK_a$ in the case of the 4-monosubstituted-3-phenyl-5-pyrazolones shows a gradual increase (Table IV). For example, 3-phenyl-5-pyrazolone has a $pK_a$ value of 7.4 and the corresponding 4-decyl pyrazolone has a value of 11.0. The other members of the series have $pK_a$ values intermediate between these and it is possible to classify them, from the 4-propyl to the 4-decyl, as very weak acids since their dissociation constants are in the region $10^{-8}$ to $10^{-11}$.

The 4-benzyl-3-phenyl-5-pyrazolone has a $pK_a$ value of 7.7 and may therefore be classified in the group of weak acids, together with the unsubstituted and also the methyl and ethyl 3-phenyl-5-pyrazolones. It is of interest to note that the 4-benzyl substituted pyrazolone has a $pK_a$ value close to that of the 4-methyl substituted pyrazolone indicating that they are acids of about the same strength.

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TABLE IV
DISSOCIATION CONSTANTS OF 4-MONOSUBSTITUTED-5-PYRAZOLONES

| Substituent | 3-Phenyl | | 1,3-Diphenyl | |
|---|---|---|---|---|
| | Amount of substance, gm. $\times 10^2$ | $pK_a$* | Amount of substance, gm. $\times 10^2$ | $pK_a$ |
| H | 6.40 | 7.4 | 2.70 | 6.2 |
| $CH_3$ | 6.96 | 7.6 | 5.46 | 7.8 |
| $C_2H_5$ | 7.52 | 7.8 | 5.25 | 8.0 |
| $C_3H_7$ | 8.08 | 8.0 | 5.11 | 7.0 |
| $C_4H_9$ | 8.64 | 8.2 | 5.09 | 7.2 |
| $C_5H_{11}$ | 9.20 | 8.4 | 5.05 | 7.3 |
| $C_6H_{13}$ | 9.76 | 8.6 | 5.19 | 7.4 |
| $C_7H_{15}$ | 10.32 | 9.2 | 5.73 | 8.0 |
| $C_8H_{17}$ | 10.88 | 10.2 | 5.12 | 7.5 |
| $C_9H_{19}$ | 11.44 | 10.6 | 5.16 | 7.2 |
| $C_{10}H_{21}$ | 12.00 | 11.0 | 4.68 | 6.7 |
| $C_6H_5CH_2$ | 10.00 | 7.7 | 3.19 | 7.6 |

* *As determined from the curves.*

The 4-monosubstituted-1,3-diphenyl-5-pyrazolones have $pK_a$ value varying between 7 and 8 (Table IV). The unsubstituted pyrazolone is slightly more acidic as shown by its $pK_a$ value of 6.2. The variation of the $pK_a$ values for the homologous series shows a maximum value of 8.0 for the 4-ethyl and 4-heptyl compounds. Beyond this the values decrease regularly with the increase of the number of carbon atoms of the substituent.

Here again the 4-benzyl-1,3-diphenyl-5-pyrazolone has a $pK_a$ value intermediate to that of the other compounds and as in the case of the 3-phenyl-5-pyrazolones it has an acidity very close to that of the corresponding methyl substituted compound.

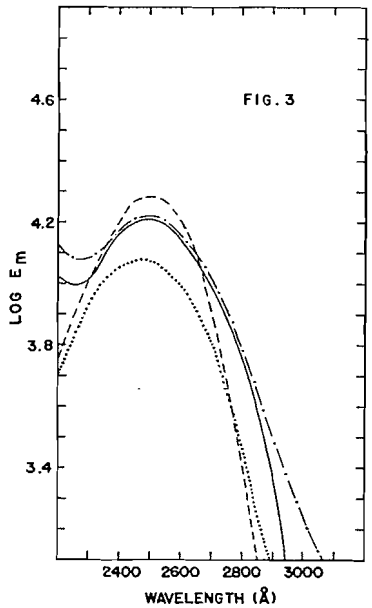
If a comparison is made between the 3-phenyl and 1,3-diphenyl pyrazolones it is noted that the latter are slightly more acidic than the former. The unsubstituted members of both series show slightly more acidic properties than the rest of the series. This is especially true in the 1,3-diphenyl pyrazolone series where the $pK_a$ value of the unsubstituted compound is 6.2 and that of the adjacent member in the series is 7.8. Comparing the 3-phenyl-5-pyrazolone with the 1,3-diphenyl-5-pyrazolone we note that the latter has a $pK_a$ value of 6.2 as compared to 7.4 for the former. It is evident therefore that the diphenyl pyrazolone is more acidic than the monophenyl compound and since both molecules differ but by one phenyl group then this difference in acidity may be attributed to the effect of the phenyl group.

*Ultraviolet Absorption Spectra*

The ultraviolet absorption spectra of the pyrazolones were determined in neutral and acid solution. The results obtained are given in Tables II and III and shown graphically in Figs. 3 and 4.

A close inspection of the absorption curves shows that the spectra of the 4-monosubstituted-3-phenyl-5-pyrazolones (Fig. 3) are almost identical. In neutral solution, they all possess, in the 2500 Å region, a single absorption maximum of high intensity, log $E_m$ varying from 4.10 to 4.21. In acid solution,

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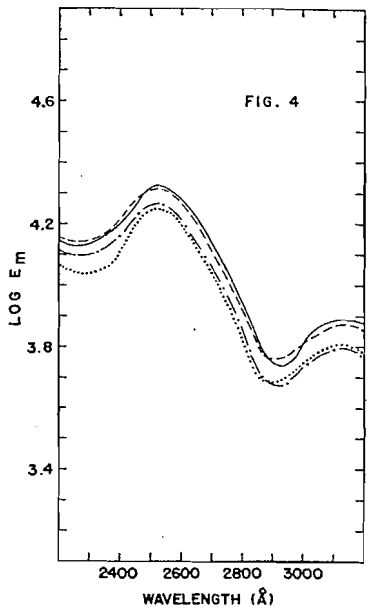
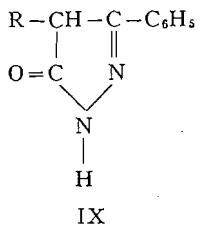



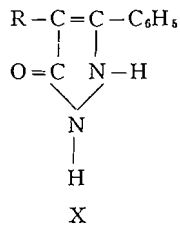

FIG. 3. Ultraviolet absorption spectrum of:
3-Phenyl-5-pyrazolone: ———— in neutral solution; – – – – in acid solution.
4-Decyl-3-phenyl-5-pyrazolone: –·–·–·– in neutral solution; ..... in acid solution.
FIG. 4. Ultraviolet absorption spectrum of:
4-Amyl-1,3-diphenyl-5-pyrazolone: ———— in neutral solution; – – – – in acid solution.
4-Nonyl-1,3-diphenyl-5-pyrazolone: –·–·–·– in neutral solution; ..... in acid solution.

the maxima are at slightly shorter wave lengths while the intensity remains nearly the same.

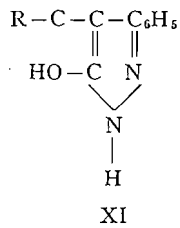
The 4-monosubstituted-3-phenyl-5-pyrazolones may exist under the following possible tautomeric forms:




IX




X




XI

It has been reported that pyrazolones showing high intensity absorption maxima at short wave lengths have a double bond between two carbon atoms, whereas those with low intensity maxima at long wave lengths have a 2:3 double bond (6, 7, 9, 10). Shifts in the position of the maxima to longer or shorter wave lengths in acid solution were interpreted in terms of resonance effects (9). Small shifts in either direction may be due to a solvent effect, to the formation of a salt, or to a combination of several of these possibilities (18).

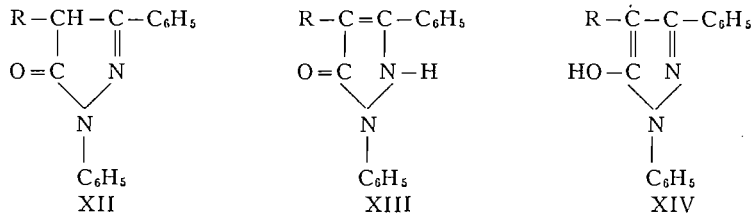
From these results one may assume that the 4-monosubstituted-3-phenyl-5-pyrazolones exist under structures X or XI, in neutral and acid solution,

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since they possess a single high intensity maxima at short wave lengths and no appreciable shift occurs in acid media.

However, a subsequent study of the infrared absorption spectra of these pyrazolones seems to indicate that they possess the hydroxy form as shown by structure XI. This is of particular interest since previous work (8, 9) indicated that the hydroxy form existed only in alkaline solution.

4-Monoalkyl-1,3-diphenyl-5-pyrazolones, in which the position of the N-phenyl group is fixed by the method used to prepare the compound, may exist only under the following isomeric structures:




The 4-monoalkyl-1,3-diphenyl-5-pyrazolones (Fig. 4) exhibited two maxima in neutral solution, one of high intensity with log $E_m$ = 4.39 at about 2500 Å and a second of low intensity, log $E_m$ 3.91, in the longer wave length region at 3100 Å. In acid media the maxima were not shifted and the intensity remained nearly the same. The high intensity maximum at short wave length implied the presence of an ethylenic bond whereas the low intensity maxima at long wave lengths indicated a 2:3 double bond. From these results one may conclude that the 4-monoalkyl-1,3-diphenyl-5-pyrazolones may exist, in both neutral and acid media under the three structures XII, XIII, and XIV. Structures XIII and XIV may be discarded however since infrared absorption measurements show the presence of a C=N bond and the absence of a hydroxyl group.

*Infrared Absorption Spectra*

The infrared absorption spectra of the pyrazolones were determined with a Perkin-Elmer spectrophotometer. The results obtained are given in Table V and some of the data are plotted in Figs. 5 and 6.

The 4-monosubstituted-3-phenyl-5-pyrazolones have absorption curves which are very similar. They show a band of relatively high intensity at about 1600 cm.$^{-1}$ and several other bands of smaller intensity in the double bond region, that is, between 1850 and 1470 cm$^{-1}$. In most of the cases, another weak band occurs in the hydrogen stretching region around 3300 cm$^{-1}$.

The most striking conclusion to be reached from these results is that apparently the C=O group is not present, since its characteristic frequency at approximately 1700 cm.$^{-1}$ is absent. The absence of this functional group, however, offers a satisfactory explanation for the band at 3300 cm$^{-1}$. It is well known that pyrazolones can exist under the hydroxy form and, therefore, the band at 3300 cm.$^{-1}$ could be interpreted as the characteristic frequency of the hydroxyl group. This band, however, has but a small intensity and in some cases it occurs as an inflection point only. The 4-benzyl-3-phenyl-5-

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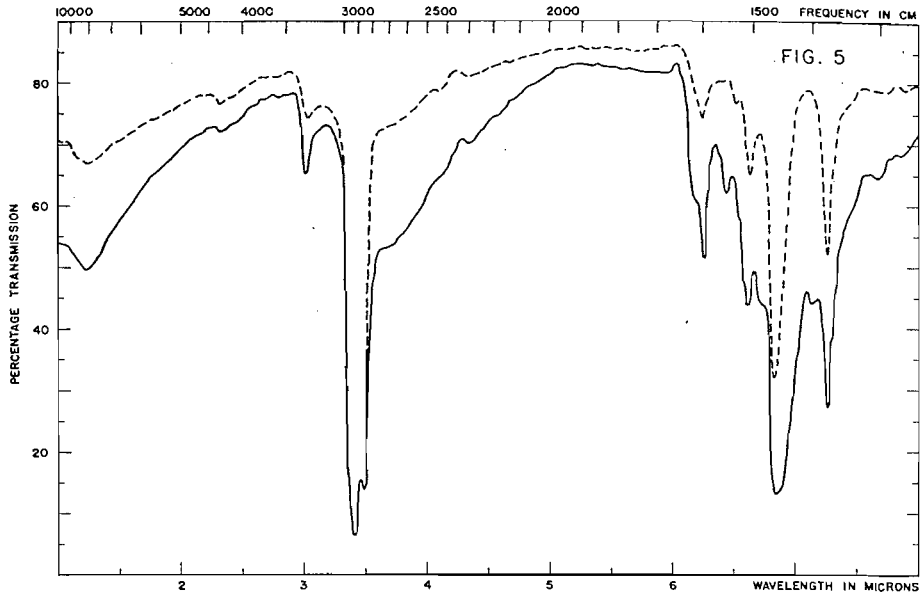



FIG. 5. Infrared absorption spectrum of:
– – – – 4-Octyl-3-phenyl-5-pyrazolone.
———— 4-Benzyl-3-phenyl-5-pyrazolone.

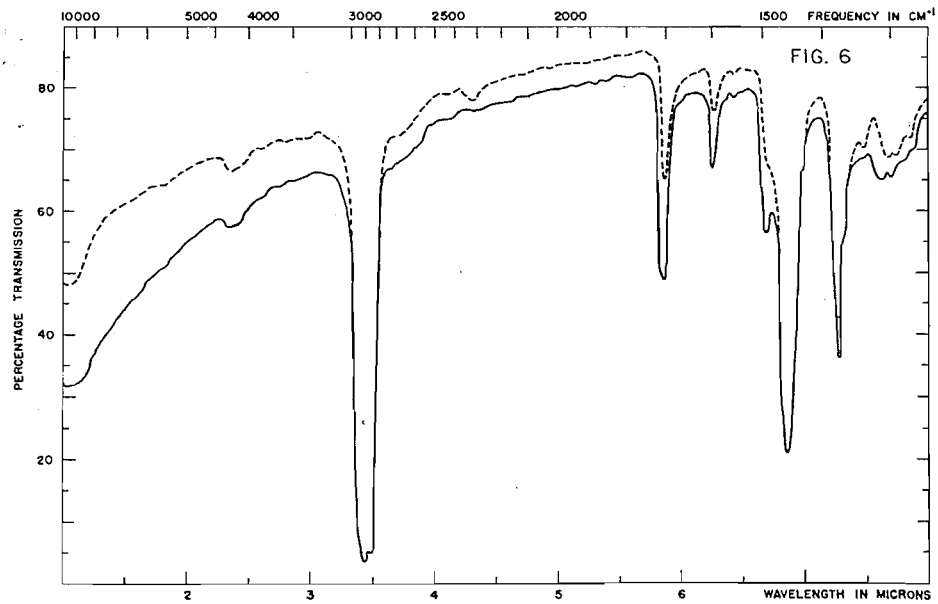



FIG. 6. Infrared absorption spectrum of:
– – – – 4-Ethyl-1,3-diphenyl-5-pyrazolone.
———— 4-Heptyl-1,3-diphenyl-5-pyrazolone.

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pyrazolone is an exception since it shows a band of relatively high intensity at 3300 $cm^{-1}$. This is in agreement with corresponding absorption in this region of another type of pyrazolone, the 4-benzyl-3-amino-5-pyrazolone. It must be noted that the NH frequency also falls in this region, but the absence of the C=O band offers a good indication for the correct assignment of the 3300 $cm.^{-1}$ band to the hydroxyl group.

The remainder of the spectrum is made up of several bands of small intensity. The fact that more than one band is observed in the double-bond region is a fair indication of the presence of conjugation. The most intense absorption in this region occurs at 1600 $cm^{-1}$. If we refer to the results obtained by Randal and his co-workers (17) then this band must be assigned to a cyclic C=N group. The above named authors reported the presence of such a band at about 1610 $cm.^{-1}$ for 3-methyl-5-pyrazolone. The other bands present in this region of the spectra have a very small intensity. They may be tentatively assigned to an ethylenic band or to characteristic phenyl and ring vibrations.

From these assignements, the 4-monosubstituted 3-phenyl-5-pyrazolones may be assumed to exist under structure XI, which is shown in the discussion of the ultraviolet spectra.

The infrared absorption spectra of the 4-monosubstituted-1,3-diphenyl-5-pyrazolones are similar and comparatively less complicated than those of the 3-phenyl-5-pyrazolones since they show but two absorption bands in the double-bond region. The 4-benzyl-1,3-diphenyl-5-pyrazolone is an exception since it shows but one band which is apparently resolved into a triplet with frequencies of 1635, 1615, and 1590 $cm^{-1}$.

A high intensity absorption band appears between 1700 $cm.^{-1}$ and 1710 $cm^{-1}$. Since this is the region in which the C=O group absorbs, this vibration can be attributed to this grouping. This is in accord with the vibration frequency of the C=O in cyclic compounds such as lactamus (17).

The other band, of slightly less intensity, occurs at a frequency of about 1600 $cm^{-1}$. This absorption occurs in the region characteristic of the C=N group. Randal and his co-workers (17) studied a number of cyclic derivatives such as thiazolidines, imidazolines, pyridines, and oxazolones, together with the 3-methyl-5-pyrazolone already mentioned, and they assigned the C=N vibration to the region between 1680 $cm.^{-1}$ and 1590 $cm^{-1}$. From these results the absorption band at 1600 $cm.^{-1}$ can be attributed to the presence of a cyclic C=N group.

The structure of the 4-monosubstituted-1,3-diphenyl-5-pyrazolones can therefore be represented as by formula XII, given in the ultraviolet section.

*X-ray Powder Diffraction*

The use of X-ray powder diffraction for analytical purposes has been extensively used to supplement other procedures. X-ray diffraction may be relied upon to provide a simple, rapid, and direct method of analysis. There are many analytical problems for which only X-ray diffraction can give the required results. This stems from the fact that X-ray diffraction patterns are characteristic of the compounds rather than of the elements or chemical groups present.

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The success of this analytical method is dependent upon an adequate set of reference standards. This remains a fundamental limitation to the method since there are compounds for which crystallographic data are not yet available. The vast majority of published data (1, 11) have been limited to inorganic compounds, very few being for organic compounds.

X-ray powder diffraction patterns for organic compounds are much more complex and exhibit wider diffraction bands than do inorganic compounds. The success of this method for identifying individual members of a homologous series depends upon the extent to which an additional methylene group affects the powder pattern of a typical member of a series. This ability of the analytical method to distinguish between homologues was demonstrated for the anilides of the saturated aliphatic acids by Matthews and Michell (14) and later for the amides of these acids by Wurg and Sharples (19).

To our knowledge no data have been published on the X-ray powder diffraction of pyrazolones. The present work deals with the diffraction patterns of 4-monosubstituted-3-phenyl-5-pyrazolones and 4-monosubstituted-1,3-diphenyl-5-pyrazolones. The results obtained are given in Tables VI and VII and some of the patterns are shown in Figs. 7 to 10. As expected, the patterns are sufficiently different to allow distinction between the members of the homologous series and, therefore, offer a convenient method for the identification of the pyrazolones.

## EXPERIMENTAL PART*

### *Ethyl α-Monosubstituted-α-benzoylacetate*

Ethyl benzoylacetate (1.0 mole) was added to a cold solution of sodium ethoxide (0.5 mole, 300 ml. of absolute alcohol) and the mixture was refluxed for one hour. The required *n*-alkyl bromide (0.5 mole) was then slowly added to the boiling solution and the reaction mixture was refluxed until nearly neutral to moist litmus paper. The precipitated sodium bromide was filtered off and washed with ethanol. The alcoholic filtrate, concentrated under reduced pressure, was poured into cold water (500 ml.) acidified with hydrochloric acid (25 ml.). The viscous layer was decanted and the aqueous layer extracted three times with ether. The extracts were added to the viscous material. The resulting solution was washed with water three times and dried over anhydrous sodium sulphate. The ether was removed under reduced pressure and the residue was fractionated. The esters are listed, together with their boiling points, indices of refraction, and analyses in Table I.

### *4-Monosubstituted-3-phenyl-5-pyrazolones*

Ethyl α-monosubstituted-α-benzoylacetate (0.02 mole) was added to an excess of hydrazine hydrate (0.06 mole) and the mixture was refluxed for five hours in a wax bath maintained at 115°C. The resulting viscous liquid was heated under reduced pressure (10 mm.) at 120 to 130°C. for three hours in order to remove the excess hydrazine hydrate together with the water and ethanol formed in the reaction. The solid obtained was cooled and dissolved

* *All melting points are uncorrected.*

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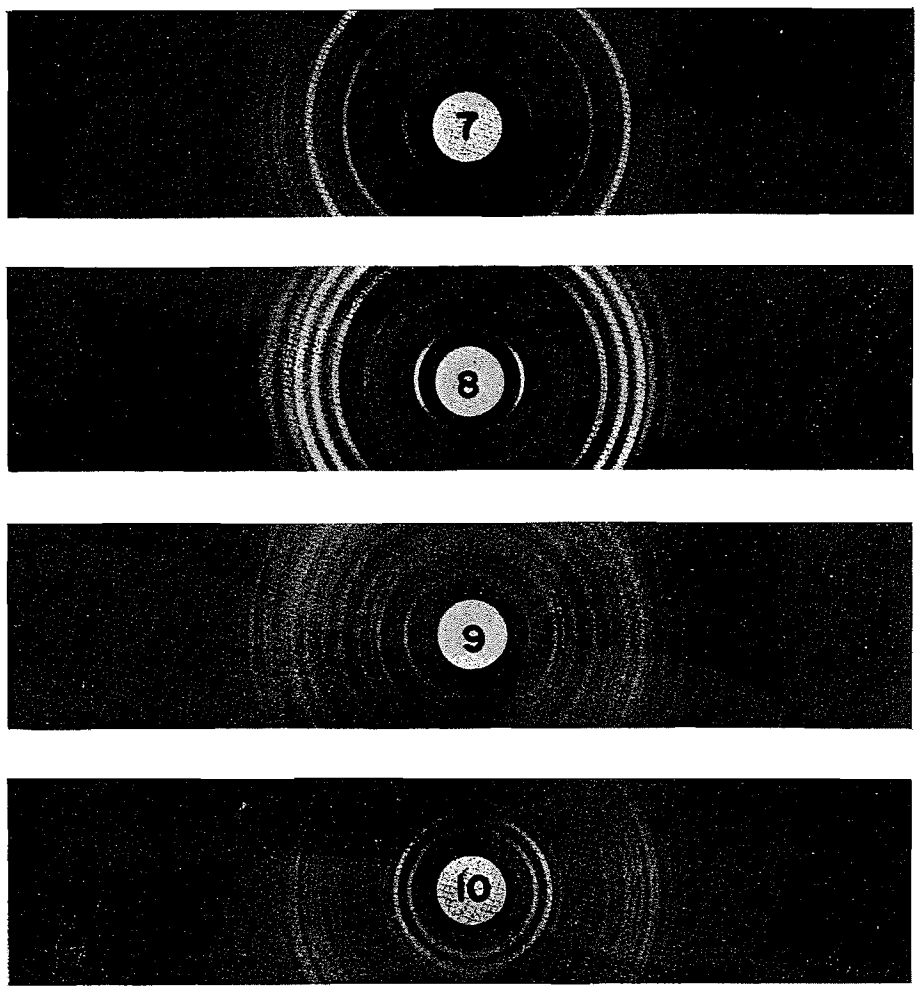



FIG. 7. X-ray powder diffraction pattern of 3-phenyl-5-pyrazolone.
FIG. 8. X-ray powder diffraction pattern of 4-propyl-3-phenyl-5-pyrazolone.
FIG. 9. X-ray powder diffraction pattern of 4-methyl-1,3-diphenyl-5-pyrazolone.
FIG. 10. X-ray powder diffraction pattern of 4-butyl-1,3-diphenyl-5-pyrazolone.

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in sodium hydroxide (5%, 200 ml.). The solution was diluted with water (100 ml.) and washed with ether until the extracts were no longer colored. The alkaline solution was cooled and acidified with acetic acid (50%). The precipitate was filtered, washed with water, and dried. The product was purified by crystallization from ethanol, petroleum ether, or a mixture of the two. The pyrazolones are listed, together with their melting points, analyses, and ultraviolet absorption maxima in Table II. Their infrared absorption bands are given in Table V and their X-ray powder diffraction data in Table VI.

*4-Monosubstituted-1,3-diphenyl-5-pyrazolones*

A mixture of ethyl α-monosubstituted-α-benzoylacetate (0.01 mole) and phenylhydrazine (0.01 mole) was heated for four hours at 110 to 120°C. and for one hour at 180°C. The red viscous liquid obtained was cooled and dissolved in sodium hydroxide (10%, 100 ml.). The solution was diluted with water (100 ml.), filtered to remove the insoluble material, and washed with ether until the extracts were no longer colored. The alkaline solution was cooled to about 0°C. and acidified with acetic acid (50%). The precipitate was filtered, washed with water, and dried. The product was dissolved in ether and the ethereal solution washed with water three times and dried over anhydrous sodium sulphate. The ether was distilled off and the residue obtained was purified by crystallization from a small quantity of ethanol. The pyrazolones are listed together with their melting points, analyses, and ultraviolet absorption maxima in Table III. Their infrared absorption bands are given in Table V and their X-ray powder diffraction data in Table VII.

TABLE V
INFRARED ABSORPTION MAXIMA OF 4-MONOSUBSTITUTED-5-PYRAZOLONES

| R | Absorption bands, $cm.^{-1}$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 3-Phenyl | | | | | | | | 1,3-Diphenyl | | | | |
| H | 3150 | 1590 | 1565 | 1530 | 1500 | 1305 | 1285 | 1260 | 1710 | 1595 | | 1320 | 1275 |
| $CH_3$ | 3290 | 1595 | 1565 | 1530 | 1500 | 1305 | 1285 | 1258 | 1708 | 1600 | | 1305 | |
| $C_2H_5$ | 3200 | 1590 | 1565 | 1530 | 1500 | 1305 | 1285 | 1260 | 1705 | 1598 | 1305 | 1295 | 1275 |
| $C_3H_7$ | | 1600 | 1570 | 1535 | 1510 | 1300 | 1285 | 1265 | 1708 | 1600 | 1315 | 1300 | 1275 |
| $C_4H_9$ | 3300 | 1600 | 1570 | 1535 | 1510 | 1305 | 1285 | 1265 | 1705 | 1595 | 1305 | 1295 | 1260 |
| $C_5H_{11}$ | | 1600 | 1565 | 1530 | 1510 | 1305 | 1275 | 1260 | 1712 | 1602 | 1320 | 1300 | 1280 |
| $C_6H_{13}$ | 3300 | 1600 | 1570 | 1530 | 1508 | 1305 | 1285 | 1265 | 1710 | 1595 | 1305 | 1282 | 1260 |
| $C_7H_{15}$ | 3300 | 1600 | 1570 | 1530 | 1500 | 1305 | 1285 | 1265 | 1705 | 1600 | 1315 | 1298 | 1280 |
| $C_8H_{17}$ | 3330 | 1600 | 1570 | 1530 | 1505 | 1300 | 1285 | 1265 | 1708 | 1600 | 1310 | 1300 | 1275 |
| $C_9H_{19}$ | | 1600 | 1565 | 1555 | 1510 | 1300 | 1285 | 1265 | 1708 | 1600 | 1310 | 1295 | 1272 |
| $C_{10}H_{21}$ | | 1600 | 1575 | 1535 | 1510 | 1300 | 1290 | 1270 | 1708 | 1600 | 1315 | 1300 | 1275 |
| $C_6H_5CH_2$ | 3310 | 1600 | | 1555 | 1510 | 1300 | 1290 | 1270 | | 1625<br>1615<br>1590 | 1325 | 1310 | 1270 |

*Potentiometric Titrations*

The potentiometric titrations were made by a method already described (5). The pyrazolones ($4 \times 10^{-4}$ mole) were dissolved in sodium hydroxide (0.1 *N*, 25 ml.). In the case of the 1,3-diphenyl-5-pyrazolones a small quantity of alco-

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TABLE VI

X-RAY POWDER DIFFRACTION DATA OF 4-MONOSUBSTITUTED-3-PHENYL-5-PYRAZOLONES, $RC_9H_7N_2O$

| R = H | | $CH_3$ | | $C_2H_5$ | | $C_3H_7$ | | $C_4H_9$ | | $C_5H_{11}$ | | $C_6H_{13}$ | | $C_7H_{15}$ | | $C_8H_{17}$ | | $C_9H_{19}$ | | $C_{10}H_{21}$ | | $C_6H_5CH_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I |
| 10.5 | 4 | 8.7 | 6 | 13.3 | 8 | 12.2 | 8 | 12.9 | 5 | 11.0 | 6 | 11.5 | 5 | 15.7 | 5 | 16.6 | 5 | 16.8 | 10 | 18.7 | 7 | 13.2 | 3 |
| 5.40 | 5 | 7.0 | 4 | 10.0 | 2 | 9.9 | 2 | 10.1 | 2 | 8.1 | 3 | 8.2 | 3 | 9.9 | 1 | 9.4 | 2 | 15.1 | 6 | 16.5 | 7 | 8.3 | 1 |
| 4.69 | 1 | 6.33 | 4 | 6.7 | 8 | 7.5 | 4 | 8.2 | 1 | 6.6 | 2 | 6.8 | 2 | 7.9 | 5 | 7.5 | 5 | 7.1 | 4 | 13.1 | 5 | 7.40 | 3 |
| 4.45 | 2 | 5.54 | 2 | 5.81 | 1 | 7.0 | 4 | 7.5 | 1 | 5.93 | 2 | 6.05 | 2 | 7.2 | 2 | 7.1 | 1 | 5.63 | 3 | 10.2 | 2 | 6.30 | 3 |
| 4.16 | 10 | 5.02 | 10 | 5.39 | 4 | 6.45 | 4 | 6.9 | 5 | 5.24 | 5 | 5.37 | 5 | 6.5 | 5 | 6.05 | 3 | 5.11 | 4 | 8.7 | 3 | 5.42 | 5 |
| 3.58 | 3 | 4.78 | 6 | 4.98 | 1 | 5.65 | 2 | 5.56 | 2 | 4.90 | 4 | 5.04 | 3 | 5.50 | 2 | 5.65 | 5 | 4.39 | 10 | 6.65 | 3 | 4.93 | 3 |
| 3.43 | 3 | 4.61 | 10 | 4.54 | 8 | 5.23 | 1 | 5.27 | 5 | 4.35 | 10 | 4.55 | 10 | 4.97 | 5 | 5.26 | 1 | 4.14 | 10 | 5.63 | 5 | 4.66 | 7 |
| 3.24 | 3 | 4.03 | 10 | 4.24 | 8 | 4.96 | 6 | 4.83 | 4 | 4.14 | 2 | 4.32 | 8 | 4.71 | 10 | 4.81 | 5 | 3.55 | 5 | 5.12 | 5 | 4.35 | 10 |
| 3.12 | 2 | 3.65 | 10 | 4.03 | 10 | 4.72 | 1 | 4.48 | 5 | 3.92 | 6 | 4.03 | 9 | 4.34 | 7 | 4.57 | 5 | 3.29 | 1 | 4.73 | 5 | 4.03 | 8 |
| 2.86 | 1 | 3.53 | 2 | 3.70 | 8 | 4.43 | 1 | 4.30 | 7 | 3.58 | 6 | 3.80 | 8 | 4.17 | 8 | 4.45 | 10 | 2.81 | 2 | 4.40 | 10 | 3.53 | 5 |
| 2.71 | 2 | 3.40 | 5 | 3.46 | 4 | 4.27 | 8 | 4.10 | 3 | 3.22 | 4 | 3.33 | 3 | 3.89 | 10 | 4.22 | 1 | 2.46 | 1 | 4.14 | 4 | 3.27 | 5 |
| 2.62 | 1 | 3.25 | 5 | 3.27 | 4 | 3.87 | 10 | 3.86 | 10 | 2.86 | 3 | 2.85 | 3 | 3.74 | 5 | 4.05 | 8 | 8.67 | 1 | 3.97 | 4 | 2.68 | 2 |
| 2.51 | 3 | 2.97 | 4 | 2.99 | 2 | 3.64 | 5 | 3.44 | 4 | 2.72 | 3 | 2.58 | 1 | 3.52 | 3 | 3.95 | 10 | 8.38 | 1 | 3.76 | 5 | 2.22 | 1 |
| 2.41 | 1 | 2.88 | 2 | 2.84 | 1 | 3.29 | 5 | 3.24 | 3 | 2.61 | 2 | 2.04 | 1 | 3.37 | 3 | 3.57 | 5 | | | 3.49 | 3 | 1.92 | 1 |
| 2.33 | 1 | 2.79 | 3 | 2.51 | 1 | 3.01 | 2 | 3.05 | 3 | 2.49 | 1 | | | 3.24 | 1 | 3.30 | 3 | | | 3.30 | 2 | | |
| 2.27 | 1 | 2.72 | 3 | 2.39 | 1 | 2.87 | 4 | 2.91 | 3 | 2.33 | 2 | | | 3.10 | 2 | 3.02 | 6 | | | 3.01 | 1 | | |
| 2.10 | 2 | 2.54 | 1 | 2.01 | 1 | 2.66 | 1 | 2.76 | 3 | 2.20 | 2 | | | 2.76 | 2 | 2.81 | 1 | | | 2.82 | 4 | | |
| 2.005 | 1 | 2.48 | 1 | | | 2.55 | 3 | 2.64 | 4 | | | | | 2.07 | 1 | 2.66 | 1 | | | 2.62 | 1 | | |
| 1.945 | 1 | 2.37 | 1 | | | 2.37 | 2 | 2.54 | 2 | | | | | | | 2.40 | 1 | | | | | | |
| 1.840 | 2 | 2.26 | 1 | | | 2.23 | 1 | 2.23 | 4 | | | | | | | | | | | | | | |
| 1.780 | 1 | 2.165 | 2 | | | 2.10 | 4 | 2.13 | 1 | | | | | | | | | | | | | | |
| 1.738 | 1 | 2.100 | 2 | | | 1.895 | 1 | 1.815 | 1 | | | | | | | | | | | | | | |
| 1.121 | 1 | 2.050 | 1 | | | 1.822 | 1 | | | | | | | | | | | | | | | | |
| 0.865 | 1 | 2.000 | 1 | | | 1.735 | 2 | | | | | | | | | | | | | | | | |
| 0.839 | 1 | 1.781 | 2 | | | 1.683 | 1 | | | | | | | | | | | | | | | | |

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TABLE VII

X-RAY POWDER DIFFRACTION DATA OF 4-MONOSUBSTITUTED-1,3-DIPHENYL-5-PYRAZOLONES, $RC_{15}H_{11}N_2O$

| R = H | | $CH_3$ | | $C_2H_5$ | | $C_3H_7$ | | $C_4H_9$ | | $C_5H_{11}$ | | $C_6H_{13}$ | | $C_7H_{15}$ | | $C_8H_{17}$ | | $C_9H_{19}$ | | $C_{10}H_{21}$ | | $C_6H_5CH_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I | *d/n* | I |
| 9.5 | 8 | 10.6 | 10 | 10.1 | 10 | 10.4 | 9 | 10.4 | 10 | 10.5 | 9 | 9.8 | 1 | 10.5 | 10 | 10.8 | 10 | 11.3 | 10 | 13.5 | 8 | 11.4 | 5 |
| 8.4 | 8 | 7.4 | 10 | 7.5 | 10 | 7.9 | 10 | 8.5 | 10 | 9.0 | 10 | 8.6 | 10 | 9.1 | 1 | 10.3 | 10 | 10.4 | 10 | 12.1 | 10 | 8.9 | 10 |
| 7.0 | 9 | 6.8 | 10 | 7.2 | 10 | 7.3 | 3 | 7.9 | 2 | 8.0 | | 7.9 | 2 | 8.3 | 1 | 8.6 | 3 | 7.6 | 9 | 9.3 | 2 | 7.1 | 2 |
| 5.9 | 9 | 6.3 | 9 | 5.3 | 9 | 6.7 | 3 | 7.4 | 9 | 7.5 | 9 | 7.4 | 1 | 6.9 | 8 | 7.4 | 5 | 7.1 | 7 | 8.7 | 10 | 6.7 | 1 |
| 5.6 | 7 | 6.1 | 10 | 4.94 | 9 | 6.0 | 1 | 6.3 | 3 | 6.5 | 2 | 7.0 | 1 | 6.2 | 1 | 6.9 | 5 | 6.6 | 2 | 8.3 | 2 | 5.9 | 9 |
| 5.2 | 7 | 5.18 | 9 | 3.92 | 9 | 5.7 | 3 | 6.0 | 3 | 6.1 | 2 | 6.7 | 1 | 5.9 | 1 | 5.5 | 1 | 5.9 | 4 | 7.3 | 9 | 5.6 | 7 |
| 4.91 | 9 | 4.55 | 9 | 3.77 | 7 | 5.2 | 9 | 5.5 | 4 | 5.7 | 2 | 6.4 | 1 | 5.6 | 2 | 5.31 | 9 | 5.6 | 4 | 5.8 | | 5.4 | 8 |
| 4.22 | 7 | 4.13 | 9 | 3.53 | 10 | 4.67 | 3 | 5.21 | 3 | 5.2 | 8 | 5.7 | 4 | 5.4 | 2 | 4.79 | 9 | 5.4 | 7 | 5.3 | 9 | 5.1 | 8 |
| 4.14 | 9 | 3.89 | 2 | 3.35 | 9 | 4.32 | 3 | 4.91 | 7 | 4.85 | 10 | 5.2 | 3 | 5.2 | 1 | 4.34 | 1 | 4.91 | 4 | 5.0 | 9 | 4.86 | 6 |
| 3.99 | 8 | 3.79 | 10 | 3.16 | 1 | 4.04 | 9 | 4.57 | 4 | 4.35 | 4 | 4.69 | 6 | 4.94 | 9 | 4.20 | 7 | 4.73 | 4 | 4.8 | 1 | 4.69 | 8 |
| 3.60 | 10 | 3.63 | 2 | 3.02 | 1 | 3.73 | 8 | 4.28 | 8 | 4.16 | 4 | 4.24 | 2 | 4.64 | 1 | 4.05 | 8 | 4.40 | 1 | 4.6 | 5 | 4.56 | 8 |
| 3.32 | 9 | 3.56 | 1 | 2.86 | 1 | 3.58 | 8 | 4.06 | 8 | 4.05 | 4 | 4.12 | 2 | 4.15 | 1 | 3.79 | 7 | 4.06 | 3 | 4.4 | 1 | 4.37 | 5 |
| 3.19 | 8 | 3.35 | 3 | 2.59 | 1 | 3.45 | 8 | 3.91 | 8 | 3.75 | 8 | 3.89 | 9 | 4.05 | 1 | 3.58 | 7 | 3.89 | 2 | 4.2 | 9 | 4.18 | 9 |
| 2.99 | 5 | 3.27 | 3 | 2.48 | 1 | 2.86 | 1 | 3.71 | 9 | 3.61 | 7 | 3.81 | 8 | 3.74 | 7 | 3.46 | 8 | 3.61 | 1 | 4.0 | 9 | 4.05 | 10 |
| 2.80 | 5 | 3.15 | 1 | 2.26 | 1 | 2.60 | 1 | 3.58 | 8 | 3.43 | 7 | 3.58 | 7 | 3.58 | 1 | 3.26 | 1 | 3.52 | 1 | 3.8 | 5 | 3.91 | 2 |
| 2.54 | 5 | 3.05 | 1 | 2.22 | 1 | | | 3.37 | 7 | 3.30 | 1 | 3.44 | 7 | 3.43 | 7 | 2.83 | 1 | 3.35 | 1 | 3.7 | 3 | 3.75 | 8 |
| 2.32 | 1 | 2.89 | 1 | | | | | 3.29 | 2 | | | 3.14 | 6 | 3.17 | 1 | 2.11 | 1 | 3.26 | 1 | 3.6 | 9 | 3.64 | 8 |
| | | 2.71 | 1 | | | | | 3.13 | 4 | | | 2.88 | 6 | 2.98 | 1 | | | | | 3.5 | 2 | 3.52 | 9 |
| | | 2.58 | 1 | | | | | 2.89 | 1 | | | | | 2.82 | 1 | | | | | 3.4 | 2 | 3.32 | 7 |
| | | 2.41 | 1 | | | | | 2.82 | 1 | | | | | 2.11 | 1 | | | | | 2.9 | 2 | 3.14 | 8 |
| | | 2.26 | 1 | | | | | 2.73 | 1 | | | | | | | | | | | 2.6 | 1 | 3.07 | 8 |
| | | 2.10 | 1 | | | | | 2.03 | 1 | | | | | | | | | | | | | 2.94 | 2 |
| | | 1.91 | 1 | | | | | | | | | | | | | | | | | | | 2.69 | 2 |
| | | 1.78 | 1 | | | | | | | | | | | | | | | | | | | 2.57 | 1 |
| | | | | | | | | | | | | | | | | | | | | | | 2.52 | 4 |

hol was added to increase their solubility. The solution was diluted with water (200 ml.) and titrated with standard hydrochloric solution (0.1 *N*). The pH values were recorded with a Beckman pH meter, Model H 2. The results are given in Table IV and shown graphically in Figs. 1 and 2.

*Ultraviolet Absorption Spectra*

The ultraviolet absorption spectra of the pyrazolones were taken on a Beckman Spectrophotometer Model DU in the same way as previously described (9). The values obtained were plotted as log $E_m$ against the wave lengths in Angstrom units. The solvents employed were ethanol (95%) and a solution of hydrochloric acid (0.01 *N*) in ethanol. The results are listed in Tables II and III and some of the data are plotted in Figs. 3 and 4.

*Infrared Absorption Spectra*

All the infrared absorption spectra of the pyrazolones were obtained with a Perkin-Elmer Model 21 double-beam null principle recording spectrophotometer. The pyrazolones were mulled in Nujol in an agate mortar until a uniform paste was obtained. The mulled samples were placed between two freshly polished rock salt plates and spread out into a uniform film by applying normal pressure. Visual observation of the sample through the plates quickly indicated whether a satisfactorily dispersed film had been obtained.

Infrared absorption spectra were then run and the resulting spectra interpreted. Over the whole range of the spectrum, from 10,000 to 650 $cm.^{-1}$, a given slit width was used for every wave length and these slit widths were the same for each pyrazolone. Only the portion of the spectra covering the range from 10,000 to 1250 $cm.^{-1}$ is given in Figs. 5 and 6. The curves all show the four specific bands of Nujol, a strong doublet at 2950 and 2850 $cm.^{-1}$ and two medium strong absorptions at 1460 and 1375 $cm^{-1}$. The other bands are given in Table V and have been discussed in the theoretical part.

*X-ray Powder Diffraction*

The pyrazolones were ground to a suitable state of subdivision in an agate mortar and mounted on Lindeman glass fibers with the aid of a little vaseline. The procedure was found adequate for the identification of the substances concerned.

The photographs were taken in a cylindrical camera having a diameter of 114.59 mm. All the samples were rotated during the 2.5 to 3.0 hr. exposure. The determinations were made on a North American Phillips diffraction unit with the copper K$\alpha$ ($\lambda$ = 1.5387 *kx*) radiation.

The values recorded in Tables VI and VII were determined from the patterns in the usual manner.

The calculated interplanar spacings are expressed in *kx* units. The corresponding intensities were determined visually and the values recorded are the relative intensities, the most intense line being taken as 10 units. Some of the patterns are shown in Figs. 7 to 10.

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# THE ALPHA AND BETA 1,3,4,6-TETRAACETYL-D-GLUCOPYRANOSES AND THEIR CHLOROACETYL DERIVATIVES[1]

By R. U. Lemieux and G. Huber[2]

ABSTRACT

Reaction of 3,4,6-triacetyl-β-D-glucopyranosyl chloride with silver acetate in acetic acid gave 1,3,4,6-tetraacetyl-α-D-glucopyranose, m.p. 97–98°C., $[\alpha]_D$ +145° (chloroform). 3,4,6-Triacetyl-α-D-glucopyranosyl chloride, m.p. 93–94°C., $[\alpha]_D$ +185° (chloroform), prepared from the β-anomer by isomerization in acetone, with silver acetate in acetic acid gave 1,3,4,6-tetraacetyl-β-D-glucopyranose, m.p. 137–138°C., $[\alpha]_D$ +26° (chloroform). The structures of these glucose tetraacetates were established by the interconversion of chloroacetyl derivatives.

Our studies of the properties of the pentaacetylglucopyranoses (16, 17, 18) have established the strong activating effect of C2-acetoxy group participation in dissociation of the Cl to acetoxy group bond of the 1,2-*trans*-β-anomer. It was now of interest to examine the effect of altering the C2-substituent on the ease of dissociation and for this the anomeric 1,3,4,6-tetraacetyl-D-glucopyranoses were desirable starting materials.

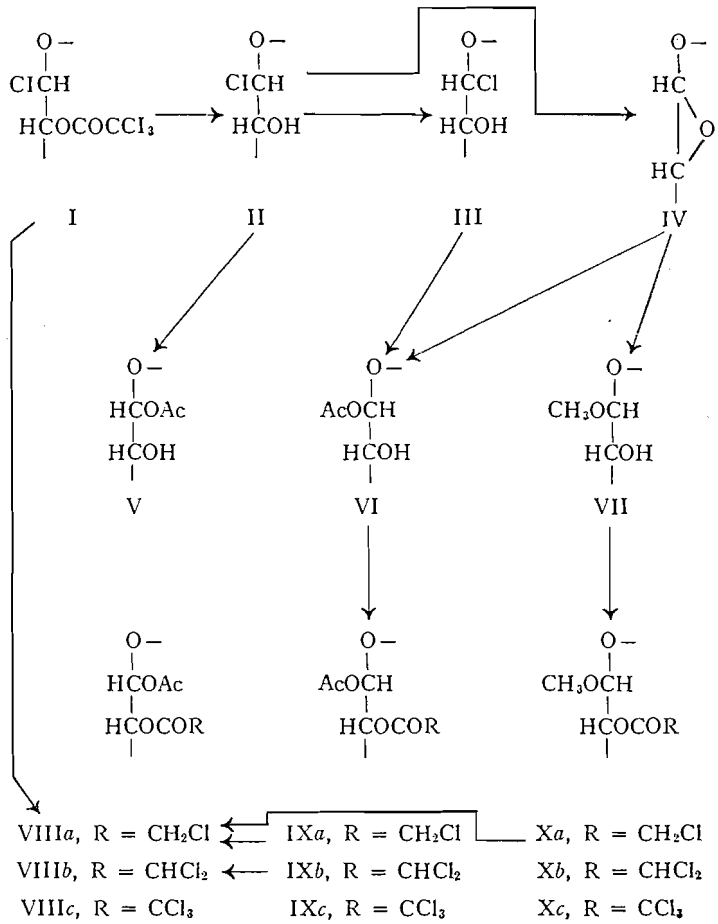
In 1921, Brigl (5) reported the preparation of 2-trichloroacetyl-triacetyl-β-D-glucopyranosyl chloride (I) by reaction of pentaacetyl-β-D-glucopyranose with phosphorus pentachloride. Ammonia in ether was shown to preferentially remove the trichloroacetyl group to yield 3,4,6-triacetyl-β-D-glucopyranosyl chloride (II). The chloride (II) was shown to mutarotate in acetone solution to yield a strongly dextrorotatory sirupy product presumed to be the α-anomer (III). In re-examining these reactions we have found the yield of I to be much more reproducible and substantially increased by lengthening the reaction time from 2.5 hr. to 5 hr. and by adding carbon tetrachloride to hasten attainment of homogeneity. Further, we have crystallized III, and its chemical properties agree with the structure proposed by Brigl.

Later, Brigl (6) reported the preparation of triacetyl-D-glucosan ⟨1,5⟩ α ⟨1,2⟩ (Brigl's anhydride) (IV) by treating the β-chloride (II) with an excess of ammonia in dry benzene. Brigl (6) discovered that the anhydride (IV) reacts with methanol at room temperature to yield methyl 3,4,6-triacetyl-β-D-glucopyranoside (VII). Hardegger and de Pascual (10) found that reaction of the anhydride (IV) with acetic acid gave a glucose tetraacetate, m.p. 131°C., $[\alpha]_D$ +28° (chloroform), which was presumed to be 1,3,4,6-tetraacetyl-β-D-glucopyranose (VI). We have obtained the same substance, m.p. 137–138°C., $[\alpha]_D$ +26° (chloroform), in high yield by reaction of the 3,4,6-triacetyl-α-D-glucopyranosyl chloride (III) with silver acetate in acetic acid. Gakhokidze (8) has reported the preparation of 1,3,4,6-tetraacetyl-β-D-glucopyranose with melting point 138°C. The rotation

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was not reported and an error may have been made (7, p. 40) in reporting the preparative procedure. Reaction of 3,4,6-triacetyl-β-D-glucopyranosyl chloride (II) with silver acetate in acetic acid gave 1,3,4,6-tetraacetyl-α-D-glucopyranose (V), m.p. 97–98°C., $[\alpha]_D$ +145° (chloroform), in high yield. The yield was much lower when ether was used as solvent. Proofs for the structures of these glucose tetraacetates (V and VI) are described below.

Trichloroacetylation of the α-tetraacetate (V) yielded a trichloroacetyl-tetraacetyl-α-D-glucose (VIII*c*) which was identical to that obtained on reaction of 2-trichloroacetyl-triacetyl-β-D-glucopyranosyl chloride (I) with silver acetate in acetic acid. Therefore, the substance (V) must be 1,3,4,6-tetraacetyl-α-D-glucopyranose. Monochloroacetylation of V gave a product (VIII*a*) which was also obtained by anomerization of the product from the monochloroacetylation of the β-tetraacetate (VI). Therefore, the latter substance (VI) must be 1,3,4,6-tetraacetyl-β-D-glucopyranose. These conclusions were substantiated in a variety of ways. Trichloroacetylation of VI yielded a

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product (IX*c*) with the physical constants reported by Brigl (5) for 2-trichloroacetyl-tetraacetyl-β-D-glucopyranose. Dichloroacetylation of VI yielded 2-dichloroacetyl-tetraacetyl-β-D-glucopyranose (IX*b*) and anomerization of this product gave a substance identical to that (VIII*b*) obtained on dichloroacetylation of the α-tetraacetate (V). Finally, the 2-monochloroacetyl-tetraacetyl-β-D-glucopyranose (IX*a*) was shown to be different to the monochloroacetyl-tetraacetyl-β-D-glucopyranoses which contain the monochloroacetyl group at positions 1, 4, or 6. This precaution seemed warranted since acetyl migrations are known (12, 13) which involve positions 1, 2, 4, and 6 of the glucopyranose molecule.

The 2-monochloroacetyl, 2-dichloroacetyl, and 2-trichloroacetyl derivatives (X*a*, X*b*, and X*c*, respectively) of methyl 3,4,6-triacetyl-β-D-glucopyranoside were prepared (see Table I). The structure of the monochloroacetyl derivative (X*a*) was corroborated by acetolysis to the 2-monochloroacetyl-tetraacetyl-α-D-glucopyranose (VIII*a*).

## THEORETICAL CONSIDERATIONS

Lemieux (16) has pointed out that participation of the C2-acetoxy group in replacement of the Cl-acetoxy group of pentaacetyl-β-D-glucopyranose affords a reasonable account for the preferential chlorination of the C2-acetoxy group by phosphorus pentachloride to yield 2-trichloroacetyl-triacetyl-β-D-glucopyranosyl chloride (I). Abramovitch (1) has suggested that the preferential chlorination of the C2-acetoxy group may be due to the −I effect of a chlorine atom at Cl.

The formation of the 1,2-*cis*-α-anomer (VIII*c*) as the main product from the reaction of 2-trichloroacetyl-triacetyl-β-D-glucopyranosyl chloride (I) with silver acetate in acetic acid should be contrasted with the usual tendency for acetohalogenosugars to yield 1,2-*trans*-acetates under these reaction conditions (19). This result is in agreement with the conclusion (17) that the trichloroacetyl group has little tendency for participation in replacements at a neighboring carbon atom. Hickinbottom (14) has prepared α-glucosides by reaction of 2-trichloroacetyl-triacetyl-β-D-glucopyranosyl chloride (I) under the conditions of the Koenigs-Knorr reaction. The formation of the α-tetraacetate (V) from the β-chloride (II) in 81% yield by reaction with silver acetate in acetic acid was to be expected on the basis of the conclusion reached by Winstein and Grunwald (20) that neighboring hydroxyl groups show little tendency for participation in replacement reactions. The formation of the β-tetraacetate (VI) from the α-chloride (III) in 79% yield under the same reaction conditions indicates that this reaction was also free of appreciable neighboring group participation. This result could not be predicted since evidence exists (2) that the C6-oxygen atom of glucose can participate in replacement reactions at the anomeric center. It is of interest to note that Hardegger and Montavon (11) have prepared ethyl α-D-isorhamnoside from 3,4-diacetyl-β-D-isorhamnosyl chloride and ethyl β-D-isorhamnoside from 3,4-diacetyl-α-D-isorhamnosyl chloride. The high yields of the Walden inversion products obtained in these reactions suggest that the transformations took

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TABLE I
SOME DERIVATIVES OF D-GLUCOPYRANOSES

| Compound | M.p., °C. | $[\alpha]_D^a$ | $[M]_D$ | $A^b$ | $B^b$ | % Carbon | | % Hydrogen | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calc. | Found | Calc. | Found | |
| Derivatives of tetraacetyl-D-glucopyranoses | | | | | | | | | | |
| α-1,3,4,6- (V) | 97–98 | 145° | 50,500 | ±20,700 | 29,800 | 48.27 | 48.57 | 5.78 | 5.82 | |
| β-1,3,4,6- (VI) | 137–138 | 26 | 9000 | | | | | | | *c* |
| α-2-Monochloroacetyl (VIII*a*) | 143–144 | 98 | 41,600 | ±18,700 | 22,900 | 45.23 | 45.19 | 4.98 | 5.01 | |
| β-2-Monochloroacetyl (IX*a*) | 118–118.5 | 9.8 | 4200 | | | | 45.03 | | 5.02 | |
| α-2-Dichloroacetyl (VIII*b*) | 128–129 | 97 | 44,500 | ±18,800 | 25,700 | 42.00 | 41.87 | 4.38 | 4.39 | |
| β-2-Dichloroacetyl (IX*b*) | 134–135 | 15.3 | 6900 | | | | 41.84 | | 4.36 | |
| α-2-Trichloroacetyl (VIII*c*) | 121–123 | 93 | 45,900 | ±18,600 | 27,400 | 38.92 | 39.08 | 3.88 | 3.89 | *d* |
| β-2-Trichloroacetyl (IX*c*) | 165–166 | 17.9 | 8800 | | | | 38.99 | | 3.88 | *e* |
| β-1-Monochloroacetyl | 134–134.5 | −1.39 | | | | | | | | (4) |
| β-4-Monochloroacetyl | 117–118 | 3 | | | | 45.23 | 44.98 | 4.98 | 4.93 | |
| β-6-Monochloroacetyl | 145–145.5 | 10 | | | | 45.23 | 45.03 | 4.98 | 4.95 | |
| Derivatives of methyl triacetyl-β-D-glucopyranoside | | | | | | | | | | |
| 2-Monochloroacetyl (X*a*) | 97.5–98 | −5.3 | | | | 45.40 | 45.63 | 5.34 | 5.32 | |
| 2-Dichloroacetyl (X*b*) | 101–102 | 4.4 | | | | 41.77 | 41.55 | 3.72 | 4.68 | |
| 2-Trichloroacetyl (X*c*) | 108.5–109 | 8 | | | | 38.68 | 38.57 | 4.11 | 4.11 | |

[a] *Unless otherwise stated the rotations were measured in chloroform, (c, 0.8–1 in the temperature range 22–26°C).* [b] *Values calculated on the basis of Hudson's rules of isorotation.* [c] *Lit. (10), m.p. 131°C.,* $[\alpha]_D$ *+28° (c, 1.3 in chloroform).* [d] *Lit. (5), m.p. 120°C.,* $[\alpha]_D^{14}$ *+101.5° (c, 2.5 in nitrobenzene).* [e] *Lit. (5), m.p. 167°C.,* $[\alpha]_D^{15}$ *+28.8° (c, 3 in nitrobenzene).*

place by the $S_N2$ type of mechanism proposed by Isbell and Frush (15) for the reaction of α-acetobromoglucose with methanol in the presence of silver carbonate.

## EXPERIMENTAL

### *Methods*

The specific rotations were measured at room temperature, 22–26°C. The melting points are corrected.

*2-Trichloroacetyl-triacetyl-β-D-glucopyranosyl Chloride* (I) (*5*)

Pentaacetyl-β-D-glucopyranose, 78 gm., phosphorus pentachloride, 177 gm., and 40 ml. of carbon tetrachloride were heated under reflux for five hours. The mixture was evaporated in the vacuum of a water aspirator to a bath temperature of about 85°C. The sirupy residue was dissolved in 160 ml. of dry ether and the clarified solution was left overnight at −10°C. The crystalline deposit was washed first with 20 ml. of cold methanol then with 20 ml. of dry ether. The yield was 38 gm., 40%, of material, m.p. 132–138°C., $[\alpha]_D$ +14° (chloroform). After two recrystallizations from ether, the substance, $[\alpha]_D$ +8.9° (*c*, 1.4 in chloroform) melted at 140–142°C. Brigl (5) has reported m.p. 142°C., $[\alpha]_D$ +2.95° (*c*, 7.4 in benzene).

*3,4,6-Triacetyl-α-D-glucopyranosyl Chloride*

3,4,6-Triacetyl-β-D-glucopyranosyl chloride (5), 4.00 gm., was dissolved in 250 ml. of dry acetone. After four days at room temperature (5), the solution was evaporated *in vacuo* to sirup which was dissolved in ether. Hexane was added to near turbidity and the solution was left at 0°C. for several days. There was deposited 3.70 gm., 92.5% yield, of crystalline compound, m.p. 90–91.5°. Four recrystallizations from ether–hexane mixture raised the melting point to 93–94°C. with $[\alpha]_D$ +185° (*c*, 1.2 in chloroform). Calc. for $C_{12}H_{17}O_8Cl$: C, 44.38; H, 5.28; Cl, 10.9%. Found: C, 44.18; H, 5.22; Cl, 11.0%.

*1,3,4,6-Tetraacetyl-α-D-glucopyranose* (V)

3,4,6-Triacetyl-β-D-glucopyranosyl chloride (II), m.p. 156–158°C., $[\alpha]_D$ +28.7° (*c*, 1.1 in chloroform) (5), 1.95 gm., and silver acetate, 1.08 gm., were shaken with 20 ml. of acetic acid for six hours. The silver salts were removed by filtration and the acetic acid by distillation *in vacuo* to yield a sirup which was dissolved in a little ether. The solution was clarified and left overnight at −10°C. A crystalline product, m.p. 90–96°C., 1.40 gm., was formed. A second crop, 0.30 gm., was obtained from the mother liquor to raise the yield to 81%. The purified material is reported in Table I. Reaction of 3,4,6-triacetyl-β-D-glucopyranosyl chloride (II) 1 mM., with silver acetate, 3 mM., in 5 ml. ether for two hours gave the same material in 43% yield. Gakhokidze (8) has reported the use of silver carbonate instead of silver acetate under these conditions to yield 1,3,4,6-tetraacetyl-β-D-glucopyranose. It has been suggested (7, p. 40) that silver acetate was probably the reagent actually used. However, Gakhokidze's product melted at 138°C. and was probably of low specific rotation since he believed the substance to be a β-D-anomer.

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*1,3,4,6-Tetraacetyl-β-D-glucopyranose* (VI) (10)

(*a*) The following reaction conditions are essentially those reported by Hardegger and de Pascual (10). Pure Brigl anhydride (IV), m.p. 59–60°C., $[\alpha]_D$ +73° (*c*, 0.8 in chloroform), was prepared by the method of Gladding and Purves (9). The anhydride, 5.8 gm., was dissolved at 20°C. in 50 ml. of pure acetic acid. After five hours, the acetic acid was removed by distillation *in vacuo* at 30°C. The sirupy product crystallized from ether at −10°C. to yield 5.2 gm., 74%, of product, m.p. 128–130°C. Several recrystallizations from ethanol gave a pure substance, m.p. 136–137°C., $[\alpha]_D$ +26° (*c*, 0.8 in chloroform). Hardegger and de Pascual have reported, m.p. 131°C., $[\alpha]_D$ +28° (*c*, 1.3 in chloroform).

(*b*) A mixture of 650 mgm. 3,4,6-triacetyl-α-D-glucopyranosyl chloride, 350 mgm. silver acetate and 10 ml. of acetic acid was shaken at room temperature for six hours. Benzene, 10 ml., was added, the silver salts were removed by filtration, and the filtrate was evaporated *in vacuo* to a crystalline residue. The substance was dissolved in ether and hexane was added to turbidity. On standing at 0°C., 550 mgm., 79% yield, of a crystalline substance, m.p. 133–134°C., was deposited. Five recrystallizations from ethanol–hexane mixture raised the melting point to 137–138°C., $[\alpha]_D$ +26° (*c*, 0.9 in chloroform). The substance did not depress the melting point of the above described preparation and gave the same monochloroacetyl derivative (IX*a*).

*Methyl 3,4,6-Triacetyl-β-D-glucopyranoside* (VII)

This substance, m.p. 94–95°C., $[\alpha]_D$ +19° (*c*, 1 in chloroform), was prepared in the manner described by Gladding and Purves (9).

*Monochloroacetylations*

The glucose derivative, 4 mM., was dissolved in 15 ml. of dry benzene and 2 ml. of dry pyridine. Monochloroacetic anhydride, 10 mM., was added to the solution cooled to 0°C. After one hour, the mixture was left at room temperature for two hours. Chloroform, 50 ml., was added and the solution washed twice with ice-cold 20% hydrochloric acid, once with cold water, and finally with aqueous sodium bicarbonate solution. The colorless chloroform solution was evaporated *in vacuo* to a sirupy residue which was crystallized from ethanol. The yields of crude crystalline product were in the range 85–95%. The purified products from the monochloroacetylations of IV, V, VI, 1,2,3,6-tetraacetyl-β-D-glucopyranose (13) and 1,2,3,4-tetraacetyl-β-D-glucopyranose (13) are reported in Table I.

*Dichloroacetylations*

Dichloroacetyl chloride, b.p. 107–108°C., $n_D^{25}$ 1.481, was used as acylating agent. The reaction conditions were essentially the same as described above for the monochloroacetylations. The reaction mixtures developed a dark reddish brown coloration. Consequently, the chloroform extract, freed from pyridine, was decolorized by percolation through Magnesol before concentration. The yields of crude crystalline product were in the range 75–80%. The purified compounds derived from IV, V, and VI are reported in Table I.

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*Trichloroacetylations*

Trichloroacetyl chloride, b.p. 116–118°C., $n_D^{25}$ 1.468, was used as acylating agent and the reaction conditions were essentially as described above for the monochloroacetylations. The yields of crude crystalline product were in the range 80–95%. The purified derivatives obtained from IV, V, and VI are reported in Table I.

*Anomerizations and Acetolyses*

The substance, 1 mM., was dissolved in 10 ml. of 50: 50 acetic acid – acetic anhydride mixture 0.5 *M* with respect to sulphuric acid (3). The solution was kept at 25°C. for the specified time and then poured into ice-water mixture which contained sufficient sodium acetate to combine with the sulphuric acid. In each case, a crystalline precipitate formed on allowing the solution to stand overnight at 4°C.

2-Monochloroacetyl-tetraacetyl-β-D-glucopyranose (IX*a*), 0.425 gm., after 7.5 hr. reaction time gave 0.32 gm., 78%, of material, m.p. 138–139°C. After several recrystallizations from ethanol the melting point was 142–144°C. This melting point was not depressed by admixture of the 2-monochloroacetyl-tetraacetyl-α-D-glucopyranose (VIII*a*).

Acetolysis of methyl 2-monochloroacetyl-triacetyl-β-D-glucopyranoside (X*a*), 400 mgm., for 6.5 hr. gave 0.21 gm., 48%, of material, m.p. 138–140°C. and this melting point was not depressed by 2-monochloroacetyl-tetraacetyl-α-D-glucopyranose (VIII*a*).

2-Dichloroacetyl-tetraacetyl-β-D-glucopyranose (IX*b*), 460 mgm., after 24 hr. reaction time gave 300 mgm., 65%, of material, m.p. 114–120°C. Several recrystallizations from ethanol raised the melting point to 127–129°C. and this melting point was unchanged by 2-dichloroacetyl-tetraacetyl-α-D-glucopyranose (VIII*b*).

*2-Trichloroacetyl-tetraacetyl-α-D-glucopyranose*

2-Trichloroacetyl-triacetyl-β-D-glucopyranosyl chloride (I), 4.7 gm., was shaken with silver acetate, 1.8 gm., in 100 ml. of acetic acid for 14 hr. at room temperature. The product, isolated in the usual manner, was crystallized from ethanol to yield 4.8 gm., 82%, of material, m.p. 114–118°C. After several recrystallizations from ether, the melting point was 120–122°C. and $[\alpha]_D$ +93° (*c*, 0.8 in chloroform). The melting point was not changed by admixture of 2-trichloroacetyl-tetraacetyl-α-D-glucopyranose (VIII*c*) (see Table I).

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# THE TAUTOMERISM OF 2-NITRAMINOPYRIDINES[1]

By Alfred Taurins and Silvio J. Viron[2]

ABSTRACT

The nitration of 2-amino-4,6-dimethylpyridine with a mixture of nitric and sulphuric acids gives 4,6-dimethyl-2-nitramino-5-nitropyridine (III). 2-Nitraminopyridine (I), 4-methyl-2-nitraminopyridine (II), and (III) produce with diazomethane methyl derivatives of their tautomeric nitramino and nitrimino forms. Diazoethane gives with (I) both the expected ethyl derivatives. However, from (II) only the ethyl derivative of the nitramino form has been obtained. Diazopropane produces with (I) or (II) the propyl derivatives of the nitramino forms only. The resonance structures of the two tautomeric forms of 2-nitraminopyridine have been advanced.

## INTRODUCTION

The study of nitraminopyridines (2–8, 10, 11, 13) was started by Tschitschibabin in 1914 with the nitration of 2-aminopyridine and its derivatives using a mixture of nitric and sulphuric acids as the nitrating agent.

Two of the chemical properties of 2-nitraminopyridines are of great interest; firstly, their ability to rearrange into 2-amino-3-nitro-, and 2-amino-5-nitropyridines by the action of concentrated sulphuric acid at moderate temperature, and secondly, their acidic nature. The acidic nature of 2-nitraminopyridines is associated with the mobility of the hydrogen atom of the nitramino group and formation of tautomeric nitramino (IA) and nitrimino (IB) forms.

Tschitschibabin and his co-workers studied the tautomerism of 2-nitraminopyridines by methylation with dimethyl and diethyl sulphate in alkaline solution. From 2-nitraminopyridine he obtained only alkyl derivatives of the nitrimino form (12). However, 5-nitro-2-nitraminopyridine (9) and 3,5-dibromo-2-nitraminopyridine (10) on methylation gave methyl derivatives of both the nitramino and nitrimino forms.

Although the methylated derivatives of both tautomeric forms of 2-nitraminopyridines in most cases were obtained, no actual proof of the original structure of these compounds was presented, because dimethyl sulphate actually methylated the sodium salt of these compounds in which 2-nitraminopyridines existed in the form of anions. Therefore we decided to investigate the direct alkylation of the three 2-nitraminopyridines with diazomethane, diazoethane, and diazopropane.

## DISCUSSION

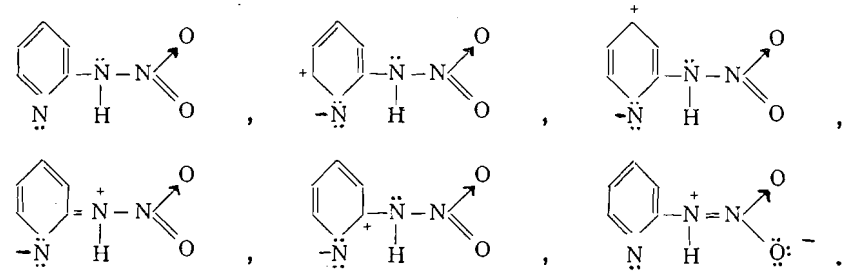
Several resonating structures can be assigned to both of the tautomeric forms of 2-nitraminopyridine, taking into account the mobility of the unshared electron pairs of both nitrogen atoms and $\pi$-electrons of the pyridine ring (Chart I). The consideration of the resonance hybrid structures (IA) and (IB)

[1] *Manuscript received May 13, 1953.*
*Contribution from the Organic Chemistry Laboratory, McGill University, Montreal, Quebec, with the financial assistance of the National Research Council of Canada, Ottawa. Presented before the 36th Annual Conference of the Chemical Institute of Canada, June 5, 1953, Windsor, Ontario.*

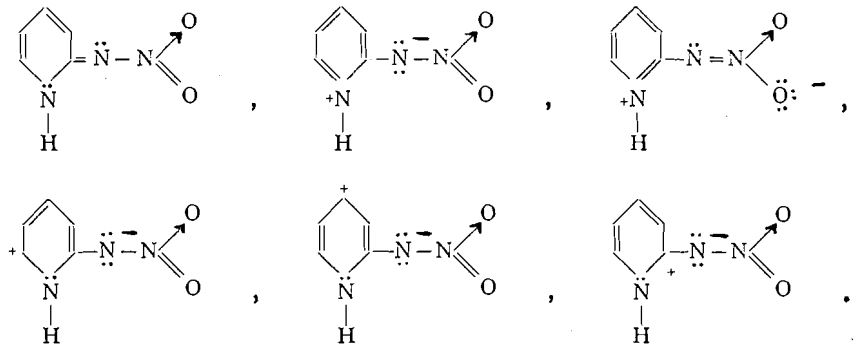
[2] *Holder of a National Research Council Studentship 1951–1952.*



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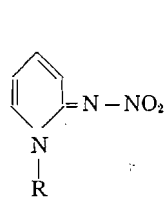


(IA) 2-Nitraminopyridine

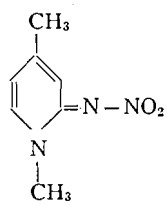


(IB) 2-Nitriminopyridine

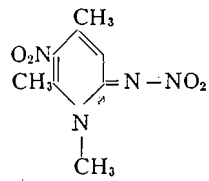
CHART I. The electronic structure of 2-nitraminopyridine.



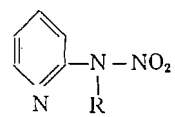
IV: R = $CH_3$
X: R = $C_2H_5$



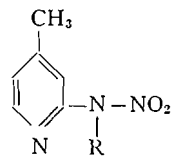
V



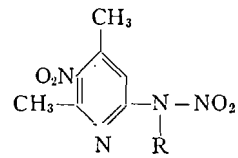
VIII



VI: R = $CH_3$
XI: R = $C_2H_5$
XIII: R = $C_3H_7$



II: R = H
VII: R = $CH_3$
XII: R = $C_2H_5$
XIV: R = $C_3H_7$



III: R = H
IX: R = $CH_3$

CHART II

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reveals that both of them must be approximately of the same stability because the competitive −M effects of the nitro group and pyridine nitrogen atom favor the existence of equal number of resonance structures of each tautomeric form. Therefore it seems reasonable to predict that the alkylating agents like diazomethane would produce alkyl derivatives of both nitrimino and nitramino forms of 2-nitraminopyridine.

The methylation of 2-nitraminopyridine (I) with diazomethane in ether yielded an ether-insoluble and an ether-soluble product. The ether-insoluble product proved to be 1,2-dihydro-1-methyl-2-nitriminopyridine (IV) as evidenced by its conversion to 1-methyl-2(1H)pyridone and nitrous oxide with hot alkali and by its identity with the product described by Tschitschibabin (12).

The oily ether-soluble product was soluble in dilute hydrochloric acid and formed a crystalline mercuric chloride double salt, but not a picrate. It must be 2-(1′-methylnitramino)pyridine (VI).

The methylation of 4-methyl-2-nitraminopyridine (II) and 4,6-dimethyl-2-nitramino-5-nitropyridine (III) with diazomethane also gave in each case the two methyl derivatives (V), (VIII) and (VII), (IX) respectively. However, unlike the methyl derivatives (VI) and (VII), 4,6-dimethyl-2-(1′-methylnitramino)-5-nitropyridine (IX) was not soluble in hydrochloric acid.

While the ethylation of 2-nitraminopyridine (I) with diazoethane in ether also gave ethyl derivatives of both tautomeric forms (X) and (XI), the propylation of (I) with diazopropane in ether produced only the ether-soluble propyl derivative of the nitramino form (XIII).

The ethylation and propylation of 4-methyl-2-nitraminopyridine (II) with the reagents mentioned above yielded only the derivatives (XII) and (XIV) of the nitramino forms, isolated as the mercuric chloride salts.

In the nitration of 2-amino-4,6-dimethylpyridine it was surprising to find that the reaction product contained a nitro group on the ring as well as the nitramino group in the two position. It is not known conclusively whether the nitro group occupies the three or five position. But from the behavior of such compounds as 2-nitraminopyridine and 4-methyl-2-nitraminopyridine which yield the 5-nitro derivatives predominantly when isomerized with sulphuric acid it seems very probable that the nitration product contains the nitro group in five position and can be named as 4-6-dimethyl-2-nitramino-5-nitropyridine (III).

## EXPERIMENTAL

### *4,6-Dimethyl-2-nitramino-5-nitropyridine* (III)

Sulphuric acid (40 ml.) was added dropwise to 44 ml. of 90–95% nitric acid at the temperature below 5°. Forty grams of 2-amino-4,6-dimethylpyridine were dissolved in 70 ml. of concentrated sulphuric acid while the flask was cooled in an ice bath. This solution was added carefully to the nitrating mixture at the temperature below 5°. After complete addition, the mixture was allowed to stand with constant stirring for three hours and then poured onto 100 gm. of crushed ice. The precipitate which separated had a distinct

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yellow color and after filtration and drying weighed 27.9 gm. (57.5%). It was recrystallized twice from ethanol and obtained in the form of yellow plates melting at 174–175° (decomp.).

Anal. Calc. for $C_7H_8N_4O_4$: C, 39.62; H, 3.78; N, 26.41%.

Found: C, 40.05; H, 3.90; N, 26.40%.

*Methylation of 2-Nitraminopyridine*

(*a*) *1,2-Dihydro-1-methyl-2-nitriminopyridine* (IV)

To the solution of diazomethane in 40 ml. ether prepared from 20 gm. of methylnitrosourea was added portionwise 7 gm. of (I). The reaction was allowed to proceed with occasional shaking until gassing had ceased. The reddish insoluble product after filtration and drying weighed 4.3 gm. (55.8%). After recrystallization from ethanol it melted at 156–157°. A mixed melting point with a sample of (IV) prepared by interaction of dimethylsulphate on (I) showed no depression.

(*b*) *2- (1'-Methyl)-nitraminopyridine* (VI)

The ether filtrate from the previous reaction was added to 50 ml. of dilute hydrochloric acid (1:1) and shaken. The acid layer was separated and rendered alkaline with sodium carbonate depositing a dark colored oil. The oil was extracted with two 25 ml. portions of ether and the ether distilled off on a steam bath. An attempt to distill the residual oil at 0.5 mm. pressure resulted in an explosion. The oil obtained from a second run was dissolved in 5 ml. of ethanol and added to 15 ml. of saturated solution of mercuric chloride in 95% ethanol. A crystalline mercuric chloride salt was deposited. The yield was 2.6 gm. (11.6%). The product crystallized from water into gleaming white plates, m.p. 151.5–152°.

Anal Calc. for $C_6H_7N_3O_2HgCl_2$: C, 16.98; H, 1.65; N, 9.91%.

Found: C, 17.35; H, 1.62; N, 9.84%.

*Methylation of 4-Methyl-2-nitraminopyridine* (II)

(*a*) *1,2-Dihydro-1,4-dimethyl-2-nitriminopyridine* (V)

Seven grams of (II) was methylated with a solution of diazomethane in ether. The insoluble reaction product (3.9 gm.) was recrystallized twice from ethanol and had a melting point 161–162°.

Anal. Calc. for $C_7H_9N_3O_2$: C, 50.30; H, 5.37; N, 25.15%.

Found: C, 49.92; H, 5.32; N, 25.37%.

The substance (V) was readily decomposed by warming with a dilute solution of potassium hydroxide with the evolution of nitrous oxide.

(*b*) *2-(1'-Methyl)-nitramino-4-methylpyridine* (VII)

The ethereal filtrate was shaken with 50 ml. of dilute hydrochloric acid (1:1) in a separatory funnel. The acid layer was separated and neutralized with sodium carbonate. Extraction with 25 ml. of ether followed by distillation of the ether on a steam bath yielded an oily residue. Half of it was added to 50 ml. of saturated solution of mercuric chloride in ethanol with the deposition

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of 1.7 gm. of a salt. The obtained mercuric chloride salt crystallized from water into long, fibrous white crystals, melting at 146–147°.

Anal. Calc. for $C_7H_9N_3O_2HgCl_2$: C, 19.62; H, 2.10; N, 9.81%.

Found: C, 19.19; H, 2.19; N, 9.39%.

The other half of the oil was added to 10 ml. of a saturated solution of picric acid in ethanol. The precipitate (picrate of VII) was recrystallized from acetone and alcohol. It formed yellow crystals which melted at 92–93°.

Anal. Calc. for $C_{13}H_{12}N_6O_9$: C, 41.91; H, 3.03; N, 21.21%.

Found: C, 42.05; H, 3.15; N, 20.56%.

*Methylation of 4,6-Dimethyl-2-nitramino-5-nitropyridine* (III)

(*a*) *1,2-Dihydro-2-nitrimino-5-nitro-1,4,6-trimethylpyridine* (VIII)

Four grams of (III) was allowed to react with a solution of diazomethane in ether prepared from 15 gm. of methylnitrosourea. After gassing had ceased the brownish insoluble substance was collected on a filter and dried. The yield was 0.7 gm. After two recrystallizations from ethanol, the melting point of (VIII) was 213–214°.

Anal. Calc. for $C_8H_{10}N_4O_4$: C, 42.48; H, 4.43; N, 24.77%.

Found: C, 42.86; H, 4.68; N, 24.35%.

(*b*) *4,6-Dimethyl-2-(1'-methyl)-nitramino-5-nitropyridine* (IX)

The ethereal filtrate was extracted with 50 ml. of hydrochloric acid (1:1) and the acid layer separated. No basic product could be isolated from this solution after neutralization with sodium carbonate. The ether solution remaining after the hydrochloric acid extraction was distilled on a steam bath to an oil which deposited crystals after standing for two days. Five milliliters of ethanol was added to facilitate filtration. The product weighed 0.9 gm. (18.9%). It was recrystallized from ethanol and obtained in the form of white crystals which melted at 104–105°.

Anal. Calc. for $C_8H_{10}N_4O_4$: C, 42.48; H, 4.43; N, 24.47%.

Found: C, 43.11; H, 4.10; N, 24.35%.

*Interaction of Diazoethane with* (I) *and* (II)

(*a*) *1,2-Dihydro-1-ethyl-2-nitriminopyridine* (X)

Seven grams of (I) was added to the diazoethane solution in ether prepared from 25 gm. of ethyl nitrosourethane. The solution slowly took on a deep red color and the solid started to dissolve. After gassing had ceased the insoluble product was filtered and dried. It weighed 1.8 gm. After two recrystallizations from ethanol the melting point was 126–127° (identical with the melting point reported in the literature (12)). It liberated nitrous oxide on being warmed with dilute potassium hydroxide solution.

(*b*) *2-(1'-Ethyl)-nitraminopyridine* (XI)

The ether filtrate was treated in the same manner as the filtrate from the methylation of (I). The oil obtained in this procedure formed a mercuric chloride salt which weighed 1.8 gm. It was recrystallized from 50% ethanol

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and obtained in the form of gleaming white plates melting at 125.5–126°.

Anal. Calc. for $C_7H_9O_2N_3HgCl_2$: C, 19.62; H, 2.10; N, 9.81%.

Found: C, 19.48; H, 2.25; N, 9.76%.

(*c*) *2-(1′-Ethyl)-nitramino-4-methylpyridine* (XII)

A solution of diazoethane was allowed to react with 7 gm. of (II). After the reaction was complete *no* insoluble product remained. From the ethereal solution the reaction product (XII) was isolated as mercuric chloride salt. It was recrystallized from 50% ethanol into long, white, fibrous needles melting at 131–132°.

Anal. Calc. for $C_8H_{11}N_3O_2HgCl_2$: C, 21.24; H, 2.41; N, 9.28%.

Found: C, 21.71; H, 2.67; N, 9.76%.

*Interaction of Diazopropane with* (I) *and* (II)

(*a*) *2-(1′-Propyl)-nitraminopyridine* (XIII)

In the reaction of the solution of diazopropane prepared from 30 gm. of undistilled propyl nitrosourethane with 7 gm. of (I) *no* insoluble product remained. A mercuric chloride salt was obtained (1.2 gm.) when the usual procedure for its isolation was followed. It was recrystallized from 50% ethanol and had a melting point 122.5–123.5°.

Anal. Calc. for $C_8H_{11}N_3O_2HgCl_2$: C, 21.24; H, 2.41; N, 9.28%.

Found: C, 21.33; H, 2.70; N, 9.6%.

(*b*) *2-(1′-Propyl)-nitramino-4-methylpyridine* (XIV)

The reaction of diazopropane with (II) gave no insoluble product. As usual an oil was obtained which formed a mercuric chloride salt, which after recrystallization from 75% ethanol melted at 88–89°.

Anal. Calc. for $C_9H_{13}N_3O_2HgCl_2$: C, 23.18; H, 2.78; N, 9.01%.

Found: C, 23.57; H, 2.88; N, 9.02%.

ACKNOWLEDGMENT

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# BIOCHEMISTRY OF THE USTILAGINALES

## IX. THE β-D-CELLOBIOSIDE UNITS OF THE USTILAGIC ACIDS[1]

By R. U. Lemieux, J. A. Thorn,[2] and H. F. Bauer[3]

ABSTRACT

The two D-glucose residues in the two main components of the ustilagic acid mixture are shown to be present as β-D-cellobiopyranoside units.

The glucoustilic acid mixture (6) was completely methylated by standard procedures for methylation and the product was subjected to methanolysis followed by hydrolysis to yield a mixture of methyl derivatives of D-glucose and the ustilic acids (7). The presence in the hydrolyzate of only tri-*O*- and tetra-*O*-methyl derivatives of D-glucose was established by paper partition chromatography. Semimicro amounts of the two fractions were obtained by preparative paper partition chromatography (13). Since the fractions crystallized readily and completely, there could be no doubt that each fraction contained only one component. The compounds were characterized as 2,3,6-tri-*O*-methyl-D-glucose and 2,3,4,6-tetra-*O*-methyl-D-glucose by the preparation of suitable derivatives. Quantitative estimations showed the glucose derivatives to be present, within experimental error, in equimolar amounts. The mixture of partially methylated ustilic acids isolated from the hydrolyzate possessed the composition expected for a mixture of mono-*O*-methylustilic acid A and di-*O*-methylustilic acid B. Therefore, both the ustilagic acids A and B possessed disaccharide units which were derived either from D-cellobiose or D-maltose.

The A and B components of the glucoustilic acid mixture must be present in the same proportion as are the ustilic acids A and B in the ustilic acid mixture. The ustilic acid mixture has been shown (7) to contain about 70% ustilic acid A and about 30% ustilic acid B. The molar rotations for the mixtures listed in Table I were calculated on this basis. Thus, the possible presence in these mixtures of a small amount of impurities (8) was disregarded.

Acetylation of methyl glucoustilate mixture yielded a crystalline mixture of the acetyl derivatives with molar rotation −25,100 in chloroform. Several recrystallizations of this substance gave pure methyl octa-*O*-acetylglucoustilate A with molar rotation −25,200 in chloroform. Since the lactol carbon atoms of glucose derivatives make a strong contribution to molar rotation (about ±25,000) (4), these rotations show conclusively that the corresponding anomeric centers in the glucoustilic acids A and B are of the same configuration.

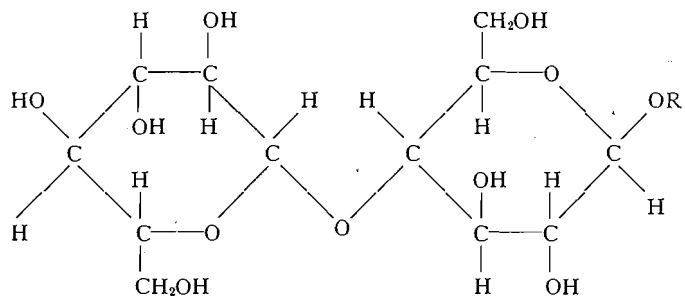
The molar rotations of acetylated glycosides of same configuration derived from a sugar and optically inactive alcohols are well-known to be remarkably constant in value. On this basis, a comparison of the molar rotation of the

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TABLE I
THE MOLAR ROTATIONS OF GLUCOUSTILIC ACID DERIVATIVES AND RELATED SUBSTANCES

| Substance | $[M]_D^{23-26}$ (chloroform) | References |
|---|---|---|
| Di-*O*-acetyl methyl ustilate A | +200° | |
| Tri-*O*-acetyl methyl ustilate B | +4600 | |
| Acetylated methyl ustilate mixture | +2000 | |
| Methyl octa-*O*-acetyl glucoustilate A | −25,200 | |
| Acetylated methyl glucoustilate mixture | −25,100 | |
| Octa-*O*-acetyl-β-D-cellobiose | −9900 | 4 |
| Octa-*O*-acetyl-α-D-cellobiose | +27,800 | 4 |
| Octa-*O*-acetyl-β-D-maltose | +42,500 | 4 |
| Octa-*O*-acetyl-α-D-maltose | +83,000 | 4 |

acetylated methyl glucoustilate mixture with the molar rotations of the α- and β-octa-*O*-acetyl derivatives of D-cellobiose and D-maltose (see Table I) would lead to the conclusion that the contribution to the rotation made by the optically active methyl ustilate portions would be −50,000 or greater (numerically) should the acetylated methyl glucoustilates possess α-D-cellobiose, β-D-maltose, or α-D-maltose residues. Since such a strong levorotation is exceedingly unlikely for residues derived from the weakly dextrorotatory acetylated methyl ustilates (see Table I), the optical rotatory data strongly suggested that the glucoustilic acids are β-D-cellobiosides. Chemical evidence was obtained which substantiated these conclusions. Acetolysis of the methyl glucoustilate mixture yielded octa-*O*-acetyl-α-D-cellobiose (1, p. 124). Therefore, the glucoustilic acids are definitely cellobiosides. It is well established (14) that hepta-*O*-acetyl-β-D-cellobiopyranosides usually can be isomerized to the α-anomers. Treatment of the levorotatory methyl octa-*O*-acetylglucoustilate A, $[M]_D$ −25,200, with boron trifluoride in chloroform solution (9) gave a dextrorotatory isomer, $[M]_D$ +24,200. These molar rotations are in excellent agreement with the values expected for anomeric cellobiopyranosides on the basis of Hudson's rules of isorotation (4). Therefore, the reaction must have effected a *beta* to *alpha* isomerization. Since the glucosidic union which joins the glucose residues in acetylated cellobiosides is known to be highly resistant to anomerization (10), the reaction must have involved the cellobiosyl to ustilic acid bond. Therefore, the glucoustilic acids must be β-D-cellobiopyranosides and their structures can be represented by the formulas I(*a*) and I(*b*).



I(*a*). Glucoustilic acid A, R = $C_{16}H_{31}O_3$.
I(*b*). Glucoustilic acid B, R = $C_{16}H_{31}O_4$.

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Although cellobiose can be considered to be a repeating unit of such substances as cellulose and lichenin, it appears that the ustilagic acids comprise the first *true* cellobiosides of biological origin to be characterized.

## EXPERIMENTAL

### *Methylation of Glucoustilic Acid Mixture*

Ustilagic acid (6), 25 gm., was methylated with dimethyl sulphate, 90 ml., and 30% sodium hydroxide, 210 ml., in the usual way. The acidified reaction mixture was extracted with ether to yield 22.4 gm. of a partially methylated derivative. After two further methylations using methyl iodide, 100 ml., and silver oxide, 75 gm., the yield was 19.4 gm. of partially crystalline material which contained 36.5% methoxyl groups. The methoxyl group content calculated for a mixture of 70% nona-*O*-methylglucoustilate A and 30% deca-*O*-methylglucoustilate B is 38.5%.

### *Quantitative Estimation of Tri-O- and Tetra-O-methyl-*D*-glucoses*

The fully methylated glucoustilic acid, 100 mgm., was heated for six hours in a sealed tube at 100°C. with 2 ml. of 5% methanolic hydrogen chloride. The solution was evaporated to dryness under reduced pressure and the residue was heated at 100°C. with 2 ml. of 10% hydrochloric acid for three hours. The hydrochloric acid was destroyed by the addition of an excess of an ethereal solution of diazomethane. The ether was removed by evaporation and the aqueous residue was filtered. The filter was washed with water to yield 25 ml. of filtrate.

Inspection of the solution by paper partition chromatography with butanol–ethanol–water (3) as developing phase showed only two reducing components detectable by the aniline phthalate reagent. The $R_f$ values indicated the presence of a tri- and a tetra-*O*-methyl-D-glucose.

A portion of the solution, 150 cmm., was developed on a sheet of Whatman 1 paper in the usual way as a 20 cm. streak across the paper. After the resultant bands were located by use of spots developed simultaneously, the zones were cut out and the methylglucoses eluted with water (2). The amounts of tri- and tetra-*O*-methyl-D-glucoses were determined by use of the anthrone reaction (2, 12). The blank was made up from the eluate of a strip of filter paper of equal area taken from the same chromatogram but which contained no reducing sugar. The transmission readings were compared to standard curves prepared from pure samples of 2,3,6-tri-*O*-methyl and 2,3,4,6-tetra-*O*-methyl-D-glucose. The ratio of tri- to tetra-*O*-methylglucose was 0.91. The yields were about 70% of theory.

### *Hydrolysis of Fully Methylated Glucoustilic Acid Mixture*

The methylated glucoustilic acid mixture, 5 gm., was heated under reflux with 50 ml. of 5% methanolic hydrogen chloride for 17 hr. The solution was added to 100 ml. of water and extracted several times with chloroform. After it was dried with sodium sulphate, the solution was evaporated to an oil. A solution of the material in 25 ml. of ethanol and 10 ml. of *N* potassium hydroxide was refluxed for half an hour. After neutralization with hydrochloric acid,

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the solution was evaporated to near dryness. The residue was stirred with sodium sulphate to yield a solid which was extracted with chloroform. Evaporation of the chloroform gave 1.7 gm. of the methylated glucoses. The residue from the extraction was dissolved in hot water, the solution was made strongly acid with hydrochloric acid and extracted with chloroform. Evaporation gave 1.75 gm. of a crystalline mixture of methylated ustilic acids, m.p. 41–55°C. After several recrystallizations from acetone the material melted at 56–70°C. Calc. for a mixture containing 60% mono-*O*-methylustilic acid A and 40% di-*O*-methylustilic acid B: neutral equiv., 314; $OCH_3$, 13.8%. Found: neutral equiv., 313; $OCH_3$, 13.8%.

The methylated glucose fraction, 400 mgm., was hydrolyzed by heating at 100°C. with 8 ml. of 10% hydrochloric acid for three hours. The solution was neutralized with diazomethane and evaporated to about a 2 ml. volume. The two methylated glucose components were separated by paper chromatography on a preparative scale (13) and characterized as follows.

*2,3,4,6-Tetra-O-methyl-α-D-glucose*

The tetra-*O*-methyl-D-glucose fraction crystallized at once on seeding with an authentic sample of 2,3,4,6-tetra-*O*-methyl-D-glucose. After two recrystallizations from petroleum ether, the material, $[\alpha]_D$ $+102 \longrightarrow +84°$ (*c*, 1 in water), melted at 95.5°C. (with some melting from 81°C.). These constants are in agreement with the published values (5) for 2,3,4,6-tetra-*O*-methyl-α D-glucose. The anilide derivative (15) melted at 137–139°C. and did not depress the melting point of an authentic sample of the same melting point.

*2,3,6-Tri-O-methyl-D-glucose*

The tri-*O*-methyl-D-glucose fraction crystallized on standing several days. A 10 mgm. sample was heated for three minutes on the steam bath with 0.5 ml. of pyridine and 20 mgm. of *p*-nitrobenzoyl chloride. Water was added, the sirup was triturated with sodium bicarbonate solution, washed with water, and dried *in vacuo*. A chloroform extract was treated with charcoal, filtered, and evaporated to yield a crystalline residue which was recrystallized from 0.8 ml. of methanol. The substance possessed the specific rotation and did not depress the melting point of 1,4-di-*O*-*p*-nitrobenzoyl-2,3,6-tri-*O*-methyl-D-glucose, m.p. 190°C., $[\alpha]_D$ $-32$ (*c*, 0.2 in chloroform).

*Acetylated Methyl Glucoustilate Mixture*

A solution of glucoustilic acid in methanol was treated with an excess of diazomethane. Addition of petroleum ether precipitated the methyl glucoustilate mixture in quantitative yield. The material was heated at 100°C. for three hours with sodium acetate and acetic anhydride. The acetyl derivative crystallized on shaking the acetylation mixture with cold water. The yield of crude material, m.p. 94–95.5°C., $[\alpha]_D$ $-25.6°$ (*c*, 4.3 in chloroform), was quantitative. Calc. for a mixture containing 70% methyl octa-*O*-acetylglucoustilate A and 30% methyl nona-*O*-acetylglucoustilate B: methoxyl, 3.17; acetyl, 36.5%. Found: methoxyl, 3.21; acetyl, 35.2%.

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*Methyl Octa-O-acetylglucoustilate A*

The mixture of acetylated methyl glucoustilates was recrystallized once from benzene – petroleum ether, three times from isopropanol, and finally three times from isopropanol – petroleum ether. The yield was 7 gm. of a substance which had reached constant physical properties, m.p. 108–109.5°C., $[\alpha]_D$ −27° (*c*, 2.3 in chloroform). Calc. for $C_{45}H_{70}O_{22}$: C, 56.12; H, 7.32%. Found: C, 56.10; H, 7.35%. Methanolysis of a sample and alkaline hydrolysis of the methyl ustilate fraction thus formed (7) to yield ustilic acid gave a substance, m.p. 110–111°C., after one crystallization from ethanol. This melting point was unchanged by admixture with ustilic acid A of the same melting point. When the melting of ustilic acid A is observed with a heating stage microscope, a transformation in crystal form is observed at 102–103°C.

*Methyl Di-O-acetylustilate A*

Pure methyl ustilate A (7) was acetylated with acetic anhydride and sodium acetate in the usual manner. The crystalline product was recrystallized from ethanol. The substance melted at 26–27°C. and $[\alpha]_D$ +0.6 (*c*, 4.3 in chloroform). Calc. for $C_{17}H_{32}O_4$ $(COCH_3)_2$: acetyl, 22.3%. Found: acetyl, 23.2%.

*Methyl Tri-O-acetylustilate B*

Acetylation of pure methyl ustilate B (7) as described above gave a sirup which resisted crystallization. The material, $[\alpha]_D$ +10.5° (*c*, 4 in chloroform), for analysis was distilled at a bath temperature of 170–180°C. at $10^{-3}$ mm. Calc. for $C_{17}H_{31}O_5(COCH_3)_3$: acetyl, 29.0%. Found: acetyl, 29.3%.

*Acetylated Methyl Ustilate Mixture*

Acetylation of purified methyl ustilate mixture (7) as described above gave a sirupy product, $[\alpha]_D$ +4.9° (*c*, 1.9 in chloroform). Calc. for a mixture containing 70% methyl di-*O*-acetylustilate A and 30% methyl tri-*O*-acetylustilate B: acetyl, 24.3%. Found: acetyl, 23.8%.

*Octa-O-acetyl-α-D-cellobiose*

The methyl glucoustilate mixture, 0.50 gm., was cooled with 1.4 ml. acetic anhydride in an ice–salt mixture. Concentrated sulphuric acid, 0.28 ml., was added to 0.60 ml. acetic anhydride cooled in the ice–salt mixture. The mixtures were combined (1, p. 124) and shaken at room temperature until solution was complete. The next day crystallization was initiated by scratching and after 2.5 days reaction time the crystals were collected, washed with ether, and recrystallized from ethanol. The yield was 20 mgm., m.p. 220–222°C. Recrystallization from ethanol raised the melting point to 226.5–228°C. and $[\alpha]_D$ +42° (*c*, 0.7 in chloroform). The substance did not depress the melting point of an authentic sample of octa-*O*-acetyl-α-D-cellobiose prepared by acetolysis of cellulose (1).

*Anomerization of Methyl Octa-O-acetylustilate A*

Methyl octa-*O*-acetylglucoustilate A, $[\alpha]_D$ −27° (chloroform), 2.90 gm., was dissolved in 50 ml. of pure chloroform and the solution was saturated with boron trifluoride. After 48 hr. at room temperature, the mixture was shaken

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with aqueous bicarbonate solution. The chloroform was washed with water, dried, and evaporated to a solid which was recrystallized from ethanol–petroleum ether mixture. The substance, 1.30 gm., $[\alpha]_D$ +8° (chloroform) was shown to be heterogeneous by chromatography on a 5:1 Magnesol-Celite column (11). The material, 1.00 gm., was treated again under the above conditions for anomerization except that the reaction time was 24 hr. The product was recrystallized from ethanol–petroleum ether mixture to yield 0.70 gm. of material, $[\alpha]_D$ +22.6° (chloroform). The substance, 100 mgm., in 2 ml. of benzene was added to the top of 140 × 35 mm. (in diam.) column of 5 parts Magnesol to 1 part Celite (11), and the chromatogram was developed with 1500 ml. of 100: 1 benzene to ethanol mixture. A band was located on the extruded column by streaking with 1% potassium permanganate in 2.5 *N* sodium hydroxide which extended from 3 mm. to 25 mm. from the top of the column. Elution with warm acetone and crystallization from ethanol gave 50 mgm. of material, m.p. 103–105°C., $[\alpha]_D$ +25.2° (*c*, 1.5 in chloroform). Calc. for $C_{29}H_{46}O_{14}(COCH_3)_8$: C, 56.12; H, 7.32; acetyl, 35.8%. Found: C, 56.22; H, 7.36; acetyl, 36.1%.

## ACKNOWLEDGMENTS

Authentic samples of 2,3,6-tri-*O*-methyl-D-glucose and its di-*O*-*p*-nitrobenzoyl derivative and the procedure for the preparation of the derivative were kindly provided by Prof. F. Smith, University of Minnesota. The microanalyses were carried out by J. A. Baignee of this laboratory.

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# A CONVENIENT SYNTHESIS OF DL-ORNITHINE[1]

By Roger Gaudry

ABSTRACT

DL-Ornithine is readily prepared in a 68% yield by condensing 3-bromopropylphthalimide with ethyl acetamidocyanoacetate and by hydrolyzing the resulting 2-acetamido-2-carbethoxy-5-phthalimidovaleronitrile into DL-ornithine, isolated as the monohydrochloride. 3-Bromopropylphthalimide is obtained in a 57% yield from 3-aminopropanol by reaction with phthalic anhydride, followed by phosphorus tribromide.

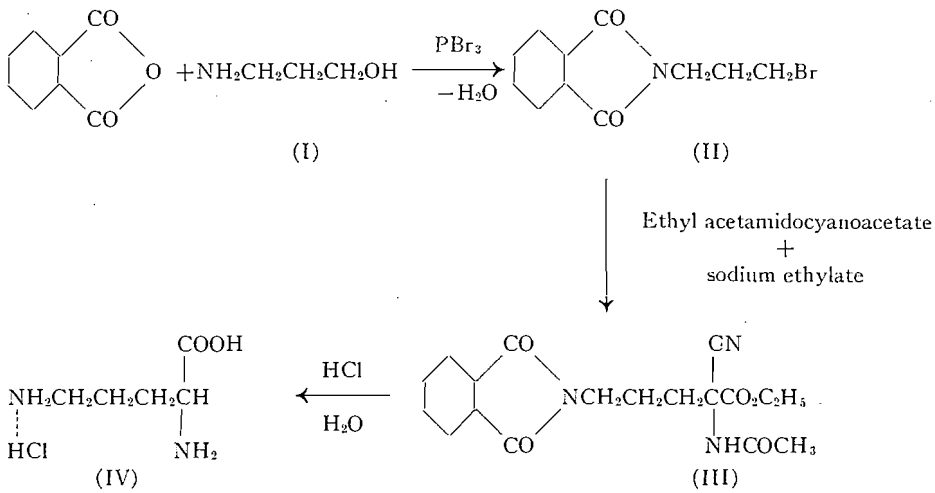
## INTRODUCTION

Many syntheses of DL-ornithine are recorded in the literature (2) but few of them are suitable for the preparation of this amino acid in important quantities.

In 1945, Albertson and Archer (1) published a satisfactory synthesis of DL-ornithine from the condensation product of acrylonitrile and ethyl acetamidomalonate. This method requires a high pressure hydrogenation to transform ethyl 2-acetamido-2-carbethoxy-4-cyanobutyrate into 3-acetamido-3-carbethoxy-piperidone, a compound which gives ornithine upon acid hydrolysis.

We have investigated the preparation of DL-ornithine from the commercially available 3-aminopropanol (I). By using an adaptation of the procedure recently described in Organic Syntheses (4) for the preparation of 2-bromoethylphthalimide, 3-aminopropanol is easily transformed into 3-bromopropylphthalimide (II). It is not necessary to isolate the intermediate 3-hydroxypropylphthalimide.

The condensation of 3-bromopropylphthalimide with ethyl acetamidocyanoacetate in the presence of sodium ethylate gives the readily isolated 2-carbe-




[1] *Manuscript received June 22, 1953.*
*Contribution from the Department of Biochemistry, Faculty of Medicine, Laval University, Quebec.*



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thoxy-2-acetamido-5-phthalimidovaleronitrile (III) in an 80% yield. Acid hydrolysis of this product gives 86% of DL-ornithine (IV), isolated as the monohydrochloride, bringing the over-all yield calculated from ethyl acetamidocyanoacetate to 68%.

The use of 3-chloropropylphthalimide instead of the corresponding bromo compound is not to be recommended because its preparation, using phosphorus trichloride or thionyl chloride, gives a lower yield of a product which is more difficult to purify, and also a lower yield of the condensation product with ethyl acetamidocyanoacetate. Ethyl acetamidomalonate was also found to be less satisfactory than ethyl acetamidocyanoacetate because its condensation product with 3-bromopropylphthalimide is not as easily isolated as 2-carbethoxy-2-acetamido-5-phthalimidovaleronitrile.

This method of synthesis is derived from the old method of Sörensen (5) with the following differences: (*1*) 3-Bromopropylphthalimide is prepared from 3-aminopropanol instead of potassium phthalimide and trimethylene dibromide (3). (*2*) Ethyl phthalimidomalonate is replaced by the much more convenient ethyl acetamidocyanoacetate. (*3*) The direct, one-step hydrolysis with hydrochloric acid allows the easiest isolation of DL-ornithine as the monohydrochloride.

## EXPERIMENTAL

### *3-Bromopropylphthalimide* (II)

(To be carried out in a well ventilated fume cupboard). In a one liter, round bottom flask are placed 148 gm. (one mole) of finely ground phthalic anhydride. Seventy-five grams (one mole) of 3-aminopropanol are added rapidly. After the spontaneous reaction has stopped, any lumps of unreacted phthalic anhydride are broken up with a glass rod or a spatula, and the flask is rotated gently by hand until a clear solution is obtained. While still hot, the flask is placed on a boiling water bath, and is fitted with a good reflux condenser. Seventy-two milliliters of freshly distilled phosphorus tribromide are now added in small portions, either through the condenser or by means of a small separatory funnel attached to a connecting tube placed between the flask and the condenser. A first portion of 15 to 20 ml. is added, and the flask is shaken gently and heated on the water bath until the reaction starts. The rest is then added in portions of approximately 10 ml., while being shaken gently and allowed enough time between each addition for the vigorous reaction to take place. When the addition of phosphorus tribromide is completed, the mixture is heated on the water bath for one additional hour, 100 ml. of ethyl alcohol are added to the hot, viscous liquid, and the solution is poured into a large volume of well stirred ice water containing broken ice. The alcohol prevents the too rapid solidification and the formation of large, hard lumps while the product is being poured into ice water. After standing overnight in the cold, the precipitate is filtered in a large Buechner funnel, and thoroughly washed with cold water until the filtrate is but faintly acidic, and allowed to dry. At this stage, the yield of crude product is approximately 200 gm. It is recrystallized from 200 ml. of ethanol. The yield of the first crop is 149 gm.

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A second crop of 5 to 6 gm. is obtained by concentrating the alcoholic filtrate to one third of its volume. Total yield: 154 gm., 57.5%. M.p.*: 74°C. (lit.: 72°–73° (3)). Calc. for $C_{11}H_{10}O_2NBr$: Br, 29.85%. N, 5.22%. Found: Br, 29.69%. N, 5.46%.

*2-Acetamido-2-carbethoxy-5-phthalimidovaleronitrile* (III)

In a one liter, three neck, round bottom flask, fitted with a mechanical stirrer, and a reflux condenser with a calcium chloride tube, are placed 500 ml. of absolute ethanol. Metallic sodium (11.5 gm., 0.5 mole) is dissolved in it. Eighty-five grams (0.5 mole) of ethyl acetamidocyanoacetate are now added. The mixture is stirred at room temperature for 15 min. and is treated with 134 gm. (0.5 mole) of dry, powdered 3-bromopropylphthalimide. The flask is placed in a water bath, and the mixture is stirred continuously while the temperature is kept at 50°C. for 24 hr. and then raised and kept at 80°C. for a second 24 hr. period. When 3-bromopropylphthalimide is first added to the cold alcoholic solution, it does not dissolve, but after the mixture has been kept at 50°C. for a few minutes, the dissolution becomes complete. After a little while, a precipitate begins to appear, which keeps increasing slowly as the reaction takes place. The mixture is then cooled by replacing the hot water bath with ice water. The precipitate is filtered on a Buechner funnel, washed with two 50 ml. portions of cold ethanol, and allowed to dry. Yield: 142 gm., 79.5%. M.p.: 210°. Calc. for $C_{18}H_{19}O_5N_3$: N, 11.76%. Found: N, 11.85%. The product can be recrystallized from a very large volume of ethanol in which it is only sparingly soluble, but the melting point and analytical results remain unchanged.

DL-*Ornithine Monohydrochloride* (IV)

In a two liter, wide neck, round bottom flask, fitted with a good reflux condenser, are placed 500 ml. of concentrated hydrochloric acid and 500 ml. of water, and the solution is heated up to the boiling point. The condenser is removed, and 118 gm. of 2-acetamido-2-carbethoxy-5-phthalimidovaleronitrile are added to the hot solution, in five or six portions, allowing enough time between each addition for the product to dissolve almost completely. Excessive foaming occurs if the portions added are too large or if the previous ones have not yet dissolved. The solution is then boiled under reflux for five hours. After standing overnight in the cold, the precipitate of phthalic acid is filtered on a Buechner funnel, washed on the filter with two 50 ml. portions of ice water, and discarded. The filtrate and washings are evaporated to dryness *in vacuo*. The residue is dissolved in 200 ml. of water, 45 ml. of concentrated ammonium hydroxide are added, and the solution is again taken to dryness *in vacuo*. Eight hundred milliliters of methanol are added to the residue, and the mixture is mechanically stirred at room temperature for one hour. The precipitate is filtered on a Buechner funnel, transferred to a beaker, and again mechanically stirred for one hour with a fresh 500 ml. portion of methanol, to dissolve any remaining ammonium chloride. The insoluble DL-ornithine monohydrochloride is filtered in a Buechner funnel, washed on the filter with two

**Melting points are uncorrected.*

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50 ml. portions of methanol and allowed to dry. Yield: 50.6 gm., 90.8%. M.p.: 222°. (lit.: 225° (1)). Calc. for $C_5H_{13}O_2N_2Cl$: N, 16.61%. Found: N, 16.47%. The product is readily recrystallized, with a loss of 5 to 6%, by dissolving it in 200 ml. of boiling water and adding 400 ml. of ethanol. Found: N, 16.63%. M.p.: 227°. The over-all yield of analytically pure DL-ornithine monohydrochloride calculated from ethyl acetamidocyanoacetate is 68%. DL-Ornithine dipicrate: M.p.: 199°, unaffected by mixture with an authentic sample.

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# THE REDUCTION OF AROMATIC NITRO COMPOUNDS BY MAGNESIUM AND METHYL ALCOHOL[1]

By Karl F. Keirstead

ABSTRACT

A study has been made of the reduction of substituted nitro compounds by magnesium in methyl alcohol. Some nitro compounds smoothly reduce to the corresponding azoxy compounds, while others yield a complex mixture of azo, azoxy, and other compounds. An investigation has been made of the various factors affecting the velocity of the reaction and the relative proportion of the products. An attempt is made to clarify the various reactions taking place.

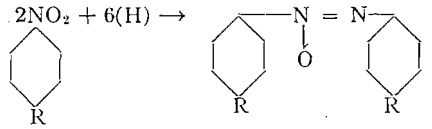
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The only reference found in the literature to the use of magnesium and methyl alcohol for the reduction of aromatic nitro compounds is a paper by Zechmeister and Rom (16). It is claimed that this method produced excellent yields of azoxy compounds from methyl, chloro, or bromo substituted nitrobenzenes, although azo compounds were present in certain reduction mixtures.

Since the reduction takes place under essentially neutral conditions, it was of interest to investigate the use of this method for the reduction of substituted nitro compounds that undergo hydrolysis, cleavage, or some similar reaction in the strong alkaline solution employed when azoxy compounds are prepared using dextrose or sodium arsenite (6).

First attempts in this study to prepare either the azo or azoxy compound from any of the compounds mentioned above failed completely. It was later established that this failure was due to the use of a stainless steel stirrer. This effect was confirmed by the addition of stainless steel turnings to a well stirred mixture of short pieces of magnesium ribbon in methyl alcohol. No visible evolution of gas took place during forty minutes. In a duplicate mixture a vigorous reaction was evident in the absence of turnings after one minute. This initial difficulty prompted a closer study of both the reaction between magnesium and methyl alcohol [I], and the reaction between magnesium, methyl alcohol, and the nitro compound [I, II, III].

$$Mg + 2CH_3OH \longrightarrow Mg(OCH_3)_2 + 2(H) \qquad [I]$$




[II]

$$2H_2O + Mg(OCH_3)_2 \longrightarrow Mg(OH)_2 + 2CH_3OH \qquad [III]$$

For the purpose of the present discussion, the reactions taking place in a mixture of methyl alcohol, magnesium, and an aromatic nitro compound may be considered separately as follows:

1. Reaction between magnesium and the methyl alcohol.

[1] *Manuscript received November 14, 1952, and, as revised, July 6, 1953.*
*Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec.*

II. Effect of the nitro compound on the reaction between the magnesium and the alcohol.

III. Reduction of the nitro compound by hydrogen and by magnesium methylate.

IV. Reduction of the azoxy compound by magnesium methylate.

I. *Reaction Between Magnesium and Methyl Alcohol*

The effect of various factors on the reaction between magnesium and methyl alcohol was studied both by the disappearance of the magnesium (Table I and Fig. 4) and by the evolution of hydrogen (Figs. 1–3).

TABLE I

LOSS OF WEIGHT OF MAGNESIUM UNDER CERTAIN CONDITIONS

| Run No. | Magnesium | Magnesium reacted, mgm. | Methyl alcohol, % water[a,b] | Stirring |
|---|---|---|---|---|
| 1 | Polished ribbon[c] | 31.3 | 0.01 | Magnetic stirrer |
| 2 | Same | 6.7 | 0.07 | Same |
| 3 | Turnings | 7.9 | 0.01 | Same |
| 4 | Same | 3.1 | 0.07 | Same |
| 5 | Polished ribbon | 17.4 | 0.01 | Shaker |
| 6 | Turnings | 3.5 | 0.01 | Same |
| 7* | Polished ribbon | 88.0<br>87.0<br>91.5 | 0.01 | Magnetic stirrer |

*Time, 15 min.; temperature, 23°–25°C.; alcohol, 25 ml.*
**Added 0.0533 gm. 4-chloronitrobenzene.*
*[a]Determined by Karl Fisher method.*
*[b]Per cent by weight.*
*[c]All magnesium ribbon used throughout was prepared immediately before use by polishing with fine emery cloth.*

It may be seen by reference to Table I that the velocity of the reaction between magnesium and methyl alcohol depends on the following factors:

(*a*) Condition of the magnesium surface.

The polished magnesium ribbon reacts four to five times as fast as magnesium turnings in the presence of 0.01% water.

(*b*) Degree of agitation.

Rapid stirring increases the velocity by a factor of approximately two.

(*c*) Amount of moisture in the methanol.

As shown in Run 1 and 2, an increase in moisture content from 0.01% to 0.07% reduces the amount of magnesium dissolved from 31.3 mgm. to 6.7 mgm. in the same time. The effect of moisture has also been observed in the presence of the nitro compound. The addition of 1 ml. of water to 250 ml. methyl

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alcohol (0.02% water) containing 0.02 mole of the aromatic nitro compound increases the reaction time from 30 min. to two–seven hours depending on the nitro compound used.

The effect of the form of the magnesium is again shown in Fig. 1. An inspection of Curves 2 and 3 shows that the magnesium ribbon reacts about

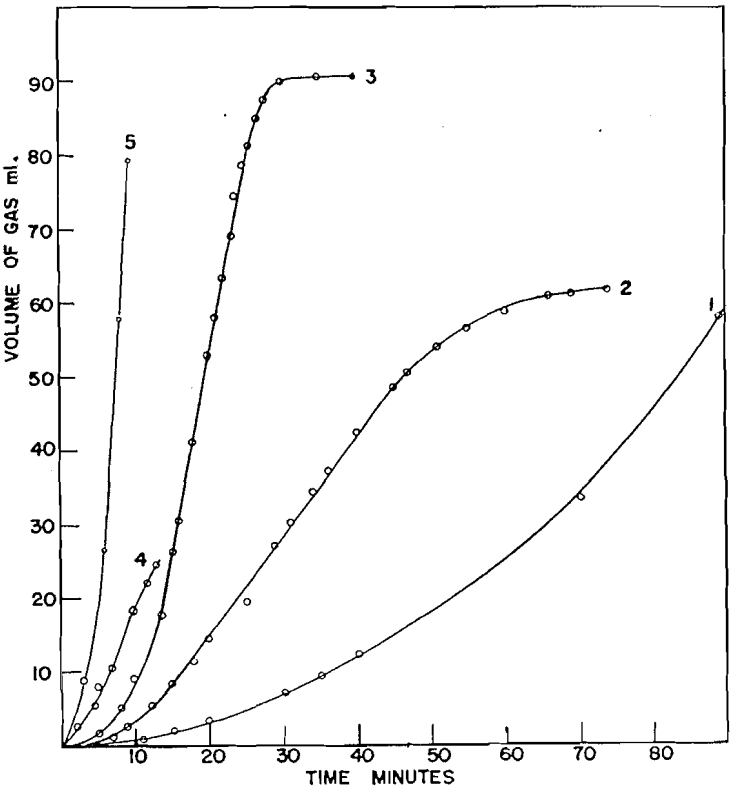



FIG. 1. Effect of water and ethyl iodide on velocity of reaction: Curve 1—Magnesium powder (0.086 gm.) in methyl alcohol (25 ml.). Water content 0.014%. Curve 2—Magnesium powder (0.0752 gm.) in methyl alcohol (25 ml.). Water content 0.007%. Curve 3—Magnesium ribbon (0.0804 gm.) in methyl alcohol (25 ml.). Water content 0.007%. Curve 4—Magnesium powder (0.0987 gm.) and ethyl iodide (0.0660 gm.) in methyl alcohol (25 ml.). Water content 0.007%. Curve 5—Magnesium ribbon (0.0799 gm.) and ethyl iodide (0.3230 gm.) in methyl alcohol (25 ml.). Temperature 25° ± 0.5°C.; rapid stirring with magnetic stirrer.

four times as fast as the magnesium powder in alcohol containing the same amount of water (0.007%). An approximate comparison of the reaction rates of magnesium ribbon, turnings, and powder in alcohol can be made more readily from the present data by estimating the weight of magnesium powder reacting in the first 15 min. (Curve 1). The volume of hydrogen produced is about 3 ml. (25°C. and 760 mm.) which corresponds to approximately 1.5 mgm. magnesium. This weight can be compared with 7.9 mgm. and 31.3 mgm. for turnings and ribbon respectively in alcohol of approximately the same water content (0.01%).

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If all the magnesium surfaces were chemically identical, the velocity of the reaction would be a function of the surface area. Since, however, the velocity of the reaction appears to decrease with increased surface area of the magnesium, it may be concluded that the difference in the reaction rates of polished ribbon, turnings, and powder is due mostly to the presence of an oxide or a hydroxide coating on the turnings and the powder.

The effect of small amounts of moisture in the alcohol on the velocity of the reaction between the magnesium and the alcohol has already been mentioned. This inhibition effect appears to be out of proportion to the small amount of water present. Considering again Runs 1 and 2 (Table I), it may be seen that the amounts of water present in the 0.01% and the 0.07% alcohol are respectively 2.0 mgm. and 13.9 mgm. Thus an increase of 11.9 mgm. of water is accompanied by a reduction of 24.6 mgm. of magnesium entering the reaction. Two alternative explanations account for the effect of the water. Firstly, the water may combine with the magnesium, be adsorbed on the surface, or otherwise tend to block contact between the magnesium and the alcohol. The second alternative would involve the combination of the water with magnesium methylate to form magnesium hydroxide [III]. Even with the most efficient stirring, the concentration of the magnesium methylate could be expected to be greater near the magnesium surface. The reaction of water with this layer would produce a layer of magnesium hydroxide in colloidal or powder form that would tend to block reaction between magnesium and the methyl alcohol.

### II. *Effect of the Nitro Compound on the Reaction Between the Magnesium and the Alcohol*

In the presence of an aromatic nitro compound a marked increase in the reaction rate is noted. The result of a typical experiment is given in Run 7, (Table I). The reaction rate has increased about three times by the addition of 0.0533 gm. 4-chloronitrobenzene. It may be seen that the effect is quite reproducible under the experimental conditions employed.

On the other hand, when a smaller amount of alcohol or when a less soluble nitro compound is used, it becomes more difficult to obtain a reproducible measure of the reaction rate. Under such conditions an adherent coating on the magnesium may result in an apparent increase in weight for a given piece of magnesium. This coating appears to be related to an unusually large increase in viscosity of the mixture.

In an attempt to account for characteristic viscosity changes that were observed during the preparation of a typical azoxy compound, measurements were carried out with a Fisher Electroviscometer. During the reaction between magnesium, 2,5-dichloronitrobenzene, and methyl alcohol, an initial increase in viscosity took place during the first 10 min. after which a decrease took place. However, this viscosity maximum was not observed in the following: (*a*) magnesium methylate, 2,5-dichloronitrobenzene, and methyl alcohol; (*b*) magnesium reacting with methyl alcohol.

It is apparent that the viscosity changes taking place during the reduction must be due to a substance not present in mixture (*a*) or mixture (*b*). An

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inspection of reactions [I–III] immediately suggests that the viscosity changes depend on the formation of water which reacts with magnesium methylate to produce colloidal magnesium hydroxide.

The aging of the colloidal magnesium hydroxide might then result in a decrease in viscosity. One might expect the magnesium hydroxide on formation to be rather heavily solvated with methyl alcohol. The loss of this alcohol of solvation would result in a reduction of viscosity. One would suspect that the coating on the magnesium is insoluble magnesium hydroxide, the final stage in the aging of the colloidal magnesium hydroxide. One would further conclude that the beneficial result of rapid stirring during the preparation of the azoxy compound is due largely to the partial removal of a thick coating of magnesium hydroxide from the surface of the magnesium.

The over-all rate of the magnesium reaction with methyl alcohol in the presence of a nitro compound is then the result of two effects: activation by the nitro compound and inhibition by water initially present or produced by the reduction of the nitro compound.

In an attempt to account for the activation of the reaction by the nitro compound it was of interest to consider the possibility that the nitro compound formed an intermediate with the magnesium. This approach was suggested by the work of Vishnyakov (13) who made a detailed study of the reaction between magnesium and methyl alcohol.

The following claims made by Vishnyakov are of interest:

(*a*) Magnesium (powder) reacts with alcohols only when other substances which activate this reaction are present.

*b*) The first portions of the gas formed are rich in hydrocarbons, the total gas corresponding closely to the equation,

$$2R'OH + Mg \rightarrow Mg(OR')_2 + H_2. \qquad [IV]$$

(*c*) With small amounts of RX (the activator, an alkyl halide) the reaction starts only after an induction period; with relatively larger amounts of Mg and RX the reaction begins quickly and exhibits two velocity maxima during its course.

Since the results of Vishnyakov are available to the present author in abstract form only, it was considered advisable to repeat some of the work reported.

The first point of variance is in the claim that the magnesium reacts only in the presence of an activator. Reference has already been made to the reaction of magnesium powder with methyl alcohol (Curves 1 and 2, Fig. 1). However, the activation of the reaction by an alkyl halide can be readily observed by comparing Curves 2 and 4, Fig. 1.

Vishnyakov suggests the following reactions to account for the hydrocarbon formation and for the activation by the alkyl halide.

$$RX + Mg \rightarrow RMgX \qquad [V]$$

$$RMgX + R'OH \rightarrow R'OMgX + RH \qquad [VI]$$

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The initial sharp velocity maximum at the end of 10 min. was attributed to the initial formation of R'OMgX which in turn was thought to activate the reaction of the alcohol with the magnesium.

In an attempt to verify the presence of the maximum described by Vishnyakov eight reactions were carried out. In each case the weight of magnesium powder was 0.07–0.09 gm. The amount of ethyl iodide was varied successively from 1.9 gm., Run 1 to 0.02 gm., Run 8. Two typical results are shown in Fig. 2. The induction period described by Vishnyakov was not evident in any

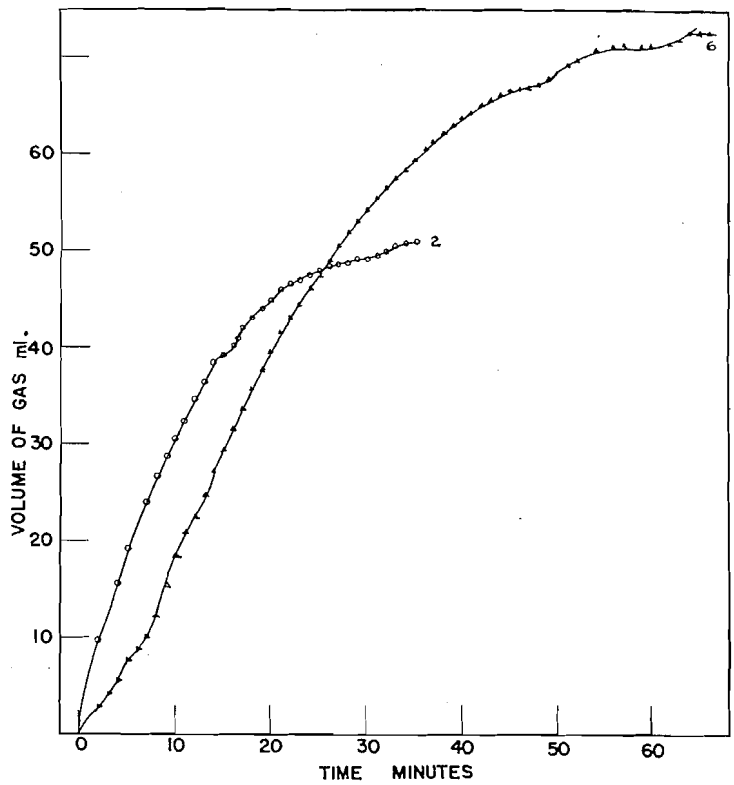



FIG. 2. Magnesium powder reacting with methyl alcohol in presence of ethyl iodide: Run 2. Magnesium powder (0.0718 gm.) and ethyl iodide (1.9224 gm.) in methyl alcohol. Run 6. Magnesium powder (0.0987 gm.) and ethyl iodide (0.0660 gm.) in methyl alcohol.

plot. The existence of velocity maxima is equally in doubt. Indeed, except for the greater velocity, the curve for magnesium powder in the presence of ethyl iodide, (Run 2, Fig. 2) does not differ greatly from the curve for magnesium alone, (Curve 2, Fig. 1).

Evidence for the occurrence of reactions involving the ethyl iodide has been found in connection with the analysis of the gas produced. This gas was examined both by infrared and by a mass spectrometer. After the usual precautions for background and a blank on the methyl alcohol, 10% ethane and 15% ethylene were found.

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According to the mechanism proposed by Vishnyakov the only hydrocarbon would be ethane. The presence of both ethane and ethylene makes it more likely that the significant reaction is a disproportionation.

$$C_2H_5I + C_2H_5MgI \rightarrow C_2H_4 + C_2H_6 + MgI_2 \qquad [VII]$$

One would conclude then that the apparent activation of the reaction between magnesium and methyl alcohol in the presence of ethyl iodide is the result of a side reaction whereby magnesium is initially consumed at a greater rate and whereby the volume of gas produced is greater than would otherwise be expected.

The activation effect produced by the addition of a nitro compound is shown in Curves 2 and 3, Fig. 3. The curves so produced resemble the plot resulting

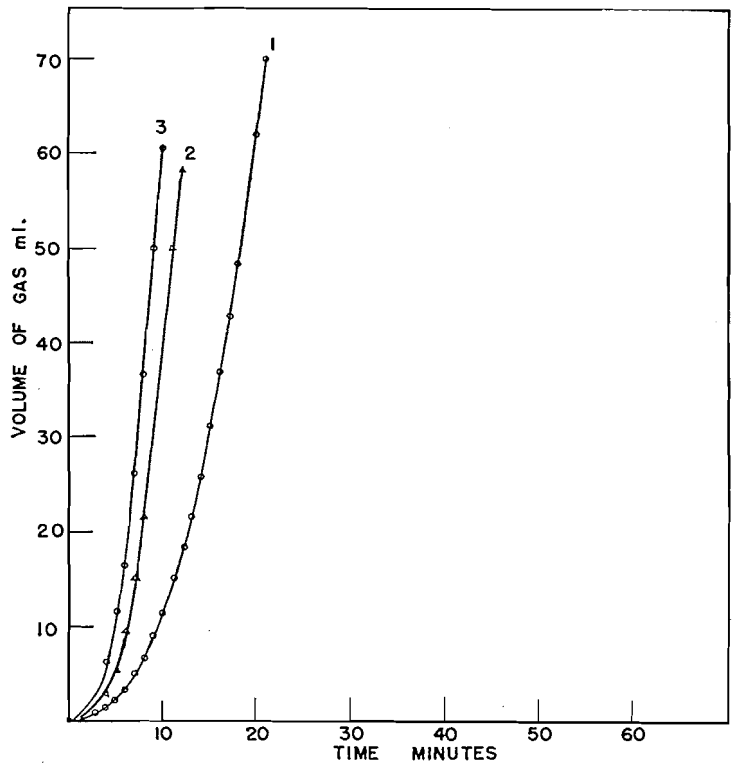



FIG. 3. Effect of 2,5-dichloronitrobenzene on reaction between magnesium ribbon and methyl alcohol: Curve 1—Polished magnesium ribbon in methyl alcohol. Curve 2—Polished magnesium ribbon and 2,5-dichloronitrobenzene (0.03 gm.) in methyl alcohol. Curve 3—Polished magnesium ribbon and 2,5-dichloronitrobenzene (0.01 gm.) in methyl alcohol.

from the activation by ethyl iodide (Curve 3, Fig. 1). Since these curves are similar to the curve for magnesium alone (Curve 3, Fig. 1) except for a shorter induction period, no useful conclusions can be drawn from these data concerning the mechanism of the activation by the nitro compound.

The presence of an intermediate compound was suggested at one stage in the work by the appearance of a highly colored substance during the reduction

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of 2,5-dichloronitrobenzene. The bright violet color formed during the first 10 min. changed later to a muddy brown. Other characteristic color changes were observed during other reductions. Efforts to isolate a possible intermediate were unsuccessful. It was later concluded that the color changes were mostly the results of adsorption of the reaction products on the colloidal magnesium hydroxide formed in the course of the reaction. As the chemical and physical properties of the magnesium hydroxide change during the reaction corresponding changes occur in the color of the adsorbed substances.

Considerable effort was spent in an attempt to relate the loss in weight of the magnesium in a fixed time (15 min.) to the weight of the nitro compound present (4-chloronitrobenzene and 4-nitroanisole). The results for 4-nitroanisole are shown in Fig. 4. Similar results were found for 4-chloronitrobenzene.

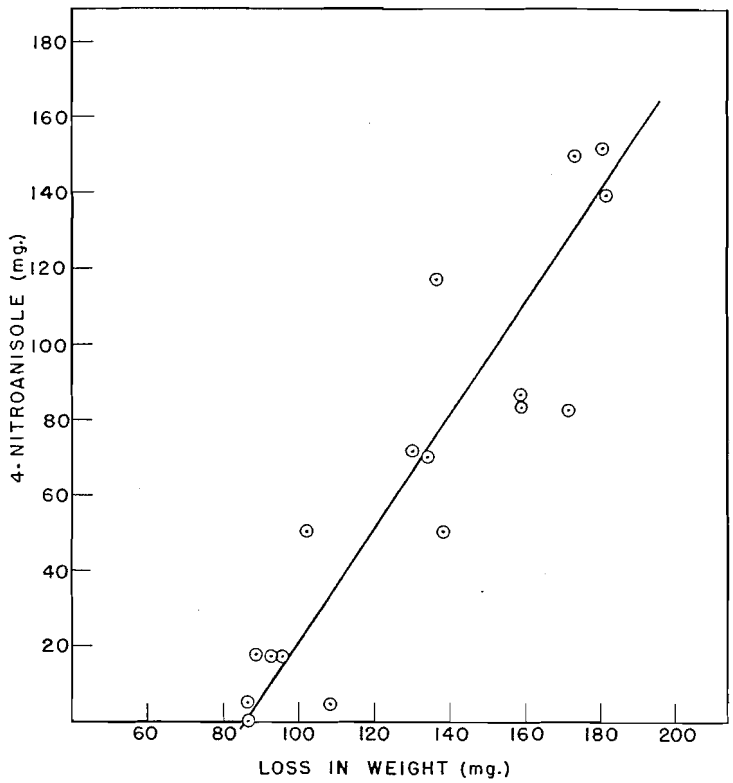



FIG. 4. Loss of weight of magnesium in solution of 4-nitroanisole and methyl alcohol (25 ml.), 15 min.

The preparation of the surface and small variations in moisture content of the alcohol are the chief factors affecting reproducibility of the results. The results show an almost linear relationship between the weight of the nitro compound and the weight of magnesium reacting in a given time.

While the mechanism by which the reaction between the magnesium and the alcohol is activated by the nitro compound remains somewhat obscure, some

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conclusions can be drawn from the data shown in Fig. 4. It is likely that the apparent linear relationship between the nitro compound and the weight of the magnesium consumed is the over-all result of several factors of which the most important are the actual activation effect together with the inhibition effect due to the water produced in the reaction. If the activation continued throughout the reaction and were in fact a function of the concentration of the nitro compound, the activation effect would decrease with time as the concentration of the nitro compound decreased. The over-all reaction rate would as a result show a marked decrease with time under the influence of a diminishing activation together with an increasing inhibition due to the water produced. Since the reaction is uniform, the hypothesis that the activation is equally effective during the whole time must be rejected. It may be concluded, then, that the activation effect of the nitro compound is most important during the first part of the reaction. Reference to Fig. 3 shows that in the absence of a nitro compound the curve for the reaction is linear after about 10 min. while in the presence of the nitro compound the curve for the reaction is linear after about three minutes. The most logical assumption appears to be that the activation produced by the nitro compound is related to the role of a depolarizer in the corrosion of a metal.

III. *Reduction of an Aromatic Nitro Compound by Magnesium and Methyl Alcohol*

It is interesting to compare reduction by magnesium and methyl alcohol with reduction by sodium methylate. According to Klinger (8) the latter reaction is:

$$4C_6H_5NO_2 + 3CH_3ONa \rightarrow 2(C_6H_5N)_2O + 3HCOONa + 3H_2O. \qquad [VIII]$$

Fry and Bowman (4) suggested that the mechanism involved first a reaction between the sodium methylate and water to form methyl alcohol and sodium hydroxide. A subsequent reaction between sodium hydroxide and methyl alcohol was thought to produce hydrogen which is the active agent.

In contrast to the above reaction [VIII] magnesium methylate was found to have a minor effect on the reduction of a nitro compound. Several days are required to produce an appreciable amount of reduction of the nitro compound whereas in the mixture of magnesium and methyl alcohol the reduction is complete in 30 min.

The conclusion that the hydrogen produced by the reaction between magnesium and the methyl alcohol is the active agent is supported by the volume of gas (1.3 moles) disappearing in the presence of the nitro compound (1 mole). The reduction of the nitro compound (1 mole) to the corresponding azoxy compound requires 1.5 moles.

IV. *Reduction of the Azoxy Compound by Magnesium Methylate*

Zechmeister and Rom (16) mentioned the presence of an azo compound in certain mixtures obtained when preparing an azoxy compound by the action of magnesium and methyl alcohol. It is likely that the azo compounds were

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produced by the reduction of the azoxy compound by the magnesium methylate. It has been found that a pure azoxy compound undergoes some reduction after being in contact for several hours with a solution of magnesium methylate in methyl alcohol.

## RESULTS AND EXPERIMENTAL PROCEDURE

The results obtained from the reduction of 12 nitro compounds on a preparative scale are shown in Table II. The yields from Experiments 1–4 confirm in a general way the results reported by Zechmeister and Rom (16). The reduction of the remaining nitro compounds by this method is reported for the first time. For the purpose of the present study, the compounds were identified by their melting points. It should be mentioned that all reactions recorded in Table II were carried out under the same experimental procedure as given for Experiment I in the experimental part.

It has already been shown that the azoxy compound may be reduced to the azo compound by magnesium methylate in methyl alcohol. It would therefore appear that the latter reaction might be inhibited by reducing the concentration of magnesium methylate in the reaction mixture. Reference to Reaction III shows that this effect can be brought about by the addition of a small amount of water to the reaction mixture. With this experimental modification, the yield of 2,2′,5,5′-tetrachloroazoxybenzene was raised from 3.7% (Expt. 7, Table II) to 35%. Similarly the yield of 2,2′-dimethyl-3,3′-dichloroazoxybenzene was raised from 52% (Expt. 10, Table II) to 68%.

Reference to the experimental part shows that the addition of water to a mixture of 2,5-dichloronitrobenzene, magnesium, and methyl alcohol reduced the reaction temperature from the usual reflux temperature to about 30°C. It may be argued that the improved yield was the result of the lower temperature rather than the smaller concentration of the magnesium methylate. The latter possibility was tested by carrying out a similar experiment at 30°C. without addition of water. The product of the reaction was a complex mixture from which no pure azoxy compound was obtained after fractional crystallization involving 15 fractions.

Inspection of Table II shows that no azoxy compound could be isolated from certain reduction mixtures. In agreement with experience, unsuccessful reductions were prominent with ortho substituted compounds, while on the other hand, the method appears to be promising for the reduction of nitroanilines where the amino group is protected by an acetyl group. Few methods exist for the reduction of nitroanilines to the corresponding azoxy compound. Since many such reductions are carried out in strong alkaline solution (3, 6), it is likely that an acetyl group would be rapidly lost by hydrolysis.

A certain similarity appears to exist in the properties of the unknown component found in reduction mixtures where the azoxy compound is absent or present in small yield. This component, usually a bright yellow or brown, was highly soluble in alcohol but unlike a tar could not be removed by treatment with activated charcoal or chromatographic alumina. No amines were found in the reduction mixtures.

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TABLE II

REDUCTION OF SOME NITROBENZENE COMPOUNDS BY MAGNESIUM AND ABSOLUTE METHYL ALCOHOL

| Expt. No. | Substituent | Recovery, % | Reagents | | | Azoxy compound | | | Azo | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Nitro comp., moles | Mg, moles | $CH_3OH$, ml. | M.p.* found, °C. | Gm. | Conversion, % | M.p.* found, °C. | Gm. | Conversion, % | |
| 1 | 4-Chloro | 10.0 | 0.02 | 0.12 | 125 | 155.5–6.5[a] | 0.94 | 39.2 | 183–4[k] | 0.76 | 33.6 | |
| 2 | Same | " | " | " | " | " | 1.40 | 58.3 | " | 0.77 | 34.0 | |
| 3 | 3-Bromo | 11.8 | 0.04 | 0.12 | 300 | 110–111[b] | 3.3 | 61.0 | — | 0 | 0 | |
| 4 | 4-Bromo | 46.0 | 0.04 | 0.12 | 300 | 173–3.5[c] | 3.7 | 98.0 | — | 0 | 0 | |
| 5 | 3-Iodo | 0 | 0.02 | 0.12 | 300 | 117–118[d] | 1.9 | 42 | — | 0 | 0 | |
| 6 | 4-Iodo | 0 | 0.02 | 0.12 | 300 | 202-203.5[e] | 1.1 | 37 | — | 0 | 0 | |
| 7 | 2,5-Dichloro | 0 | 0.02 | 0.12 | 125 | 146–7[f] | 0.124 | 3.7 | 188–9[l] | 0.19 | 6 | 2.1 gm. crude product |
| 8 | 3,4-Dichloro | 0 | 0.016 | 0.12 | 125 | 138–9[g] | 0.46 | 17 | — | 0 | 0 | 2.19 gm. crude product, m.p. 135°–137°C. |
| 9 | 2,4-Dichloro | 0 | 0.02 | 0.12 | 125 | 130.5[h] | 0.13 | 3.8 | 164–5[m] | 0.08 | 2.5 | |
| 10 | 2-Methyl-3-chloro | 0 | 0.02 | 0.12 | 125 | 121.3[i] | 1.5 | 52.0 | — | 0 | 0 | 2.0 gm. crude product, m.p. 119°–120°C. |
| 11 | 4-Acetamino | 0 | 0.02 | 0.12 | 125 | 273–4†[j] | 1.5 | 41.0 | — | 0 | 0 | |
| 12 | 3-Acetamino | 0 | 0.016 | 0.10 | 250 | 254–5[n] | 0.615 | 30.0 | — | 0 | 0 | |
| 13 | 4-Methoxy | 0 | 0.022 | 0.11 | 250 | 114[o] | 0.605 | 21.0 | | | | |

[a] *Ref.* (7), *155–6°C.*
[b] *Ref.* (1), *109–10°C.*
[c] *Ref.* (14), *175°C.*
[d] *Ref.* (10), *118–9°C.*
[e] *Ref.* (5), *119.0–9.5°C.*
[f] *Ref.* (2), *147°C.*
[g] *Ref.* (3), *137–138°C.*
[h] *Ref.* (12), *126–7°C.*
[i] *Ref.* (6), *122–3°C.*
[j] *Ref.* (11), *275°C.*
[k] *Ref.* (15), *185–6°C.*
[l] *Ref.* (2), *188–9°C.*
[m] *Ref.* (17), *161–2°C.*
[n] *Ref.* (10), *254°C.*
[o] *Ref.* (9), *116°C.*

**All melting points were checked against reliable standards.*

*†Further identified by conversion to the corresponding diaminoazoxy compounds.*

*No azoxy or azo compound could be found in the reaction mixture of the following: 2-nitroiodobenzene, 4-aminonitrobenzene, 2-nitroanisole, 3-nitroanisole, 3-nitrobenzaldehyde.*

## MATERIALS

Canadian Industries Limited reagent anhydrous absolute synthetic methyl alcohol Grade A-1 was used throughout. When first taken from the drum the alcohol contained 0.01% moisture. Alcohol containing 0.007% moisture was obtained by reaction with magnesium followed by slow distillation through an efficient column. The magnesium ribbon, turnings, and powder were Baker and Adamson, purified.

## EXPERIMENTAL

*Reaction of Magnesium with Methyl Alcohol as Measured by the Evolution of Gas (Curve 2, Fig. 1)*

Magnesium powder (0.0752 gm.) was added to methyl alcohol (25 ml., 0.007% water). Magnetic stirring was used. A water bath maintained the temperature at 25° ± 0.5°. The gas evolved was measured in the gas burette of Fisher Orsat precision model gas analyzer with the volume of gas evolved balanced against atmosphere pressure and read at one minute intervals.

*Hydrogen Consumed in the Presence of 4-Chloronitrobenzene*

(*a*) Polished magnesium ribbon (0.0800 gm.) in methyl alcohol (25 ml.) produced 66.9 ml. gas (0° C. and 760 mm.).

(*b*) Polished magnesium ribbon (0.0800 gm.) in methyl alcohol (25 ml.) containing 4-chloronitrobenzene (0.1028 gm.) produced 48.5 ml. gas (0° C. and 760 mm.).

Gas consumed = 66.9 − 48.5 = 18.4 ml. for 1 mole 4-chloronitrobenzene
= (18.4 × 157.5)/0.1028 ml.
= 1.26 moles gas/ 1 mole 4-chloronitrobenzene.

*Viscosity Changes During Reduction of 2,5-Dichloronitrobenzene by Magnesium and Methyl Alcohol*

2,5-Dichloronitrobenzene (2.6 gm.) was dissolved in methyl alcohol (150 ml.). To this solution was added freshly polished magnesium ribbon (2.37 gm.) cut into small pieces. The viscosity changes were followed by a Fisher electro-viscometer. The speed of the rotation of the spindle was checked at intervals by a stroboscope. The temperature was 24° ± 0.5° C. The relative viscosity was as follows: 130 sec.–7.0; 224 sec.–8.2; 415 sec.–12.0; 488 sec.–13.5; 552 sec.–12.7; 780 sec.–11.0; 980 sec.–10.2.

*Analysis of the Gas Produced by the Reaction Between Magnesium Powder, Ethyl Iodide, and Methyl Alcohol*

Magnesium powder (0.1675 gm.), ethyl iodide (1.7032 gm.), and methyl alcohol (25 ml.) were allowed to react. The gas was collected over mercury. Analysis by a mass spectrograph gave the following approximate results: methyl alcohol, 20%; ethane, 10%; ethylene, 15%; hydrogen, 55%. Suitable correction was made for background. The calibration for methyl alcohol was taken from a run on a pure sample while those for ethane and ethylene were taken from the average of several American Petroleum Institute spectrograms. The presence of ethylene was confirmed by infrared analysis of the same sample.

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*Reduction of 2,5-Dichloronitrobenzene by Magnesium Methylate*

Polished magnesium ribbon (2.9 gm.) was added to redistilled methyl alcohol (250 ml.). When all the magnesium had dissolved, 2,5-dichloronitrobenzene (3.8 gm.) was added to the hot solution. The mixture was allowed to stand for three days at room temperature and then diluted with water, acidified with hydrochloric acid, and then steam distilled. 2,5-Dichloronitrobenzene (2.3 gm., m.p. 52° C.) was recovered from the steam distillate. A small quantity of a product remained. Recrystallization produced a few milligrams of 2,2′,5,5′-tetrachloroazoxybenzene (m.p. 145° C.).

*Reduction of 2,2′,5,5′-Tetrachloroazoxybenzene by Magnesium Methylate*

2,2′,5,5′-Tetrachloroazoxybenzene (1 gm., m.p. 145° C.) was added to a freshly prepared solution of magnesium methylate and allowed to stand for several hours. The recovered product, melting at 142°–143°, was separated into four fractions melting respectively at 145°–146° C., 144°–145° C., 145°–146° C., and 184°–186° C. The last fraction is the reduction product, 2,2′,5,5′-tetrachloroazobenzene.

*Reduction of 4-Chloronitrobenzene by Magnesium and Methyl Alcohol (Expt. 1, Table II)*

4-Chloronitrobenzene (3.15 gm., 0.02 mole) was dissolved in redistilled methyl alcohol (125 ml.) in a 250-ml., three-necked flask provided with a reflux condenser and a pyrex stirrer with a mercury seal. Magnesium turnings or short pieces of polished ribbon (2.9 gm., 0.12 mole) were added to the solution. A rapid reaction set in and the alcohol reached the boiling point within 10 min. After the solution of the magnesium was complete, the mixture was heated at reflux temperature for two hours. It was diluted with water, neutralized with hydrochloric acid to dissolve the magnesium hydroxide, and then steam distilled. In the distillate was unchanged 4-chloronitrobenzene (0.3 gm.). The product remaining was dissolved in alcohol and separated by fractional crystallization into 4,4′-dichloroazoxybenzene (1.4 gm., m.p. 155.5°–156.5° C.) and 4.4′-dichloroazobenzene (0.77 gm., m.p. 183°–184° C.).

*Reduction of 2,5-Dichloronitrobenzene by Magnesium and Methyl Alcohol in the Presence of Water*

Water (1 ml.) was added to 2,5-dichloronitrobenzene (3.8 gm., 0.02 mole) dissolved in methyl alcohol (0.06% water) in a 250-ml., three-necked flask provided with a reflux condenser and a pyrex stirrer with a mercury seal. Freshly polished magnesium ribbon (2.9 gm., 0.12 mole) cut into small pieces was added. The reaction began at once but the temperature did not exceed 31° C. At the end of 30 min., water (1 ml.) was again added and after two hours the temperature was raised to 45°. At the end of five hours the reaction was complete.

The mixture, after being diluted with water and neutralized with hydrochloric acid to dissolve the magnesium hydroxide, was steam distilled. In the distillate was unchanged 2,5-dichloronitrobenzene (1.2 gm.). The residue from the steam distillation was dissolved in methyl alcohol and treated with Norite.

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Fractional crystallization of the product gave 2,2′,5,5′-tetrachloroazoxybenzene (m.p. 144°–145° C.). The yield was 0.7878 gm. or 35% calculated on the 2,5-dichloronitrobenzene converted.

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# CONSTRUCTION AND USE OF A SEMIMICRO LIGHT-SCATTERING APPARATUS[1]

By D. A. I. Goring

ABSTRACT

A light-scattering apparatus requiring only 4 ml. of liquid was designed and built. The device has permitted the measurement of intensity for angles between $37\frac{1}{2}°$ and 135° to the incident beam. In this range the unpolarized, horizontal, and vertical components of the light emitted from a solution of fluorescein were constant to within ±0.2%, 0.4%, and 0.6% respectively. The apparatus was calibrated with a suspension of Ludox colloidal silica which absorbed no light for $\lambda$ = 3800 Å to 6000 Å. The suspension was found to possess all the properties of a Rayleigh scattering system except randomness. This condition was achieved by extrapolating the light-scattering and spectrophotometric functions to zero concentration when computing the calibration factor. The molecular weight of a sample of sodium carrageenate, determined by the method of Zimm, was 1,700,000. The distribution of intensity at zero concentration fell between that for stiff rods and polydisperse coils.

## INTRODUCTION

No description has yet been published of a light-scattering apparatus specifically designed for a small volume of liquid. The present device evolved directly from an earlier model briefly described in a previous publication (10).

Construction of a geometric photometer similar to that of Brice, Halwer, and Speiser (1) was not attempted; the precise optical system required would be difficult to combine with a small cell volume and a continuous observation of the angular variation of intensity. Instead the apparatus was calibrated with a liquid the turbidity of which was measured spectrophotometrically. Provided a suitable calibrating liquid is chosen this method has been shown to give reliable values of the molecular weight (10).

To illustrate the use of the device a measurement of particle size has been given for the polysaccharide, carrageenin. The molecular weight, $M$, was determined from the usual equation

$$[1] \qquad H\left(\frac{c}{\tau}\right)_{c=0} = \frac{1}{M}$$

where $\tau$ is defined as the turbidity, due to scattering alone, which the solution would show if the particles obeyed the Rayleigh law and therefore produced a symmetrical distribution of intensity. In Eq. [1] $c$ is the concentration and the constant $H$ has the usual significance.

Since the polysaccharide solution showed a large dissymmetry of scattering the more accurate method of Zimm (17) was used. The intensity of scatter, $I_\theta$, was measured for different values of the angle, $\theta$, defined by the direction of scattering and the transmitted beam. A graph of $c/I_\theta$ vs. $\sin^2\frac{1}{2}\theta + \kappa c$ was drawn where $\kappa$ was a constant chosen to separate the distribution of intensity

[1] *Manuscript received July 29, 1953.*
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for each concentration. The value of $\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}}$ was found by extrapolation. The value of $(c/\tau)_{c=0}$ was obtained from

$$[2] \qquad \left(\frac{c}{\tau}\right)_{c=0} = C\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}}$$

where $C$ was the calibration factor determined with a Ludox suspension. To obtain $M$, $(c/\tau)_{c=0}$ was substituted in Eq. [1].

The distribution of intensity at $c = 0$ was computed from the Zimm plot and was compared with theoretical distributions predicted for spheres, coils, and rods.

## THE LIGHT-SCATTERING APPARATUS

A photograph and a plan of the light-scattering apparatus are shown in Figs. 1 and 2 respectively.

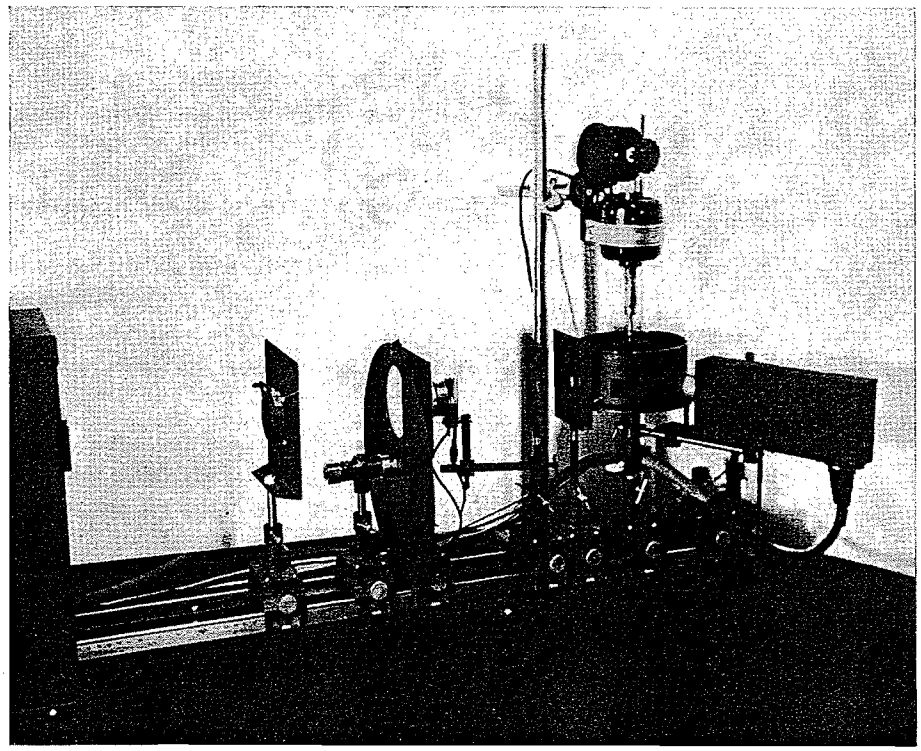


FIG. 1. Photograph of the light-scattering apparatus.

Light from source B was focused on slit C. An image of C was produced by lens E in the center of the scattering cell Q. Scattered light from the center of Q was focused by lens T through slit U on photomultiplier tube V.

The components for the primary beam (A → P) were mounted on a 125 cm. optical bench. The cell was immersed in a cylindrical water bath, K, which

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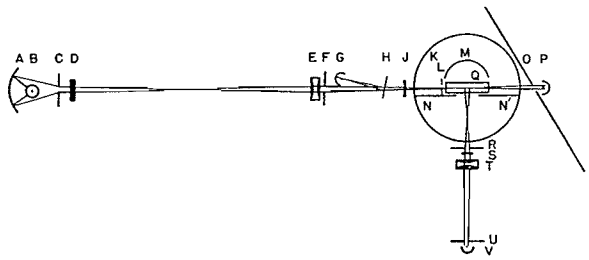



FIG. 2. Plan of the light-scattering apparatus. The letters corresponding to various parts are referred to in the text.

rested on a circular table mounted on the optical bench. The components for the scattered beam (R → V) were mounted on a rotatable arm centered below the table.

*Light Source*

The light source was a General Electric AH-4 mercury arc. Current to the lamp was drawn from the 110 v. mains and stabilized with a 500 w. Sola constant-voltage transformer. The operating current was adjusted to the recommended value of 0.9 amp. by means of a Variac transformer. After the lamp had been running 15 min. variations in the current were less than 0.5%.

As shown in Fig. 2, a concave spherical mirror, A, with a radius of curvature of 64 mm. focused an image of the lamp on slit C. The mirror proved more effective than a condensing lens for increasing the incident intensity.

A filter, D, in the incident beam gave monochromatic light. Wratten filters 77A and 76 were used for the 5461 Å and the 4358 Å lines respectively.

The lamp, mirror, and slit were enclosed in a ventilated, light-proof housing with filter D covering the opening for the incident beam.

*The Incident Beam*

To reduce the size of the beam in the cell, the distance between slit C and lens E was approximately twice that between the center of the cell, Q, and lens E. Slit C was 8 mm. high by 3 mm. wide, making the dimensions of the incident beam in the cell 4 mm. high by 1.5 mm. wide.

Lens E was a Schneider-Zenir f 4.5, with a focal length of 150 mm. A rectangular stop, F, set the convergence in the horizontal and vertical planes at 2.5° and 8° respectively.

The incident beam entered the water bath, K, through a cylindrical surface. To counteract the convergence produced in the horizontal plane, a plano-concavo cylindrical spectacle lens, J, was set adjacent to the entrance window. A sharp image of slit C was thereby produced in the scattering cell.

After traversing the scattering cell, the incident beam passed through a baffle O on to a phototube P. Comparative measurements of the transmitted intensity were made with P in order to compute the decrease in intensity of the incident beam on traversing the half-length of the cell. A correction for the decrease was applied to the intensity. This correction is important when colored solutions are studied (10).

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Fluctuations in incident intensity were measured by a phototube, G, on to which was focused light reflected from a microscope cover glass, H, set at 7° to the incident beam. No polarization was found in the incident light after passage through the cover glass. During an experiment the variation in lamp intensity measured at G was less than 1%, so that for routine work the monitor was removed from the apparatus and was only used when highest accuracy was desired.

*The Cell and Water Bath*

The cylindrical water bath (K in Fig. 2) was a pyrex crystallizing dish, 125 mm. in diameter, selected visually to be free from optical aberration. As shown in Fig. 3, the position of the bath on the table was adjusted by three centering screws.

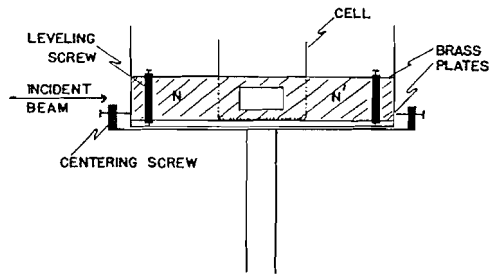



FIG. 3. Section of the table and cylindrical water bath showing the position of the cell and the baffle NN'.

Two brass plates, held 24 mm. apart by three pillars, fitted exactly into the dish and supported the cell and the baffles L, M, and NN'. The cell fitted closely through a rectangular hole cut in the center of the upper plate and a rectangular recess in the lower plate. Leveling screws were fitted through the pillars separating the plates. If desired, the temperature of the water bath could be controlled by flat coils of copper tubing above the top plate and below the bottom plate.

The cells were made of optical glass* 2 mm. thick and had inside dimensions of length, height, and width equal to 40 mm., 50 mm., and 5 mm. respectively. With 4 ml. of liquid in the cell the height of the meniscus cleared the top of the incident beam by 6 mm.

The system of baffles is shown in Figs. 2 and 3. The baffle NN' shielded from the photomultiplier tube the path of the incident beam through the bath and the ends of the cell. The scattered light was viewed through a rectangular hole, 12 mm. high and 19.5 mm. wide in NN'. The size of the hole and position of the baffle were chosen to permit unbroken passage of the scattered beam between $\theta = 37\frac{1}{2}°$ and $\theta = 135°$.

A semicircular baffle, M (Fig. 2), was placed behind the cell to prevent reflections from the back of the water bath entering the photomultiplier. A plate, L, with a rectangular hole, 7.5 mm. high by 2.5 mm. wide, was set in the path of the incident beam near the cell. This baffle stopped any diffuse light

*Cells were supplied in pyrex and soft glass by the Pyrocell Manufacturing Co.

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from entering the cell. Baffles and bath were painted flat black; small windows were left clear for the primary beam and scattered light.

*The Scattered Beam*

The distance between slit U and lens T (Fig. 2) was twice the distance between the center of the scattering volume and T. Slit U was 12 mm. high by 6 mm. wide and therefore the area in the cell from which scattered light was received was 6 mm. high by 3 mm. wide. The position of lens T was adjusted so that an image of U (obtained by substituting a galvanometer lamp for the photomultiplier tube) was in sharp focus in the center of the cell. A rectangular stop, R, reduced the convergence to 8° in the vertical plane and to 3° in the horizontal plane.

Lens T was a Schneider-Componar f-4.5, with a focal length of 50 mm. As in the incident beam, a plano-concavo cylindrical spectacle lens, S, was included to counteract the convergence of the water bath and thereby to permit a sharp image of slit U in the center of the scattering cell. Therefore the scattering volume was defined by the height (4 mm.) and width (1.5 mm.) of the incident beam and the width (3 mm.) of the image of U in the cell.

From an angular scale on the edge of the table, the direction of the analyzing arm was determined. To prevent stray light entering the photomultiplier, the components S → V of the analyzing arm were enclosed in a light-proof box with stop R as the only opening.

The photomultiplier was an R.C.A. 1P21 phototube. A potential of 90 v. was maintained across the dynodes and between the anode and dynode 9 a potential of 45 v. was used. Dry cells were found to be a stable and reliable source of power.

The output of the photomultiplier was read directly on a d'Arsonval galvanometer and the sensitivity was controlled with an Ayrton shunt. Dark currents were 0.004 μamp. The additional output for $I_{90}$ from a dust-free solution of 0.1 *M* sodium acetate was 0.004 μamp. which corresponded to 10 mm. on the galvanometer scale. Thus the sensitivity was adequate even for the extremely small intensity scattered by 0.1 *M* aqueous sodium acetate.

*Correction and Normalizing Factors*

It was necessary to apply several factors and small corrections to the data.

(1) *Variations in intensity and sensitivity.*—The galvanometer deflection for the light scattered was divided by the deflection for the 90° intensity from a plastic block. Thus variations in the intensity of the lamp or in the sensitivity of the photomultiplier were accurately compensated. The block was machined from a piece of Lucite which was four years old. It was kept in the dark and the scatter from it was assumed constant.

(2) *Change in scattering volume.*—For any position of the analyzing arm the scattering volume was assumed to be a right parallelapiped. A factor, $\sin\theta$, was applied to the observed intensity to allow for increase in the scattering volume for angles other than 90°.

(3) *The horizontal component.*—Unpolarized light was used in the incident beam and therefore the scattered light contained a horizontal component pro-

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portional to $\cos^2\theta$. To normalize the intensity it is usual to apply the factor $1/(1 + \cos^2\theta)$. The 1P21 photomultiplier tube was found to be 1.013 times more sensitive to vertically than to horizontally polarized light. The normalizing factor used was, therefore, $1/(1 + 0.987\cos^2\theta)$.

(4) *Depolarization.*—The depolarization, $\rho$, was measured by means of a polaroid placed in the scattered beam in the 90° position. When the value of $\rho$ was significant ($> 0.005$) the molecular weight was multiplied by the factor $(6 - 7\rho)/(6 + 6\rho)$ (Ref. 6).

(5) *Dark current.*—With the photomultiplier in circuit, a shutter was placed across the incident beam and the galvanometer set at zero. On illuminating the solution the deflection obtained was due only to the light scattered. By this method a direct measurement of the dark current was unnecessary.

(6) *Refractive index corrections.*—If liquids of different refractive indices are used in the scattering cell, correction must be made for the change in (*a*) the scattering volume (8) and (*b*) the size of the cone of light received by the lens T (Fig. 2) on the analyzing arm (8, 10). Only dilute aqueous solutions were used in the present work; it was assumed that the refractive index remained constant thereby precluding the necessity of a correction.

(7) *Scatter of solvent.*—Intensities for the solvent were measured and subtracted from those for the solution.

(8) *Reflection.*—As pointed out by Sheffer and Hyde (14) the reflection in a *backward direction* from flat surfaces at the end of the cell can alter the distribution when a large dissymmetry exists. In the present device the two water–glass interfaces produced a back reflection of 0.8% of the incident beam which was assumed negligible.

*Testing the Apparatus*

The symmetry of the apparatus was tested by observing the distribution of intensity emitted by a solution of 1 mgm. per liter of fluorescein in 0.1 *M* sodium acetate solution. Using an unpolarized incident beam, measurements were made of the unpolarized and the vertically and horizontally polarized components of the fluorescence. With fluorescein, the intensity of fluorescence is equal in all directions and therefore the factor $1/(1 + 0.987\cos^2\theta)$ was not applied; the intensity was corrected by the factor, $\sin\theta$, for the change in scattering volume and the horizontal component was multiplied by the factor 1.013.

As shown in Fig. 4, $I_\theta$ was constant within ±0.2% for the unpolarized light. The horizontal and vertical components were constant within ±0.4% and ±0.6% respectively. This result showed that the apparatus was set up in a symmetrical manner and that the correction for the variation of the scattering volume with $\theta$ was accurate.

As a final test for absence of secondary reflections the distribution of intensity scattered by a 0.1 *M* aqueous solution of sodium acetate was measured. In Fig. 5 the unpolarized and horizontally and vertically polarized components of the envelope are given: for comparison, the unpolarized envelope of a phosphate buffer obtained with the apparatus described by Goring and Johnson (10) is given also.

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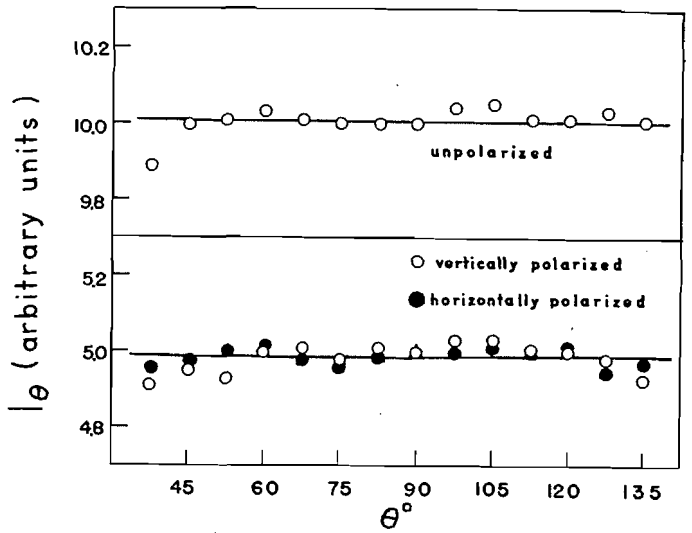



FIG. 4. Distribution of intensity of light emitted by a solution of 1 mgm. per liter of fluorescein in 0.1 *M* sodium acetate solution. The scale of the ordinate was chosen to magnify the errors.

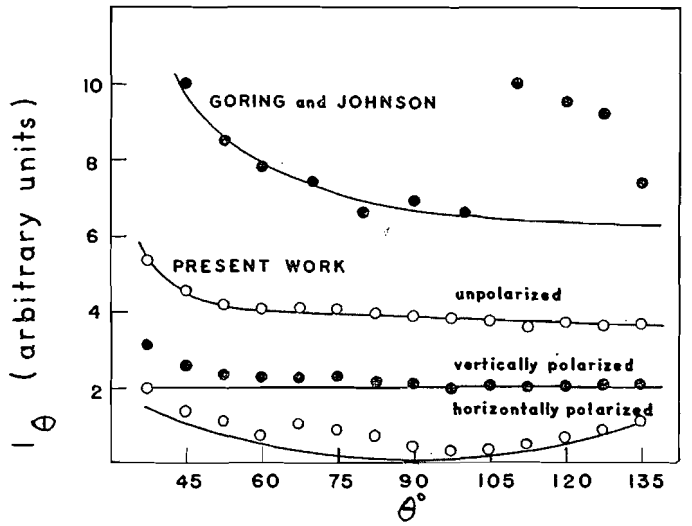



FIG. 5. Unpolarized and vertically and horizontally polarized components for a 0.1 *M* solution of sodium acetate; and on the same absolute scale the envelope of a phosphate buffer (pH = 7.7; I = 0.05) determined by Goring and Johnson on the previous apparatus (10).

As shown in Fig. 5, the absence of large irregularities for the distributions obtained with the present device indicated that secondary reflections were almost completely eliminated. There was a small anomalous increase in the horizontal component for $\theta = 67\frac{1}{2}°$ to $\theta = 90°$. This effect was reproducible and was probably due to minute reflections from various parts of the instrument. Comparison of the unpolarized distribution with the previously obtained envelope showed a marked improvement in regularity. The difference in absolute intensities was not significant since different solutions were used.

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*Calibration*

The apparatus was calibrated with suspensions of Ludox colloidal silica the turbidities of which were determined spectrophotometrically. Ludox has been used by Tietze and Neurath (15) and is recommended by Oster (12) as a calibrating solution. An electron micrograph of its particles (Fig. 6) shows a fairly

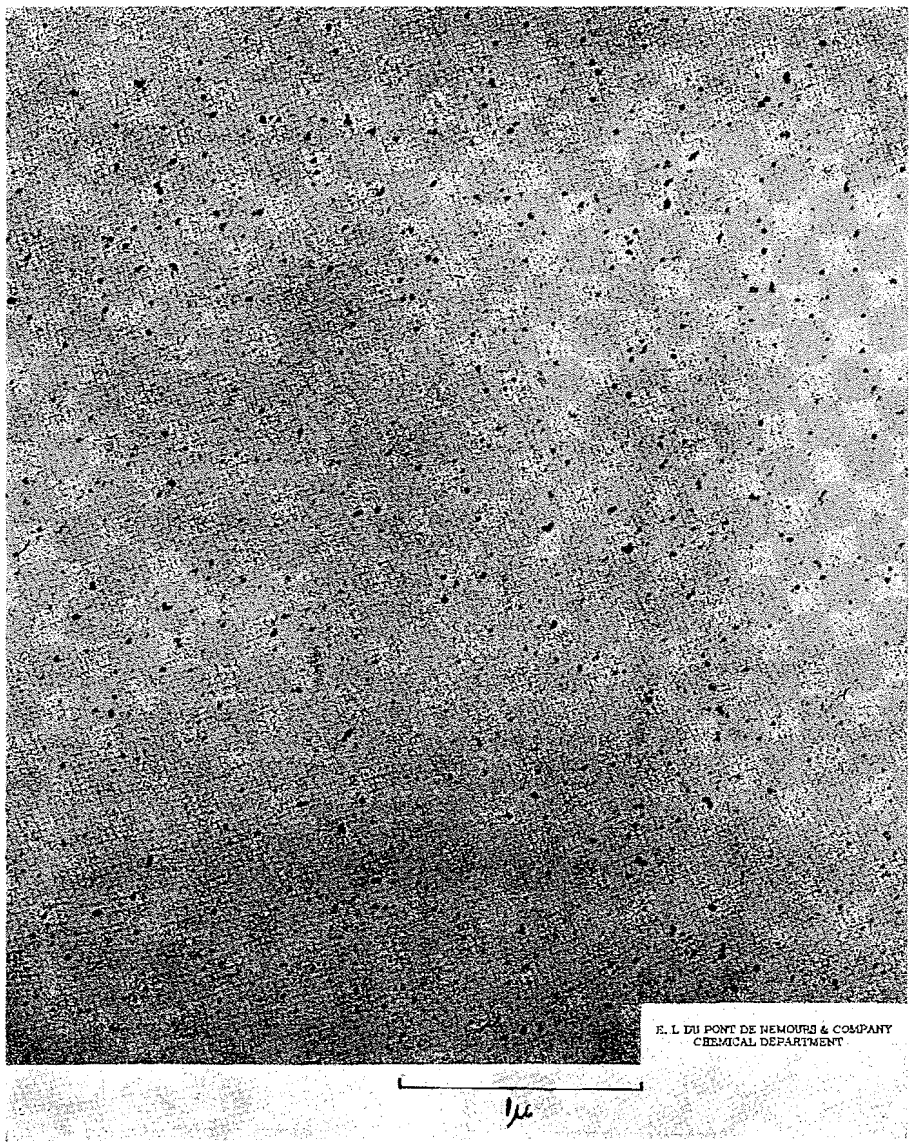



FIG. 6. An electron micrograph of Ludox particles (reproduced by kind permission of Mr. J. M. Rule of DuPont).

uniform particle size with an average diameter of about 200 Å. Such a suspension would approximate to a simple Rayleigh system and therefore would be a

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good calibrating liquid provided there was no absorption of light and the total dissipation in the transmitted beam was due to scattering alone.

For a given solution in which $c$, $M$, and the interaction constant, $B$, do not vary, the light-scattering equation (6) may be written

$$[3] \qquad \frac{\lambda^4\tau}{(n_0 dn/dc)^2} = \text{constant}$$

where $\lambda$ is the wave length of the incident beam, $n_0$ is the refractive index of the solvent, and $dn/dc$ is the refractive index increment. If the solution is a Rayleigh scattering system showing no absorption, the spectrophotometrically determined values of $\tau$ should give a constant value of $\lambda^4\tau/(n_0\, dn/dc)^2$ for a range of wave lengths.

To test the constancy of $\lambda^4\tau/(n_0\, dn/dc)^2$ for Ludox,* the variation of $\tau$, $n_0$, and $dn/dc$ with $\lambda$ was required. The variation of $\tau$ was measured with a Beckman DU spectrophotometer using 5 cm. cells. A tungsten filament was used as a source. A vertical slit, 2 mm. wide by 10 mm. high, was set in front of the photocell on the spectrophotometer. The slit was 8 cm. from the center of the 5 cm. cell. The area of the slit was 1/500 the area of the spherical surface containing the slit about the center of the 5 cm. cell. Thus a relatively negligible quantity of light scattered at low angles to the beam could enter the slit and reach the photocell. Although the slit decreased the sensitivity of the instrument, an accurate balance could be obtained for all wave lengths from 3800 Å to 6000 Å with a spread of 20 Å in the wave length of the monochromator beam.

The change of $n_0$ with $\lambda$ was assumed to be the same as that for water. The refractive index increment was measured at 4358 Å and 5461 Å with a Bellingham and Stanley critical angle refractometer; the values of $dn/dc$ at different wave lengths were obtained by assuming a linear variation of $dn/dc$ with $\lambda$. The error involved in this assumption was small since $dn/dc$ for Ludox decreased by only 1.5% from $\lambda$ = 4358 Å to $\lambda$ = 5461 Å.

The graph of $\lambda^4\tau/(n_0\, dn/dc)^2$ vs. $\lambda$ for a Ludox suspension is given in Fig. 7. The value of $\lambda^4\tau/(n_0\, dn/dc)^2$ is constant to within $\pm 1.2\%$. The small regular increase at the higher wave lengths would result if a nonlinearity existed in the relationship between $dn/dc$ and $\lambda$.

A series of four Ludox suspensions of concentrations from 7% to 1.8% (by dry weight) were used to determine the calibration factor. The turbidity of each was measured in the Beckman at the wave length of the highest intensity emitted from the green line of the mercury arc. From the graph of $c/\tau$ vs. $c$ shown in Fig. 8 $(c/\tau)_{c=0}$ was obtained.

A distribution of scattered intensity for each of these concentrations was measured in the light-scattering apparatus. The data were represented as a Zimm plot part of which is shown in Fig. 9. The $\theta = 0$ and $c = 0$ lines extrapolated to a common intercept to give $\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0 \\ c=0}}$.

*Kindly donated by Mr. J. M. Rule of Du Pont de Nemours, Delaware.*

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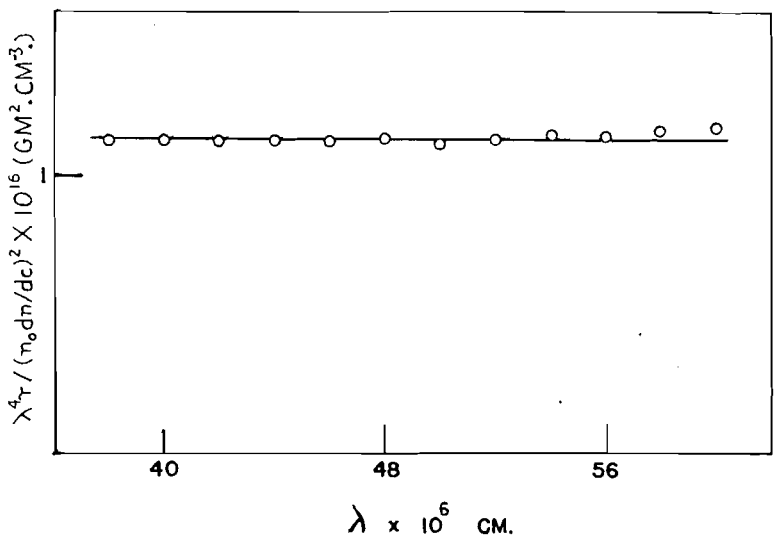



FIG. 7. $\lambda^4\tau/(n_0\, dn/dc)^2$ vs. $\lambda$ for a 7% suspension of Ludox colloidal silica.

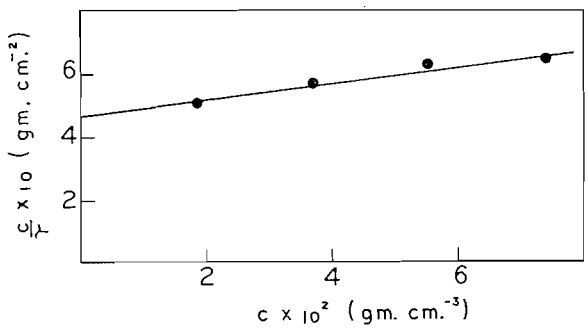



FIG. 8. $c/\tau$ vs. $c$ for Ludox suspensions.

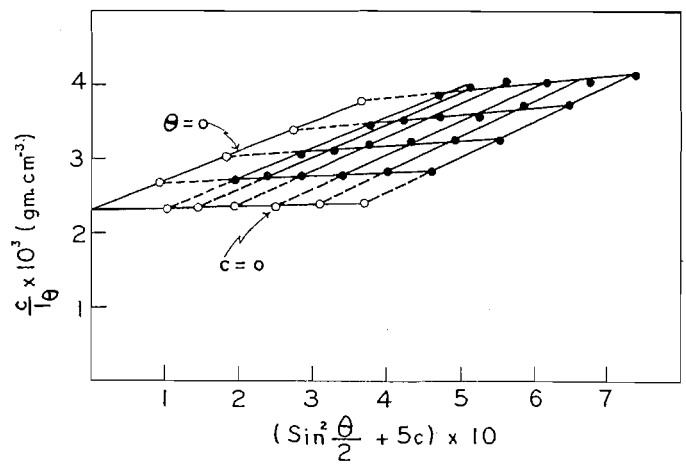



FIG. 9. Zimm plot for Ludox. The range of concentration was from $7.4 \times 10^{-2}$ to $1.8 \times 10^{-2}$ gm.cm.$^{-3}$; the range of $\theta$ was from $37\frac{1}{2}°$ to 75°.

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It was necessary to make a small adjustment to allow for the dissymmetry. The turbidity in Eq. [1] used for computing $M$ is taken as that which the solution would have had if interference had not caused a decrease of scatter in the backwards direction. Therefore, in calibrating, the relationship between $\tau$ and $I_\theta$ should be that for a Rayleigh system. If a dissymmetry exists, the value of $\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}}$ will be smaller than that for an ideal system having the observed $(c/\tau)_{c=0}$. By a graphical integration it was found that for spheres showing a small dissymmetry, the error can be corrected by using

$$\tfrac{1}{2}\left[\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}} + \left(\frac{c}{I_\theta}\right)_{\substack{\theta=180\\c=0}}\right]$$

instead of $\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}}$. The calibration factor, $C$, was then obtained from

[4] $$\left(\frac{c}{\tau}\right)_{c=0} = \frac{C}{2}\left[\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}} + \left(\frac{c}{I_\theta}\right)_{\substack{\theta=180\\c=0}}\right].$$

The value of $C$ was decreased 4.2% by this correction for dissymmetry.

## MOLECULAR WEIGHT OF CARRAGEENIN

Sodium carrageenate was prepared from Irish moss by aqueous extraction and dialysis (2, 16). For light-scattering the polysaccharide was dissolved in acetate buffer (pH = 5.5; I = 0.05) made up by the method of Green (11). Dilutions were made in the cell. Motes were removed by centrifuging in stainless steel cups at 27,000 g. for 20 min. Ultrafiltration (9) was not successful because the polysaccharide clogged the filter.

The Zimm plot is given in Fig. 10. From $\theta = 135°$ to $\theta = 75°$ readings were taken every 15°; from 75° to $37\frac{1}{2}°$ readings were taken every $7\frac{1}{2}°$ to facilitate extrapolation to $\theta = 0$. For constant angle, $c/I_\theta$ varied linearly with $c$ and the

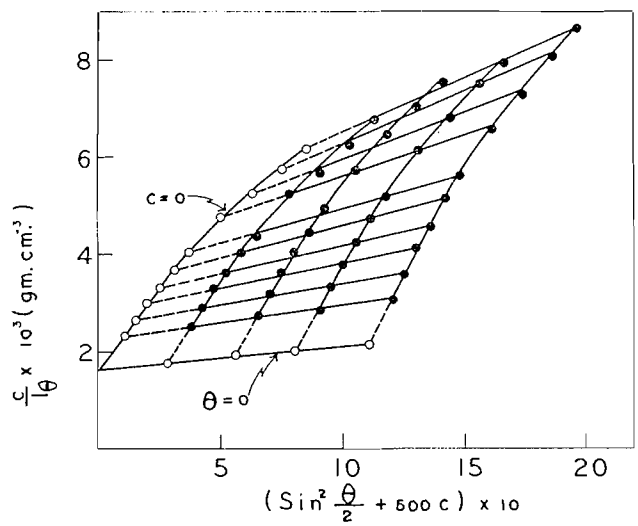



FIG. 10. Zimm plot for sodium carrageenate in sodium acetate buffer (pH = 5.5; I = 0.05). The range of concentration was from $2.2 \times 10^{-3}$ to $0.6 \times 10^{-3}$ gm.cm.$^{-3}$; the range of $\theta$ was from $37\frac{1}{2}°$ to 135°.

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best straight line between the four points at different concentrations was used for extrapolation. The variation of $c/I_\theta$ with $\sin^2\frac{1}{2}\theta$ at constant concentration showed a curvature for higher values of $\theta$. From $\theta = 67\frac{1}{2}$ to $\theta = 37\frac{1}{2}$ the graph was essentially linear and extrapolation of these five points was used to determine $(c/I_\theta)_{\theta=0}$.

The extrapolations of the curves for $\theta = 0$ and $c = 0$ gave a common intercept for $\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}}$ which equalled 0.0016. From this value and the calibration factor, $(c/\tau)_{c=0}$ was 0.31 gm. cm.$^{-2}$. The refractive index increment for sodium carrageenate was found to be 0.131 gm.$^{-1}$ cm.$^3$ from which $H$ was computed. By substituting these results in Eq. [1] a molecular weight of 1,700,000 ($\pm$100,000) was obtained.

## DISCUSSION

### *Performance*

In several ways the present apparatus was superior to its predecessor (10). It required only 4 ml. whereas in the previous model a volume of 15 ml. was necessary. It was more stable and sensitive and could be used over a wider range of angular distribution. Also, as shown in Fig. 5, it was freer from secondary reflections.

It was anticipated that reflection from the flat sides of the cell would distort the distribution. From Fresnel's laws it was computed that for $\theta = 37\frac{1}{2}°$, 4.1% of the light is reflected back from the two glass–water interfaces. For $\theta = 90°$, the intensity of reflection is 0.8%. Thus, a distribution of intensity should show an appreciable decrease for angles away from the 90° position.

Because of the long, narrow shape of the scattering cell, this error was compensated by a similar reflection from the back of the cell. The effect is illustrated in Fig. 11. A secondary scattering volume may be defined as the volume emitting light which, when reflected from the back of the cell, is received by the analyzing arm. If the incident beam is assumed to be parallel and the width

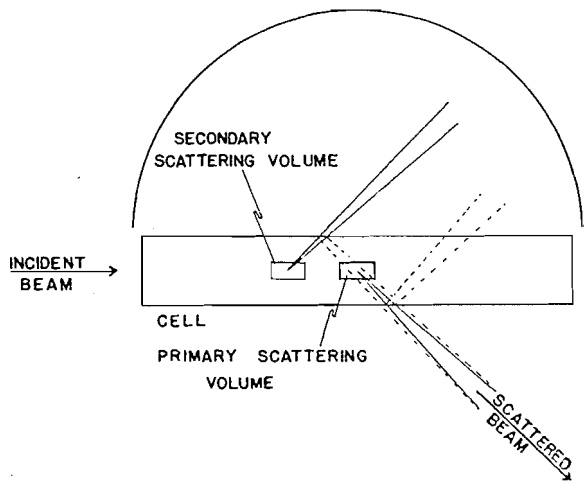



FIG. 11. Illustrating the manner in which part of the light scattered in the secondary scattering volume is reflected from the back of the cell and reinforces the main scattered beam.

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of the cell (5 mm.) is small compared with the distance between the scattering volume and lens T (90 mm., see Fig. 2) the primary and secondary scattering volumes are the same size. Thus the reflected light received by the analyzing arm from the secondary scattering volume will be similar in intensity and composition to the light lost from the primary scattering volume due to back reflection. This compensation occurred in the present apparatus since $I_\theta$ was found constant for the range of angles studied as shown in Fig. 4.

The incomplete removal of motes was assumed to cause the dissymmetry found in the distribution for 0.1 *M* sodium acetate (Fig. 5). Alternate causes were (*a*) diffuse secondary reflections at angles near the incident beam or (*b*) a dissymmetry in the solution itself. In any case the intensity was very small in comparison with that scattered by the solutions of carrageenin ($I_{90}$ for a buffer was $I_{90}/100$ for a 0.3% solution of sodium carrageenate) and any error was further reduced by subtraction.

It is interesting to note that, as shown in Fig. 5, the vertically and horizontally polarized components for the sodium acetate solution were approximately a Rayleigh distribution. The turbidity was $2.17 \times 10^{-5}$ cm.$^{-1}$; this value equals that for a 0.1% solution of a protein having a molecular weight of 6000.

*Calibration*

The turbidity of the calibrating solution should be related to intensity of scatter in the unique manner defined by the Rayleigh equation. Therefore the scatterers should be small, random, and isotropic. The further condition of nonabsorption is imposed because the turbidity is determined spectrophotometrically.

The constancy of $\lambda^4\tau/(n_0\, dn/dc)^2$ for the Ludox suspension (Fig. 7) indicated that no absorption of light occurred in the range of wave lengths from 3800 Å to 6000 Å. The depolarization was small (0.007) showing negligible anisotropy. From the Zimm plot (Fig. 9) $I_{45}/I_{135}$ was 1.06. Thus the envelope was almost symmetrical indicating that the particle size was small enough to give a near approximation to Rayleigh scattering; the error involved was eliminated by the correction mentioned earlier.

Randomness could not be assumed since concentrations as high as 0.074 gm. cm.$^{-3}$ were used. The slope of $(c/I_\theta)_{\theta=0}$ vs. $c$ in Fig. 9 showed that intermolecular interaction occurred. However, from the Zimm plot the limiting relationship between $\left(\frac{c}{\tau}\right)_{c=0}$ and $\left(\frac{c}{I_\theta}\right)_{\substack{\theta=0\\c=0}}$ was obtained in which the scatterers were completely random. This was the main advantage of the extrapolation method.

It was interesting to compare the extrapolation method of calibration with the more usual technique based on a determination of the 90° intensity.* For each concentration of Ludox, $C_{90}$ was calculated from

$$[5] \qquad \frac{1}{\tau} = C_{90} \times \frac{1}{I_{90}}.$$

**With the 90° method of calibration it is more accurate not to apply a dissymmetry factor since, for a suspension of spheres showing a small dissymmetry, $I_{90}$ is a good approximation to the constant value of $I_\theta$ for the ideal system of equivalent turbidity. The earlier apparatus (10) was calibrated by the 90° method and a correction for dissymmetry was made. The discrepancy observed in the calibrating factors for different solutions was probably due in part to this error.*

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If each calibrating solution obeyed the Rayleigh law, the $C_{90}$ values should be constant and equal to $C$ determined by the extrapolation method. As shown in Fig. 12, $C_{90}$ increased from 162 to 181 cm. when $c$ decreased from 0.074 to 0.018 gm. cm.$^{-3}$. The variation in $C_{90}$ may have been due to inapplicability of the Rayleigh equation at high concentration because of nonrandom-

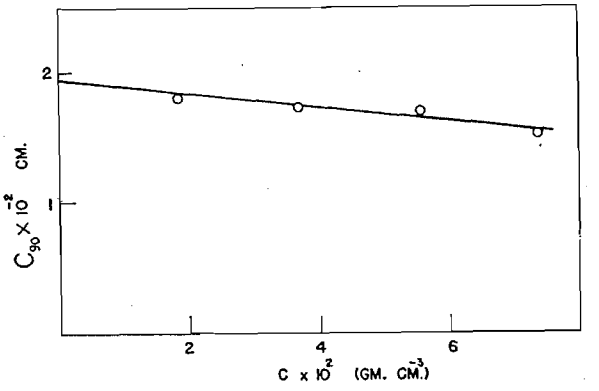



FIG. 12. $C_{90}$ vs. $c$ for Ludox solutions.

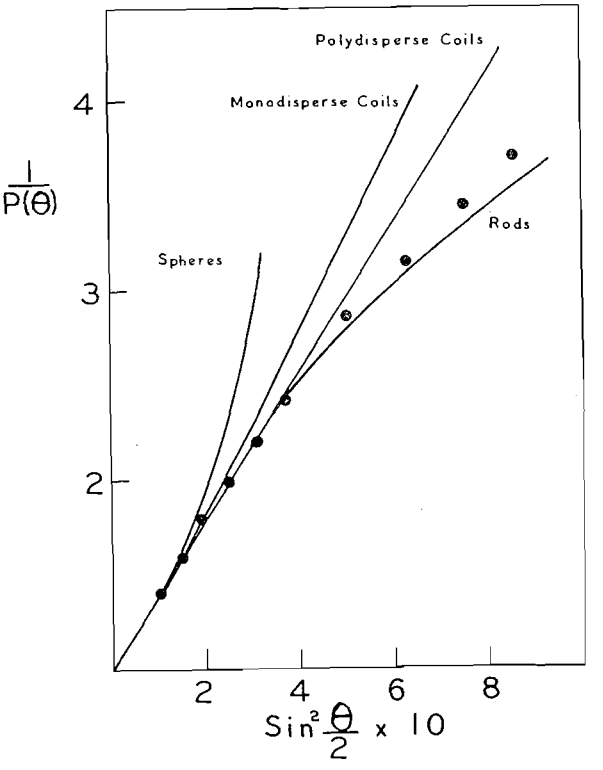



FIG. 13. Graph of $1/P(\theta)$ vs. $\sin^2\frac{1}{2}\theta$. The points are for sodium carrageenate derived from the data in Fig. 10. The lines are computed for various shapes from the figures published by Doty and Steiner (7).

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ness. In Fig. 12, $(C_{90})_{c=0}$ was 194 cm. in good agreement with the factor 195 cm. obtained by the extrapolation method.

*Molecular Size and Shape of Carrageenin*

The molecular weight of 1,700,000 was higher than the values of 100,000 to 500,000 reported by Cook, Rose, and Colvin (3) for samples of carrageenin of various degrees of degradation. The higher value may have resulted from a milder extraction of the polysaccharide in the present work.

As noted by Doty and Bunce (5) and by Peterlin (13) the angular distribution of intensity can indicate the shape and characteristic dimension of the molecule. In Fig. 13 the distribution at $c = 0$ is given as $1/P(\theta)$ vs. $\sin^2\frac{1}{2}\theta$. The data are compared with theoretical curves for various shapes computed from the figures published by Doty and Steiner (7).

The distribution was nearest to that for a stiff rod; the length of the rod was 3700 Å. Peterlin (13) has shown that for a chain in which the orientation from link to link is not random, the graph of $1/P(\theta)$ vs. $\sin^2\frac{1}{2}\theta$ approaches that of a stiff rod. The carrageenin molecule is believed to contain one branch point for every 10 hexose residues (4) and therefore a straight chain configuration is unlikely. However an extended branched structure, flexible in its major axis, could give the observed distribution.

It is always possible that the shape of the envelope was distorted by a small concentration of heavy aggregates not removed by centrifuging. Thus more detailed interpretation is postponed until the dispersion in particle size has been determined.

ACKNOWLEDGMENTS

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# STUDIES ON THE GLYCOPROTEINS OF THE DOMESTIC FOWL

## I. A MODIFICATION OF THE METHOD OF ELSON AND MORGAN FOR THE DETERMINATION OF HEXOSAMINE, AND ITS APPLICABILITY TO TISSUE HYDROLYZATES[1]

By P. A. Anastassiadis and R. H. Common

ABSTRACT

The method of Elson and Morgan for the determination of hexosamine has been studied spectrophotometrically with the object of applying the method to the analysis of tissue hydrolyzates. It has been shown that it is possible by appropriate blanks to correct for interference due to humin. It has been found necessary (*a*) to increase the strength of the buffer solution in order to stablize the pH and, in extreme cases, first to neutralize the dried hydrolyzate; and (*b*) to increase the amount of acetylacetone. These modifications also reduce interference by hydroxyproline to a minimum. The use of an appropriate excess of acetylacetone was found to depress the formation of the secondary chromogen during acetylation. A procedure based on these findings is proposed for the direct determination of hexosamine in acid hydrolyzates of tissues.

## INTRODUCTION

The colorimetric method of Elson and Morgan (2) for the determination of hexosamine depends on acetylation of the hexosamine with acetylacetone in the presence of sodium carbonate. This treatment is said to yield a pyrrole derivative. On treating the solution with excess ethanolic hydrochloric acid containing *p*-dimethylaminobenzaldehyde (Ehrlich reagent), the pyrrole derivative yields a red color. Subsequent workers, including Immers and Vaseur (5), have noted that the red solutions display an absorption peak in the region 530 mμ to 535 mμ (*vide* also Fig. 4 in the present paper). Elson and Morgan reported interference by indole compounds, but stated that these yield a color with Ehrlich reagent also when the acetylation step is omitted. Various workers have sought to apply the Elson and Morgan method directly to tissue hydrolyzates. Some (8) have removed excess hydrochloric acid from hydrolyzates by neutralization with sodium hydroxide; others (3, 6) have preferred drying the hydrolyzate *in vacuo* over solid sodium hydroxide. Most workers, however, have reported erratic results. Ogston *et al.* (7) suggested that this might be due in part to loss of acetylacetone by evaporation during acetylation; they, therefore, recommended carrying out the acetylation under reflux. Johnston *et al.* (6) have preferred to obviate such loss by acetylating in sealed glass tubes at 100° C. The effects of varying the time of acetylation and concentration of the acetylating medium have also been studied. Both Blix (1) and Immers and Vaseur (5) have favored a stronger concentration than that originally recommended by Elson and Morgan (2). Schloss (9) studied the effect of varying pH on the acetylation and demonstrated that at least two chromogens are produced. It has been shown also that sugars and sugar – amino acid mixtures interfere seriously, and this again hampers the application of the method to biological material (4, 5).

[1] *Manuscript received June 24, 1953.*
*Contribution from the Faculty of Agriculture of McGill University, Macdonald College, Que. Macdonald College Journal Series No. 333.*



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The present communication deals with a further attempt to apply the method directly to tissue hydrolyzates. Since the ultimate object of the work has been an investigation of the distribution of mucopolysaccharide material in the tissues of the fowl, most of the studies on tissues reported in the present paper were made using avian oviduct, a tissue likely to contain appreciable amounts of hexosamine.

## EXPERIMENTAL

### *Interference of Colored Material Formed During Hydrolysis with the Colorimetric Determination of Hexosamine*

In order to study this interference, samples of freeze-dried avian oviduct were hydrolyzed with 25 times their fresh weight of 4 *N* hydrochloric acid for hours at 100° C. in sealed glass tubes. The hydrolyzates were light brown in color; small amounts only of insoluble humin were formed. For the purpose of studying interference, this small amount of insoluble humin was not removed. The acid was then removed *in vacuo* over solid sodium hydroxide, and the residue taken up in water. Acetylation and color development were performed as suggested by Johnston *et al.* (6), and the final solution after the color reaction was diluted so that each milliliter corresponded to 10 mgm. fresh tissue.

The light absorption curves of these solutions were measured in a Beckman DU spectrophotometer. The average values for such curves are presented in Fig. 1. The curves did not display any distinct peak around 530 mμ to 535 mμ.

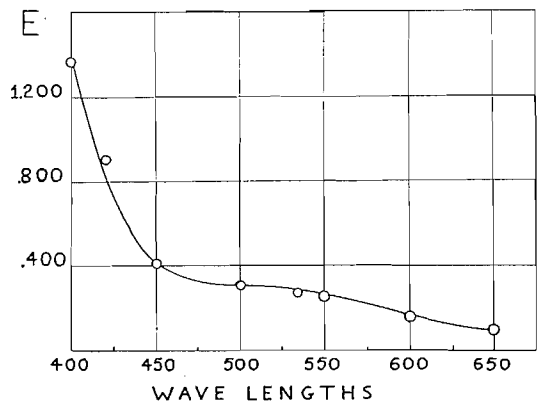



FIG. 1. Light absorption curve of acetylated tissue hydrolyzates treated with *p*-dimethylaminobenzaldehyde.
Size of sample: 10 mgm. fresh tissue per ml. of final solution.
Acetylating medium: 0.083 *M* sodium carbonate and 0.66% acetylacetone. (Level of Elson and Morgan and of Johnston *et al.*)

Even in this region, most of the absorbency appeared to be irrelevant and in all probability was due to colored material formed during hydrolysis (e.g. humin) and acetylation.

In order to study the absorbency due to the products of hydrolysis of protein and to reaction of such products of hydrolysis during acetylation, the foregoing analytical procedure was also performed on samples of casein

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(Champlain Chemical Company). Casein was chosen as a protein known to be very low in hexosamine. At the same time absorption curves were prepared using a solution of hexosamine only. The results are summarized in Table I.

TABLE I

COMPARISON OF LIGHT ABSORPTION BY TISSUE HYDROLYZATES AND CASEIN HYDROLYZATES WITH THE LIGHT ABSORPTION BY GLUCOSAMINE IN THE COLORIMETRIC METHOD OF ELSON AND MORGAN

| | Extinctions (1 cm. cell) | | | | |
|---|---|---|---|---|---|
| | 450 mμ | 500 mμ | 535 mμ | 550 mμ | 600 mμ |
| *a*. Tissue hydrolyzates (11 samples) | 0.390 | 0.298 | 0.269 | 0.238 | 0.133 |
| *b*. Casein hydrolyzates (4 samples) recalculated to same extinction at 450 mμ as tissue hydrolyzates | 0.390 | 0.251 | 0.185 | 0.162 | 0.091 |
| *c*. Difference of (*a*) and (*b*) | 0.000 | 0.047 | 0.084 | 0.076 | 0.042 |
| *d*. Standard hexosamine solution (extinctions recalculated to basis of 0.084 at 535 mμ) | 0.014 | 0.049 | 0.084 | 0.069 | 0.049 |

The light absorption curve for hexosamine alone displayed low absorbency in the region 450 mμ (*vide* Fig. 4 for typical hexosamine absorption curve). On the other hand, at 450 mμ the absorbencies of tissue and casein hydrolyzates were falling off from high values in the near ultraviolet. In order to facilitate comparisons, the extinctions for the casein hydrolyzates were recalculated to give the same extinction at 450 mμ as was given by the tissue hydrolyzates, and these values are presented in Table I, line (*b*). The difference, (*c*), between (*a*) and (*b*) in Table I might then be expected to provide some measure of the hexosamine in the tissue hydrolyzates, i.e. the values obtained by difference as above ought to display some degree of correspondence with the values obtained for hexosamine only. A comparison of the values in line (*c*) with those in line (*d*) of Table I shows that the values obtained by difference did in fact correspond to a curve of the same shape as that obtained with hexosamine only. Hence this preliminary work suggested that it might be possible by suitable choice of blanks to arrive at corrections for the irrelevant absorptions.

Accordingly, tissue samples were hydrolyzed and treated as follows, color development being carried out as before:—

A. Acetylated hydrolyzate plus Ehrlich reagent.
   Read against complete reagent blank.
B. Acetylated hydrolyzate treated as was A, but with the *p*-dimethylaminobenzaldehyde omitted from the Ehrlich reagent.
   Read against blank of water plus acetylacetone.
C. Acetylated hydrolyzate plus Ehrlich reagent.
   Read against hydrolyzate similarly treated but with the *p*-dimethylaminobenzaldehyde omitted from the Ehrlich reagent.

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D. Water plus acetylacetone plus Ehrlich reagent.
Read against similar solution but with the *p*-dimethylaminobenzaldehyde omitted from the Ehrlich reagent.

Standard. Glucosamine solution acetylated and treated with Ehrlich reagent.
Read against complete reagent blank.

The experimental data are summarized in Table II.

TABLE II
COMPARISON OF ESTIMATES OF LIGHT ABSORPTION DUE TO HEXOSAMINE IN PROTEIN HYDROLYZATES ANALYZED BY METHOD OF ELSON AND MORGAN WITH LIGHT ABSORPTION OBTAINED USING GLUCOSAMINE SOLUTIONS

| | No. of analyses | Extinction (1 cm. cell) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 400 mμ | 420 mμ | 450 mμ | 500 mμ | 535 mμ | 550 mμ | 600 mμ | 650 mμ |
| A | 11 | 1.287 | 0.900 | 0.390 | 0.298 | 0.269 | 0.238 | 0.133 | 0.087 |
| B | 11 | 0.654 | 0.529 | 0.397 | 0.238 | 0.166 | 0.146 | 0.097 | 0.070 |
| "Hexosamine *a*" | — | 0.633 | 0.471 | **−0.007** | **0.060** | **0.103** | **0.088** | **0.036** | **0.017** |
| C | 11 | 1.445 | 0.484 | 0.018 | 0.072 | 0.120 | 0.113 | 0.042 | 0.022 |
| D | 11 | 0.833 | 0.122 | 0.006 | 0.010 | 0.018 | 0.019 | 0.006 | 0.002 |
| "Hexosamine *b*" | — | 0.622 | 0.369 | **0.012** | **0.062** | **0.102** | **0.094** | **0.036** | **0.019** |
| Standard hexosamine | 12 | 0.061 | 0.060 | **0.016** | **0.058** | **0.103** | **0.081** | **0.037** | **0.005** |
| Difference curve from Table I | | | — | 0.000 | 0.047 | 0.084 | 0.076 | 0.042 | — |

The difference (A − B) is also reported as "Hexosamine *a*" and the difference (C − D) as "Hexosamine *b*".

A satisfactory feature of the results presented in Table II is that the values for "Hexosamine *a*" agreed rather closely with the values for "Hexosamine *b*", and that both sets of values agreed closely with the curve for hexosamine. This agreement suggested that no serious interference from side reactions had taken place over the range 450 mμ to 650 mμ, and that the use of the correction blank was justifiable.

The next step was to study whether the use of large samples of hydrolyzate would give proportionate increases in the extinction attributable to hexosamine when the foregoing corrections were applied. It was found that the increases in extinction were not proportional. As will be shown below, this failure to attain proportionality was due to lowering of the pH by the larger samples, the intensity of the color maximum being sensitive to pH.

*The Sensitivity of the Acetylation of Hexosamine to pH and the Effect of Dried Hydrolyzates on the pH of the Acetylating Medium*

The dependence of the acetylation step upon close control of pH became apparent in the course of experiments undertaken to compare extinctions obtained with casein plus known amounts of hexosamine with the extinctions obtained with hexosamine alone.

The determinations were carried out as described above, the acetylations being performed in a solution 0.083 *M* as to sodium carbonate and 0.66% as to

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acetylacetone, i.e. the levels used by Elson and Morgan (2) and by Johnston *et al.* (6).

The extinction maxima for hexosamine were calculated from the following relation:—

$$EM = Et_{530} - Eu_{530} - \tfrac{1}{2}[Et_{600} - Eu_{600}] - \tfrac{1}{2}[Et_{450} - Eu_{450}]$$

where $EM$ = extinction maximum for hexosamine
$Et$ = extinction of sample treated with Ehrlich reagent
$Eu$ = extinction of sample not treated with Ehrlich reagent
Subscript numerals = wave length in mμ.

The results are presented in Table III. Recoveries of the added hexosamine were irregular and low. Attempts to improve recoveries by increasing the

TABLE III

RECOVERIES OF HEXOSAMINE HYDROCHLORIDE (H.H.) ADDED TO CASEIN AND WITH USE OF WEAK ACETYLATING MEDIUM (0.083 *M* SODIUM CARBONATE AND 0.66% ACETYLACETONE)

| Material, weight per ml. of final solution | Number of samples | Extinction at 535 mμ, corrected for irrelevant absorptions | | | | Recovery, % |
|---|---|---|---|---|---|---|
| | | Casein hydrolyzate | Casein hydrolyzate +H.H. | Column 4–3 | Standard H.H. | |
| 2 mgm. casein + 20 μgm. H.H. | 2 | 0.055 | 0.095 | 0.040 | 0.309 | 12.9 |
| 2 mgm. casein + 30 μgm. H.H. | 2 | 0.055 | 0.114 | 0.059 | 0.611 | 9.7 |
| 4 mgm. casein + 20 μgm. H.H. | 2 | 0.052 | 0.076 | 0.024 | 0.306 | 7.8 |

amounts of acetylacetone were unsuccessful, but suggested the desirability of studying the control of pH, because an increase of the amount of acetylacetone without a simultaneous increase of the carbonate content of the acetylating medium led to lowered "recoveries".

Accordingly, series of determinations of extinction of hexosamine solutions were carried out where constant levels of acetylacetone (0.66% of the acetylating medium) and of total carbonate (0.083 *M*) were employed, but where the pH was adjusted to various values by hydrochloric acid. The pH was measured before and after acetylation, but the change was always less than 0.02 pH units.

A representative series of results is presented in Fig. 2. Maximal extinction at 530 mμ was realized within the narrow range of pH 9.2 to pH 9.6. The intensity of the color fell off rapidly below pH 9.0 and above pH 10.5. Schloss (9) has also noted that the color maximum is only realized within a narrow range of pH.

In view of the narrow pH range for maximal color development, it was decided to study the possibility of stabilizing the pH during acetylation by using a more strongly buffered medium. The influence of buffer concentration on the Elson and Morgan reaction was examined in the first place with hexosamine alone. The concentrations of sodium carbonate and acetylacetone were increased simultaneously so that the acetylation mixture before reaction

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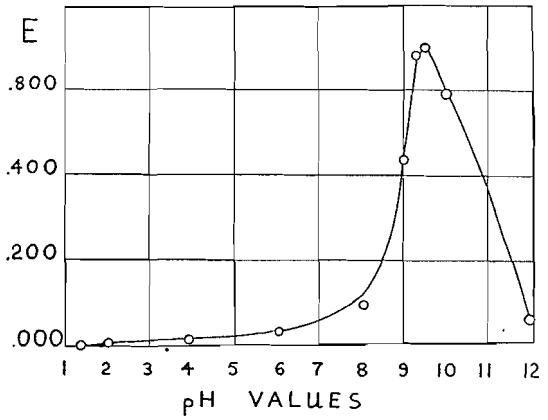



FIG. 2. Effect of the pH during acetylation on the intensity of the color given by the reaction of the acetylated hexosamine with *p*-dimethylaminobenzaldehyde.
Extinction at 530 mμ of 20 μgm. hexosamine hydrochloride per 1 ml. final solution.
Acetylating medium: 0.083 *M* sodium carbonate plus 0.66% acetylacetone.

had a pH = 9.5 approx. The results are summarized in Fig. 3. The extinction increased as the level of acetylacetone in the reaction mixture increased from 0.66% (the level used by Elson and Morgan) to 1.8%. Between 1.8% and 3% the extinction remained relatively steady, but above 3.0% the extinction began to fall off. Working levels of 1.83% acetylacetone and 0.33 *M* sodium carbonate were selected provisionally. Similar concentrations were adopted by Immers and Vaseur (5) in order to reduce interference by sugar – amino acid interactions.

Recoveries of hexosamine added to casein or to tissue hydrolyzates and obtained by the use of the more strongly buffered acetylation medium are presented in Tables IV and V. Recoveries were improved quantitatively (comparison of recoveries in Tables III and IV) when the stronger buffer was used. However, reproducibility was found still to be erratic, not only as between

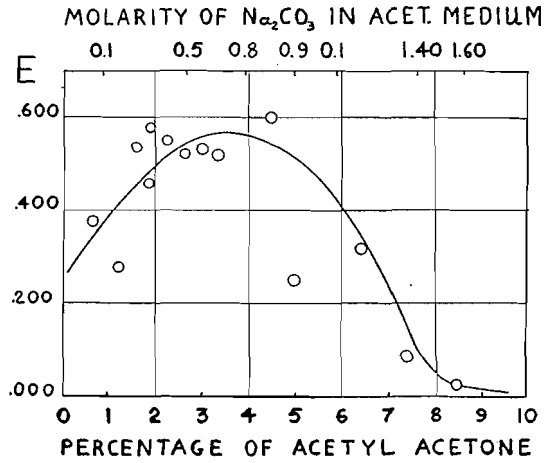



FIG. 3. Effect of acetylacetone buffer concentration on the intensity of the color at the iso-pH 9.50. [The value of the molarity of $Na_2CO_3$ following 0.9 should read 1.0, not 0.1]

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TABLE IV

RECOVERIES OF HEXOSAMINE HYDROCHLORIDE (H.H.) ADDED TO CASEIN AND WITH USE OF STRONG ACETYLATING MEDIUM (0.33 *M* SODIUM CARBONATE AND 1.83% ACETYLACETONE)

| Material, weight per ml. of final solution | Number of samples | Extinction at 535 mμ, corrected for irrelevant absorptions | | | | Recovery, % |
|---|---|---|---|---|---|---|
| | | Casein hydrolyzate | Casein hydrolyzate +H.H. | Column 4–3 | Standard H.H. | |
| 0.43 mgm. casein +13.3 μgm. H.H. | 3 | 0.075 | 0.583 | 0.508 | 0.428 | 118.7 |
| 1 mgm. casein +10 μgm. H.H. | 1 | 0.211 | 0.544 | 0.333 | 0.365 | 91.2 |
| 2 mgm. casein +10 μgm. H.H. | 1 | 0.336 | 0.715 | 0.379 | 0.365 | 103.8 |

TABLE V

RECOVERIES OF HEXOSAMINE HYDROCHLORIDE (H.H.) ADDED TO TISSUES AND ACETYLATED IN A STRONG MEDIUM (0.33 *M* SODIUM CARBONATE AND 1.83% ACETYLACETONE)

| Material, weight per ml. of final solution | Number of samples | Extinction at 535 mμ corrected for irrelevant absorptions | | | | Recovery, % |
|---|---|---|---|---|---|---|
| | | Tissue hydrolyzate | Tissue hydrolyzate +H.H. | Column 4–3 | Standard H.H. | |
| 0.45 mgm. tissue +11 μgm. H.H. | 4 | 0.276 | 0.567 | 0.291 | 0.344 | 84.6 |
| 1.00 mgm. tissue +10 μgm. H.H. | 3 | 0.506 | 0.816 | 0.310 | 0.297 | 104.4 |
| 2.00 mgm. tissue +16.7 μgm. H.H. | 3 | 0.849 | 1.594 | 0.745 | 0.548 | 135.9 |

different levels of acetylacetone (*vide* Table IV) but also as between different determinations on one and the same sample (results not shown here).

*Effect of Acetylacetone Concentration on Relative Development of Chromogens Formed During Acetylation*

Schloss (9) has shown that at least two chromogens are formed by the acetylation of hexosamine with acetylacetone, and that the optimal conditions for development of their color maxima differ rather widely. Schloss found that one chromogen gave a color maximum at 530 mμ when the acetylation time was one hour and time of the color reaction was a few minutes; a second chromogen gave a color maximum at 512 mμ when time of acetylation was 20 min. and the time of color reaction was 24 hr. Thus the original Elson and Morgan method appears to have been based principally on the color given by the first chromogen. Schloss suggested that the second chromogen might afford a more satisfactory basis for the determination of hexosamine. It seemed probable, therefore, that modification of the acetylation conditions so as to restrict chromogen development to one chromogen only might contribute to improved reproducibility and proportionality between extinction and amount of hexo-

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samine present. Experiments showed that an increase of the acetylacetone concentration led to substantial elimination of formation of the second chromogen.

The results of a series of measurements obtained by increasing the acetylacetone concentration *without* changing the buffering capacity of the acetylating medium are given in Table VI. With a color reaction time of one hour, the

TABLE VI

EFFECT OF ACETYLACETONE CONCENTRATION ON THE RELATIVE YIELD OF THE TWO CHROMOGENS
Concentration of sodium carbonate in the acetylating medium:—0.33 *M*;
hexosamine hydrochloride per ml. final solution:—13.5 μgm.

| Acetylacetone concentration in the acetylating medium | | Extinction due to hexosamine HCl | | Ratio of extinction at 512 mμ to extinction at 530 mμ |
|---|---|---|---|---|
| % | pH | At 530 mμ after 1 hr. color reaction | At 512 mμ after 24 hr. color reaction | |
| 3.03 | 9.25 | 0.714 | 0.373 | 0.522 |
| 2.27 | 9.41 | 0.739 | 0.440 | 0.595 |
| 1.97 | 9.51 | 0.664 | 0.428 | 0.645 |
| 1.72 | 9.60 | 0.740 | 0.510 | 0.689 |
| 1.30 | 9.70 | 0.665 | 0.516 | 0.776 |
| 1.10 | 9.81 | 0.550 | 0.505 | 0.918 |
| 0.89 | 9.90 | 0.561 | 0.540 | 0.963 |
| 0.49 | 10.18 | 0.240 | 0.374 | 1.558 |

extinction at 530 mμ increased steadily with increasing amounts of acetylacetone, whereas with a color reaction time of 24 hr. the extinction at 512 mμ decreased as acetylacetone concentration increased.

The effect became clearer on studying the complete absorption curves (*vide* Fig. 4). The lowest pair of curves shows that there was not any displacement of the maximum towards lower wave lengths when the time of color reaction was prolonged to 24 hr. and the concentration of acetylacetone was highest. The intermediate pair of curves showed no appreciable displacement. The highest pair of curves shows that the lowest concentration of acetylacetone resulted in a marked displacement of the maximum towards 512 mμ when the color reaction was prolonged for 24 hr. These observations were confirmed in a further series of experiments where an acetylation time of 20 min. was used for the purpose of emphasizing development of color from the second chromogen, and of 1 hr. for the purpose of emphasizing color development from the first chromogen.

Neither series of experiments, however, showed whether the results were due to the change of pH or to the change in acetylacetone concentration *per se*. Accordingly, experiments were made in which the sodium carbonate concentration was further increased, so as to maintain the pH at or slightly above pH 9.5, although the concentration of acetylacetone was also further increased. The results are presented in Table VII. Development of the second chromogen was almost completely absent at pH 9.7 when the medium contained 7.8% acetylacetone. At pH 9.9, and with a relatively high concentration (viz. 5.2%)

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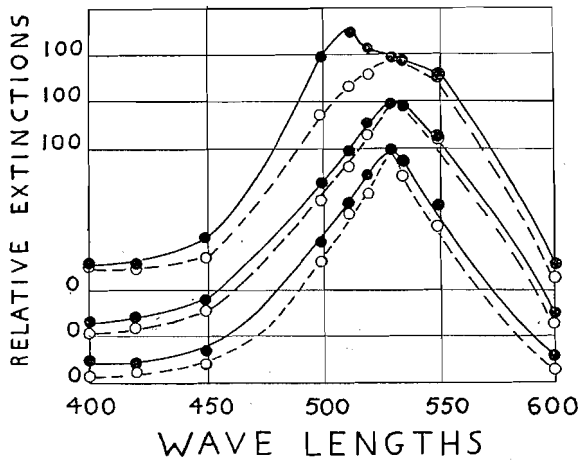



FIG. 4. Effect of acetylacetone concentration on the development of the two chromogens formed during the acetylation of hexosamine. 100 = Extinction at 530 mμ.
Acetylating medium buffered with 0.33 *M* sodium carbonate.
Lowest pair of curves: acetylacetone concentration 3.03%, pH 9.25.
Intermediate pair of curves: acetylacetone concentration 2.27%, pH 9.41.
Highest pair of curves: acetylacetone concentration 0.89%, pH 9.90.
Broken lines: extinction curves after 1 hr. color reaction.
Full lines: extinction curves after 24 hr. color reaction.

acetylacetone, formation of the second chromogen was almost completely suppressed. This is of interest in view of the fact that formation of the second chromogen is relatively favored at pH 9.9 with low concentrations of acetylacetone (9). The results strongly suggest that formation of the second chromogen was depressed by increasing the acetylacetone concentration, and that this effect took place whether the acetylation was performed (*a*) in a solution

TABLE VII
EXTINCTION OF HEXOSAMINE HYDROCHLORIDE (H.H.)ACETYLATED IN 0.5 *M* SODIUM CARBONATE BUFFER MEDIUM WITH DIFFERENT CONCENTRATIONS OF ACETYLACETONE

| Acetylacetone concentration, % | pH values | Concentration of H.H.μgm./ml. final solution | Extinction values | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 20 min. acetylation | | | | 1 hr. acetylation | | | |
| | | | 1 hr. color reaction | | 24 hr. color reaction | | 1 hr. color reaction | | 24 hr. color reaction | |
| | | | 512 mμ | 530 mμ | 512 mμ | 530 mμ | 512 mμ | 530 mμ | 512 mμ | 530 mμ |
| 7.83 | 9.60 | 6.7 | 0.262 | 0.355 | 0.204 | 0.263 | 0.314 | 0.425 | 0.572 | 0.337 |
| | | 13.4 | 0.561 | 0.753 | 0.428 | 0.552 | 0.640 | 0.850 | 0.522 | 0.652 |
| | | 20.0 | 0.842 | 1.150 | 0.628 | 0.810 | 0.944 | 1.290 | 0.758 | 0.961 |
| 5.21 | 9.90 | 6.7 | 0.263 | 0.345 | 0.246 | 0.275 | 0.325 | 0.430 | 0.313 | 0.355 |
| | | 13.4 | 0.480 | 0.615 | 0.440 | 0.490 | 0.642 | 0.848 | 0.600 | 0.698 |
| | | 20.0 | 0.815 | 1.070 | 0.722 | 0.822 | 0.915 | 1.200 | 0.842 | 0.960 |

buffered with a constant amount of sodium carbonate, and therefore at a lower pH, or (*b*) in a solution where the sodium carbonate was increased simultaneously with the acetylacetone, so as to keep the pH constant. Furthermore, increase of acetylacetone tended to give improved proportionality between extinction and hexosamine concentration. Notwithstanding these improve-

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ments, reproducibility was not completely satisfactory. This may be exemplified by the following results for 16 separate determinations of hexosamine alone at each of two levels of concentration.

| Hexosamine taken per ml. final solution, μgm. | Average extinction of hexosamine (1 cm. cell) and its standard error | Coefficient of variation |
|---|---|---|
| 4 | 0.270 ± 0.010 | 14.2 |
| 10 | 0.599 ± 0.012 | 8.2 |

The average ratio (Extinction of 4 μgm. hexosamine × 2.5)/(Extinction of 10 μgm. hexosamine) for 16 separate determinations was found to be 1.139 ± 0.044 and the percentage of standard deviation on the average ratio (coefficient of variation) was 15.4%.

The foregoing results support the recommendation given below that at least six aliquots from each hydrolysis should be run in order to reduce error from variability.

*Interference by Hydroxyproline and its Elimination*

Interference by sugar – amino acid interactions has been studied by Immers and Vaseur (5) and by Horowitz *et al* (4). Immers and Vaseur pointed out the possibility of making a rough correction for this interference by heating the hydrolyzate solution with sodium carbonate alone in absence of acetylacetone and then applying the color reaction. Experiments in this laboratory support this view.

Possible interference by hydroxyproline does not seem to have been mentioned in the literature. Preliminary experiments in this laboratory showed that hydroxyproline gave about 2% as much color at 530 mμ in the Elson and Morgan reaction as did an isomolecular amount of hexosamine. Even this small interference might be appreciable when analyzing collagenous tissues of high hydroxyproline content. The absorption curve for hydroxyproline in the reaction was found to exhibit a maximum at 550 mμ; the height of the peak increased with increasing time of the color reaction and at the same time moved towards longer wave lengths (*vide* Fig. 5). Fortunately, increasing the concentration of acetylacetone also reduces the extinction at 550 mμ due to the presence of hydroxyproline. Hence the proposed increase of the concentration of acetylacetone also reduces this interference by four-fifths, i.e. to values at which it is negligible in practice. This is also evident from the results presented in Fig. 5.

*Application of (a) Correction Blanks, (b) Increased Buffering Capacity of Acetylation Medium, and (c) Increased Amount of Acetylacetone to Determinations of Hexosamine in Tissue Hydrolyzates*

Tissue hydrolyzates (hen's oviduct) were dried over solid sodium hydroxide *in vacuo* and dissolved in water. The pH of the solutions ranged from pH 1.70 to pH 1.80. The effects of varying the size of sample on the pH of the acetyla-

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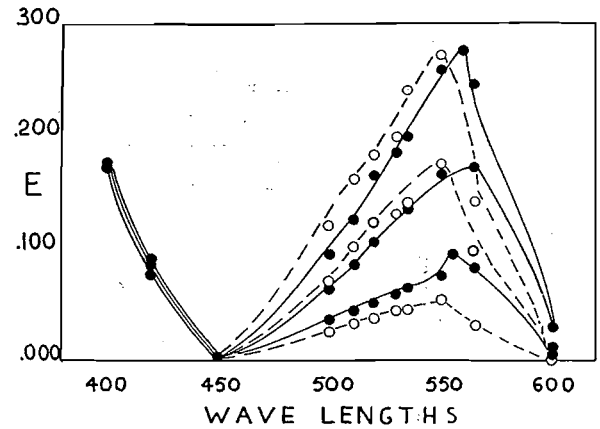



FIG. 5. Effect of acetylacetone concentration and time of color reaction on the extinction curve of the color given by acetylated hydroxyproline plus *p*-dimethylaminobenzaldehyde.
Hydroxyproline concentration 600 μgm. per ml. final solution.
Acetylating medium buffered with 0.33 *M* sodium carbonate.
Lower pair of curves: acetylacetone concentration 3.03%.
Intermediate pair of curves: acetylacetone concentration 1.93%.
Highest pair of curves: acetylacetone concentration 0.50%.
Broken lines: extinction curves after 1 hr. color reaction.
Full lines: extinction curves after 24 hr. color reaction.

tion mixture are illustrated in Table VIII. It will be noted that 0.50 *M* sodium carbonate maintained the pH of the acetylating mixture at a sufficiently steady level for a useful range of size of tissue hydrolyzate samples (to a level as high as 2 mgm. per ml. of acetylating medium).

The corresponding extinctions of the color reaction, corrected for presence of humin as described above ("hexosamine extinction"), are presented in Table IX. Improved consistency of results was attained as the acetylacetone concentration was increased. The proportionality between extinction and amount

TABLE VIII
EFFECT OF THE SIZE OF TISSUE SAMPLES ON THE pH OF ACETYLATION

| Size of the samples (dried tissue) | | Acetylating medium* | | | |
|---|---|---|---|---|---|
| Wt. per ml. of the acetylating medium | Wt. per ml. of final solution | 0.66/0.085/9.50 | 1.88/0.33/9.60 | 2.47/0.50/9.62 | —/0.50/11.02 |
| | | pH after acetylation | | | |
| 0.0 mgm. | 0.00 mgm. | 9.31 | 9.61 | 9.62 | 10.69 |
| 2.2 " | 0.67 " | 8.58 | 9.51 | 9.59 | 10.70 |
| 4.4 " | 1.34 " | 8.08 | 9.39 | 9.49 | 10.50 |
| 6.6 " | 2.10 " | 7.70 | 9.21 | 9.41 | — |
| Hexosamine HCl 22 μgm. | 6.70 μgm. | 9.31 | 9.62 | 9.63 | 10.90 |

**The first number indicates percentage of acetylacetone, the second molarity of sodium carbonate, and the third the pH of the acetylating medium.*

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TABLE IX
EFFECT OF THE ACETYLATING MEDIUM ON THE PROPORTIONALITY BETWEEN SIZE OF TISSUE SAMPLES AND HEXOSAMINE EXTINCTION

| Size of sample (dried tissues), wt. per ml. of acetylating medium | Acetylating media* | | | |
|---|---|---|---|---|
| | 0.66/0.085/9.50 | 1.88/0.33/9.60 | 2.47/0.50/9.62 | —/0.50/11.02 |
| | Hexosamine extinctions | | | |
| 2.2 mgm. tissue | 0.292 | 0.442 | 0.479 | |
| 4.4 " " | 0.267 | 0.790 | 0.874 | 0.014 |
| 6.6 " " | 0.239 | 1.070 | 1.242 | 0.030 |
| 2.2 mgm. tissue +22 μgm. H.H. | 0.440 | 0.638 | 0.741 | 0.021 |
| 4.4 mgm. tissue +44 μgm. H.H. | 0.421 | 1.248 | 1.372 | 0.063 |
| 6.6 mgm. tissue +66 μgm. H.H. | 0.378 | — | 1.905 | — |
| 22 μgm. hexosamine HCl (H.H.) | 0.360 | 0.354 | 0.426 | 0.004 |

**The first number indicates percentage of acetylacetone; the second molarity of sodium carbonate, and the third the pH of the acetylating medium.*

of hexosamine, although by no means perfect, was better than that obtained previously, and suggested that the proposed modifications would enable the Elson and Morgan method to give useful results on tissue hydrolyzates.

The average ratio (Extinction of A mgm. tissues × 2.5)/(Extinction of 2.5 × A mgm. tissues) for 17 separate determinations on different samples of hen's oviducts was found to be 1.063 ± 0.059. Consequently, the standard deviation expressed as a percentage of the average ratio was 22.9% as compared with a value of 14.8% for determinations of hexosamine alone. The weight of tissue A taken for the above 17 determinations was of the order of 2 mgm. The close approximation of the average value of ratio of tissues (1.063) to the average value of ratio of hexosamine alone (1.139) suggests that, for the level of tissues hydrolyzates used in these determinations, the effect of the dried hyrdolyzate on the pH of the strongly buffered acetylating medium had little influence on the depression of the extinction.

Relatively large samples must be taken for acetylation whenever the tissue is low in hexosamine. It may then be advisable carefully to adjust the pH of the solution of dried hydrolyzate to pH 9.5 before proceeding with the acetylation. Appropriate experiments showed that, provided this neutralization is carried out slowly and with continual mixing using sodium hydroxide, no appreciable deamination of hexosamine takes place.

## SUGGESTED PROCEDURE

The following procedure is recommended on the basis of the work described above.

*Reagents*

(*a*) Hydrochloric acid 4 *N*.

(*b*) Acetylacetone, Eastman Kodak, 4% in 0.75 *M* sodium carbonate and made immediately before use.

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(*c*) Sodium carbonate, 0.75 *M* in water.

(*d*) Ehrlich's reagent:—0.8 gm. *p*-dimethylaminobenzaldehyde is dissolved in 30 ml. aldehyde-free ethanol and 30 ml. hydrochloric acid, reagent grade, is added. Store in refrigerator in amber bottle with ground glass stopper. The *p*-dimethylaminobenzaldehyde should be purified by recrystallization from solution in hydrochloric acid by addition of saturated sodium acetate solution. The recrystallization should be performed immediately before the Ehrlich reagent is made up. The Ehrlich reagent should not exhibit any absorbency at 530 mμ.

(*e*) Alcoholic hydrochloric acid:—30 ml. aldehyde-free ethanol plus 30 ml. hydrochloric acid conc.

(*f*) Standard hexosamine:—

Stock solution; 1 gm. glucosamine hydrochloride dissolved and made to 100 ml. in water. Store in a 250 ml. flask in the deep freeze.

Working standard; thaw out stock standard and dilute 1 ml. to 100 ml. in water. Replace stock solution in deep freeze.

*Procedure*

Hydrolyze samples of tissue containing approximately 500 μgm. hexosamine with 5 ml. 4 *N* hydrochloric acid by heating in sealed pyrex tubes 13 mm. × 100 mm. for four hours in a boiling water bath. If quantities greater than 0.1 gm. dry matter are necessary in order to have hexosamine in amounts of the order of 500 μgm., then larger quantities of hydrochloric acid should be used in larger tubes.

Open the tubes and remove the acid by evaporation at low pressure over solid sodium hydroxide. Care is necessary to avoid a reduction of the pressure to a level lower than the vapor pressure of the 4 *N* hydrochloric acid at the maximal prevailing temperature, otherwise the sample may spurt on boiling.

Add 5 ml. of water and dissolve the residue, using a stirring rod. If insoluble humin has been formed, remove this by centrifuging.

For each analysis the determination is made at two levels of concentration of hydrolyzate (H) and two levels of concentration of standard (S) are set up at the same time, together with the necessary blanks (Bl). Set up these subsamples in fifteen 5-ml. glass stoppered pyrex volumetric flasks according to the following scheme:—

| Quantities in ml. | $H_1$ | $Bl_1$ | $H_2$ | $Bl_2$ | $H_3$ | $Bl_3$ | $S_1$ | $S_2$ | $Bl_4$ |
|---|---|---|---|---|---|---|---|---|---|
| No. of flasks set up | 3 | 1 | 3 | 1 | 1 | 1 | 2 | 2 | 1 |
| Hydrolyzate solution | 0.2 | 0.2 | 0.5 | 0.5 | 0.5 | 0.5 | — | — | — |
| Hexosamine standard | — | — | — | — | — | — | 0.2 | 0.5 | — |
| Water | 0.3 | 0.3 | — | — | — | — | 0.3 | — | 0.5 |
| Acetylacetone in sodium carbonate | 1.0 | 1.0 | 1.0 | 1.0 | — | — | 1.0 | 1.0 | 1.0 |
| Sodium carbonate | — | — | — | — | 1.0 | 1.0 | — | — | — |

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Close the flasks firmly by turning the ground glass stoppers and immobilize them with the help of rubber stoppers or otherwise in a wire basket. Immerse the basket in a constant level boiling water bath so arranged that the level of the water is 1 cm. lower than the tops of the volumetric flasks. Leave the flasks in the boiling water bath for one hour. Cool the flasks in ice-water for 10 min. Add 3 ml. aldehyde-free alcohol to each flask and mix well. Warm the flasks in a water bath at 37°C. for three minutes.

Now add 0.5 ml. Ehrlich reagent to flasks $H_1$, $H_2$, $H_3$, $S_1$, $S_2$, and $Bl_4$, and add 0.5 ml. alcoholic hydrochloric acid to flasks $Bl_1$, $Bl_2$, $Bl_3$.

Make up the flasks to 5 ml. by addition of alcohol, mix well, and leave them in a water bath at 37°C. for 60 min.

Read the extinctions at 530 m$\mu$ of the sets of solution $H_1$, $H_2$, and $H_3$ against their corresponding blanks.

Correct the values of $H_1$ and $H_2$ for any extinction in $H_3$.

If flask $H_3$ displays a substantial extinction (i.e. if it be more than one-tenth of the extinction of $H_2$), this indicates serious interferences by combination of sugars and amino acids and by indole compounds.

The extinctions of the standards are read against $Bl_4$.

If the extinctions for $H_1$ and $H_2$ per microgram display appreciable and systematic divergences, much larger than the average divergence of the standard, then the analysis should be repeated with careful adjustment of the solution of dried hydrolyzate to pH 9.5 by means of 1.0 *N* sodium hydroxide before proceeding with the subsequent steps.

It is most important that the flasks to be used for correction for sugar and amino acid interference (i.e. $H_3$ and $Bl_3$) be not in the slightest degree contaminated with acetylacetone. For this reason the manipulation and heating of these flasks is preferably carried out apart from the other flasks.

In this procedure the acetylation is carried out in stoppered 5 ml. Pyrex flasks and not in sealed glass tubes.

The investigation described in this paper was based on acetylation in sealed glass tubes, but towards the end of the work it was found that the acetylation could equally well be carried out in sufficiently securely stoppered 5 ml. volumetric flasks, which are capable of withstanding the pressure developed. Their use has the advantage of avoiding a troublesome sealing and transfer, while retaining the advantages of acetylating in a closed vessel.

## DISCUSSION

The difficulty experienced in obtaining adequate reproducibility of results seems to be due to the following circumstances. Firstly, whereas the amino group of hexosamine is readily split off by heating in alkaline solution (10), the acetylation of hexosamine cannot be carried out except in hot alkaline solution. Secondly, the acetylation of hexosamine does not yield a unique product; not all the products of acetylation are chromogenic and the relationship between the two main chromogenic products varies with the pH, the acetylacetone concentration, and the strength of the buffer, and there are also indications that the acetylation products are not particularly stable.

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Thirdly, the acetylation reaction can only be carried out with the free amino group of hexosamine. The amino group must be freed by acid hydrolysis since alkaline hydrolysis would destroy hexosamine. Subsequent neutralization with alkali introduces the danger of localized decomposition of hexosamine. Removal of excess acid from the hydrolyzates by drying is consequently the only alternative, but this also leaves the amino acids as the acid salts. The results of the present study strongly suggest that the first and second of these circumstances may be overcome by increasing the amount of acetylacetone, and the third by increasing the buffering capacity of the acetylating medium.

Where it is necessary to neutralize the solution of dried hydrolyzate, care is necessary in bringing the reaction to pH 9.5 lest there be local decomposition of hexosamine.

The stronger concentrations of acetylacetone and buffer have the further advantage of affording an excess of acetylating agent such that the eventual acetylation of amino and hydroxy groups of amino acids and carbohydrate does not lower the yield of acetylated hexosamine. Acetylation of the samples in the strong acetylacetone buffer medium has been shown also to restrict the hydroxyproline interference and the possibility of correcting for interference by the sugars – amino acid reactions.

Strict standardization of the procedure and a number of replicates in the stage subsequent to hydrolysis are regarded as essential if reasonably reliable results are to be secured.

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# THE USE OF A DIFFUSION CLOUD CHAMBER TO CHARACTERIZE CONDENSATION NUCLEI[1, 2]

By Daphne Schiff, H. I. Schiff,[3] and P. R. Gendron

ABSTRACT

The original Langsdorf diffusion cloud chamber has been modified so that the temperature gradient obtained can be controlled. The supersaturations thus produced can be calculated from a diffusion equation. The effectiveness of various inorganic nuclei in causing condensation in this supersaturated vapor has been studied.

## INTRODUCTION

It is generally believed that the efficiency of a nucleus in causing condensation of water vapor is governed solely by particle size. However, until now no experimental investigation has been undertaken to ascertain the role played by other physical or chemical properties. By characterizing nuclei according to the degree of supersaturation which they will tolerate, it was hoped that the property responsible for nucleation power would become evident.

A diffusion cloud chamber was used for this work, since it will produce a gradient of supersaturation. The diffusion cloud chamber was first described by Langsdorf (3) who used it to study ion tracks in a medium of air supersaturated with methanol vapor. Schiff and Gendron (5) later modified the apparatus so that the temperature gradient obtained could be regulated. The present paper deals with a similar cloud chamber in which conditions are even more carefully controlled. The temperature gradient can be measured and from a suitable diffusion equation the resulting supersaturations present in the chamber may be calculated.

## EXPERIMENTAL

Fig. 1 is a diagram of the cloud chamber used. The vapor was supplied by heating the liquid in the evaporator E at a constant temperature (as indicated by $T_3$) by means of a nichrome heating element $H_2$, wound around the outside of the evaporator. This evaporator had a large surface area to ensure that the vapor depleted by cloud formation was continuously renewed. The level in the evaporator was maintained constant by the reservoir R. To prevent spray droplets from entering the chamber the top wall was kept independently hot by means of a ring heater, $H_1$, soldered to the top of the chamber. Thermocouple $T_1$ indicated the temperature of the chamber ceiling. To facilitate cleaning and assembly the upper portion of the chamber was made in two sections bolted together and rendered leak-tight with a Teflon gasket.

[1] *Manuscript received July 7, 1953.*
*Contribution from the Department of Chemistry, University of Montreal, Montreal, Quebec. Based on a paper presented at the 36th annual conference of the Chemical Institute of Canada, June 3rd, 1953, Windsor, Ontario.*
[2] *The research reported in this paper has been sponsored by the Geophysics Research Division of the Air Force Cambridge Research Center under Contract AF19(122)380.*
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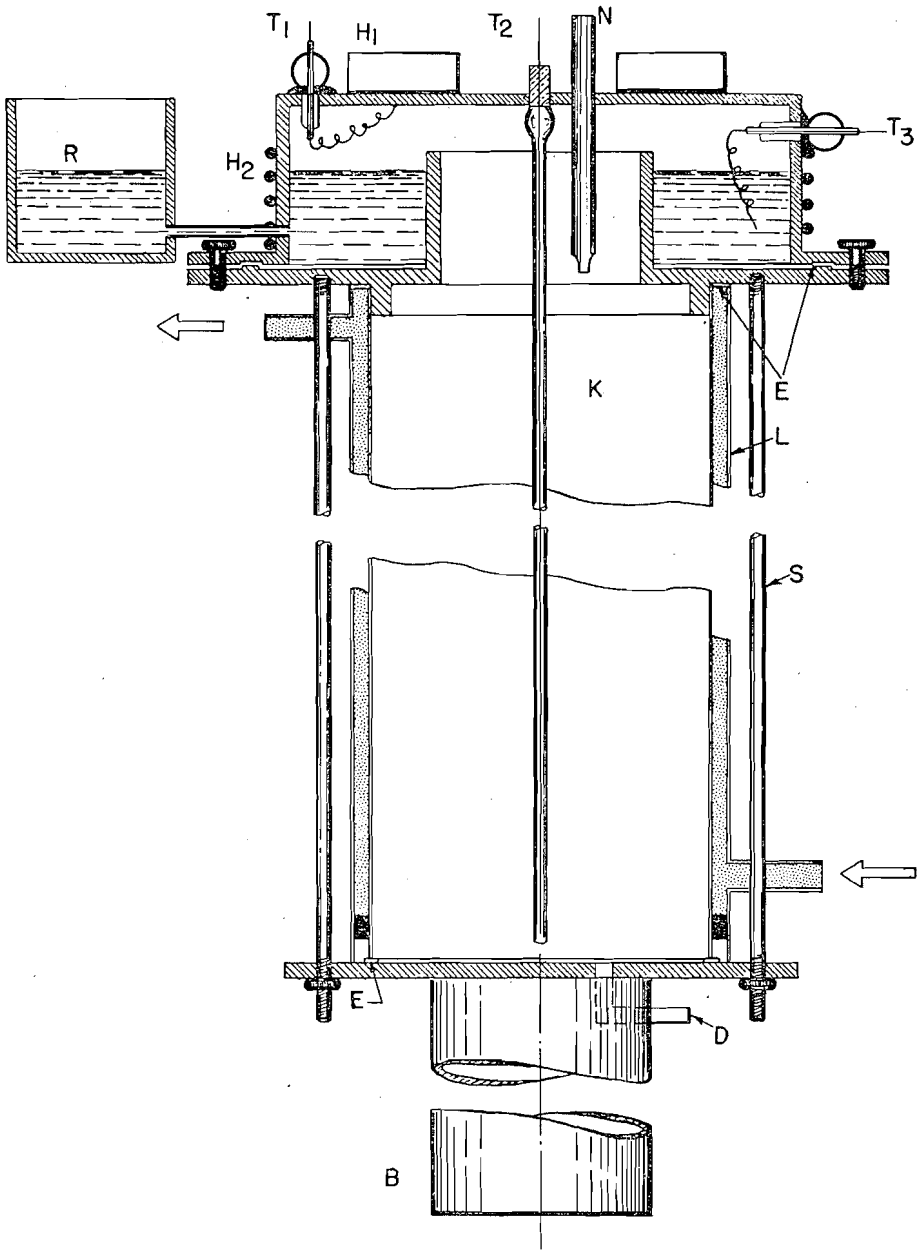



FIG. 1.

The floor of the chamber is cooled by immersing the 6 in. brass rod B in a dewar flask containing a freezing mixture of dry ice and acetone. The condensate may be removed from the floor through the drain tube D. The top and bottom parts of the chamber are made of nickel coated brass and are held together by four threaded rods.

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The sensitive portion of the chamber K is constructed of a 10 in. length of Corning electrically conducting glass, 60 mm. in diameter. A temperature gradient was produced along this tubing by allowing a low viscosity, high flash point, water white oil with a constant initial temperature to flow at a constant rate between the glass jacket L and the electrically conducting glass, through which a constant current was passed. The chamber was made airtight by pressing the glass tube between teflon gaskets E, placed below the evaporator and above the cold floor. It was easy to dismantle and clean the chamber so that spurious condensation caused by contamination could be avoided. The outer jacket was separated from the chamber by a rubber gasket. The temperature at any height in the center of the chamber could be measured by raising or lowering thermocouple $T_2$ in the pyrex tube. N was a brass tube through which nuclei were added to the chamber.

To start an experiment, the oil, heated in a constant temperature bath, entered the jacket at a temperature of about 60°C. The rate of flow of the oil and the current in the chamber wall were regulated so that the oil was about 90° at the top. $H_1$ and $H_2$ were controlled so that the water in the evaporator was at 90–95°C. and the ceiling was approximately the same. The brass rod B was immersed about one-half inch in a freezing mixture. These conditions were kept constant for about four hours until a steady state was reached. By this time any foreign particles in the enclosed air which caused condensation had fallen to the floor and the temperature gradient as measured in the center of the chamber by $T_2$ was constant. Also a cloud caused by the self nucleation of the water vapor is about 2 cm. from the floor. That is, the water vapor produced at the top of the chamber had diffused downwards becoming more and more supersaturated until it reached the critical point at which self nucleation occurred. A gradient of supersaturation was thus present in the chamber.

When these conditions were established, a few cubic centimeters of the nuclei were injected from a heated syringe into the top of the chamber slowly. The tube N was constructed so that the particles were injected horizontally. These particles could not be seen until they caused condensation of the water vapor. When viewed with a parallel beam of light at an angle of 120° this condensation was easily visible especially after the particles had fallen some distance and had time to grow. The upper limit of the cloud was ascertained by gradually moving the light upward until the cloud was no longer evident. Then thermocouple $T_2$ was moved to this height and the temperature at which condensation apparently initiates was recorded. The number of nuclei injected was sufficient to keep the height of the cloud constant for at least 10 min. It took at least an hour for all the cloud particles to settle out but then more nuclei could be added and a new estimate of the cloud height made.

The salt to be studied was coated evenly on the chromel nuclei coil. This was done by repeatedly dipping the coil in a solution or, in the case of insoluble compounds, a slurry of the salt. The wire was then heated in a flask in a stream of clean dry air and a few cubic centimeters of this air taken with the syringe for nucleating the chamber. An extensive study by electron micro-

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graphs of the nuclei produced (1) has shown that their size and monodispersity vary with the current in the coil and the rate of flow of the carrier air. Although the size and monodispersity of the nuclei used did not affect the height of the cloud, they affected its visibility. Consequently, for each salt used various conditions of nuclei production were tried until the one giving the most distinct cloud was found. Then an electron micrograph was made of these nuclei so that their size would be known accurately.

The flux of water vapor in the chamber was measured at the end of each day by melting the ice collected on the floor and allowing it to drain through D into a graduated cylinder.

## RESULTS

In Table I are given the results for the six types of nuclei used. The temperature of the cloud top is given in column 3 and the temperature of the water evaporator is given in column 2. The last column shows the supersaturation of water vapor corresponding to these clouds.

TABLE I

| Nucleus | Water, °C. | Cloud top, °C. | $S$ | Nucleus | Water, °C. | Cloud top, °C. | $S$ |
|---|---|---|---|---|---|---|---|
| NaCl | 91.5 | 89 | 1.09 | AgI | 92 | 82.5 | 1.15 |
| | 93.5 | 92 | 1.04 | | 92 | 91 | 1.06 |
| | 93 | 90 | 1.08 | | 92 | 85.5 | 1.12 |
| | 93.5 | 93 | 1.02 | | 91.5 | 85.5 | 1.12 |
| | 92.5 | 91 | 1.06 | | 91.5 | 84 | 1.14 |
| | 93 | 90.5 | 1.07 | | 91 | 83 | 1.14 |
| | 91 | 89 | 1.09 | | 93 | 85 | 1.13 |
| $CaCl_2$ | 91 | 91 | 1.06 | $MnCl_2$ | 91.5 | 90 | 1.07 |
| | 91.5 | 91.5 | 1.05 | | 91.5 | 91.5 | 1.05 |
| | 91 | 89 | 1.09 | | 92 | 89.5 | 1.08 |
| | 91.5 | 92 | 1.04 | | 93.5 | 92 | 1.04 |
| | | | | | 93 | 90 | 1.07 |
| $CuSO_4$ | 93 | 87 | 1.11 | | 93 | 89 | 1.09 |
| | 92 | 90 | 1.08 | | 93 | 90.5 | 1.07 |
| | 92 | 86 | 1.12 | | 93.5 | 91.5 | 1.05 |
| | 91 | 85 | 1.13 | | | | |
| | 91 | 85 | 1.13 | LiCl | 92 | 93.5 | 1.01 |
| | 94.5 | 90 | 1.08 | | 93 | 93 | 1.02 |
| | 94 | 87 | 1.11 | | 93 | 93.5 | 1.01 |
| | 94 | 85 | 1.13 | | 93 | 93 | 1.02 |
| | 94 | 85 | 1.13 | | 93 | 93.5 | 1.01 |
| | 94 | 86.5 | 1.12 | | | | |
| | 93.5 | 89 | 1.09 | | | | |
| | 92 | 90 | 1.08 | | | | |

The flux measured for several eight hour periods averaged $14 \pm 0.4$ cc./eight hours, that is $1.75 \times 10^{-5}$ cc./cm.$^2$ cross section/sec.

The calculations of the degree of supersaturation existing at cloud formation were made from the following considerations. It is necessary to know both the vapor pressure and the saturation pressure at that point. Direct experimental measurements of the vapor pressure cannot be made, however, without either disturbing the system or involving very elaborate techniques. Langsdorf (3)

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treated this problem theoretically for his cloud chamber. By considering the energy flux he obtained an expression for the temperature distribution in the chamber. Upon introducing this distribution into the Kuusinen equations (2) for mass flux he derived an expression for the degree of supersaturation as a function of the distance from the chamber floor. His expression however, includes the energy flux, which is difficult to determine, and the thermal conductivity coefficient of the gas to which no unique value can be given since the coefficient is a complex function of both the temperature and composition. An additional criticism arises out of his neglect of self-nucleation which certainly exists in his chamber and which provides an additional mechanism for mass transfer. In a more recent paper Shutt (6) also used the Kuusinen equations but was primarily concerned with the conditions inside the cloud.

By taking advantage of our ability to determine the temperature distribution experimentally we have been able to obviate the need of knowing the energy flux and thermal conductivity coefficient. If we also assume that we can apply Kuusinen's one dimensional, isothermal, diffusion equations we get:

[1] $$c_2 = w D_2 - \frac{k dD_2}{dx}.$$

[2] where $$w = c_1 v_1 + c_2 v_2,$$

$c_1$ and $c_2$ are the mass flux and $v_1$ and $v_2$ are the partial specific volumes of water vapor and air respectively,

$D_2$ is the concentration of the air,

$k$ is the diffusion coefficient of water in air,

$x$ is the distance from the bottom of the chamber.

Since there is no flux of air $c_2 = 0$. Substituting [2] into [1] and using the perfect gas law value for $D_2$ we get:

$$0 = c_1 v_1 p_2 - (k\, dp_2/dx)$$

where $p_2$ is the partial pressure of air.

But $$v_1 = RT/M_1 p_0$$

where $M_1$ is the molecular weight of water vapor and $p_0$ is the pressure in the chamber = 1 atm. and then

$$0 = \frac{c_1 RT\, p_2}{M_1 p_0} - k \frac{dp_2}{dx}.$$

Now the variation of $k$ with temperature and pressure can be represented as:

$$k = \frac{k_0}{p_0} \frac{(T)^{1+\alpha}}{T_0}$$

where $T_0$ is the temperature of the self-nucleated cloud at which $k$ equals $k_0$ and $\alpha$ is a constant.

Making this substitution we get:

$$0 = \frac{c_1 RT\, p_2}{M_1} - k_0 \frac{(T)^{1+\alpha} dp_2}{T_0 \quad dx}$$

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Upon rearranging:

$$\frac{dp_2}{p_2} = \frac{c_1 R\,(T_0)^{1+\alpha}\,dx}{M_1 k_0\ T_\alpha}.$$

For water in air $\alpha$ can be taken as unity.

Integrating between the conditions at the self-nucleated cloud ($p_2^0$, $x_0$) and any point in the chamber ($p_2$, $x$) then gives:

$$\ln \frac{p_2}{p_2^0} = \frac{c_1 R T_0^2}{M k_0} \int_{x_0}^{x} \frac{dx}{T}.$$

For our experiments $c_1 = 1.75 \times 10^{-5}$ cc. cm.$^{-2}$ sec.$^{-1}$
$R = 82.06$ cc. atm. mole$^{-1}$ deg.$^{-1}$
$M = 18$ gm. mole$^{-1}$
$k_0 = 0.219$ cm.$^2$ atm. sec.$^{-1}$
$T_0 = 333$°A.

The integral was evaluated by measuring the area under the temperature distribution curve. The equation thus gives a value for the partial pressure of air and hence the partial pressure of water vapor at any point in the chamber. The degree of supersaturation was then obtained as the ratio of the calculated pressure to the saturation pressure of water at that temperature (Fig. 2).

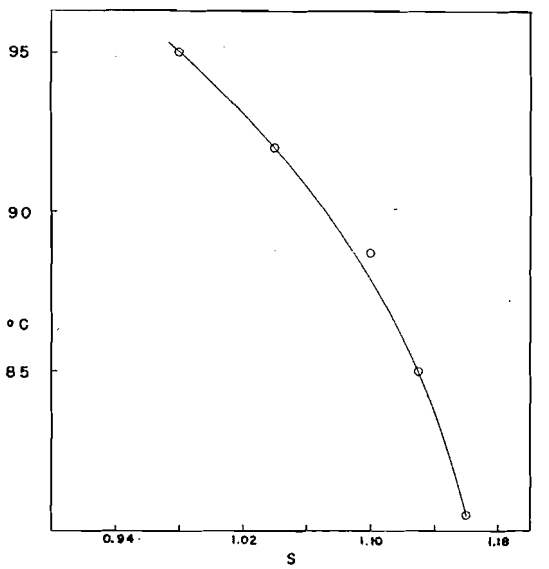



FIG. 2. Supersaturation ratio as a function of temperature.

In practice, the temperature distribution in the chamber did not vary markedly from experiment to experiment so only one representative curve of $1/T$ (°A) vs. height was used for evaluation of the integral (Fig. 3). The error in $S$ introduced by this simplification was at the most 1%.

The water evaporator was not always at the same temperature. However this temperature does not come into our equation and only affects $S$ in so far

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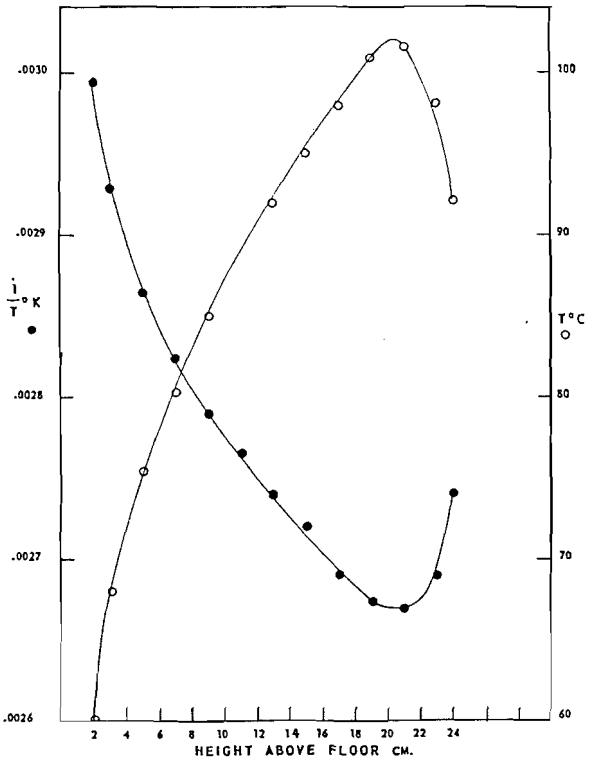



FIG. 3. Temperature distribution in the chamber.

as it changes $T_0$. $T_0$ had an average value of 60°C. and this was used in the calculations. It is estimated that the use of this average value for $T_0$ may cause $S$ to be in error by 4%. Table II was obtained by averaging the values of $S$ in Table I.

TABLE II

| Nucleus | Supersaturation |
|---|---|
| LiCl | 1.02 ± .01 |
| NaCl | 1.06 ± .02 |
| $CaCl_2$ | 1.06 ± .02 |
| $MnCl_2$ | 1.07 ± .01 |
| $CuSO_4$ | 1.11 ± .02 |
| AgI | 1.12 ± .02 |

Again, if variations of the flux are taken into account the resulting variation in supersaturation is at the most 2%.

Summarizing, the total maximum variation in the supersaturation values caused by variations in the flux, the temperature of the self-nucleated cloud, and the temperature distribution are 7%. However this error will occur consistently for each salt investigated and therefore will not affect their relative differences.

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Fig. 4 is taken from the electron micrographs and shows the variation of size of the NaCl nuclei with temperature of the coil. The magnification used is 40,000. These sizes did not affect the height of the cloud but only its visibility.

Fig. 5 shows comparative size of the six nuclei used. From the magnification (40,000) the minimum size of each nucleus was above $10^{-6}$ cm.

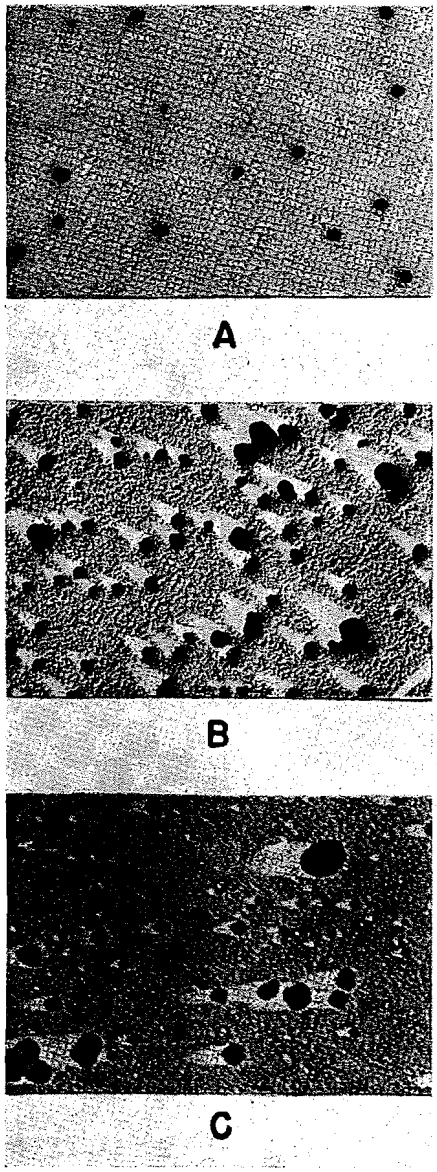



FIG. 4. NaCl nuclei (40,000 ×).
*A*. 330°C. *B*. 410°C. *C*. 470°C.

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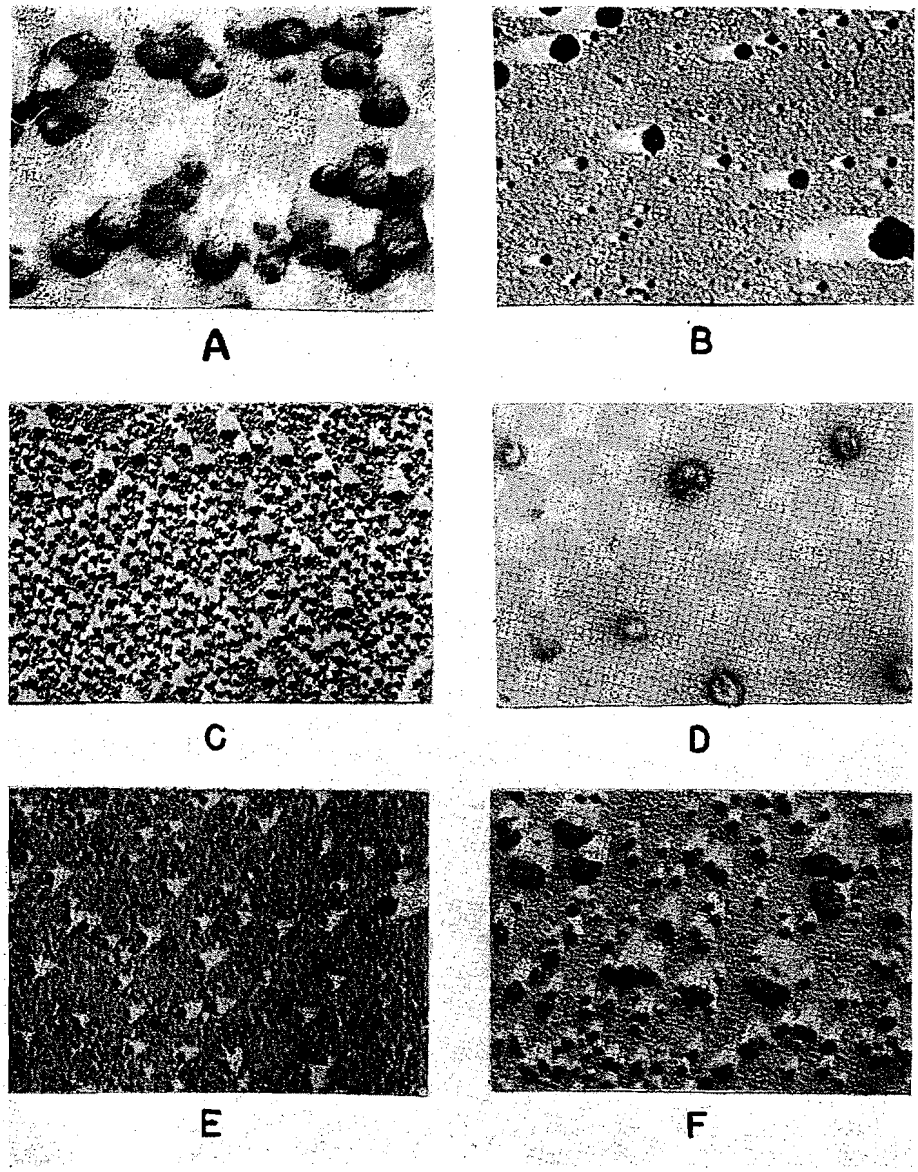



FIG. 5. Condensation nuclei (40,000 ×).
*A*. LiCl *C*. $CuSO_4$ *E*. AgI
*B*. NaCl *D*. $CaCl_2$ *F*. $MnCl_2$

## DISCUSSION

The results in Table II indicate that there is a total of a 10% difference in the supersaturations that these nuclei will tolerate. The average deviations, shown in the table, which, we feel are a measure of the reducability of these values, are at the most 2%. Therefore the difference in nucleating efficiency is

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a real one. This difference was also found, but in a qualitative manner, in the original diffusion cloud chamber (5).

In our experiments, this difference is independent of particle size. According to Pound's theory of heterogeneous nucleation (4), the nucleation rate is not affected by particles greater than $10^{-7}$ cm. The electron micrographs indicate that the minimum size of particles used in our experiments was of the order of $10^{-6}$ cm. so we were operating well out of the critical size range. In fact, this was proved since the height of the cloud did not vary for the three very different sizes of NaCl shown in Fig. 4.

This difference in nucleating efficiency does not seem to be explained by any of the more obvious physical and chemical properties of these compounds such as solubility, crystal structure, hygroscopicity, and the like. The only order observed is that the nucleation power varies as the weight of the cation used. This might lead to many properties such as density and charge to mass ratio. A more extensive list of compounds would have to be studied before the property responsible for nucleation efficiency was clearly defined.

As already stated, the assumptions involved in developing and applying our diffusion equation may alter the absolute values that we have given for the supersaturation tolerances of these nuclei. However, we feel that the *differences* indicated are real and significant. The diffusion cloud chamber is an effective way of measuring such differences in nucleating efficiency.

ACKNOWLEDGMENTS

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# THE ELECTRODE BEHAVIOR OF COPPER[1]

By A. K. Wiebe and C. A. Winkler

ABSTRACT

Potentials ranging from −0.063 volt to +0.044 volt were observed for freshly prepared copper electrodes in sulphuric acid. The potential was dependent upon concentration of the electrolyte, the gas with which the electrolyte was saturated, the nature of the electrode surface, and the intensity of the stirring. The rate of potential decay was influenced by the nature of the dissolved gas and concentration of the electrolyte. When current was passed for the first time across a freshly prepared electrode face, the potential build-up was nonlinear, but subsequent passage of current gave a linear build-up of potential. The apparent capacitance at a copper cathode increased with the time allowed for the potential to decay after current had been passed. It was also dependent upon the current used to measure it, and appeared to be somewhat affected by the area of the cathode. Reliable estimates of the surface areas of the electrodes appeared to be possible from the times required for the electrodes to reach maximum potentials.

## INTRODUCTION

Potential change and rates of potential change associated with overvoltage phenomena have often been interpreted in terms of a parallel mesh of resistance and capacitance at or near the electrode surface (cf. 4). Earlier work in this laboratory (8) with copper and silver electrodes appeared to support this view. Two distinct types of potential build-up curves were observed, one of which (the initial curve) was tentatively associated with the deposition of a close-packed monatomic film of hydrogen on the electrode surface and the other with the charging of a condenser.

The results of recent studies with electrodes of mercury (9) and platinum (10) made it desirable to reinvestigate the electrode behavior of copper.

## EXPERIMENTAL AND RESULTS

The cathode ray oscilloscope unit and Leeds and Northrup type K potentiometer arrangement used have been described in previous papers from this laboratory (5,7–10). The electrolytic cell and experimental methods were also essentially similar.

The copper electrodes were prepared by cementing turned plugs into a small female ground joint, using a solution of lucite in chloroform as the cement. The female joint was sealed to a larger male joint which fitted into the cell. Experiments showed that electrodes prepared in this way gave the same results as those in which seepage of electrolyte between the metal and glass was prevented with a small pressure of hydrogen gas behind the electrode. The electrode face was ground until a uniform surface was obtained. The electrode cross section was 0.37 cm$^2$.

All potential measurements were made as before, with reference to a saturated calomel electrode.

[1] *Manuscript received July 24, 1953.*
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As with platinum (10), the potential of a freshly prepared copper electrode immersed in hydrogen saturated electrolyte approached a steady state value (zero potential) from more positive potentials, but at a much slower rate (curve I, Fig. 1A). With platinum, the zero potential in hydrogen saturated

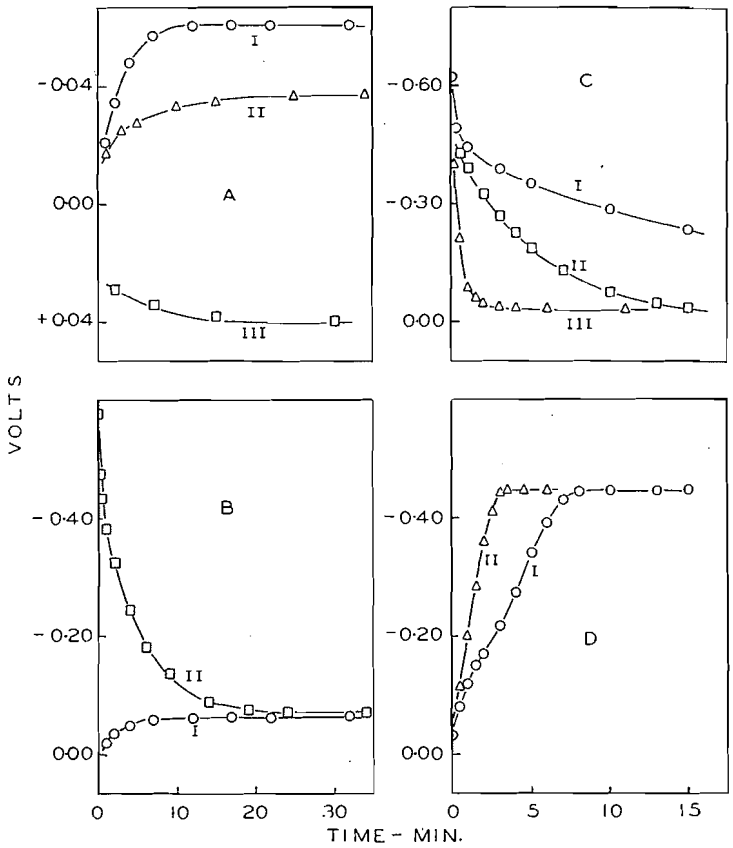



FIG. 1. A. Potential behavior of a copper cathode in $N/5$ sulphuric acid.
Curve I: Electrolyte saturated with hydrogen.
Curve II: Electrolyte saturated with nitrogen.
Curve III: Electrolyte saturated with oxygen.
B. Potential–time curves for a copper cathode in $N/5$ sulphuric acid saturated with hydrogen.
Curve I: Attainment of steady state (zero) potential.
Curve II: Potential decay.
C. Potential decay curves for a copper cathode in electrolytes of different acid concentrations, saturated with nitrogen.
Curve I: $N/1000$ sulphuric acid.
Curve II: $N/100$ sulphuric acid.
Curve III: $N/5$ sulphuric acid.
D. Potential build-up curves for a copper cathode in $N/5$ sulphuric acid saturated with nitrogen (solutions unstirred).
Curve I: Initial curve on a fresh copper surface prepared by grinding with No. 225 optical compound and water on glass. The electrode was left in contact with the solution for 130 min. before switching on the current.
Curve II: Subsequent curve obtained after allowing the potential to decay from the maximum of Curve I.

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electrolyte was steady within 30 sec. of immersion, whereas 15 to 20 min. were required with a copper electrode.

In electrolyte saturated with nitrogen, copper, like platinum, gave a negative change of potential which was complete in about 20 min., and attained a steady state potential more positive than in electrolyte saturated with hydrogen (curve II, Fig. 1A). The behavior of copper in oxygen saturated electrolyte was also similar to that of platinum, with the potential changing to a more positive value with time. The steady state potential was considerably more positive than in electrolyte saturated with either nitrogen or hydrogen (curve III, Fig. 1A).

The zero potential of a copper cathode immersed in $N/5$ sulphuric acid saturated with hydrogen was $-0.063$ volt, while that of a similar electrode immersed in oxygen saturated electrolyte was $+0.04$ volt. In marked contrast, the electrode potentials of mercury (9) and of platinum (10) were changed by about one volt when electrolyte saturated with oxygen replaced a hydrogen saturated electrolyte.

The potentials of copper electrodes varied with (i) the concentration of the electrolyte, (ii) the gas with which the electrolyte was saturated, (iii) the nature of the electrode surface, and (iv) the intensity of stirring (Table I).

TABLE I
ZERO POTENTIALS AT COPPER ELECTRODES

| Sol'n. | Sol'n. sat'd with gas | Potential | | |
|---|---|---|---|---|
| | | Sol'n. stirred | Sol'n. unstirred | Cathode surface ground with: |
| $N/5$ $H_2SO_4$ | $H_2$ | $-0.063 \pm 0.003$ | | No. 225 optical compound and water on glass |
| As above | $N_2$ | $-0.050 \pm 0.003$ | $-0.035 \pm 0.005$ | As above |
| As above | $N_2$ | $-0.033 \pm 0.003$ | $-0.024 \pm 0.004$ | 120 Mesh emery and water on glass |
| $N/100$ $H_2SO_4$ | $N_2$ | | —0.010 | No. 225 optical compound and water on glass |
| $N/1000$ $H_2SO_4$ | $N_2$ | $-0.016$ | $-0.010$ | As above |
| $4N$ $H_2SO_4$ | $N_2$ | | $-0.044$ | As above |
| $N/5$ $H_2SO_4$ | $O_2$ | $+0.044$ | $+0.032$ | As above |

However, as these potential effects were small, a study of zero potentials would seem to be of little value for the elucidation of the cathode reactions involved.

Potential decay curves were obtained as before (9), by allowing the potential to decay on open circuit after current had been passed until the maximum value of the overvoltage had been reached.

The potential of a copper cathode immersed in $N/5$ sulphuric acid saturated with hydrogen decayed to a value identical with the steady state potential observed under similar conditions (Fig. 1B). This would seem to indicate that the copper surface was in the same condition at the end of the decay process as it was when the zero potential was measured (before flow of current).

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Potential decay curves at copper cathodes were influenced by the nature of the dissolved gas and the concentration of the electrolyte. The decay process in $N/5$ sulphuric acid saturated with nitrogen (curve III, Fig. 1C) was complete in much less time than that in hydrogen saturated electrolyte of the same concentration (curve II, Fig. 1B). In nitrogen saturated solution, the potential decayed at a markedly slower rate as the concentration of the electrolyte was reduced (Fig. 1C). The rates of potential decay in $4N$ and $N/5$ sulphuric acid were approximately equal.

As with mercury (9) and platinum (10) two types of potential build-up curves could be distinguished for copper cathodes. An initial potential build-up curve, obtained when current was passed for the first time across the face of a freshly prepared electrode, was nonlinear throughout. On the other hand, when the current was switched on after the potential was allowed to decay on open circuit from the maximum of the initial curve, the subsequent curve was linear and reached the maximum potential in a much shorter period of time.

As with platinum, the initial and subsequent potential build-up curves at a copper cathode immersed in hydrogen saturated electrolyte were essentially identical unless the initial curve was obtained within 15–20 min. after the electrode was introduced into the electrolyte. In electrolyte saturated with nitrogen, the initial curve (curve 1, Fig. 1D) was independent of the time of immersion of the electrode (prior to switching on the current).

This electrode behavior would seem to indicate that on a copper surface, as on platinum, molecular hydrogen in solution is adsorbed as a monatomic film. The electrode behavior of the two metals appears to differ mainly in the rate of dissociation and adsorption of hydrogen, as indicated by the time required for the zero potential to reach a steady value. The dissociation and subsequent adsorption of hydrogen as a monatomic film at a platinum surface appears to be essentially complete in about 30 sec., whereas with copper the process apparently requires 15 to 20 min. (curve 1, Fig. 1A). This comparatively slow rate of dissociation and adsorption at a copper surface would seem to indicate that the forces between hydrogen and copper atoms are weaker than those existing between hydrogen and platinum atoms.

The initial potential build-up curves on cathodes of mercury (9) and of platinum (10) were taken to be associated with the deposition of a monatomic film of hydrogen on the electrode surfaces such that each surface atom of mercury or of platinum accommodated one atom of hydrogen when the potential reached a maximum. The time required for the potential to reach a maximum with a given current was designated $t_{max}$ and it was shown that the application of Faraday's laws to the charge passed in the interval $t_{max}$ may provide a convenient method of measuring the surface areas of platinum electrodes.

The true area of a copper electrode is unknown, so that the number of surface copper atoms cannot be calculated as with mercury (9). Moreover, since stable oxides of indefinite thickness tend to form on a copper surface, the current reversing techniques used with platinum (10) cannot be successfully applied at a copper electrode. As a result, there is no direct evidence that at $t_{max}$ each

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surface atom of copper accommodates one atom of hydrogen. However, it is interesting to compare areas obtained by application of Faraday's laws to the quantity of charge passed in the interval $t_{max}$, with those given by apparent capacitance measurements. The values of $t_{max}$ were taken directly from the initial potential build-up curves. A value of 5.2 Å$^2$ was calculated for the effective area of a copper atom, on the assumption that the atoms in solid copper are close-packed. The apparent capacitance of copper cathodes was determined from the rate of potential change in the linear sections of the subsequent potential build-up curves. From these measurements the areas of the electrodes could be calculated by the Bowden–Rideal method (3), assuming a capacitance of 20 microcoulombs per volt cm.$^2$ at a uniplanar surface (2, 5,6).

Areas of copper cathodes determined by the Bowden–Rideal method decreased with time of immersion in $N/5$ sulphuric acid as shown in Fig. 2. The

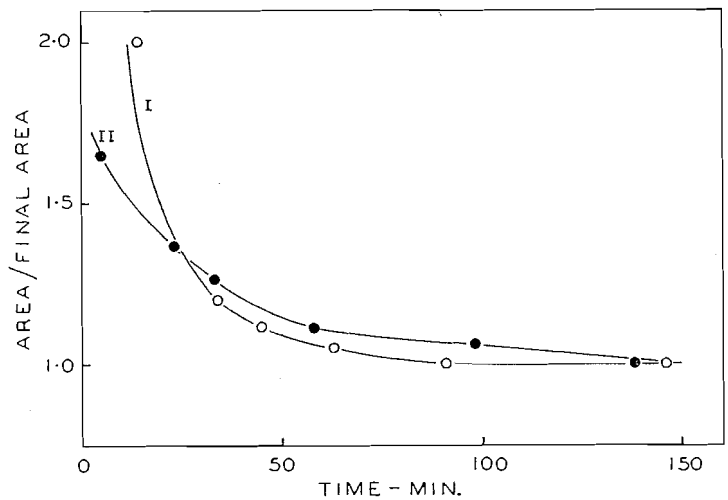



FIG. 2. Change in area of copper cathodes with time, in $N/5$ sulphuric acid saturated with nitrogen.
Curve I: Electrode surface ground with 120 mesh emery and water on glass.
Curve II: Electrode surface ground with No. 225 optical compound and water on glass.

initial change was quite rapid but appeared to be complete in about two hours. Thus, after the copper cathodes had been allowed to age for two to three hours, experiments were made to determine how the apparent capacitance was related to the current used in the measurements and to the period of potential decay prior to the switching on of the current.

The apparent capacitance at a copper cathode immersed in $N/5$ sulphuric acid increased with the time allowed for the potential to decay after current had been passed (Table II). The recorded increase in apparent capacitance corresponds to a decrease in the slope of the subsequent build-up curves. This behavior, although less pronounced, is identical with that observed at a mercury cathode with initial potentials of about −0.61 volt (9). As with mercury

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TABLE II

CHANGE OF APPARENT CAPACITANCE WITH THE TIME ALLOWED FOR POTENTIAL DECAY ($N/5$ $H_2SO_4$ SAT'D. WITH $N_2$)

| Time of potential decay, min. | Apparent capacitance, microcoulombs/volt |
|---|---|
| 1 | 310 |
| 2 | 440 |
| 3 | 410 |
| 4 | 440 |
| 6 | 450 |
| 8 | 460 |
| 10 | 470 |
| 15 | 480 |
| 20 | 510 |
| 30 | 520 |
| 60 | 510 |

*Note: The electrode surface was ground with No. 225 optical compound and water on glass. The current used for capacitance measurements was 4.36 × $10^{-5}$ amp.*

cathodes, the linear rate of potential build-up might be expected to increase with the time allowed for the potential to decay if it were the result of a true capacitance.

The apparent capacitance also varied with the current used to measure it (Fig. 3). The observed minima in the values of apparent capacitance, in

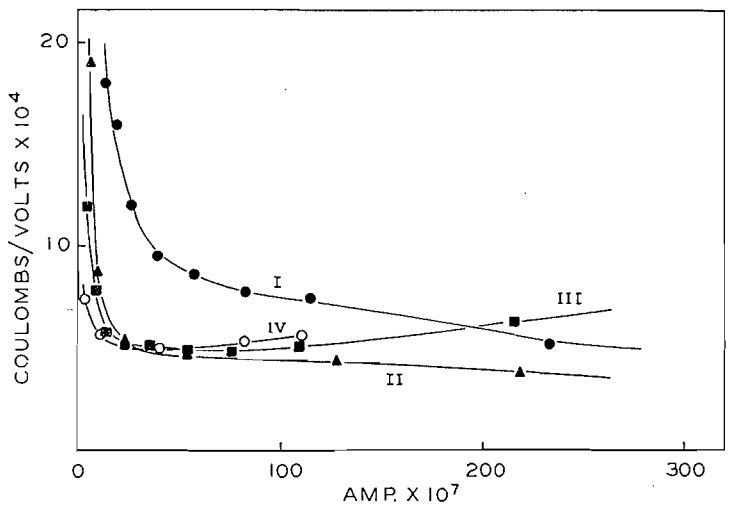



FIG. 3. Relation between apparent capacitance and current at a copper cathode in nitrogen saturated electrolytes.
Curve I: 4 $N$ sulphuric acid.
Curve II: $N/5$ sulphuric acid.
Curve III: $N/100$ sulphuric acid.
Curve IV: $N/1000$ sulphuric acid.
Electrode surfaces ground with No. 225 optical compound and water on glass.

$N/100$ and $N/1000$ acid, corresponding to maxima in the rates of potential build-up, would seem to indicate that at least two separate reactions occurred, the rates of which were altered to a different extent by change in the current.

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Insufficient evidence is available to propose a definite mechanism but possibly adsorption–desorption equilibria are involved (1), together with reactions of the type

$$H^+ (ads) + e \longrightarrow H (ads).$$

For copper electrodes ground with No. 225 optical compound and allowed to age for two hours in $N/5$ $H_2SO_4$ saturated with nitrogen before switching on the current, surface areas determined by rate of potential build-up agreed well with those determined from the charge passed during $t_{max}$, over a range of current of $4.19 \times 10^{-5} - 3.03 \times 10^{-6}$ amp. The values of apparent capacitance presented in the last column of Table III were obtained by dividing the total apparent capacitance by the area estimated from the quantity of charge passed in $t_{max}$ (i.e. by hydrogen packing). When similar experiments were made with electrodes ground with 120 mesh emery and water on glass (Table IV), the areas measured by the two methods differed by a factor of about four. Furthermore, the total apparent capacitance for electrodes ground with 120 mesh emery (Table IV) was only slightly larger than for electrodes ground with No. 225 optical compound (Table III) whereas measurements by hydrogen packing showed the former surfaces to have almost six times the area of the latter.

TABLE III

AREA BY H PACKING COMPARED WITH AREAS BY RATE OF POTENTIAL BUILD-UP

| Area by H packing | | | Area by rate of potential build-up | | Apparent capacitance | |
|---|---|---|---|---|---|---|
| | | | Area | | Microcoulombs/volt | |
| $I$, amp. $\times 10^6$ | $t_{max}$, min. | Area, cm.² | × Planar | Cm.² | Total | Per cm.² |
| 41.9 | 2.7 | 22.0 | 63 | 23.4 | 460 | 21 |
| 17.5 | 6.4 | 21.8 | 57 | 21.2 | 410 | 19 |
| 17.5 | 3.0 | 10.3 | 60 | 22.2 | 430 | 42 |
| 17.4 | 7.7 | 26.0 | 59 | 21.8 | 440 | 17 |
| 17.4 | 6.3 | 21.4 | 79 | 29.2 | 580 | 27 |
| 17.2 | 7.3 | 24.4 | 56 | 20.8 | 420 | 17 |
| 8.05 | 10.4 | 16.4 | 58 | 21.4 | 440 | 27 |
| 5.56 | 9.0 | 10.0 | 53 | 19.6 | 390 | 39 |
| 5.56 | 11.0 | 12.0 | 60 | 22.5 | 440 | 37 |
| 5.55 | 24.5 | 26.6 | 78 | 28.6 | 530 | 22 |
| 5.40 | 19.5 | 20.8 | 71 | 26.3 | 520 | 25 |
| 3.03 | 39.0 | 22.8 | 60 | 22.2 | 460 | 20 |
| Average | | 19.5 | | 23.3 | 460 | 26 |

*Note: Apparent area of the cathode = 0.37 cm.²*
*The cathodes were ground with No. 225 optical compound.*
*Current used for the area measurements by rate of potential build-up = $4.2 \times 10^{-5}$ amp.*

This would indicate that the apparent capacitance is affected to some extent by the area of the cathode but that the relation is by no means linear. Hence, the Bowden–Rideal method would seem to be of doubtful value for the estimation of true surface areas of electrodes.

Since the Bowden–Rideal method did not appear to give a reliable estimate of true surface areas, it seemed possible that the observed change of area with

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TABLE IV

AREAS BY HYDROGEN PACKING COMPARED WITH AREAS BY RATE OF POTENTIAL BUILD-UP

| Area by hydrogen packing | | | Area by rate of potential build-up | | Apparent capacitance | |
|---|---|---|---|---|---|---|
| | | | Area | | Microcoulombs/volt | |
| $I$, amp. $\times 10^5$ | $t_{max}$, min. | Area, cm.$^2$ | $\times$ Planar | cm.$^2$ | Total | Per cm.$^2$ |
| 19.8 | 2.5 | 96 | 47 | 17 | 350 | 3.7 |
| 11.2 | 5.8 | 130 | 80 | 30 | 600 | 4.7 |
| 7.18 | 8.1 | 114 | 86 | 32 | 650 | 5.7 |
| 4.20 | 15.8 | 130 | 69 | 26 | 510 | 3.9 |
| 2.34 | 19 | 87 | 76 | 28 | 570 | 6.5 |
| 1.25 | 47 | 114 | 75 | 28 | 560 | 4.8 |
| Average | | 112 | | 27 | 540 | 4.9 |

*Note: Apparent area of cathode = 0.37 cm.$^2$*
*The cathodes were ground with 120 mesh emery and water on glass.*
*Current used for area measurements by rate of potential build-up = 4 $\times$ $10^{-5}$ amp.*

time of aging (Fig. 2) might also be apparent rather than real. To examine this possibility, the current was switched on 10 min. after the introduction of the copper electrodes into nitrogen saturated electrolyte. Areas by the Bowden–Rideal method were then determined immediately following $t_{max}$. For electrodes ground with No. 225 optical compound (Table V), the Bowden–Rideal

TABLE V

AREAS BY H PACKING COMPARED WITH AREAS BY RATE OF POTENTIAL BUILD-UP ($N$/5 $H_2SO_4$)

| Area by H packing | | | Area by rate of potential build-up | | Apparent capacitance | |
|---|---|---|---|---|---|---|
| | | | Area | | Microcoulombs/volt | |
| $I$, amp. $\times 10^5$ | $t_{max}$, min. | Area, cm.$^2$ | $\times$ Planar | Cm.$^2$ | Total | Per cm.$^2$ |
| 4.38 | 3.7 | 31.7 | 87 | 32 | 640 | 20 |
| 2.55 | 6.2 | 30.8 | 93 | 34 | 690 | 22 |
| 2.55 | 5.9 | 29.0 | 98 | 36 | 730 | 25 |
| 2.55 | 6.4 | 31.8 | 88 | 33 | 650 | 20 |
| Average | | 30.9 | | 34 | 680 | 22 |

*Note: Current used for areas by rate of potential build-up = 2.55 $\times$ $10^{-5}$ amp.*
*The cathode surfaces were ground with No. 225 optical compound and water on glass.*

measurements were made 20 min. after the time of immersion. For electrodes ground with 120 mesh emery (Table VI), 25–28 min. elapsed between the time the electrodes were introduced into the electrolyte and the time the Bowden–Rideal measurements were made. The values of apparent capacitance per cm.$^2$ obtained for electrodes that were aged for 10 min. (Tables V and VI) were in reasonable agreement with those obtained on similarly prepared electrodes that had been allowed to age for two hours (Tables III and IV). The apparent capacitance per cm.$^2$ appeared to increase slightly as the area decreased. Hence, the Bowden–Rideal method appears to give a fairly reliable indication of changes of area, although the magnitude of the change may be somewhat underestimated.

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TABLE VI
AREAS BY H PACKING COMPARED WITH AREAS BY RATE OF POTENTIAL BUILD-UP ($N/5$ $H_2SO_4$)

| Area by H packing | | | Area by rate of potential build-up | | Apparent capacitance | |
|---|---|---|---|---|---|---|
| | | | Area | | Microcoulombs/volt | |
| $I$, amp. $\times 10^4$ | $t_{max}$, min. | Area, cm.$^2$ | $\times$ Planar | Cm.$^2$ | Total | Per cm.$^2$; |
| 1.14 | 11.0 | 244 | 123 | 46 | 910 | 3.9 |
| 1.14 | 11.4 | 254 | 121 | 45 | 900 | 3.5 |
| 1.15 | 8.7 | 195 | 95 | 35 | 700 | 3.6 |
| 1.15 | 11.7 | 262 | 122 | 45 | 900 | 3.5 |
| Average | | 236 | | 43 | 850 | 3.6 |

*Note: Current used for areas by rate of potential build-up = 1.14 $\times$ $10^{-4}$ amp. The cathode surfaces were ground with 120 mesh emery and water on glass.*

Cathode areas determined from the charge passed in time $t_{max}$ in $N/100$ sulphuric acid (Table VII) and in $N/5$ sulphuric acid (Table V) were in good agreement. It would seem, therefore, that this quantity of charge is independent of the acid concentration and is a function of the cathode surface area only. Thus the application of Faraday's laws to the product $It_{max}$ appears to provide a method of determining the true surface area of an electrode.

TABLE VII
AREAS BY H PACKING IN $N/100$ $H_2SO_4$ SAT'D. WITH $N_2$

| Time of aging in sol'n., min. | Current, amp. $\times 10^5$ | $t_{max}$, min. | Area, cm.$^2$ |
|---|---|---|---|
| 45 | 2.63 | 5.9 | 30 |
| 10 | 2.68 | 6.5 | 34 |
| 10 | 2.73 | 7.0 | 37 |
| 10 | 2.70 | 6.6 | 34 |
| 10 | 2.70 | 6.2 | 33 |
| Average | | | 33.5 |

*Note: The cathodes were prepared by grinding with No. 225 optical compound and water on a glass surface.*

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# THE REACTION OF CYANOGEN BROMIDE WITH THE SODIUM SALTS OF CARBOXYLIC ACIDS

## I. THE REACTION OF CYANOGEN BROMIDE WITH SODIUM BENZOATE[1]

By D. E. Douglas, Jean Eccles,[2] and Anne E. Almond[3]

ABSTRACT

The main products of the reaction of cyanogen bromide with sodium benzoate at 250° to 300°C. are carbon dioxide, benzonitrile, and sodium bromide. Tracer studies have shown that the carbon of the carbon dioxide is derived almost entirely from the cyanogen bromide.

Zappi and Bouso (3) have investigated the reaction of cyanogen chloride with the sodium salts of several carboxylic acids, both aliphatic and aromatic, at 200 to 300°C. to form the corresponding nitriles:

$$RCOONa + ClCN \rightarrow NaCl + CO_2 + RCN.$$

Since good yields of nitriles were obtained they proposed this reaction as a method of synthesis of these compounds.

The corresponding reaction of cyanogen bromide with the sodium salts of various carboxylic acids is being investigated because of its potential application in the synthesis of labelled molecules. By the use of carbon-14-labelled reactants, it has been found that, depending on the carboxylic acid employed, the carbon of the product carbon dioxide may be derived from the carboxyl group or the cyanogen bromide. With sodium acetate and propionate the carbon dioxide carbon originates in the carboxyl group (1).

In this paper, the reaction of cyanogen bromide with sodium benzoate is described. Data are presented to show that in this case the carbon dioxide is derived almost entirely from the cyanogen bromide. Observations on the reaction of cyanogen bromide with the sodium salts of homologous fatty acids will be published later.

### EXPERIMENTAL

Cyanogen bromide-$C^{14}$ was prepared from aqueous sodium cyanide-$C^{14}$ and bromine by a vacuum-line modification of the method Graf *et al.* (2). Benzoic acid-carboxyl-$C^{14}$ was prepared by carbonation of phenylmagnesium bromide by standard vacuum-line procedure.

*Reaction of Cyanogen Bromide with Sodium Benzoate*

The apparatus (Fig. 1) consisted of a tube for the cyanogen bromide connected by a ground joint and stopcock to a U tube with a by-pass between its arms. The U tube was joined through a glass spiral to a vacuum manifold with an attached mercury manometer. A weighed sample (one to two millimoles)

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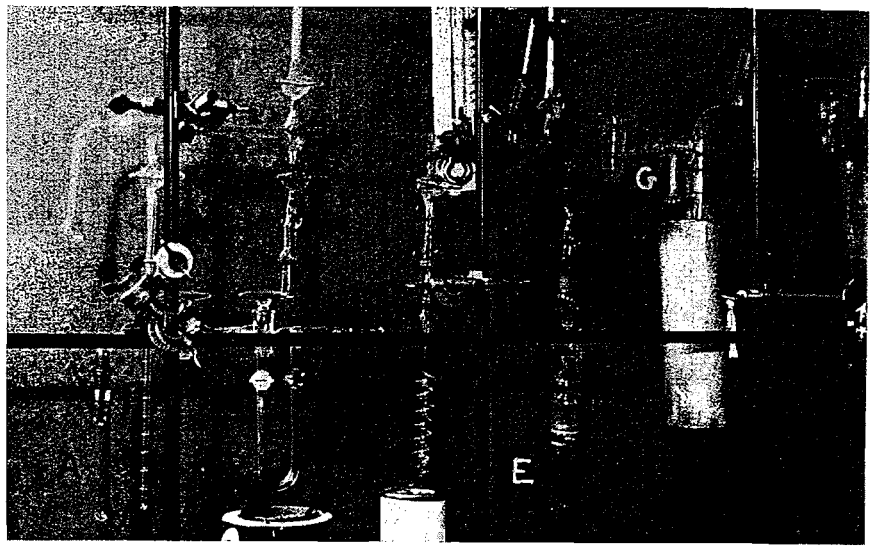



FIG. 1. Vacuum reaction apparatus.
A—Tube to contain cyanogen bromide.
B—U tube.
C—Electrically heated Wood's metal bath.
D—Spiral trap.
E—Carbon dioxide absorption trap.
F—Graduated tube for estimating yield of nitrile.
M—Mercury manometer.
G—Vacuum manifold.

of sodium benzoate was suspended on a mixture of 0.5 gm. each of powdered glass and ignited fuller's earth by evaporating an aqueous slurry of the three materials with stirring. The dried powder was confined to the bottom of the U tube with two plugs of glass wool. The bottom of the U tube was immersed in an electrically heated Wood's metal bath controlled by a Powerstat transformer.

An excess of cyanogen bromide was weighed into the glass stoppered tube, which was then connected to the apparatus, and surrounded by a bath of liquid nitrogen. The whole train was evacuated by means of a fore-pump and mercury diffusion pump. The glass spiral was cooled with liquid nitrogen, and the cyanogen bromide was allowed to volatilize and pass slowly through the contents of the U tube. The process took between 10 and 20 min. No significant pressure change occurred during reaction. The contents of the spiral were later fractionated. Carbon dioxide and unreacted cyanogen bromide were frozen into a trap containing excess 0.5 *N* sodium hydroxide (or, 0.2 *N* sodium sulphide saturated with barium hydroxide when active cyanogen bromide was reactant). The nitrile was condensed with a liquid nitrogen bath into a graduated tube. A varying amount of white or brownish crystalline material condensed in the cooler part of the exit of the U tube during the reaction.

*Treatment of the Reaction Products*

Barium hydroxide solution in a slight excess was added to the heated solution of carbonate in sodium hydroxide from the carbon dioxide trap, and the precipitate of barium carbonate was filtered, dried, weighed, and counted.

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For final activity determination, a sample of the carbonate was decomposed with lactic acid in a vacuum transfer apparatus, and the carbon dioxide reconverted to barium carbonate. A small amount of activity was usually found in the filtrate from the first precipitation.

When the carbon dioxide was absorbed in 0.2 *M* sodium sulphide saturated with barium hydroxide, the barium carbonate was filtered off, weighed, and counted and a sample was decomposed with lactic acid and reconverted to barium carbonate as described above. An aliquot of the original filtrate, which contained the excess cyanogen bromide-$C^{14}$ from the reaction as thiocyanate, was counted.

The nitrile was washed from the graduated tube with ethanol into a bomb tube and hydrolyzed by heating with an excess of 2 *N* sodium hydroxide. Benzoic acid was recovered by acidification of an aqueous solution of the sodium salt with hydrochloric acid, and recrystallized from hot water. M.p. 121.5°–122°C.; mixed m.p. with authentic benzoic acid 121–122°C.

To confirm the identification of the reaction product as benzonitrile, in experiment No. 5 the nitrile was divided into two portions one of which was hydrolyzed as described above. The other portion in dry ether was added to an excess of lithium aluminum hydride in the same solvent. After a few hours, the mixture was decomposed with water, and a few drops of saturated sodium hydroxide added. The solution was extracted continuously with ether. A crystalline hydrochloride formed on passing hydrogen chloride into the dried ether extract. The chloride content of this compound, determined by titration with mercuric nitrate was in good agreement with the theoretical value for benzylamine hydrochloride. Calc. for $C_7H_{10}N$: Cl, 24.7; found: Cl, 24.55.

A sample of the crystalline material from the exit side of the U tube of the train (experiment No. 5) was recrystallized from toluene-cyclohexane. After sublimation, it melted at 100–104°C. By hydrolysis with concentrated hydrochloric acid at 220°–230°C., benzoic acid was obtained, with a specific activity of 249 counts/min./mgm. as compared with 253 counts/min./mgm. for the starting material. This material probably consisted of benzamide and kyaphenin, the trimer of benzonitrile, both of which yield benzoic acid under the hydrolytic conditions employed. Kyaphenin has been identified among the products of the reaction of cyanogen chloride with sodium benzoate (3).

Sodium bromide was identified in the nonvolatile residue remaining in the bottom of the U tube by extracting the fuller's earth and glass with water and precipitating bromide as the silver salt with silver nitrate.

Counting was carried out with a helium flow-type windowless counter and an Atomic Instrument Model 101-A scaler. Corrections were applied for self-absorption in the various substances counted.

## RESULTS AND DISCUSSION

Data for several typical experiments are given in Tables I and II. Owing to the difficulty of obtaining reproducible conditions in heterogeneous pyrolytic reactions of this type, there is considerable variation in the experimental results. Specific activity data show conclusively that the carbon of the product

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TABLE I

DATA FOR THE REACTION OF SODIUM BENZOATE-CARBOXYL-$C^{14}$ WITH CYANOGEN BROMIDE

| Expt. no. | Temp., °C. | Specific activity of original $C_6H_5COOH$, counts/min./mmole | Specific activity $C_6H_5COOH$ from hydrolyzate, counts/min./mmole | Specific activity of $BaCO_3$, counts/min./mmole | Per cent yield of $BaCO_3$ | Per cent yield of $C_6H_5$ |
|---|---|---|---|---|---|---|
| 2 | 280–285 | 160,600 | 139,900 | 4240 | 72.2 | 47 |
| 4 | 296–297 | 39,500 | 28,500 | 356 | 68.1 | 35 |
| 5 | 284–288 | 30,450 | 32,170* | 197 | 77.8 | 34 |

**Benzylamine hydrochloride obtained by reduction of the benzonitrile had a specific activity of 25,400 counts/min./mmole.*

TABLE II

DATA FOR THE REACTION OF SODIUM BENZOATE WITH CYANOGEN BROMIDE-$C^{14}$

| Expt. no. | Temp., °C. | Specific activity of CNBr, counts/min./mmole | Specific activity of $BaCO_3$, counts/min./mmole | Per cent yield of $BaCO_3$ | Specific activity of $C_6H_5$-COOH from hydrolyzate, counts/min./mmole | Per cent activity recovered as $BaCO_3$ and thiocynate | Per cent yield of $C_6H_5CN$ |
|---|---|---|---|---|---|---|---|
| 6 | 289 | 314,600 | 267,900 | 86.7 | 9,060 | 74.5 | 20 |
| 7 | 296–302 | 314,600 | 272,800 | 49.5 | 490 | 50.1 | 46 |

carbon dioxide is derived almost entirely from the cyanogen bromide. The presence of low activity in the barium carbonate when carboxyl-labelled sodium benzoate is a reactant (Table I) and in the recovered benzoic acid when cyanogen bromide alone is labelled (Table II) reveals that a small fraction of the carbon dioxide has its origin in the carboxyl group, probably through a simultaneously occurring alternate reaction yielding the same end products. The occurrence of a side reaction of this type also could explain the trend towards lower activity per millimole of the active product as compared with the active reactant, but this difference may include errors in correcting for self-absorption in the different materials counted.

In the absence of sufficient data on the reaction of cyanogen bromide with sodium salts of other carboxylic acids, a mechanism explaining the derivation of the carbon dioxide from cyanogen bromide is difficult to postulate. At the temperatures employed (250–300°C.), cyanogen bromide should be largely dissociated into CN radicals and bromine atoms, and it is almost certain that a free radical heterogeneous reaction takes place.

Further work should make possible a correlation of the genesis of the carbon dioxide with the general behavior of the carboxyl group of various acids, and thus suggest a mechanism for this reaction.

ACKNOWLEDGMENT

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# FATTY ACIDS OF FILBERT OIL AND NASTURTIUM SEED OIL[1]

By Mary J. Chisholm and C. Y. Hopkins

ABSTRACT

The fatty acids of a sample of filbert kernel oil (*Corylus avellana* L.) were examined by means of ester distillation and low-temperature crystallization. Stearic, oleic, and linoleic acids were identified but eicosenoic acid was not found although earlier workers had reported its presence in considerable amount in samples from the same species. Nasturtium seed oil (*Tropaeolum majus* L. var.), examined in the same way, was found to contain about 20% of 11-eicosenoic acid. An estimate is given of the fatty acid composition of the two oils.

## INTRODUCTION

During a study of the occurrence of *n*-eicosenoic acid in plants, attention was drawn to a report of its presence in substantial amount in the oil of filbert kernels (4). This genus (*Corylus*) had been studied by earlier workers without yielding evidence of the presence of eicosenoic acid (3, 9). Accordingly, a new examination of filbert oil was undertaken to determine its value as a source of the acid in question.

The occurrence of eicosenoic acid in the seed oils of several Cruciferae species has been well established (2, 7, 8). The chief component acid in these oils is docosenoic (erucic) acid and it is evident that oils containing a fairly large proportion of docosenoic acid are likely to contain an appreciable amount of eicosenoic acid as well. An apparent exception was nasturtium seed oil (*Tropaeolum*), which was reported to consist almost entirely of oleic and erucic acids (6), with small amounts of saturated and linoleic acids. It seemed desirable, therefore, to reinvestigate this oil also.

## EXPERIMENTAL

### A. *Filbert Oil*

Filberts were purchased locally and were identified as *Corylus avellana* L. var. Barcelona. The kernels (555 gm.) were crushed and extracted by petroleum ether, yielding 354 gm. of bright yellow oil (63.7%). The oil had iodine value 88.1, saponification value 192.3, and unsaponifiable matter 0.5%. It was converted to methyl esters directly by methanol with dry hydrogen chloride as catalyst. A portion of the mixed methyl esters (308 gm.) was distilled through a heated column, packed with metal rings, at a pressure of 0.1 mm. or less. The distillation data are given in Table I.

The course of the distillation showed that the fatty acids were predominantly 18 carbons in chain length. There was no evidence of a $C_{20}$ fraction. The residue was so small as to signify a very small content of $C_{20}$ or $C_{22}$ acids, if any.

A portion of fraction 1 was saponified. The mixed acids had equivalent weight 274, indicating a mixture of $C_{16}$ and $C_{18}$ acids. The remainder of the fraction (19 gm.) was fractionally crystallized from acetone, giving 11 gm. of solid esters, iodine value 3.6; 5.0 gm. of liquid esters, iodine value 85; and 2.3 gm. of liquid esters, iodine value 117.

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TABLE I
DISTILLATION OF METHYL ESTERS OF FILBERT OIL

| Fraction | Vapor temp., °C. (approx.) | Wt. of fraction, gm. | Iodine value | $n_D^{25°}$ |
|---|---|---|---|---|
| 1 | 100–110 | 24.0 | 42.2 | 1.4448 |
| 2 | 110–115 | 24.2 | 85.5 | 1.4505 |
| 3 | 115–116 | 38.4 | 93.0 | 1.4515 |
| 4 | 116–117 | 14.4 | 98.9 | 1.4515 |
| 5 | 117–119 | 41.6 | 98.8 | 1.4515 |
| 6 | 119–120 | 43.4 | 93.9 | 1.4515 |
| 7 | 120–121 | 42.5 | 92.7 | 1.4515 |
| 8 | 121–123 | 40.2 | 91.3 | 1.4512 |
| 9 | 123–126 | 12.7 | 89.2 | 1.4510 |
| | (Residue distilled from smaller flask) | | | |
| 10 | 124–126 | 16.4 | 83.5 | 1.4508 |
| 11 | (a) | 1.5 | — | 1.4520 |
| Residue | — | 6.0 | — | — |

(a) *Portion obtained by rinsing the column packing.*

Fraction 4 was fractionally crystallized from acetone. The most soluble portion (1.7 gm.) was subjected to the hexabromide test but failed to show evidence of linolenic acid.

On crystallizing 20 gm. of fraction 5 from acetone at −35°, methyl stearate, m.p. 37.5–38° was obtained (0.3 gm.). Succeeding lots of crystals had iodine value 86.7 (13 gm.), 87.7 (2.7 gm.), and 153 (2.7 gm.). The methyl stearate, after hydrolysis and crystallization, gave stearic acid, m.p. 69.2–69.8°, equivalent weight 284.2.

The portion of iodine value 86.7 was oxidized by alkaline permanganate giving dihydroxystearic acid, m.p. 129.5–130.5° alone and mixed with an authentic sample. Thus this fraction contained ordinary oleic acid.

The portion of iodine value 153 was oxidized similarly and the solid product was recrystallized from ethyl acetate. It melted at 172–173°, alone and mixed with an authentic sample of tetrahydroxystearic acid, proving the presence of linoleic acid in the fraction.

The mixed acids of fraction 9 had equivalent weight 284. Crystallization of 9 gm. of the esters from acetone gave 1.7 gm. of iodine value 68, 4.0 gm. of iodine value 86, and 1.9 gm. of iodine value 112.5. The middle portion gave dihydroxystearic acid on oxidation, m.p. 129–130°, alone and mixed with an authentic sample.

Fraction 11 (1.5 gm.) also gave dihydroxystearic acid on oxidation.

The residue was saponified and separated from the unsaponifiable matter. The mixed acids had iodine value 72.7, equivalent weight 297. Upon recrystallizing from acetone, the products were as follows:

| Temp. of cryst'n., °C. | Yield, gm. | M.p., °C. | Equivalent weight | Iodine value |
|---|---|---|---|---|
| 0° | 0.35 | 64–66° | 333 | |
| −40° | 0.4 | Semisolid | 296 | |
| Filtrate | 3.1 | — | 293 | 85.3 |

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The solid portion apparently contains one or more of the higher saturated acids (C > 18). The portion from the filtrate was oxidized by permanganate, freed of saturated acids, and crystallized from ethyl acetate and finally from ethanol, giving dihydroxystearic acid, m.p. 129–130°. Its identity was confirmed by mixed melting point. Accordingly, the major unsaturated acid, even in the residue, is oleic acid. Oleic was identified as the principal acid also in fractions 5, 9, and 11.

Estimation of the fatty acid composition from the above data gives the following percentages: palmitic 3, stearic 4, higher saturated acids, less than 1, oleic 82, linoleic 11.

B. *Nasturtium Oil*

Nasturtium seed (4.5 kilograms) was purchased from a local seed house. It was the ordinary dwarf garden variety, stated by Bailey (1) to be a variety of *Tropaeolum majus* L.

The husks were removed by abrading and aspirating. The seeds were ground further and extracted by petroleum ether, yielding 318 gm. of oil (7%). The oil had iodine value 74.5, saponification value 158.7, and unsaponifiable matter 3.8%. A portion of the mixed methyl esters (270 gm.) was distilled *in vacuo* as described in part A for filbert oil (Table II).

TABLE II
DISTILLATION OF METHYL ESTERS OF NASTURTIUM SEED OIL

| Fraction | Vapor temp., °C. (approx.) | Wt. of fraction, (gm.) | Iodine value | $n_D^{25°}$ |
|---|---|---|---|---|
| 1 | (*a*) 115–140 | 8.1 | 65.2 | 1.4510 |
| 2 | 140–142 | 10.0 | 100.7 | 1.4529 |
| 3 | 142–151 | 4.8 | 93.9 | 1.4529 |
| 4 | 151–157 | 4.7 | 80.0 | 1.4530 |
| 5 | 157–158 | 12.8 | 78.2 | 1.4529 |
| 6 | 158–160 | 15.0 | 78.2 | 1.4529 |
| 7 | 160–162 | 9.7 | 76.8 | 1.4529 |
| 8 | (*b*) 137–140 | 9.6 | 76.9 | 1.4530 |
| 9 | 140–148 | 13.1 | 75.1 | 1.4537 |
| 10 | 148 | 12.4 | 72.5 | 1.4540 |
| 11 | 148–149 | 40.0 | 71.9 | 1.4541 |
| 12 | 149–153 | 53.5 | 71.9 | 1.4540 |
| 13 | 153–155 | 29.4 | 71.8 | 1.4541 |
| 14 | 155–160 | 7.4 | 70.9 | 1.4541 |
| 15 | 160–162 | 4.4 | 70.0 | 1.4542 |
| 16 | (*c*) | 5.0 | 62.2 | 1.4598 |
| Residue | | 30.0 | | |

(*a*) *Pressure 0.5 mm.*
(*b*) *Pressure reduced to 0.1 mm.*
(*c*) *Portion obtained by rinsing the column packing.*

By plotting iodine number and refractive index of each fraction against the aggregate amount of distillate (Fig. 1), it is seen that there is a small proportion of $C_{18}$ esters (chiefly in fractions 1–4), a larger amount of $C_{20}$ esters (fractions 5–8) and a still larger amount of $C_{22}$ esters. The peak in the iodine value curve occurs in the fractions containing methyl linoleate.

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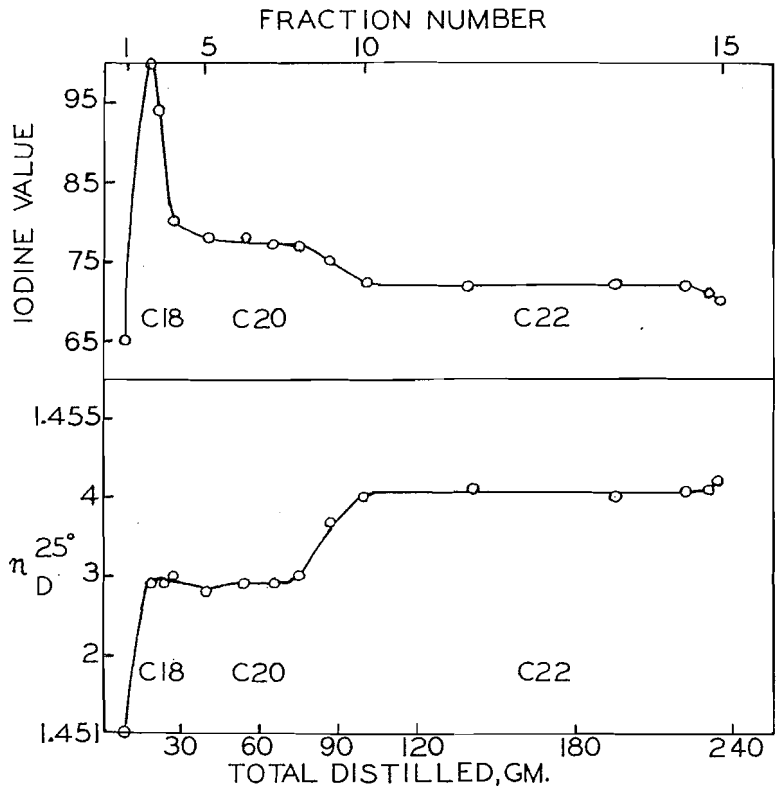



FIG. 1. Methyl esters of nasturtium seed oil. Constants of successive fractions plotted against aggregate weight of distillate.

Fraction 1 was crystallized from acetone and gave 2.2 gm. of solid esters, iodine value 5.7. Upon hydrolysis to acids, this portion had m.p. 62–64° and equivalent weight 269, indicating that it is a mixture of palmitic and stearic acids.

Fraction 2 gave 0.3 gm. of solid acids and the remainder evidently consisted of oleic and linoleic acids.

Fraction 6 (iodine value 78.2) was fractionally crystallized from acetone, with the following results:

| Fraction | Temp. of cryst'n., °C. | Yield, gm. | Iodine value |
|---|---|---|---|
| 6–1 | −24° | 0.5 | 74.5 |
| 6–2 | −30° | 6.7 | 77.8 |
| 6–3 | −45° | 5.3 | 77.7 |
| 6–4 | Filtrate | 1.2 | 80.3 |

Fractions 6–2 and 6–3 were united and hydrolyzed. The resulting acid was crystallized from acetone at −12° and gave 5.0 gm. of eicosenoic acid, m.p. 24°. (Found, iodine value 81.5, equivalent weight 310.6; $C_{20}H_{38}O_2$ requires

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iodine value 81.7, equivalent weight 310.5). Hydroxylation of the acid by permanganate gave dihydroxyeicosanoic acid, m.p. 129–130°. The melting point was unchanged on admixture with 11,12-dihydroxyeicosanoic acid prepared from jojoba oil.

Cleavage of the dihydroxy acid by periodate gave nonaldehyde (the semicarbazone melted at 99–100°) and 10-aldehydodecanoic acid (the semicarbazone melted at 160–161°). The melting points were unchanged in admixture with authentic samples. The original acid is therefore 11-eicosenoic acid.

Fraction 16 and the residue were combined, saponified, and freed from unsaponifiable matter. The acids (22 gm.) had iodine value 70.7 (erucic acid has iodine value 75.0). They were crystallized from acetone as follows:

| Fraction | Temp. of cryst'n., °C. | Yield, gm. | Iodine value |
|---|---|---|---|
| *R*1 | −10° | 10.6 | 69.5 |
| *R*2 | −37° | 4.3 | 72.2 |
| *R*3 | −50° | 2.1 | 73.4 |
| *R*4 | Filtrate | 2.5 | 69.8 |

Fraction *R*1 melted at 30–35° and its equivalent weight was 341. It was recrystallized as follows:

| Fraction | Temp. of cryst'n., °C. | Yield, gm. | Properties |
|---|---|---|---|
| *R*11 | 4° | 1.0 | M.p. 69–71° |
| *R*12 | −50° | 8.0 | I.V. 72.2<br>Equiv. wt. 337 |
| *R*13 | Filtrate | 0.3 | I.V. 71.1 |

*R*11 is evidently a saturated acid. After recrystallization, the equivalent weight was 360, indicating a mixture of behenic and lignoceric acids. *R*12 is almost pure docosenoic acid. Upon hydroxylation by permanganate it gave 13,14-dihydroxybehenic acid, m.p. 130–130.5° alone and mixed with an authentic sample, showing that the original material was erucic acid.

Tetracosenoic acid may be present in *R*2 and *R*3 but if so, it constitutes a relatively small proportion of the total acids.

From these data, the percentage composition of the fatty acids is estimated as follows: palmitic 0.5, stearic 0.5, higher saturated acids 1, oleic 7, linoleic 2, eicosenoic 20, erucic 69.

## DISCUSSION

*A*. Filbert oil from nuts grown in Europe was examined by Schuette and Chang in 1933 (9) and by Bertram in 1936 (3). These authors carried out a partial separation of the fatty acids but neither found positive evidence of acids higher than $C_{18}$. Fang and Bullis (1949) extracted the oil from two varieties of North American filberts and carried out a distillation of the methyl esters (4). Calculations based on the saponification number of the ester frac-

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tions indicated that the fatty acids of the Barcelona variety contained 21% of eicosenoic acid and that the Du Chilly variety contained 15%. However, the acid was not isolated or identified.

The present study of oil from a sample of the Barcelona variety has not confirmed the presence of eicosenoic acid, although the procedure is the same as that employed for the identification of the acid in other oils, in amounts from 3 to 20% of the total acids (7, 8). It is judged, therefore, that the content of eicosenoic acid in our sample is much less than the 21% reported by Fang and Bullis. The possibility of as much as one per cent of this acid being present is not entirely excluded but it is believed that any greater amount would have been detected.

The oil therefore contains the common octadecoic acids, oleic and linoleic, which constitute about 93% of the total; the remaining acids are saturated. These values agree well with those of Bertram (3) and show that the oil is similar to olive oil in composition.

*B.* Nasturtium seed oil (*Tropaeolum majus*) was shown by Gadamer to have erucic acid as its chief constituent (5) and this was confirmed in 1926 by Sudborough and co-workers (10). A further study of oil from a dwarf variety was made in 1938 by Hilditch and Meara (6), including the distillation of a small volume of the methyl esters. They reported the presence of oleic, linoleic, and erucic acids, along with a little saturated acid, and placed the content of erucic acid at 81.8% of the total fatty acids.

In the present work, also with the dwarf variety, 11-eicosenoic acid has been isolated and identified. The amount is substantial and is estimated as 20% of the total acids. This is the highest proportion yet found in a glyceride oil from plants. However, the low content of oil in the seed (7%) renders it unsuitable as a source of eicosenoic acid in quantity. The content of oleic and erucic acids in the oil is calculated to be somewhat lower than that reported by Hilditch and Meara but the total content of monoenoic acids is about the same (96%). Saturated acids are present in unusually small amount.

Although the main purpose of this work was to determine the presence or absence of eicosenoic acid in the two oils, the data are sufficient for a rough estimate of the fatty acid compositions, excluding some minor components which may be present in amounts less than one per cent (Table III).

TABLE III
ESTIMATED FATTY ACID COMPOSITION

| Acid | Per cent of total fatty acids | |
|---|---|---|
| | Filbert oil | Nasturtium seed oil |
| Palmitic | 3 | 0.5 |
| Stearic | 4 | 0.5 |
| Higher saturated acids | <1 | 1 |
| Oleic | 82 | 7 |
| Eicosenoic | | 20 |
| Erucic | | 69 |
| Linoleic | 11 | 2 |

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# DINITRO-ISOBUTYLPHENOL AND DINITRO-ISOAMYLPHENOL[1]

By G. G. S. Dutton, T. I. Briggs,[2] and E. Merler

ABSTRACT

An unequivocal synthesis of ortho- and para-isobutyl and isoamyl phenols by the method of Klages is described. The resulting phenols were nitrated and characterized as their amine salts. The nitrophenols were prepared as part of a program for testing potential herbicides.

## INTRODUCTION

It has been generally accepted that branching an alkyl side chain in a phenol lowers its phenol coefficient (6, 17). This has also proved to be true in the case of dinitroalkyl phenols as far as their herbicidal activity is concerned, with the exception of the ortho-(*sec*-butyl) isomer (5). In view of this apparent anomaly we desired to extend our previous work on the synthesis of dinitro-*n*-alkyl phenols (8) to isomers containing *sec*-alkyl groups.

Since rearrangements are known to occur when alcohols are condensed with an aromatic nucleus (10) we have preferred to use a modification of the method of Klages (11) whereby the desired alkyl group may be built up by reacting a methoxycarbonyl compound with a Grignard reagent. The resulting alcohol may then be dehydrated, the substituted ethylene hydrogenated, and on replacing the methoxyl group by hydroxyl the required phenol is obtained.

Since the isobutyl and isoamyl compounds were also needed for testing as herbicides the preparation of these phenols by the method of Klages and their subsequent nitration is described in this paper. A later communication will extend the use of this method to the preparation of *sec*-amyl and *sec*-hexyl phenols.

## EXPERIMENTAL*

### *2-Isobutylphenol*

(a) *2-Methyl-1-(o-methoxyphenyl)-1-propanol*

A Grignard reagent was prepared in the usual manner in an atmosphere of nitrogen using magnesium (37 gm., 1.5 moles), ether (250 cc.), and isopropyl bromide (196 gm., 1.5 moles) dissolved in ether (350 cc.). The reagent thus formed was treated with 2-methoxybenzaldehyde (102 gm., 0.75 mole) in ether (100 cc.) at 0°C. with vigorous stirring and then refluxed for five hours. The cooled solution was then slowly poured onto cracked ice and ammonium chloride. The ether layer was separated, washed, and dried. A small portion was evaporated and gave a negative test with 2,4-dinitrophenylhydrazine. Removal of the solvent from the main portion and distillation of the residual

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*Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, B.C.*
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**All melting and boiling points uncorrected.*
*Carbon and hydrogen analyses by Drs. Weiler and Strauss, Oxford; others by authors.*



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oil under vacuum gave 2-methyl-1-(*o*-methoxyphenyl)-1-propanol (98 gm., 73%) as a clear liquid boiling at 96°C. (1 mm.) and having $n_D^{19}$, 1.5235. Literature (12) b.p. 133°C. (14 mm.) and $n_D^{16}$, 1.524. Anal. calc. for $C_{11}H_{16}O_2$: $OCH_3$, 17.21%. Found: $OCH_3$, 17.30%. *Phenylurethane* m.p. 148°C. (from carbon tetrachloride). Anal. calc. for $C_{17}H_{21}NO_3$: N, 4.68; $OCH_3$, 10.36%. Found: N, 4.76; $OCH_3$, 10.30%.

(b) *2-Methyl-1-(o-methoxyphenyl)-1-propene*

2-Methyl-1-(*o*-methoxyphenyl)-1-propanol (5 gm.) was refluxed three hours with 20% sulphuric acid. There was thus obtained 2-methyl-1-(*o*-methoxy phenyl)-1-propene (4 gm., 90%) having b.p. 77°C. (1 mm.) and $n_D^{23}$, 1.5435. Literature (12) b.p. 109°C. (14 mm.) and $n_D^{17}$, 1.545. Anal. calc. for $C_{11}H_{14}O$: $OCH_3$, 19.13%. Found: $OCH_3$, 17.88, 17.80%. *Nitrosylchloride*, obtained in poor yield, m.p. 129°C. Anal. calc. for $C_{11}H_{14}ClNO_2$: N, 6.61%. Found: N, 7.00%.

(c) *2-Isobutylanisole*

2-Methyl-1-(*o*-methoxyphenyl)-1-propene (21 gm.) was dissolved in 95% ethanol (25 cc.) and Raney nickel catalyst added (about 5 gm.). Hydrogenation was carried out in an Aminco microhydrogenator at 500 p.s.i. and 50°C. yielding 2-isobutylanisole (16 gm., 76%) boiling at 55°C. (0.1 mm.) and having $n_D^{25}$, 1.5005. Anal. calc. for $C_{11}H_{16}O$: $OCH_3$ 18.89%. Found: $OCH_3$, 18.40, 18.45%. The *sulphonamide* m.p. 103°C. was prepared by treating the alkylanisole with chlorosulphonic acid and ammonia according to the method of Huntress and Carten (9). Anal. calc. for $C_{17}H_{17}NO_3S$: N, 5.76, $OCH_3$, 12.75%. Found: N, 5.71; $OCH_3$, 12.62%.

(d) *2-Isobutylphenol*

2-Isobutylanisole (9 gm.) was treated with pyridine hydrobromide (11.5 gm.) and glacial acetic acid (1.3 cc.) and the whole heated under reflux at 200°C. for five hours (15). The cooled mixture was then poured into water and the organic layer extracted with ether. The ether layer was successively washed with dilute hydrochloric acid, sodium bicarbonate solution, and water. After drying and removal of solvent, fractionation gave a quantitative yield of 2-isobutylphenol b.p. 51°C. (0.01 mm.) and $n_D^{24}$, 1.5171. Literature (3) b.p. 86°C. (6 mm.). Anal. calc. for $C_{10}H_{14}O$: C, 80.0; H, 9.33%. Found: C, 79.8, 79.7; H, 9.24, 9.24%. *3,5-Dinitrobenzoate* m.p. 84°C. Anal. calc. for $C_{17}H_{16}N_2O_6$: N, 8.13%. Found: N, 8.09%.

*4-Isobutylphenol*

(a) *2-Methyl-1-(p-methoxyphenyl)-1-propanol*

By means of a Grignard reaction from isopropyl bromide and anisaldehyde there was obtained 2-methyl-1-(*p*-methoxyphenyl)-1-propanol (67%) boiling at 103°C. (1 mm.) and having $n_D^{24}$, 1.5215. Literature (16) b.p. 157°C. (21 mm.) and $n_D^{20}$, 1.5210. Anal. calc. for $C_{11}H_{16}O_2$: $OCH_3$, 17.21%. Found $OCH_3$, 17.40%. Phenylurethane m.p. 77°C. Literature (16) 82°C. Anal. calc. for $C_{17}H_{21}NO_3$: N, 4.68%. Found: N, 4.58%.

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(b) *2-Methyl-1-(p-methoxyphenyl)-1-propene*

The above carbinol was dehydrated with 20% sulphuric acid to give 2-methyl-1-(*p*-methoxyphenyl)-1-propene (71%) boiling at 81°C. (1 mm.) and having $n_D^{24}$, 1.5470. Literature (4) b.p. 118°C. (15 mm.). Anal. calc. for $C_{11}H_{14}O$: $OCH_3$, 19.13%. Found: $OCH_3$, 18.90%. The *nitrosyl chloride*, obtained in very poor yield, melted at 133°C. Anal. calc. for $C_{11}H_{14}ClNO_2$: N, 6.61%. Found: N, 6.53%.

(c) *4-Isobutylanisole*

The ethylene obtained above was hydrogenated as before, yielding 4-isobutylanisole (72%) boiling at 68°C. (1 mm.) and having $n_D^{25}$, 1.4975. Literature (4) b.p. 123°C. (15 mm.) and $n_D^{24}$, 1.4980 (19). Anal. calc. for $C_{11}H_{16}O$: $OCH_3$, 18.89%. Found: $OCH_3$, 18.95, 18.88%. The *sulphonamide* m.p. 205°C., was obtained in poor yield. Anal. calc. for $C_{11}H_{17}NO_3S$: N, 5.76%. Found: N, 5.65%.

(d) *4-Isobutylphenol*

4-Isobutylanisole was demethylated as before yielding 4-isobutylphenol (75%) boiling at 60°C. (0.01 mm.). On standing the oil solidified and recrystallization gave the pure phenol m.p. 52°C. This phenol was first reported as a solid by Barber and Haslewood (2) who give m.p. 51–52°C. Anal. calc. for $C_{10}H_{14}O$: C, 80.0; H, 9.33%. Found: C, 80.0, 80.1; H, 9.36, 9.30%. *3,5-Dinitrobenzoate* m.p. 131°C. Anal. calc. for $C_{17}H_{16}N_2O_6$: N, 8.13%. Found: N, 8.08%.

*2-Isoamylphenol*

(a) *3-Methyl-1-(o-methoxyphenyl)-1-butanol*

By means of a Grignard reaction from isobutyl bromide and 2-methoxybenzaldehyde there was obtained the impure alcohol as a tan colored solid. Recrystallization from benzene – petroleum ether (30–60°C.) yielded pure *3-methyl-1-(o-methoxyphenyl)-1-butanol* as a white solid melting at 73°C. (Attempted distillation caused dehydration.) Anal. calc. for $C_{12}H_{18}O_2$: $OCH_3$, 15.97%. Found: $OCH_3$, 15.93, 15.95%. *Phenylurethane* m.p. 107°C. Anal. calc. for $C_{18}H_{23}NO_3$: N, 4.47; $OCH_3$, 9.90%. Found: N, 4.40; $OCH_3$, 9.90, 9.92%.

(b) *3-Methyl-1-(o-methoxyphenyl)-1-butene*

The above carbinol was dehydrated as before yielding *3-methyl-1-(o-methoxyphenyl)-1-butene* (50%) boiling at 82°C. (1 mm.) and having $n_D^{18}$, 1.5430. Anal. calc. for $C_{12}H_{16}O$: $OCH_3$, 17.60%. Found: $OCH_3$, 17.51, 17.55%. The *nitrosyl chloride*, obtained in good yield, melted at 137°C. Anal. calc. for $C_{12}H_{16}ClNO_2$: N, 5.79; $OCH_3$, 12.80%. Found: N, 5.98; $OCH_3$, 12.67, 12.61%.

(c) *2-Isoamylanisole*

The ethylene obtained above was hydrogenated giving a quantitative yield of 2-isoamylanisole b.p. 75°C. (0.5 mm.) and $n_D^{18}$, 1.4995. Anal. calc. for $C_{12}H_{18}O$: $OCH_3$, 17.40%. Found: $OCH_3$, 17.43, 17.37%. *Sulphonamide* m.p. 113°C. Anal. calc. for $C_{12}H_{19}NO_3S$: N, 5.44; $OCH_3$, 12.06%. Found: N, 5.37; $OCH_3$, 12.09%.

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TABLE I

DINITRO-ISOBUTYL AND ISOAMYL PHENOLS AND THEIR AMINE SALTS*

| Dinitrophenol | B.p., °C. (0.1 mm.) | Yield, % | Piperidine salt | | | | Morpholine salt | | | | Cyclohexylamine salts | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Formula | M.p., °C. | Nitrogen, % | | Formula | M.p., °C. | Nitrogen, % | | Formula | M.p., °C. | Nitrogen, % | |
| | | | | | Calc. | Found | | | Calc. | Found | | | Calc. | Found |
| 4,6-Dinitro-2-isobutyl** | 130 | 66 | $C_{15}H_{23}N_3O_5$ | 187 | 12.92 | 12.84 | $C_{14}H_{21}N_3O_6$ | 168 | 12.84 | 12.84 | $C_{16}H_{25}N_3O_5$ | 193 | 12.38 | 12.39 |
| 2,6-Dinitro-4-isobutyl | 143 | 55 | $C_{15}H_{23}N_3O_5$ | 189 | 12.92 | 12.95 | $C_{14}H_{21}N_3O_6$ | 164 | 12.84 | 12.82 | $C_{16}H_{25}N_3O_5$ | 192 | 12.38 | 12.32 |
| 4,6-Dinitro-2-isoamyl** | 140 | 57 | $C_{16}H_{25}N_3O_5$ | 167 | 12.39 | 12.48 | $C_{15}H_{23}N_3O_6$ | 190 | 12.32 | 12.29 | $C_{17}H_{27}N_3O_5$ | 188 | 11.90 | 11.89 |
| 2,6-Dinitro-4-isoamyl | 154 | 55 | $C_{16}H_{25}N_3O_5$ | 176 | 12.39 | 12.47 | $C_{15}H_{23}N_3O_6$ | 169 | 12.32 | 12.32 | $C_{17}H_{27}N_3O_5$ | 185 | 11.90 | 11.94 |

*All the salts are yellow, orange, or red.

**Ref. (13).

(d) *2-Isoamylphenol*

2-Isoamylanisole was demethylated giving a quantitative yield of 2-isoamylphenol b.p. 64°C. (0.01 mm.) and $n_D^{24}$, 1.5120. Anal. calc. for $C_{11}H_{16}O$: C, 80.5; H, 9.82%. Found: C, 80.2, 80.4; H, 9.70, 9.71%. *3,5-Dinitrobenzoate* m.p. 92°C. Anal. calc. for $C_{18}H_{18}N_2O_6$: N, 7.82%. Found: N, 7.75%.

*4-Isoamylphenol*

(a) *3-Methyl-1-(p-methoxyphenyl)-1-butanol*

By means of a Grignard reaction from isobutyl bromide and anisaldehyde there was obtained 3-methyl-1-(*p*-methoxyphenyl)-1-butanol in crude form as an oil (60 gm., 68%). Attempted distillation caused obvious dehydration. It was not possible to obtain a phenylurethane.

(b) *3-Methyl-1-(p-methoxyphenyl)-1-butene*

The above carbinol was dehydrated giving *3-methyl-1-(p-methoxyphenyl)-1-butene*, in high yield, boiling at 91°C. (1 mm.) and having $n_D^{27}$, 1.5390. Anal. calc. for $C_{12}H_{16}O$: $OCH_3$, 17.60%. Found: $OCH_3$, 17.43, 17.43%. The *nitrosyl chloride* was obtained in good yield, m.p. 153°C. Anal. calc. for $C_{12}H_{16}ClNO_2$: N, 5.79; $OCH_3$, 12.80%. Found: N, 5.74; $OCH_3$, 12.16, 12.08%.

(c) *4-Isoamylanisole*

3-Methyl-1-(*p*-methoxyphenyl)-1-butene (75 gm.) was hydrogenated in the usual way and gave 4-isoamylanisole (58 gm., 78%) boiling at 78°C. (1 mm.) and having $n_D^{27}$, 1.4940. The literature (1) gives b.p. 121°C. (14 mm.) and $n_D^{22}$, 1.4995 (19). Anal. calc. for $C_{12}H_{18}O$: $OCH_3$, 17.40%. Found: $OCH_3$, 17.50, 17.50%. The *sulphonamide* was obtained in good yield and melted at 103°C. Anal. calc. for $C_{12}H_{19}NO_3S$: N, 5.45; $OCH_3$, 12.06%. Found: N, 5.51; $OCH_3$, 12.09, 12.05%.

(d) *4-Isoamylphenol*

4-Isoamylanisole (34 gm.) was demethylated as described above and yielded 4-isoamylphenol (29 gm., 94%) as an oil boiling at 68°C. (0.01 mm.) and having $n_D^{25}$, 1.5060. The literature (14) gives b.p. 245–250°C. (760 mm.) and $n_D^{27}$, 1.505. Anal. calc. for $C_{11}H_{16}O$: C, 80.5; H, 9.82%. Found: C, 80.3, 80.3; H, 9.80, 9.59%. The *3,5-dinitro-benzoate* melted at 124°C. Anal. calc. for $C_{18}H_{18}N_2O_6$: N, 7.82%. Found: N, 7.80%.

*Nitration of the Phenols*

The four phenols described above were then nitrated in the usual manner and the dinitrophenols thus formed were characterized as their piperidine, morpholine, and cyclohexylamine salts as described in an earlier communication (7). The relevant data are summarized in Table I.

ACKNOWLEDGMENTS

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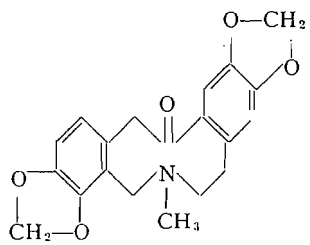
# INTERACTION OF KETO- AND TERTIARY AMINO-FUNCTION IN MEDIUM RINGS[1, 2]

By Edward H. Mottus,[3] Hans Schwarz,[4] and Léo Marion

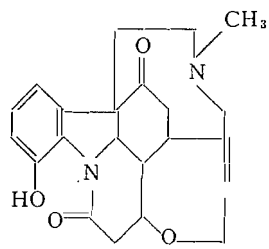
ABSTRACT

The ultraviolet and infrared absorption spectra of protopine and some of its derivatives have been studied. The interaction between a keto group and a tertiary nitrogen in a 10-membered ring is illustrated by the study of these spectra. On the basis of these studies a quaternary carbinolamine structure (V) is suggested for protopine and cryptopine salts. Some of the reactions of protopine, cryptopine, and vomicine are discussed.

Medium rings containing both tertiary amino- and carbonyl-function have been found to occur in nature in the alkaloids protopine (I), cryptopine[5], and vomicine (II). Perkin (6), in his studies on the structure of protopine and cryptopine, noted that reactions without analogy occurred. Many of the reactions in the chemistry of vomicine could not be explained by Huisgen, Wieland, and Eder (5) on the basis of Robinson's (1) structure without assuming some kind of unusual interaction between the carbonyl and the tertiary amine function.




I




II

In order to study the interaction of the carbonyl- with the tertiary amino-function we measured the ultraviolet and infrared spectra of protopine and some of its derivatives. Protopine (I) was chosen since it contained a 10-membered ring which offered possibilities for interaction between the keto-

[1] *Manuscript received July 24, 1953.*
*Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3092.*
[2] *For classification of rings see Ref. (2).*
[3] *National Research Council of Canada Postdoctoral Fellow, Present address: Monsanto Chemical Company, Dayton, Ohio.*
[4] *National Research Council of Canada Postdoctoral Fellow. Present address: Cleveland Clinic, Research Division, Cleveland, Ohio.*
[5] *Ten-membered ring structure is present in the alkaloids of the cryptopine sub group. See Ref. (3).*

and the amino-function. Since the keto group is conjugated with an aromatic system, any change in the electronic configuration of the carbonyl should change the ultraviolet absorption. Furthermore, because of the absence of methoxyls in protopine it should be possible to determine the formation of a methoxy group in a derivative without difficulty.

The spectra of I, its perchlorate, and its methiodide were chosen as examples. The ultraviolet absorption of I would be expected to be a composite of the two chromophoric systems present in the molecule. Fig. 1 shows that such is not

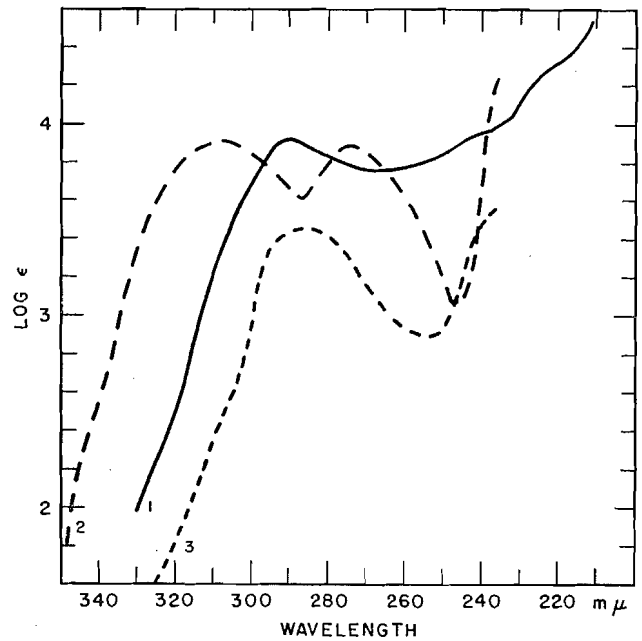



FIG. 1. Ultraviolet spectra in alcohol, curve 1, protopine; curve 2, α-ketodihydrosafrol (spectrum copied from Ref. (4); curve 3, dihydrosafrol (spectrum copied from Ref. (4)).

the case. To obtain the protopine curve the absorption due to the α-ketodihydrosafrol portion of I should be shifted to shorter wave lengths. This would be the case if in I either the keto group is not in the plane of the benzene ring or there is interaction between the keto- and the amino-function. A study of the Fisher-Taylor-Hirschfelder model of I indicates that it could exist in three forms. One is energetically improbable since the two aromatic nuclei would lie one on top of the other. The second possibility (Fig. 2) shows that the nitrogen and the carbonyl oxygen are very close resulting in a repulsion tending to force the carbonyl out of the plane of the benzene ring. By inverting the nitrogen of the second form, the third form (Fig. 3) is obtained in which the carbonyl is very nearly in the plane of the benzene ring, and there is a facile approach of the nitrogen to the carbonyl carbon. Bond formation between the nitrogen and the carbonyl would then be possible without any further steric change so that an effect similar to that of intramolecular hydrogen bonding (III (*a*)) might be expected (III (*b*)).

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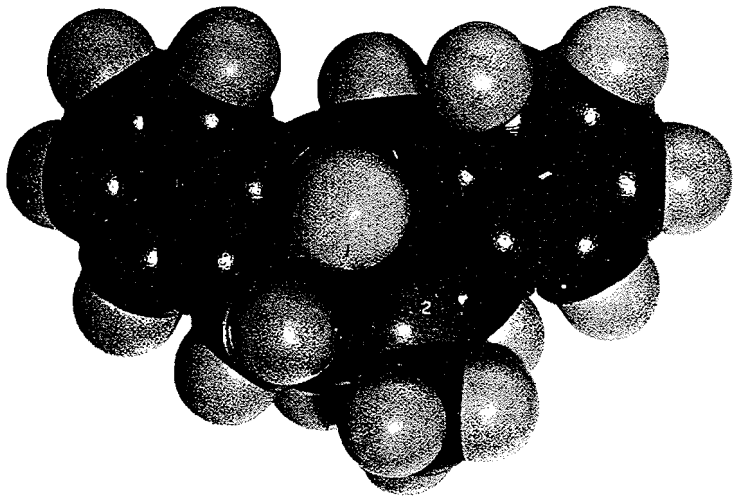



FIG. 2. Photograph of Fisher-Taylor-Hirschfelder model of form 2 of protopine (shown without methylene-dioxy groups); 1, oxygen atom; 2, nitrogen atom.

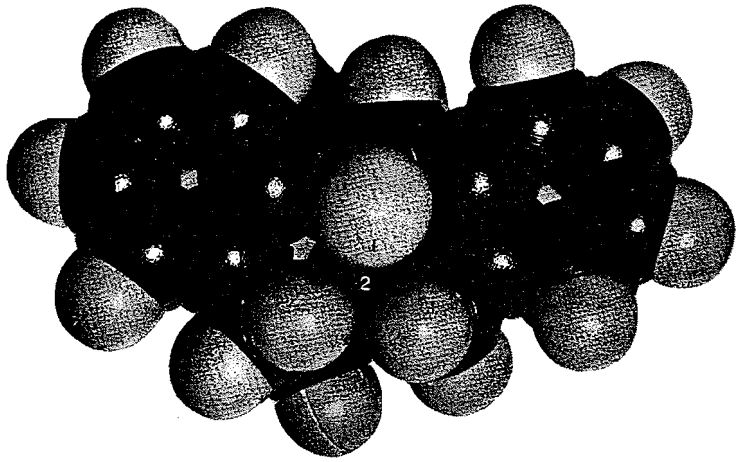
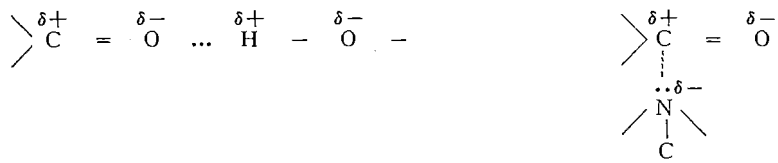



FIG. 3. Photograph of Fisher-Taylor-Hirschfelder model of form 3 of protopine (shown without methylene-dioxy groups); 1, oxygen atom; 2, nitrogen atom.

Both of the possible forms of protopine would be expected to explain the hypsochromic shift observed in the ultraviolet spectrum. However, the effect on the carbonyl band in the infrared is different which allows us to differen-




(*a*) (*b*)

III

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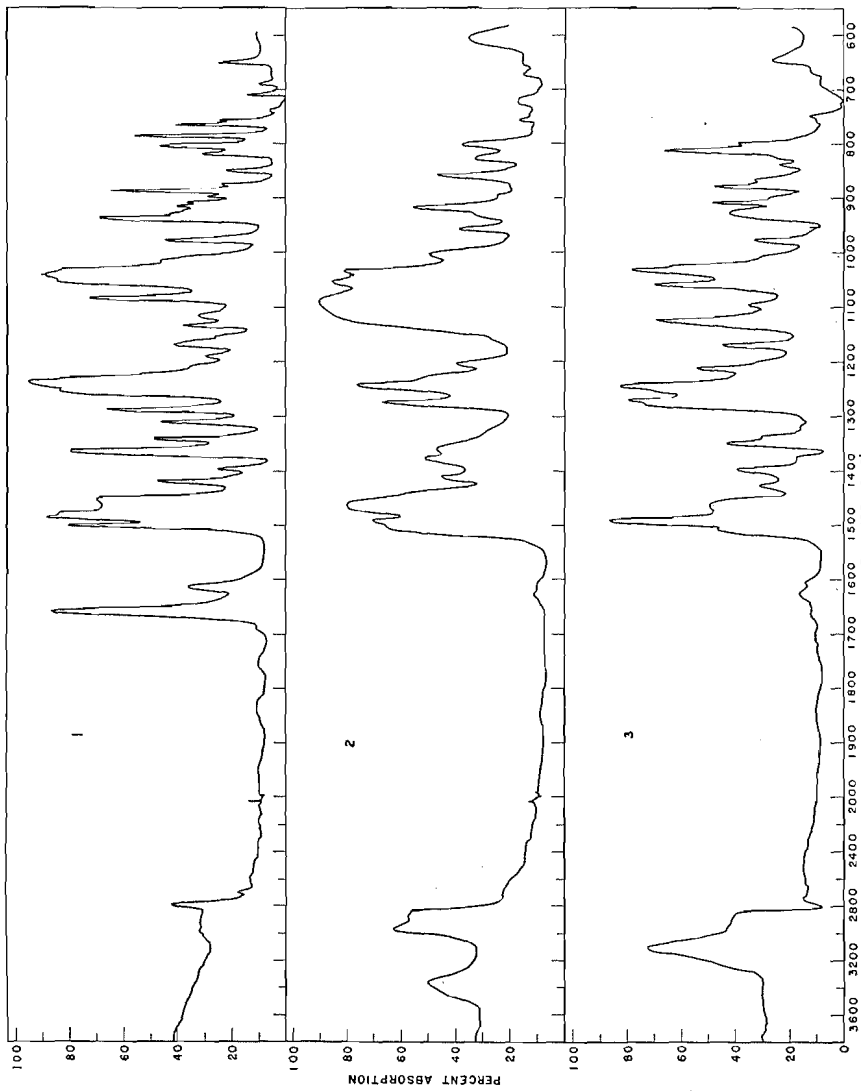
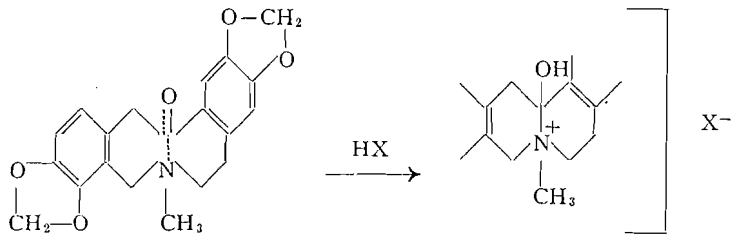



FIG. 4. Infrared spectra in nujol mulls, curve 1, protopine; curve 2, protopine perchlorate; curve 3, protopine methiodide.

tiate between the two forms. Loss of conjugation (form 2) should result in a shift to higher frequency. "Nitrogen bonding"[6] (form 3, III(*b*)) on the other hand results in absorption at lower wave numbers. Since the carbonyl peak in the infrared spectrum of protopine (1658 cm.$^{-1}$, Fig. 4, curve 1) is lower than that of acetophenone (1690 cm.$^{-1}$) we believe that the third form is favored and we therefore propose IV for protopine[7].




IV V

In this form the nitrogen will be quite inert since it is pretty well buried in the molecule. (Protopine does not give a methiodide at 42°; for the preparation of this derivative, heating for 10 hr. at 100° in a sealed tube is necessary (6).)

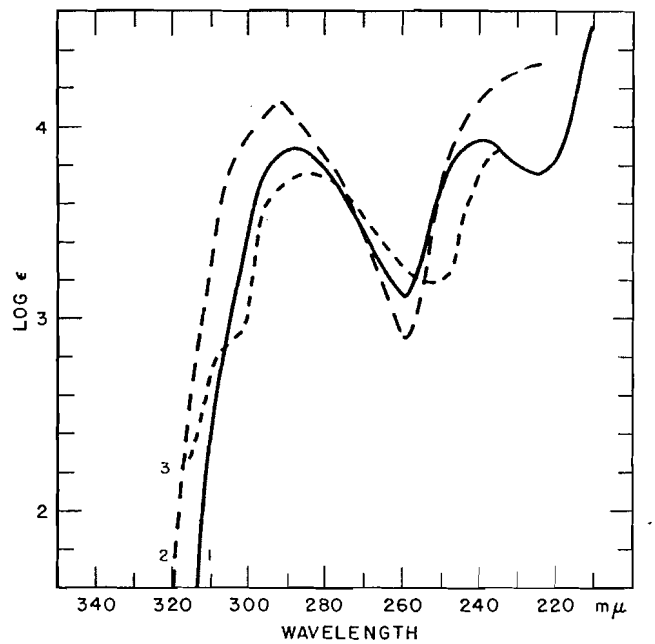


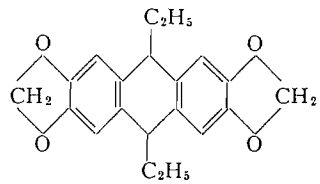

FIG. 5. Ultraviolet spectra in alcohol, curve 1, protopine salt (as hydrochloride); curve 2, diisosafrol (spectrum copied from Ref. (4); curve 3, two moles of dihydrosafrol (curve calculated from Ref. (4)).

[6] *In analogy to hydrogen bonding we suggest the term "nitrogen bonding" for this similar effect.*

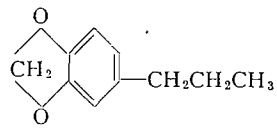
[7] *It is proposed that the structure of vomicine and its salts is modified in the same way.*

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A salt of protopine derived from structure IV has structure V, which is in agreement with our findings. The infrared spectrum of protopine perchlorate shows the strong band at 3385 cm.$^{-1}$ indicating the presence of an OH group[8] and no absorption in the carbonyl region (Fig. 4, curve 2). The molecular absorption (E) in the ultraviolet of V is in close agreement with the molecular absorption of diisosafrol (VI) and the sum of the molecular absorptions of two moles of dihydrosafrol (VII) (Fig. 5).

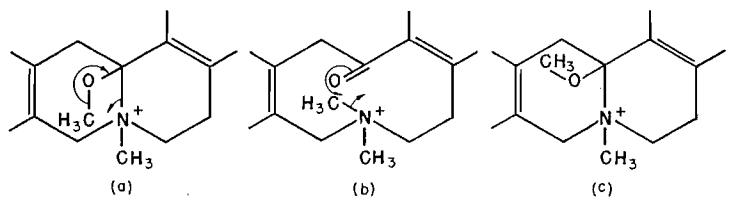



VI




VII

The methiodide derived from IV would be expected to contain a methoxyl and an N-methyl. This agrees very well with the infrared spectrum taken in a nujol mull, which shows neither OH nor carbonyl band (Fig. 4, curve 3).




VIII

From the study of the models of I (Figs. 2 and 3) it becomes clear that the methiodide could exist in three different forms, two derived from the model in Fig. 2 (VIII*a*, 1 O-$CH_3$; 1 N-$CH_3$ and VIII*b*, 2 N-$CH_3$), and one derived from the model in Fig. 3 (VIII*c*, 1 O-$CH_3$; 1 N-$CH_3$). In crystalline form either VIII*a* or VIII*c* or both are present (see above). In solution, however, the equilibrium

$$\overline{\underline{\text{VIII}c}} \rightleftharpoons \overline{\underline{\text{VIII}a}} \rightleftharpoons \overline{\underline{\text{VIII}b}}$$

is more likely.

Of the two equilibria involved, one $\overline{\underline{\text{VIII}c}} \rightleftharpoons \overline{\underline{\text{VIII}a}}$ is an inversion of the nitrogen. The other, $\overline{\underline{\text{VIII}a}} \rightleftharpoons \overline{\underline{\text{VIII}b}}$ does not involve an actual migration of the methyl group but only a change in the binding electrons as can be decuced from Fig. 2 (and represented by arrows in formula VIII). This is supported by the ultraviolet spectrum of the methiodide which is intermediate between

[8] *The enol form is not considered since, if this enol were the predominant form in acid solution the ultraviolet spectrum of a salt should resemble that of a correspondingly substituted stilbene derivative, and this has not been found to be the case (see spectra in Ref. 7).*

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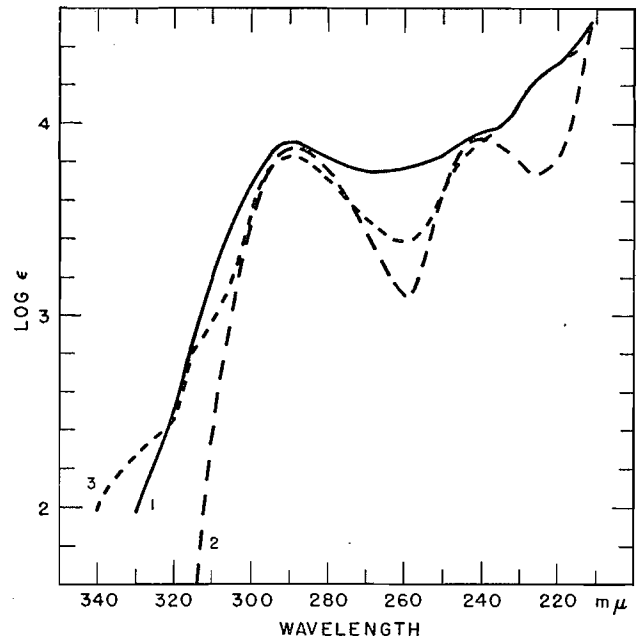
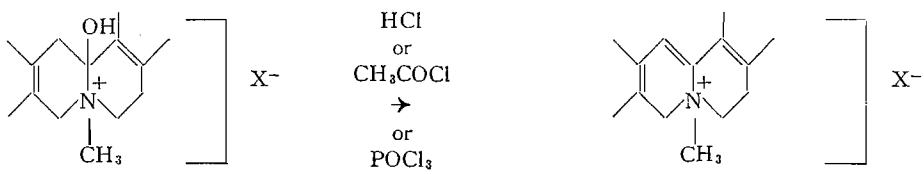



FIG. 6. Ultraviolet spectra in alcohol, curve 1, protopine; curve 2, protopine salt (as hydrochloride); curve 3, protopine methiodide.

that of protopine and that of its salt. Under the conditions of a Zeisel determination Form VIII(*b*) only seems to be present (no $OCH_3$; 2 N-$CH_3$). Huisgen *et al.* (5) came to the same conclusions: methyl vomicinium salts (no $OCH_3$; 2 N-$CH_3$) on reduction with sodium amalgam gave rise to methylvomicine (1 $OCH_3$; 1 N-$CH_3$).

These new observations throw some light on many of the unusual reactions observed with vomicine and cryptopine derivatives. They are in agreement with Huisgen, Wieland, and Eder's (5) explanations for the reactions of vomicine except that whereas these authors call the quaternary form a canonical form (mesomeric grenzform) we consider it as the form present in all salts of vomicine. All reactions in acidic solution are therefore carried out with the quaternary form.

The quaternary form V for protopine and cryptopine in acid media helps to interpret some of the unusual reactions observed by Perkin (6). For example, the formation of isocryptopine and isoprotopine salts is simply a dehydration of V rather than a rearrangement of the enol as proposed by Perkin.




V

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The reaction of protopine and cryptopine in acid solution with sodium amalgam was found by Perkin to give the dihydro-compounds. This is more likely an Emde degradation rather than the reduction of the carbonyl.

## EXPERIMENTAL

### *Spectra*

The ultraviolet spectra were determined with a Beckmann Spectrophotometer Model DU. The infrared spectra were all taken in nujol mulls with a Perkin-Elmer double beam infrared Recording Spectrophotometer, Model 21.

### *Protopine Perchlorate*

To protopine, dissolved in dilute acetic acid, was added perchloric acid. The perchlorate, recrystallized from water, melted at 321–322°. Calc. for $C_{20}H_{19}O_5N.HClO_4$: C, 52.93; H, 4.43; N, 3.09. Found: C, 53.00; H, 4.46; N, 3.33%.

### *Protopine Methiodide*

The methiodide was made according to Perkin (6). Calc. for $C_{20}H_{19}O_5N.CH_3I$: N, 2.83; 2 N-$CH_3$, 6.07. Found: N, 3.01; N-$CH_3$, 6.25; $OCH_3$, 0.0.

## ACKNOWLEDGMENTS

The authors express their gratitude to Dr. H. J. Bernstein of the National Research Laboratories for revealing discussions, and to Mr. R. Lauzon and Dr. R. N. Jones, also of these laboratories, for the determination of the infrared spectra.

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# THE DECOMPOSITION OF CRYSTALLINE SODIUM AZIDE BY X RAYS[1]

BY H. G. HEAL[2]

ABSTRACT

Sodium azide is decomposed by X rays. The yields of nitrogen gas, ammonia, and hydroxyl ion obtained when irradiated crystals are dissolved in water are proportional to total dose and independent of dose rate, for small amounts of decomposition. The yields per unit dose at 102° are 1.3 times those at 51°. The nature of the decomposition products in the crystals is uncertain, but the absorption spectrum seems to rule out the formation of sodium. A mechanism for the decomposition is suggested.

## INTRODUCTION

The decomposition of solid azides by heat and by ultraviolet light, as well as the chemiluminescence accompanying the thermal decomposition, have been investigated in some detail. Apart, however, from a very few observations on barium azide (6), little is known of the decomposition of solid azides by ionizing radiation. The alkali metal azides form an attractive point of entry into the little explored field of radiation-induced reactions in solids. Among the reasons for this are the fact that their heats of formation are approximately zero, which makes it unlikely that decomposition will be thermally propagated at ordinary temperatures from points where it is initiated by radiation, and the general similarity of their structure to that of the alkali halides, the behavior of which under irradiation is beginning to be well understood.

The objectives of the present investigation were:

(*a*) To determine, as far as possible, the chemical nature of the products formed in solid sodium azide by X irradiation, using a combination of chemical analysis and spectrophotometry.

(*b*) To study the variation of yields with total dose, dose rate, and temperature, in the hope of arriving at a mechanism for the decomposition.

## EXPERIMENTAL

### *Preparation of Materials*

B.D.H. sodium azide was recrystallized once by allowing a solution saturated at about 70°, and filtered, to cool to room temperature. The product was

[1] *Manuscript received June 23, 1953.*
*Contribution from the Chemistry Department, University College of the West Indies, Mona, St. Andrew, Jamaica, B.W.I.*

[2] *Present address, Queen's University, Belfast, Northern Ireland.*



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filtered. The crystals were washed successively with pure ethanol and pure acetone, air-dried, and stored in a desiccator.

*Analysis of Starting Material*

Samples of about 0.1 gm. of the recrystallized azide were dissolved in an excess of pure 1*N* hydrochloric acid, and the solution evaporated to dryness under an infrared lamp. The residue was moistened with more hydrochloric acid, again dried under the lamp, and weighed. The weight ratio NaCl: $NaN_3$ should be 0.899. Values found were 0.893, 0.909.

*Irradiation Arrangements*

Irradiations were carried out by means of a Siemens "Dermopan" skin therapy unit. This has a beryllium-windowed X-ray tube operating at 50 KVP and 25 ma. maximum. The tube is supplied with unrectified alternating high voltage. All irradiations were performed at 50 KVP.

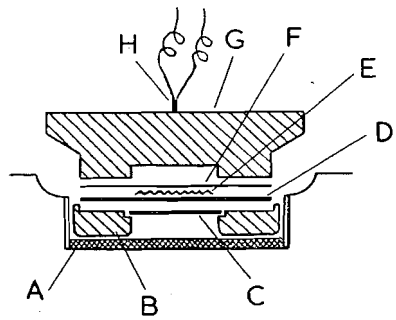



FIG. 1. Vertical section through sample holder (one and two-thirds times actual size).

The sample holder is shown in Fig. 1. A circular brass ring *B* rests directly on the window *A* of the X-ray tube. *C* is an aluminum disk, the thickness of which can be selected to provide the desired degree of filtration. *D* is a disk of 0.08 mm. aluminum foil, on which the sample *E* rests. *F* is a disk of 0.04 mm. aluminum foil, placed over the sample. The whole arrangement is weighted down by means of the brass block *G*, which presses the foil disks *D* and *F* firmly down on the ring *B* around their periphery. The sample is thus enclosed in a lens-shaped cavity, and is entirely surrounded by aluminum. *H* is a copper-constantan thermocouple junction soldered to *G*.

Very small samples were used in order to take advantage of the intense radiation field existing close to the window of the X-ray tube. By keeping the samples thin, it was possible to irradiate them uniformly with quite soft X radiation, so that the amount of filtration could be kept to a minimum, and the intensity correspondingly increased. Samples were irradiated for periods ranging from half an hour to five hours. The largest amount of decomposition achieved was approximately 2.5%.

*Irradiation Procedure*

The sodium azide consisted largely of platelets 1–3 $mm.^2$ in area and 0.05–0.1 mm. thick. A few milligrams of these were spread out on black paper.

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For each irradiation, approximately 2 mgm. of platelets free from thick places were selected by means of a small glass probe, and spread out over the central area of disk *D* (Fig. 1) in such a way that no two platelets overlapped.

The current and voltage were manually controlled in all irradiations.

The heat generated by the X-ray tube in normal operation was allowed to determine the sample temperature. Two different temperatures (51° and 102°) were obtained by operating the tube with 8.3 ma. and 25 ma. current respectively. One hundred and two degrees is far below the temperature at which sodium azide begins to decompose thermally (4). Two to three minutes' operation were required before the temperature became steady. Since none of the irradiations done in the course of the chemical work lasted less than thirty minutes continuously, and the temperature coefficient of the decomposition rate is not large, it was not necessary to correct for the short period during which full operating temperature had not been reached. The room temperature, which, of course, partly determined the sample temperature, was always within ±2° of 28°. It is unlikely that the sample temperatures deviated more than ±3° from the figures given above.

The effect of intensity upon the decomposition rate, at constant temperature, was determined by changing the thickness of the filter *C*, which enabled the rate of energy absorption in the sample to be varied by a factor up to 3.5. The highest intensities at 51° overlapped with the lowest intensities at 102°, so that the decomposition rates at the two temperatures could be compared for equal intensities. The relative intensities for different filter thicknesses were calculated, using De Waard's formula (3) for the spectral energy distribution, and tabulated values for the mass absorption coefficients of beryllium, aluminum, sodium, and nitrogen (7). Characteristic lines in the spectrum were neglected. If, as is almost certainly the case,* the target is tungsten, the only such lines concerned are the *L*-lines, which fall at wave lengths near the middle of the spectrum of radiation absorbed by the salt, so that their intensity would vary with filtration in roughly the same way as that of the 'white' radiation. In any case, the integrated intensity in the characteristic lines should be small compared with that of the 'white' radiation.

Sodium azide does not deliquesce unless the relative humidity is very high. All irradiations were performed during the dry season, and at temperatures of 51° or 102°. The salt therefore remained perfectly dry, and there was no visible corrosion of the aluminum foil where it had touched the crystals, even after many irradiations.

*Analysis of Samples*

The volume of gas evolved when the sample dissolved in water, and the amounts of hydroxyl ion and ammonia in the resulting solution, were determined.

The method of gas analysis has been described in a recent Note (8). Rather than weigh the samples, it was found convenient to determine the amount of

*No information on this point could be obtained.

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azide in them colorimetrically. The solution from the gas determination was washed into a 25 ml. volumetric flask. To it were added 2.5 ml. of a solution containing 10 gm. A.R. ferric ammonium sulphate and 10 ml. of $3N$ sulphuric acid per liter. The solution was diluted to 25 ml. and its transmission measured by means of an EEL photoelectric colorimeter, with blue filter. The ferric azide color was found to be stable for the few minutes required for transmission measurements.

Attempts to determine hydroxyl ion and ammonia by titration with a microburette were abandoned after a few trials. It was not practicable to titrate the hydroxyl ion from 2 mgm. samples in a volume greater than about 0.2 ml., and such small volumes were difficult to protect adequately from atmospheric carbon dioxide during a titration. Moreover, the ammonia present spoiled the end point, and was partly lost by volatilization during the time required for a titration, so that it could not easily be corrected for. Nevertheless, the results obtained for both hydroxyl ion and ammonia by titration methods agreed substantially with those given by the methods now to be described.

*Hydroxyl Ion* was determined colorimetrically. In these determinations it was necessary to keep the solutions decidedly alkaline throughout, in order to prevent hydrolysis of the undecomposed sodium azide. The sample was added to a solution of phenolphthalein containing about half the indicator in the acid form and half in the alkaline form. The number of equivalents of phenolphthalein present was made much greater than the number of equivalents of hydroxyl ion given by the sample. Under these conditions it can be shown that the change in concentration of the pink alkaline form is approximately a linear function of the quantity of hydroxyl ion added. Experimentally, two eight-milliliter portions of a nearly saturated aqueous phenolphthalein solution were placed in matched colorimeter tubes, each of which contained a thin glass stirrer so contrived as not to interfere with the passage of the light beam in the colorimeter. Decinormal baryta (0.01 ml.) was added to each tube from a micropipette. The purpose of this was to convert nearly half the indicator to the alkaline form, and at the same time to remove dissolved carbon dioxide as barium carbonate. The solutions were stirred, left to stand five minutes, stirred again, and measured in the colorimeter with green filter, using tube 1 as a blank with which tube 2 was compared. The azide sample, about 2 mgm. of the irradiated salt, was then added to tube 2. The contents of both tubes were stirred simultaneously and in the same manner, after which the transmission of tube 2 was again compared with that of tube 1. The identical treatment of the two ensured that atmospheric carbon dioxide picked up during the operations could not affect the result, which depended, to a first approximation, only on the *difference* between the transmissions of the two tubes. The method was calibrated by means of known amounts of standard baryta. It proved to be quite convenient for the determination of amounts of hydroxyl ion up to about 0.6 microequivalent. Since the concentrations of acid and alkaline forms of the indicator were never far from equality, the pH of the solutions must always have been close to pK for phenolphthalein,

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which is 9.6. This made it possible to correct satisfactorily for the hydroxyl ion formed from ammonia in the solution by the reaction.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

for it follows from the equilibrium constant for this reaction that one third of the total ammonia present in solutions of pH 9.6 is in the form of $NH_4^+$ and the rest as $NH_3$. On account of the comparatively large volume of solution, no appreciable amount of ammonia could be lost during measurements (2).

The unirradiated azide gave a very small quantity of hydroxyl ion, for which all results were corrected.

After measurement of the optical transmission of the phenolphthalein solution containing the irradiated azide, the quantity of azide in the solution was found simply by adding the ferric sulphate reagent and measuring the transmission of the ferric azide with a blue filter. The color of the phenolphthalein was, of course, discharged by the acid in the reagent, and so did not interfere.

The quantities of *ammonia* given by the samples never exceeded 0.3 microequivalent. The irradiated samples were dissolved in 0.2 ml. water, 0.02 ml. Nessler's reagent added, and the precipitates compared with those given by a series of standards made up with unirradiated sodium azide and known amounts of ammonium chloride, all in small matched test tubes.

Like ammonia, hydrazine gives a brown precipitate with Nessler's reagent. Hydroxylamine, the only other likely reaction product, gives on the other hand a grey precipitate. The following tests showed that a little hydrazine was present in the solutions of irradiated azide, but that nearly all the precipitate with Nessler's reagent was due to ammonia. A sample of sodium azide irradiated sufficiently to decompose about 2% of it was dissolved in 0.1 ml. water. Comparison samples containing the same weight of unirradiated sodium azide in the same volume, and in addition known amounts of hydrazine, were also prepared. Ammoniacal silver nitrate solution (0.1 ml.) was added to each. The irradiated sample gave a scarcely visible stain of silver on the walls of the tube. By visual comparison with the standards, the number of moles of hydrazine responsible for this was estimated. This quantity, when added to Nessler's reagent in the presence of 2 mgm. of unirradiated sodium azide, gave only a faint yellow coloration, in place of the substantial brown precipitate given by a sodium azide sample, which had been irradiated with the same dose as previously. The number of moles of hydrazine formed was not more than about one-sixth the number of moles of ammonia. The coloration given with Nessler's reagent by the hydrazine alone was not strong enough to justify any attempt to correct for it, and it was ignored in the ammonia determinations.

*Measurement of Spectra*

A Unicam quartz spectrophotometer was employed.

## RESULTS AND DISCUSSION

*General*

The sodium azide turned brown when irradiated. The color of thin crystals about 0.3% decomposed was scarcely visible. Samples 2.5% decomposed

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were dark in color, but still transparent in a thickness of 0.1 mm. Under the microscope, with 50 diameters magnification, the color appeared uniform, and no nuclei were seen.

Irradiated samples dissolved in water with effervescence, forming a mist of fine gas bubbles. The speed of dissolution increased with the dose received. It was very fast for samples 2.5% decomposed. If, however, samples which had been irradiated at 51° were heated for several hours at 100° before dissolving, they dissolved very much more slowly than crystals similarly irradiated and not heated. The total volume of gas evolved was slightly increased by the heating.

The evolution of gas during dissolution continued steadily from each crystal until the last minute particle had dissolved. This shows that the decomposition took place throughout the bulk of the material, and was not confined to external surfaces or their immediate neighborhood.

*The Chemical Data*

These are plotted in Figs. 2 and 3. The energy values on the abscissae were not measured, but have been calculated from figures for the roentgen intensity of radiation from the "Dermopan" given by Graul (5). Graul's values are only for intensities 5 cm. and 10 cm. from the target. The azide samples were irradiated at 1.45 cm. from the target. The intensity at this distance was taken to be the mean of values calculated from the intensities at 5 cm. and 10 cm. by applying the inverse square law. This, of course, is only a rough estimate, and an error of ±25% is certainly possible. The *relative* energy absorptions for the different experimental points in Figs. 2 and 3, however, are correct within ±5%.

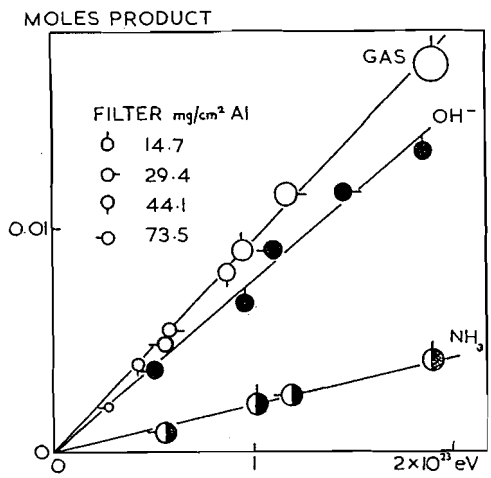



FIG. 2. Dependence of yields of gas, hydroxyl ion, and ammonia, per mole azide, upon X-ray energy absorbed per mole, at 51°. (Radii of circles represent estimated probable analytical errors.)

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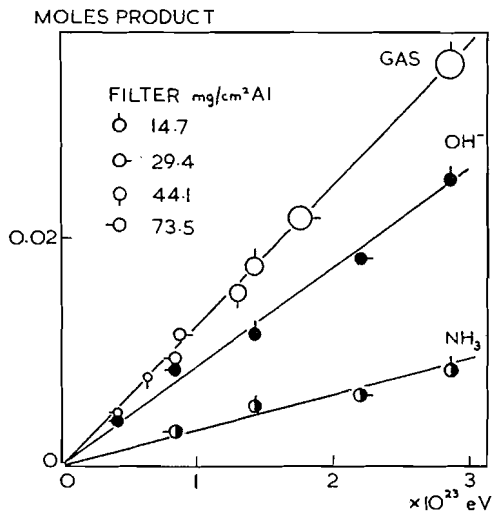



FIG. 3. As Fig. 2, but at 102°.

*The Influence of Total Dose and Dose Rate on the Yield*

At 51° and 102° the yields of gas, hydroxyl ion, and ammonia all seem to be proportional to the total dose. This conclusion can be stated with less confidence for the ammonia yields than for the others, on account of the large experimental error in this case. The points for all filters lie on or near the same straight lines. Hence the yield for a given dose is practically independent of the dose rate, over the ranges of dose rates studied. The dose rates at 51° ranged from $0.28 \times 10^{23}$ ev./mole/hr. to $0.96 \times 10^{23}$ ev./mole/hr. Those at 102° ranged from $0.85 \times 10^{23}$ ev./mole/hr. to $2.87 \times 10^{23}$ ev./mole/hr.

In view of this behavior, and since the gas determinations in particular are easily carried out, sodium azide seems worthy of further study as a chemical dosimeter for intense radiation fields.

The $G'$ value (1) (number of molecules of sodium azide decomposed per estimated 100 ev. absorbed) is 5.2 at 102° and 4.0 at 51°. The possible error in these values is of the order of 1.0, but cannot be estimated accurately.

*The Influence of Temperature*

For a given dose rate, the rates of formation at 102° of the three products analyzed for averaged 1.3 times the corresponding rates at 51°. This corresponds to a thermal activation energy of 500 cal./mole.

*Significance of the Chemical Data*

The yields of gas, hydroxyl ion, and ammonia were in the ratio 1 : 0.81 : 0.22 at 51°, and in the ratio 1 : 0.72 : 0.25 at 102°.

At least two simple modes of decomposition could give these values. The ammonia in the aqueous solution might have come from nitride ion formed in the reaction

$$3\,N_3^- \rightarrow N^{3-} + 4\,N_2$$

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followed by

$$N^{3-} + 3\ H_2O \rightarrow NH_3 + 3\ OH^-,$$

which would give four moles nitrogen : three equivalents hydroxyl ion : one mole ammonia, assuming no nitrogen to be lost during irradiation. The experimental ratios are 4 : 3 : 1 within the error of measurement.

Alternatively, the ammonia may have been formed through the reduction of azide ion in solution by the hydrogen atoms formed when free electrons or minute aggregates of sodium metal come in contact with water.

$$Na + H_2O \rightarrow Na^+ + OH^- + H$$

or

$$e + H_2O \rightarrow OH^- + H.$$

Since the concentration of azide ions in the solution next to the dissolving crystal surface is so much higher at all times than that of hydrogen atoms, reduction of azide ion to ammonia may well occur much more often than the union of hydrogen atoms to hydrogen molecules. If, then, the reaction occurring under irradiation were

$$NaN_3 \rightarrow Na + 3/2\ N_2$$

and the sodium were fairly efficiently utilized in reducing azide ion to ammonia during dissolution, the relative yields of gas, hydroxyl ion, and ammonia would, as is easily shown, be the same as in the case of the previously postulated mechanism. Thus the chemical data alone provide no way of distinguishing between these two mechanisms. Still others can be imagined (such as the formation of $N^{2-}$ or $N^-$ in the crystals) which would probably lead to the same result in solution. It would evidently be very difficult to find purely chemical methods of discriminating between these alternatives. An independent line of evidence was sought in the study of absorption spectra of the irradiated crystals.

The chemical data prove:

(*a*) That the gas evolved on dissolution must have been practically pure nitrogen (since, with the observed ratio of hydroxyl ion to ammonia, little free hydrogen can have been formed).

(*b*) That little or no gas can have escaped from the crystals during irradiation (since all the nitrogen which could have been formed, in conjunction with the hydroxyl ion and ammonia found, was actually recovered on dissolution).*

*The Absorption Spectrum*

Spectra were measured for several different samples. Fig. 4 shows one set. The spectra are those of a crystal plate of mean thickness 0.13 mm., but rather irregular, the thickest places being about 0.2 mm. thick and the thinnest about 0.1 mm. It was irradiated 15 min. at 51°. 0.18% of the material was decomposed. Spectrum A was plotted immediately after irradiation. Spectrum B is that of the same sample after 18 hr. storage in the dark. The height of the peak at 3400 Å has diminished slightly. Spectrum C is that of the same sample

**Storage* after *irradiation for periods up to 48 hr. was found to have no measurable effect on the volume of gas recovered. All samples were analyzed within 48 hr. of irradiation, and nearly all within 24 hr.*

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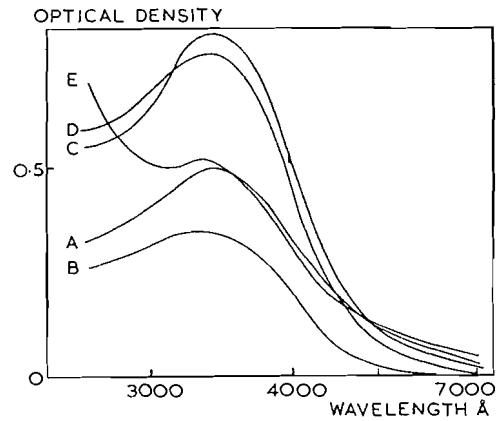



FIG. 4. Absorption spectra of irradiated sodium azide plate. (The optical densities are relative to those of the same crystal before irradiation.)

immediately after a further 15 min. irradiation, i.e. about 0.36% decomposed. Spectrum D is the same after 24 hr. storage in darkness. Again the 3400 Å peak has declined somewhat. Spectrum E was obtained after this sample had been heated 24 hr. at 100°. Here a big decline in the 3400 Å peak is in evidence.

The 3400 Å peak was the only one observed in the spectra of irradiated sodium azide crystals, between 2800 Å, where the absorption of sodium azide itself begins, and 7000 Å.

On account of the small transmission near this peak, and the irregular thickness of the crystal, these spectra are not to be relied upon in detail, but there is no doubt of the position and qualitative height changes of the absorption band, which were similar for several specimens which were similarly treated.

The band with the peak at 3400 Å probably does not arise from F centers, for the following reason. Simpson (10), and others have obtained good results for the energy of the $1s \rightarrow 2p$ optical transition in the F centers of sodium chloride, by calculations in which the only parameters required were the lattice spacing and the static and dynamic dielectric constants of the crystal. Now the azide ion is intermediate in volume between the bromide ion and the iodide ion. Hence it must be roughly as polarizable as these ions. The static and dynamic dielectric constants of sodium azide cannot, therefore, be very different from those of sodium bromide and iodide, and its lattice spacing is intermediate between those of the bromide and iodide. It is therefore unlikely that the absorption band of F centers in sodium azide can lie very far away from those of similar centers in the bromide and iodide, which occur at 5400 Å and 5880 Å respectively. Actually the 3400 Å band in irradiated sodium azide approaches in position the F band in lithium fluoride (2570 Å), the ions of which are very much smaller and less easily polarized than those of sodium azide. It is reasonable to conclude that the 3400 Å band is not an F band, (i.e. that it is not due to electrons trapped in anion vacancies). However, the *total absence* of an F band in the expected position is hard to explain. One would

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expect some F centers to be formed, even if they are not the principal product of irradiation. This suggests that some important factor may have been left out of account in the argument just given.

The band at 3400 Å is not nearly intense enough to be accounted for by an allowed transition in one of the major reaction products. If the absorption in this band is due to a major product, the oscillator strength for the transition, calculated by the formula of Smakula (11) is only 0.04 approximately. The changes in height of the peak on standing and on heating are not accompanied by any corresponding changes in the chemical gas yield. It seems more likely, therefore, that this band is due to absorption in a minor reaction product not identified, than that it is caused by a forbidden transition in a major product.

One reasonably certain conclusion from the absorption spectra is that the irradiated crystals do not contain colloidal sodium metal, which would give a broad band in the visible.

*A Possible Mechanism*

Jacobs and Tompkins (9) found that potassium azide is decomposed by ultraviolet light via a mechanism involving the reaction of two excitons, which leads to a decomposition rate proportional to the square of the radiation intensity. The rate of decomposition of sodium azide by X rays, however, is proportional to the first power of the intensity. The simplest possible mechanism consistent with this fact, and with the chemical and spectroscopic evidence as to the nature of the products, would be the dissociation of excited azide ions according to the equation

$$N_3^- \rightarrow N^- + N_2$$

at lattice imperfections of various kinds. The excitons would have to be at a higher level of excitation than those produced in the ultraviolet decomposition. The fraction of X-ray excited azide ions actually decomposing cannot be much less than 0.25 here* (in contrast with the value of 0.001 for the ultraviolet photolysis of $KN_3$) so that mechanisms requiring the interaction of two excitons seem less likely than single-exciton mechanisms.

There is no obvious reason why an assembly of $Na^+$ and $N^-$ ions should not be stable.

When the crystals dissolve, the following sequence of reactions may take place:

$$\begin{aligned}
N^- &+ H_2O \rightarrow NH + OH^- \\
NH &+ N_3^- \rightarrow NH^- + 3/2\ N_2 \\
NH^- &+ H_2O \rightarrow NH_2 + OH^- \\
NH_2 &+ N_3^- \rightarrow NH_2^- + 3/2\ N_2 \\
NH_2^- &+ H_2O \rightarrow NH_3 + OH^-
\end{aligned}$$

which would give the observed chemical products in the proper ratio. This mechanism also accounts for the trace of hydrazine found in the solutions, which could be formed by combination of pairs of $NH_2$ or NH radicals.

**Since the energy required to excite an azide ion is at least 5 ev., and only about 20 ev. are consumed per azide ion decomposed.*

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The very low thermal activation energy (500 cal/mole), deduced from the temperature coefficient of the decomposition rate, is consistent with the observed high probability of dissociation of excited azide ions.

ACKNOWLEDGMENT

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# IRRADIATION OF ONE MOLAR AQUEOUS CHLORAL HYDRATE SOLUTION WITH $Co^{60}$-GAMMA-RAYS AND BETATRON X RAYS[1]

By G. R. Freeman, A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

The production of acid by irradiation of 1 *M* chloral hydrate solutions is proportional to the dose at a given dose rate. The specific yield is the same for $Co^{60}$ $\gamma$-rays as for 23 Mev. peak energy X rays and is a linear function of the inverse of the square root of the dose rate. The reaction is apparently a chain reaction.

## INTRODUCTION

Many organic halogen compounds liberate the corresponding halogen acid when irradiated in aqueous systems and in some cases the radiation yield is quite high. Since it is relatively easy to analyze for strong acids by a variety of methods, it has been suggested that such systems might be useful as chemical radiation dosimeters or actinometers.

In addition to having a yield that is high, an acceptable dosimeter should have a yield that is, (i) zero order with respect to the concentration of the substance undergoing chemical change, (ii) independent of intensity over a wide intensity range, (iii) independent of the energy of the radiation, (iv) not too dependent on temperature, and (v) not too dependent on traces of impurities, rigorous purification of reagents, etc.

Andrews and Shore (1) studied the aqueous chloral hydrate system using 50–200 kv. X rays, and dose rates from 9 to 360 kr./hr. They found that the chief ionizable product formed was hydrochloric acid, and that a smaller amount of a weakly ionized acid was also probably formed. They found that the radiation yield was dependent on chloral hydrate concentration and on temperature, and was independent of dose rate over the range investigated.

In the present experiments the effects of photon energy and dose rate were studied using aerated one molar aqueous solutions of chloral hydrate. The dose rate was in general lower than that used by Andrews and Shore.

## MATERIALS AND METHODS

The water used in the chloral hydrate solutions was distilled from alkaline potassium permanganate, then from an alkaline suspension of manganous hydroxide, and finally from a Pyrex still equipped with a quartz condenser and a quartz receiving flask.

May and Baker's reagent grade chloral hydrate was used without further purification. Since an induction period was observed in the radiation reaction with solutions that were about four days old, the reported results were obtained using solutions which were never more than 36 hr. old.

Solutions were irradiated in Pyrex test tubes with ground-glass stoppers. These tubes were cleaned with hot chromic acid cleaning solution, rinsed repeatedly with tap water and then six times with the specially distilled water.

[1] *Manuscript received July 13, 1953.*
*Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.*



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A microburette consisting of a glass siringe and a micrometer screw (6), on which one unit corresponded to $1.5 \times 10^{-4}$ ml., was used to titrate the acid produced with 0.01 *N* sodium hydroxide. Bromcresol purple indicator was used, each irradiated solution being titrated to the color shade shown by a blank. The indicator solution was prepared according to the directions of Kolthoff and Rosenblum (7) with the pH adjusted to 3.5.

One molar chloral hydrate solutions were used in all experiments. Filtration of the solutions through glass wool did not affect the yield of acid.

Irradiations of the chloral hydrate solutions were carried out using $Co^{60}\gamma$-ray sources of 1.2 curies and 1100 curies respectively and X rays from a betatron. In order to offset any fluctuations and lack of homogeneity in the betatron X-ray beam, the samples were placed in a rotating cylindrical lucite block. (For experimental details, see (3) and (5).)

The dose rate was determined using a Victoreen Condenser r.-meter Model 70 and the usual corrections were applied for energy, temperature, and pressure (5). The energy correction factors for X rays from the betatron were calculated. They were 1.06 and 1.08 for 15 and 22 Mev. peak energies, respectively (3).

## EXPERIMENTAL RESULTS

### *Irradiation with $Co^{60}$ $\gamma$-Rays*

The effect of variations in temperature on specific yield of acid is shown in Table I. Since the system had a temperature coefficient of 2.5% per degree

TABLE I
VARIATION OF SPECIFIC YIELD OF ACID WITH TEMPERATURE

| Temp., °C. | Dose rate (kr./hr.) | Specific yield ($\mu$M./l./kr.) |
|---|---|---|
| 24 | 2.74 | 350 |
| 5 | 2.74 | 184 |

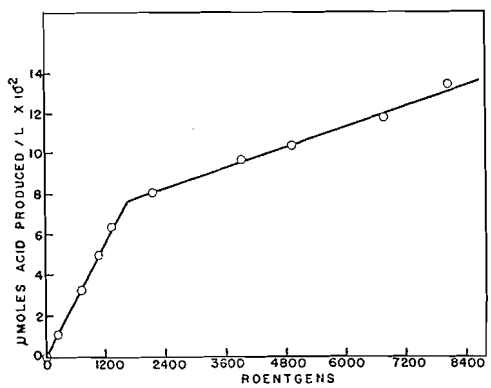



FIG. 1. Irradiation of 1 molar chloral hydrate solution with $Co^{60}$ gamma-rays (dose rate = 1.08 kr./hr.).

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centigrade, and the temperature varied by one or two degrees from experiment to experiment, the results have been corrected to 25°C. unless otherwise stated. The results of a typical irradiation experiment, using a constant dose rate of 1.08 kr./hr. are shown in Fig. 1.

It was found that the amount of acid initially varied linearly with the total dose received by the solution (at constant dose rate). However, with a dose rate of 1.08 kr./hr., after about 1600 roentgens had been received by the solution, the specific yield (μM./l./kr.) decreased to one-fifth of its original value and then stayed constant up to 8000 roentgens.* This decrease in specific yield was shown to be related to depletion of the oxygen content of the solution (see Table II and Fig. 2). When a solution that had been irradiated until the specific yield had fallen off had oxygen bubbled through it, the specific yield increased to the value shown by a fresh solution through which oxygen was bubbled before irradiation. Bubbling oxygen through a fresh solution before

TABLE II
EFFECT ON ACID PRODUCTION OF BUBBLING OXYGEN THROUGH THE SOLUTION

| Treatment with respect to oxygen | Total dose received, r. | Acid produced, μmoles acid/l. |
|---|---|---|
| No oxygen bubbled in | 900 | 438 |
| No oxygen bubbled in | 1820 | 837 |
| No oxygen bubbled in | 2860 | 878 |
| Oxygen bubbled in initially and then irradiated | 918 | 323 |
| Oxygen bubbled in after receiving 900 r. | 1860 | 775 |
| Oxygen bubbled in after receiving 900 r. | 2830 | 1139 |
| Oxygen bubbled in after receiving 2860 r. | 3770 | 1219 |

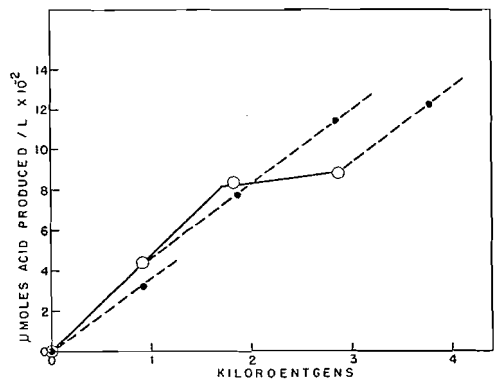



FIG. 2. Effect of oxygen on production of acid when 1 molar chloral hydrate is irradiated with $Co^{60}$ gamma-rays.
——○—— No oxygen bubbled through the solution.
——●—— Oxygen bubbled through the solution.

*The initial specific acid yield with a dose rate of 1.08 kr./hr. was 467 μM./l./kr., but after about 1600 r., the specific acid yield decreased to 87 μM./l./kr.*

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irradiation decreased the yield to about 75% of the value for air saturated solutions. The reason for this decrease is not known.

Solutions which were about four days old showed an induction dose of approximately 170 roentgens and then gave specific yields about 10% greater than those for fresh solutions. No induction period was observed with fresh solutions.

It was found that the acid concentration in the irradiated chloral hydrate solution did not change appreciably for at least $17\frac{1}{2}$ hr. after irradiation, if kept in the dark at room temperature. However, if kept exposed to light, the acid concentration slowly increased.

The effect of dose rate was investigated in a series of experiments. The results are recorded in Fig. 3. It was found that plotting the specific acid yield in

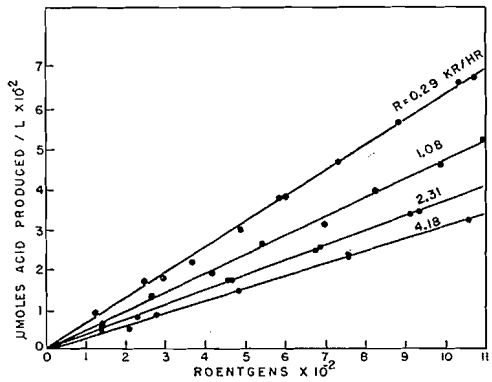



FIG. 3. Variation of yield of acid with dose rate using $Co^{60}$ gamma-rays.

$\mu$M./l./kr. ($Y$) for a given dose rate, against the inverse of the square root of the dose rate in kr./hr., ($1/\sqrt{R}$) gave a linear relationship, $Y = 138 + 346/\sqrt{R}$, down to a dose rate of one kr./hr. (See Fig. 4.)

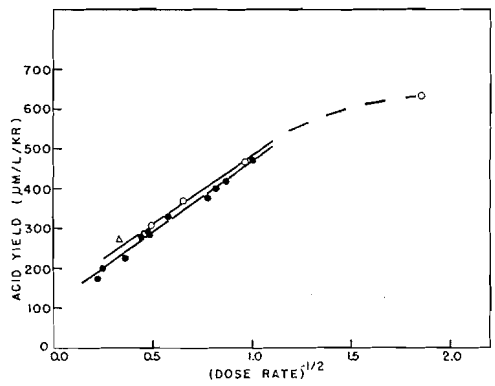



FIG. 4. Plot of yield of acid vs. (dose rate)$^{-\frac{1}{2}}$ for $Co^{60}$ gamma-rays (○) and betatron X rays (●). △, Andrews and Shore.

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*Irradiation with Betatron X rays 23 Mev. Peak Energy (Results Corrected to 25°C.)*

In experiments at a given dose rate, the acid production was proportional to the dose, as for $Co^{60}$ $\gamma$-rays. The results are recorded in Fig. 5, as the best fitting straight lines. Only 7 of the 11 dose rates tried are shown, to avoid

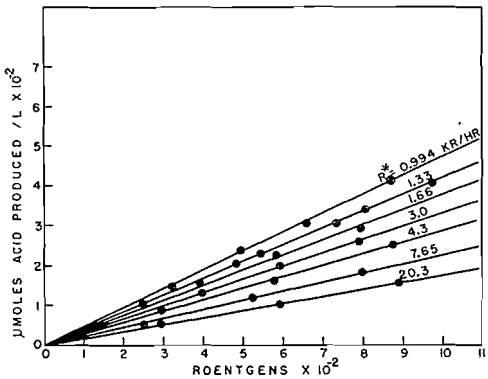



FIG. 5. Variation of yield of acid with dose rate and energy using betatron X rays, 25°C.

congestion in the figure. The precision was about the same for the betatron irradiations as for the $Co^{60}$ irradiations. A plot of the specific yield, $Y$ versus the inverse of the square root of the average dose rate $1/\sqrt{R^*}$ gave a reasonably straight line, the slope being practically the same as for $Co^{60}$ (See Fig. 4). The equation of the line is $Y = 110 + (358/\sqrt{R^*})$. Changing the energy of the incident bremsstrahlung from 15 to 23 Mev. did not produce a significant change of specific yield of acid at a given dose rate (3).

The fact that the specific yield depends on the dose rate necessitated a further examination of the possible effects of rotating the samples in the betatron beam.

The X-ray beam was quite small in cross section and at a half angle (subtended at the target) of 3 degrees, the intensity was about 60% of that in the center of the beam. At the highest dose rates (16.6 and 20.3 kr./hr.) the lucite block was so close to the target that it was as wide as the 3 degree cone of the beam. As a result, the dose rate at a given position in the block varied by 40% as the block rotated. The dose rates received by various parts of the block when it was stationary were determined and plotted on polar coordinate paper. The curve through these points could be approximated by an ellipse, $R^2 = a^2b^2/(a^2 \sin^2\theta + b^2 \cos^2\theta)$, where $R$ = dose rate, $a$ = semimajor axis of ellipse, $b$ = semiminor axis of ellipse, $\theta$ = angle between the line joining the center of the lucite block to the position of the sample and the direction of the beam through the center of the block. The angle $\theta$ varies between 0 and $2\pi$.

Using this equation and the inverse square root relation as a first approximation, the yield for a given average dose rate, $R^*$, can then be determined.

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Thus, when the elliptical variation in dose rate is taken into consideration, one obtains

$$Y = 110 + 358\,[a^2b^2/(a^2\sin^2\theta + b^2\cos^2\theta)]^{-1/4}.$$

When the block rotates, $\theta$ varies between 0 and $2\pi$. Hence, it is necessary to solve the following integral:

$$Y = \left[\int_0^{2\pi}\left\{110 + 358\left(\frac{a^2b^2}{a^2\sin^2\theta + b^2\cos^2\theta}\right)^{-1/4}\right\}d\theta\right] \Big/ \int_0^{2\pi} d\theta.$$

The solution was obtained graphically. The maximum effect due to rotating the block is about 3% and is obtained when the block is closest to the target. That is, at the highest dose rate, when the block was closest to the target, the measured specific yield was about 3% higher than would be expected for a homogeneous beam of intensity equal to the average intensity of the experimental beam across the block. As the block is moved further away from the target (i.e. at progressively lower dose rates) the variation of dose rate across the block becomes progressively less because the beam becomes wider; hence $a \rightarrow b$, and the effect due to the rotating becomes negligible. Therefore, this factor would not decrease the slope of the line in Fig. 4 more than about 1 or 2%.

## DISCUSSION

It is seen from Fig. 4 that the specific acid yield varies inversely as the square root of the dose rate down to a dose rate of about one kr./hr. Andrews and Shore (1) reported dose rate independence. However, the fact that they observed no dose rate dependence may be due to the high dose rates used and the great thickness of sample used in the experiments. The Andrews and Shore point plotted in Fig. 4 was obtained by multiplying the slope of the 1 $M$ line in Fig. 1 of their paper by 1.30, which is the average ratio for (total acid from titration)/(HCl from conductance) obtained from Table I of their paper (1). Although this point was determined using 200 kv. X rays most of the difference between their result and those reported here is probably due to the dose rate effect.

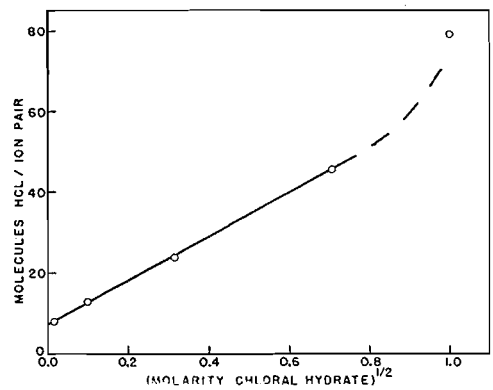



FIG. 6. Variation of specific yield of acid with chloral hydrate concentration (using the results obtained by Andrews and Shore).

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Andrews and Shore (1) investigated the dependence of the specific yield of acid upon the concentration of chloral hydrate. In Fig. 6, their results have been plotted against the square root of the chloral hydrate concentration. (The values for $M/N$ and the chloral hydrate concentration were obtained from Figs. 1 and 2 of their paper (1).) The variation is linear, except for the most concentrated solution. The equation of the line in Fig. 6 is: $M/N = 54.3\sqrt{c} + 7.3$, where $c$ = chloral hydrate concentration (molarity).

The ion pair yield for the reaction with 1 $M$ chloral hydrate is about one hundred and a free radical-chain reaction must be postulated to explain this high yield. The decrease in the yield with increasing dose rate is probably due to an increasing amount of reaction of free radicals with themselves. The fact that the yield is inversely proportional to the square root of the radiation intensity over quite a wide range of dose rates indicates that a recombination process, second order with respect to the atoms or radicals concerned, is probably playing an important part in the mechanism and in fact must be the principal process by which those atoms or radicals disappear (8). A comparison of our results with Noyes and Leighton's limiting cases 3 and 4 (8, pp. 196 and 197), seems to indicate that the recombinations of both primarily and secondarily produced radicals are of comparable importance in breaking chains.

It is also seen from Fig. 4 that for the same dose rate the yield of acid in one molar chloral hydrate solution is very nearly the same whether $Co^{60}$ $\gamma$-rays (average energy 1.25 Mev.) or betatron X rays (peak energies from 15–23 Mev. ) are used.

The $Co^{60}$ line lies above the betatron line. This difference may be due to an energy dependence of the system. On the other hand it may be due to factors such as uncertainties in Victoreen dose determinations at high energies, or the pulsed nature of the betatron X rays (emitted in pulses at the rate of 180 per second, each pulse lasting 4 $\mu$seconds). Each factor will be discussed in turn.

The possibility that the system is energy dependent does not appear to be very likely since no significant difference was noted between the yields obtained for 15, 22, and 23 Mev. peak energies with the betatron for the same dose rate. The median energies of the 15, 22, and 23 Mev. peak X rays are approximately 5, 8, and 8.8 Mev., respectively. That no significant difference was observed is reasonable since the energies for both $Co^{60}$ $\gamma$-rays and the betatron X rays are mainly in the region where energy is absorbed principally by the Compton process. Using the Compton and pair production coefficients for water and the photon energy distribution given by Cormack and Johns (2) it was calculated that about 11% of the beta particles (counting both positrons and negatrons) were produced by the pair process using 25 Mev. peak energy X rays from the betatron. The percentage of pair particles decreases with decreasing photon energy. Hence, in this energy region the chemical effect should not depend significantly on the energy of the incident radiation but only on the amount of energy absorbed by the system. A similar result has been found for several other reactions (4, 5).

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The Victoreen condenser r.-meter is accurate to 2% over the energy range, 30 kev. to 1 Mev. (9). However, the accuracy of the calculation of energy absorption from Victoreen readings for energies above 1 Mev. is not known and this is therefore a possible source of error.

The betatron X rays are emitted in 4 $\mu$ second pulses at the rate of 180 per second. Therefore, for an average dose rate of 1 kr./hr., the actual dose rate in each pulse is 1400 kr./hr. One can readily see from Fig. 4 that for a steady dose rate of 1400 kr./hr. the yield of acid would be considerably less than that actually observed for an intermittent dose rate of 1400 kr./hr. In actual fact, the yield of acid observed for the intermittent dose rate of 1400 kr./hr. was only slightly less than the yield observed for the steady dose rate of 1 kr./hr. with $Co^{60}$ gamma-rays. Thus, if the variation of acid yield with dose rate is attributed to reaction of free radicals with themselves, then the concentration of free radicals present in the solution when it is irradiated with $Co^{60}$ gamma-rays at the rate of 1 kr./hr. must be nearly the same as when it is irradiated with betatron X rays at the intermittent rate of 1400 kr./hr. (i.e. average rate of 1 kr./hr.). This must mean that the free radical-chains have a significant lifetime and that their concentration builds up as irradiation proceeds, and reaches a constant value after a certain time (8). If the average lifetime was appreciably less than 1/180 sec., their concentration would instantaneously become very large and then fall off to zero with each pulse. However, if the average lifetime of the free radicals was greater than 1/180 sec., their concentration could build up under irradiation until it reached a more or less steady state. This would tend to cancel the effect of the pulses. With $Co^{60}$ gammas, the free radical concentration would build up to a similar value for the same average dose rate, and one would expect similar acid yields. Since the acid yields observed for the same average dose rates are nearly the same, it is reasonable to suggest that the free radical-chains produced in this system have an average life greater than 1/180 sec. The effect of the pulses could easily account for the difference in the betatron and $Co^{60}$ lines in Fig. 4.

It is concluded from the foregoing considerations that in the reaction of X or gamma-rays with aqueous 1 *M* chloral hydrate solutions the specific yield is independent of the energy over the energy range used, but dependent on the intensity of the incident radiation in the range investigated. The specific yield is also dependent on the temperature of the solution. The reaction is a chain reaction.

## ACKNOWLEDGMENTS

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# SOME FATTY ACIDS OF PEANUT, HICKORY, AND ACORN OILS[1]

By C. Y. Hopkins and Mary J. Chisholm

ABSTRACT

Eicosenoic and docosenoic acids have been identified as constituents of the glycerides of peanut oil (*Arachis hypogaea* L. var. Spanish). Hexadecenoic acid could not be detected; if present, the amount in this sample of oil is judged to be less than 0.3% of the fatty acids. The oils of the bitter hickory nut (*Carya cordiformis* Koch) and acorn (*Quercus alba* L.) have the ordinary palmitate–oleate–linoleate composition. Neither contained a detectable amount of eicosenoic acid. Estimated proportions of some of the acids in these oils are given.

## INTRODUCTION

The occurrence of *n*-eicosenoic acid in plant glycerides has been noted chiefly in members of the Cruciferae family. Indications of its presence in other plant groups have been obtained but positive identification has rarely been made (3, 4, 11).

The present work was undertaken to determine whether eicosenoic acid is present in three species of seeds, representing three different plant families, namely the peanut (Leguminosae), hickory (Juglandaceae), and acorn (Fagaceae). The peanut was chosen as a probable producer of eicosenoic acid, $C_{20}H_{38}O_2$, because it is known to contain arachidic acid $C_{20}H_{40}O_2$.

An earlier report of eicosenoic acid in the filbert (4), although not confirmed (2), gave some grounds for believing that other nut trees might produce this acid. Two species of native trees were therefore included in the study.

The oils were extracted in the laboratory, converted to methyl esters and distilled fractionally *in vacuo*. The appropriate fractions were examined for eicosenoic acid and some attention was given to the other component acids.

## EXPERIMENTAL

### *A. Peanut Oil*

Raw shelled peanuts were purchased locally (*Arachis hypogaea* L. var. Spanish). On solvent extraction, they yielded 42% of oil having iodine value 100.7; saponification value 190, and unsaponifiable matter 0.7%. The oil was converted to methyl esters by methanolysis, using a variation of the method of Haller (5), as follows:

Absolute methanol (1000 gm.) was weighed with its container and dry HCl was bubbled in until 20 gm. of HCl had been absorbed. The oil (500 gm.) was added and the mixture was refluxed for 24 hr., then cooled in a separatory funnel. The upper layer (A) was removed and distilled on a steam bath until the volume was reduced to half. The concentrate was poured into four volumes of water and to this solution was added the lower layer (B). The esters were extracted from this mixture by ether.

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*Examination of Low Boiling Esters*

A quantity of the methyl esters (241 gm.) was distilled at reduced pressure through a column packed with metal rings. The first fraction, b.p. 102–107° at 0.1 mm., weight 14.4 gm., I.V. 10.4, was examined for hexadecenoate. It was crystallized from acetone, yielding mostly esters of saturated acids. The portion soluble at −60° (3.3 gm.) had I.V. 100.5. It was hydroxylated by permanganate but gave only dihydroxy- and tetrahydroxy-stearic acids, identified by mixed melting point with authentic samples. Thus the chief unsaturated acids in this fraction are oleic and linoleic. The amount of hexadecenoic acid in this sample of oil, if present at all, is estimated to be less than 0.3% of the total fatty acids.

*Identification of Eicosenoic Acid*

A quantity of methyl esters of peanut oil (780 gm.) was distilled fractionally until most of the esters of $C_{16}$ and $C_{18}$ acids had distilled off. The residual esters (88 gm., I.V. 45.6) were transferred to a smaller flask and fractionated as shown in Table I. The time:temperature curve for the distillation is plotted in Fig. 1.

TABLE I
DISTILLATION OF HIGHER-BOILING METHYL ESTERS OF PEANUT OIL

| Fraction | Vapor temp., °C. (approx.) | Wt. of fraction (gm.) | Iodine value |
|---|---|---|---|
| 1 | 127–130 | 13.4 | 99.6 |
| 2 | 130–143 | 4.0 | 72.2 |
| 3 | 143–150 | 17.9 | 42.6 |
| 4 | 150–157 | 5.7 | 15.3 |
| 5 | 157–165 | 20.0 | 4.0 |
| 6 | 165–176 | 6.2 | 5.9 |
| 7 | (*a*) | 2.4 | |
| R | Residue | 16.8 | 68.5 |
| | | 86.4 | |

(*a*) *Portion obtained by rinsing the column packing.*

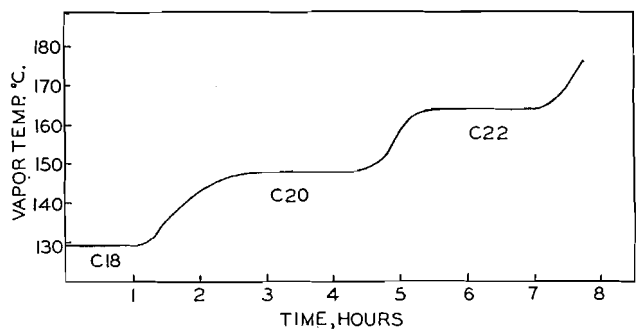



FIG. 1. Distillation of high-boiling methyl esters of peanut oil.

Fractions 1, 3, and 5 were judged from the boiling range and the time: temperature curve to contain esters of $C_{18}$, $C_{20}$, and $C_{22}$ acids respectively. Fraction 3 was crystallized from acetone and gave the following fractions:

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| Fraction | Temp. of cryst'n., °C. | Yield, gm. |
|---|---|---|
| 31 | 0 | 9.0 M.p. 44–46°C. |
| 32 | −32 | 1.6 I.V. 63.3 |
| 33 | −50 | 2.7 I.V. 71.8 |
| 34 | Filtrate | 3.2 I.V. 103.3 |

Fraction 31 is evidently the ester of a saturated acid. The melting point corresponds to that of methyl arachidate.

Fraction 33 was saponified and hydroxylated by alkaline permanganate. After removal of saturated acids by hexane, the product was crystallized from ethyl acetate. It melted at 129–130°, alone and mixed with an authentic sample of 11,12-dihydroxyeicosanoic acid.* Its equivalent weight was 344.6 (theory 344.5). The principal unsaturated acid of fraction 33 is therefore eicosenoic acid.

Fraction 2 (Table I) was hydroxylated in the same way. The product had m.p. 118–120° and equiv. wt. 329, apparently a mixture of dihydroxystearic and dihydroxyeicosanoic acids.

It is estimated from these data that the original methyl esters contained about 12 gm. of methyl eicosenoate or about 1.6% of the total esters of peanut oil.

In order to obtain a further quantity of the eicosenoic acid, 1460 gm. of the methyl esters was distilled fractionally in the usual way. The $C_{20}$ fraction was purified by crystallizing from acetone and the methyl eicosenoate was hydroxylated. The resulting dihydroxyeicosanoic acid was subjected to oxidative cleavage by sodium periodate (1). The products were nonaldehyde (the semicarbazone melted at 98–99°) and 10-aldehyodecanoic acid (the semicarbazone melted at 160–161°). The identities of both were confirmed by mixed melting points. Accordingly, the original acid is 11-eicosenoic acid.

*Arachidic Acid*

Further examination of the data indicates that the ester of the $C_{20}$ saturated acid, methyl arachidate, is concentrated in fractions 3 and 4 (Table I) and that the amount is about 1.5% of the total esters.

*Identification of Docosenoic Acid*

A portion of fraction 5 (14.5 gm.) (Table I) was crystallized from 360 ml. of acetone, giving the following fractions:

| Fraction | Temp. of cryst'n., °C. | Yield, gm. |
|---|---|---|
| 51 | 24 | 9.4 |
| 52 | 18 | |
| 53 | 6 | 2.2 |
| 54 | −5 | 0.6 |
| 55 | Filtrate | 0.8, I.V. 59 |

**Melting points are not corrected.*

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Upon hydroxylation with permanganate, fraction 55 gave an acid of m.p. 128–129°. The melting point was not depressed by mixing with pure 13,14-dihydroxybehenic acid but was lowered about 5° by mixing with dihydroxystearic or dihydroxyeicosanoic acid. Accordingly, the presence of docosenoic (erucic) acid in the original oil is established. The amount is estimated at 0.2% of the total fatty acids.

*B. Hickory Nut Oil*

Hickory nuts (*Carya cordiformis* Koch) were collected in Glengarry County, Ontario, in 1951. They were dried and shelled. The kernels, which are quite bitter, yielded 45% of oil by solvent extraction. The oil had I.V. 94.2, saponification value 191, and unsaponifiable matter 0.6%. It was converted to methyl esters and 300 gm. of the esters was distilled at a pressure of about 0.1 mm. Distillation data are given in Table II.

TABLE II
DISTILLATION OF METHYL ESTERS OF HICKORY NUT OIL

| Fraction | Vapor temp., °C. (approx.) | Wt. of fraction (gm.) | Iodine value | $n_D^{25°}$ |
|---|---|---|---|---|
| 1 | 87–105 | 3.0 | 20.6 | 1.4405 |
| 2 | 105–112 | 10.8 | 23.2 | Solid |
| 3 | 112–114 | 19.2 | 66.3 | 1.4473 |
| 4 | 114–116 | 47.4 | 95.4 | 1.4514 |
| 5 | 116 | 45.6 | 102.6 | 1.4522 |
| 6 | 116 | 16.3 | 103.6 | 1.4522 |
| 7 | 116 | 40.0 | 102.2 | 1.4521 |
| 8 | 116–117 | 33.3 | 101.5 | 1.4521 |
| 9 | 117–119 | 36.4 | 100.1 | 1.4520 |
| 10 | 119–121 | 18.6 | 97.6 | 1.4518 |
| 11 | 121–125 | 11.2 | 95.7 | 1.4518 |
| 12 | (*a*) | 3.5 | 88.1 | 1.4514 |
| R | Residue | 13.5 | | |
| | | 298.8 | | |

(*a*) *Portion obtained by rinsing the column packing.*

The course of the distillation showed that the fatty acids were predominantly 18 carbons in chain length. Fractions 1 to 3, with low iodine value and low refractive index, indicate an appreciable content of palmitic and stearic acids. Fractions 4–12 have the characteristics of a typical oleate–linoleate mixture with the iodine number decreasing gradually because of the slightly lower boiling point of the linoleate. The refractive index continues to fall even in fraction 12, showing that there is little, if any, acid higher than $C_{18}$ in this fraction.

A portion of fraction 7 was crystallized from acetone. It yielded 0.2 gm. methyl stearate, m.p. 38–39°, 6.9 gm. methyl oleate, I.V. 85.4 and 3.0 gm. of oleate–linoleate mixture, I.V. 138.4.

Fractions 3, 11, and 12 were saponified. The equivalent weight of the acids was 276, 283, and 282 respectively (oleic acid 282.5). It is unlikely, therefore, that any acids higher than $C_{18}$ are present in fractions 1–12.

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The residue from the distillation was saponified and unsaponifiable matter was removed. The acids were crystallized from acetone giving the following fractions:

| Fraction | Temp. of cryst'n., °C. | Yield, gm. | M.p., °C. | Equiv. wt. |
|---|---|---|---|---|
| R1 | +15 | 0.3 | 64–66 | 319 |
| R2 | −35 | 1.1 | 59–61 | 301 |
| R3 | −52 | 4.3 | Liq. | 286 |
| R4 | Filtrate | 4.9 | Liq. | 294 |

R1 and R2 are almost entirely saturated and consist of stearic and arachidic or behenic acids, judging by the equivalent weight.

R3 and R4 had I.V. 85.3 and 102.2 respectively. Efforts to crystallize R3 and R4 were not successful, the products being gummy. It is judged from the iodine values and equivalent weights that the content of monoenoic acids higher than $C_{18}$, if any are present, must be less than 1.0% of the total acids.

*C. Acorn Oil*

Acorns were gathered in the vicinity of Ottawa in 1951 from the white oak (*Quercus alba* L.). They were shelled and dried. The kernels yielded 4.6% of reddish-brown oil by solvent extraction. It had I.V. 109.7, saponification value 185, and unsaponifiable matter 3.7%.

The oil was converted to methyl esters (129 gm., I.V. 108.3). The esters were distilled at a pressure of about 0.1 mm. until 15 gm. remained in the pot. At this point 30 gm. of pure methyl erucate was added and the distillation was continued (Table III), in order to distill over esters of $C_{18}$ and $C_{20}$ acids if present.

TABLE III
DISTILLATION OF METHYL ESTERS OF ACORN OIL

| Fraction | Vapor temp., °C. (approx.) | Wt. of fraction (gm.) | Iodine value | $n_D^{25°}$ |
|---|---|---|---|---|
| 1 | 90–108 | 3.1 | 25.8 | 1.4430 |
| 2 | 108–112 | 10.4 | 33.3 | solid |
| 3 | 112–115 | 14.0 | 92.1 | 1.4508 |
| 4 | 115 | 12.5 | 119.1 | 1.4540 |
| 5 | 115 | 14.3 | 125.1 | 1.4550 |
| 6 | 115 | 16.0 | 125.9 | 1.4550 |
| 7 | 115–118 | 14.0 | 125.9 | 1.4550 |
| 8 | 118–120 | 16.0 | 124.4 | 1.4550 |
| 9 | 120–125 | 4.3 | 122.5 | 1.4549 |
| 10 | 125–128 | 9.0 | 119.7 | 1.4545 |
| | Added 30 gm. methyl erucate | | | |
| 11 | 110–128 | 6.8 | 101.6 | 1.4549 |
| 12 | 128–137 | 2.9 | 70.8 | 1.4550 |
| 13 | 137–146 | 3.0 | 70.8 | 1.4548 |
| 14 | 146–151 | 5.7 | 70.9 | 1.4548 |

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The distillation follows the pattern of a typical palmitate–oleate–linoleate oil, although with more linoleate than in the hickory nut oil. There was no indication of a $C_{20}$ fraction.

Fraction 1 was crystallized from acetone and then saponified, giving 1.1 gm. of solid acids, equiv. wt. 260. The mixed acids from fraction 2 had equiv. wt. 264.

Fraction 10 (methyl esters) was crystallized from acetone, giving the following portions:

| Fraction | Temp. of cryst'n., °C. | Yield, gm. | Properties of esters |
|---|---|---|---|
| 10–1 | −27 | 0.2 | M.p. 37–38 |
| 10–2 | −50 | 2.8 | I.V. 83.6 |
| 10–3 | Filtrate | 5.0 | I.V. 146.1 |

Fraction 10–1 corresponds in melting point to methyl stearate. Upon hydroxylation with permanganate, fraction 10–2 readily gave dihydroxystearic acid, m.p. 129.5–130.5° alone and mixed with 9,10-dihydroxystearic acid. Therefore, the chief monoenoic acid in this fraction was ordinary oleic acid. The iodine value of fraction 10–3 shows that it is mainly polyenoic acid, probably linoleic.

A portion of fraction 11 was crystallized from acetone at −50°C. The crystals, 2.3 gm.; I.V. 73.9, were saponified and hydroxylated by permanganate. The product, after several crystallizations, melted at 127–129°. When mixed with 9,10-dihydroxystearic acid, it melted at 127–129°; with 11,12-dihydroxyeicosanoic acid it melted at 120–124°. It is concluded that the chief monoenoic acid in fraction 11 is ordinary oleic acid. The esters from the acetone filtrate (3.4 gm.; I.V. 115.9) were also saponified and hydroxylated. The portion of the product insoluble in ethyl acetate was tetrahydroxystearic acid, m.p. 171–173° alone and mixed with an authentic sample. Thus fraction 11 is shown to contain mainly oleic and linoleic acids.

Fraction 12, on hydroxylation, gave dihydroxybehenic acid, presumably arising from the methyl erucate that was added during the distillation. There was no evidence of eicosenoic acid.

## DISCUSSION

A. Peanut oil fatty acids have been studied at various times with some variation in results attributable to varietal or regional differences. Recent workers agree fairly well on the proportions of fatty acids present except for hexadecenoic acid. The present work, however, is the first in which eicosenoic and docosenoic acids are identified.

The presence of eicosenoic acid was suspected because of the known content of $C_{20}$–$C_{24}$ saturated acids. Eicosenoic and docosenoic acids tend to occur together. In this oil, the docosenoic acid is the lesser of the two in amount.

As in most vegetable oils, the acids of lower molecular weight (below $C_{18}$) are predominately saturated. We were unable to find hexadecenoic acid in

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the present sample although it has been reported by others (6, 8). Wikoff and co-workers did not find hexadecenoic acid in their examination of peanut oil (12).

Arachidic acid is estimated in the present sample as 1.5% of the total fatty acids. This is a lower figure than is commonly quoted. Actually, peanut oil is a poor source of arachidic acid. The present data, as well as those of Wikoff (12) and others, show that the peanut contains more behenic than arachidic acid.

It is clear that peanut oil differs from many oleate-type oils in having an appreciable content of acids higher than $C_{18}$, both saturated and unsaturated. Some legume oils exhibit this characteristic in varying degrees but it is by no means universal throughout the legume family.

B. Hickory nut oil, from a bitter species given as *Carya cordifornia*, was studied by Riebsomer and co-workers (10). They reported the mean molecular weight of the unsaturated acids as 317 but found only $C_{16}$ and $C_{18}$ acids upon further analysis. Palmitic, stearic, and oleic acids were positively identified by them but the tetrabromide test for linoleic acid was negative.

The present sample of oil from the bitter species *Carya cordiformis* Koch, was found by us to contain predominately $C_{18}$ acids. Oleic acid was isolated (as the ester) and iodine values above 100 for fractions 5 to 9 are judged to be sufficient evidence for the presence of linoleic acid. The saturated acids were palmitic, stearic, and a small amount of higher acid. Neither eicosenoic nor docosenoic acids could be detected although there was an indication of a little monoenoic acid, other than $C_{18}$, in the distillation residue.

C. Acorn oils from two species of oak have been examined by earlier workers. An Indian species (*Quercus incana* Roxb.) was found to have 17% palmitic, 0.9% other saturated acid, and 82% oleic acid (9). The swamp oak (*Q. palustris* Muench) gave an oil which had 15% saturated acids, 58% oleic acid, and 27% linoleic acid (7).

In the present work, the oil of a third species, *Q. alba* L., was found to have a simple palmitate–oleate–linoleate composition. Oleic and linoleic acids were identified by chemical derivatives. Eicosenoic acid could not be detected.

## CONCLUSIONS

The analysis of the three oils, although not complete, permits estimates of the proportions of some of the fatty acids. The figures are given as percentages of the total fatty acids.

Peanut oil: archidic 1.5, behenic 3.4, eicosenoic 1.6, docosenoic 0.2; hexadecenoic could not be detected—if present, less than 0.3.

Hickory nut oil: palmitic 6, stearic 1, higher saturated acids 0.5, oleic 72, linoleic 19; higher monoenoic acids could not be identified—if present, less than 1.0.

Acorn oil: palmitic 10, stearic 2, oleic 48, linoleic and other polyenoic 40; eicosenoic could not be detected—if present, less than 0.5.

11-Eicosenoic acid is therefore a minor constituent of this sample of peanut oil, constituting about 1.6% of the total fatty acids. It could not be detected

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in the hickory and acorn oils. If present at all, the amount is judged to be less than 1.0% in the hickory oil and less than 0.5% in the acorn oil.

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# PYRIDINE DERIVATIVES

## PART VI*. MALONATIONS OF SUBSTITUTED NITROPYRIDINES[1]

By W. Gruber

ABSTRACT

5-Hydroxy-2-alkylpyridines (VII) were prepared by a sequence of reactions starting with the malonation of 2-chloro-5-nitropyridine with diethyl alkylmalonates. Malonation failed with 4-methoxy-3-nitropyridine (VIII) and 2-chloro-3-nitropyridine (XII), yielding decomposition products only. Reactivity of the methoxyl groups in 4-methoxy-3-nitropyridine (VIII) and in 2-methoxy-3-nitropyridine (XV) was compared with respect to the rearrangement to N-methylpyridone, the reaction with aromatic amines, and hydrolysis with dilute acids. Methylation of 2-hydroxy-3-nitropyridine yields either 2-methoxy-3-nitropyridine (XV) or N-methyl-3-nitro-2-pyridone (XVI) as can be expected.

In Part I of this series (5) it was shown that malonation of 2-chloro-5-nitropyridine gives in good yields diethyl(5-nitropyridyl-2)-ethylmalonate (I, R = Et). This compound was the intermediate for a synthesis of *d*-pseudoconhydrine (II), thus proving the structure of (II). In Part IV (4) the isomeric 3-hydroxy-2-alkylpyridines (III) have been synthesized by rearrangement of 2-acylfuranes with ammonia. This paper reports further applications of the malonation reaction on 2,5-, 2,3-, and 3,4-substituted pyridine derivatives.

The reaction was studied first with 2-chloro-5-nitropyridine. The best yields of (I) were obtained by heating the components without a solvent. At 80–100°C. a violent reaction took place which was moderated by gentle cooling. After the first reaction subsided the dark brown mixture was heated for one hour at 150°C. to complete the reaction. The cooled mixture was poured into water and extracted with ether. The solvent was evaporated and the residue distilled *in vacuo* so as to remove the starting material and also to distill the end product, provided its boiling point was not too high. (5-Nitropyridyl-2)-alkylmalonesters are highly viscous, yellow oils which did not crystallize. During hydrolysis of these malonesters with sulphuric acid (50% v/v) or 20% hydrochloric acid, complete decarboxylation occurred. The intermediate, (5-nitropyridyl-2)-alkylacetic acid (IV) is still more unstable than pyridyl-2-acetic acid (6,12), the nitro group in the 5-position increasing the lability. The 2-alkyl-5-nitro-pyridines (V) do not give picrates, having not enough base-strength, but some of them have been characterized as chloroplatinates.

The nitro group was reduced either with stannous chloride or by catalytical hydrogenation. Both methods yielded the 5-amino-2-alkylpyridines almost quantitatively. Except 5-amino-2-benzylpyridine (VI, R = $CH_2C_6H_5$) all of them were oils and were therefore characterized as monopicrates (Table I). By diazotization and hydrolysis of the diazoniumsulphate, the amines were converted into the 5-hydroxy-2-alkylpyridines (VII, $R_1$ = alkyl, $R_2$ = H), which showed the normal properties of aromatic phenols: Color reaction with

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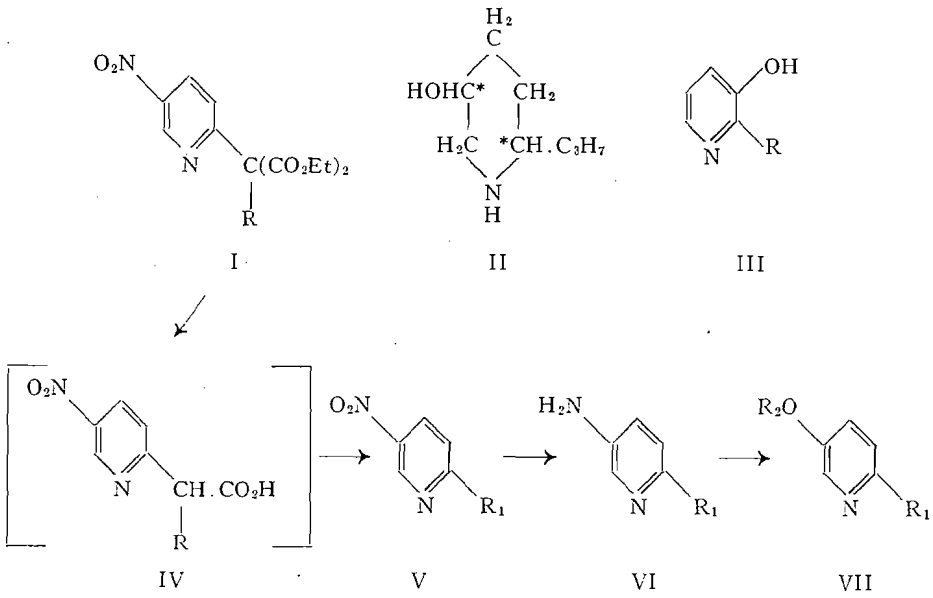



TABLE I

| 5-Amino-2-alkylpyridines VI | M.p., °C. | Analytical figures | |
|---|---|---|---|
| | | Calc., % | Found, % |
| Picrate of 5-amino-2-ethylpyridine ($R_1 = C_2H_5$) | 189–191 | $C_7H_{10}N_2.C_6H_3N_3O_7$<br>N 19.94 | 20.12 |
| Picrate of 5-amino-2-*n*-propylpyridine ($R_1 = n$-$C_3H_7$) (5) | 163–165 | | |
| Picrate of 5-amino-2-*n*-butylpyridine ($R_1 = n$-$C_4H_9$) | 142–143 | $C_9H_{14}N_2.C_6H_3N_3O_7$<br>C 47.49<br>H 4.52 | <br>47.55<br>4.41 |
| Picrate of 5-amino-2-*sec*-butylpyridine ($R_1 = sec$-$C_4H_9$) | 151–153 | $C_9H_{14}N_2.C_6H_3N_3O_7$<br>C 46.51<br>H 4.42<br>N 18.08 | <br>46.74<br>4.53<br>18.05 |
| Picrate of 5-amino-2-*n*-amylpyridine ($R_1 = n$-$C_5H_{11}$) | 150–152 | $C_{10}H_{16}N_2.C_6H_3N_3O_7$<br>C 48.85<br>H 4.87<br>N 17.81 | <br>48.65<br>4.93<br>17.65 |
| 5-Amino-2-phenylethylpyridine ($R_1 = CH_2CH_2C_6H_5$) | 113–115 | $C_{13}H_{14}N_2$<br>C 78.75<br>H 7.12<br>N 14.13 | <br>78.55<br>7.13<br>14.27 |

ferric chloride solution produced red to brown complexes, and coupling with *o*- and *p*-nitroanilines gave brown azo dyes.

Compounds of type (VII) are readily soluble in 1 *N* alkali and 1–2 *N* acids (Table II).

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TABLE II

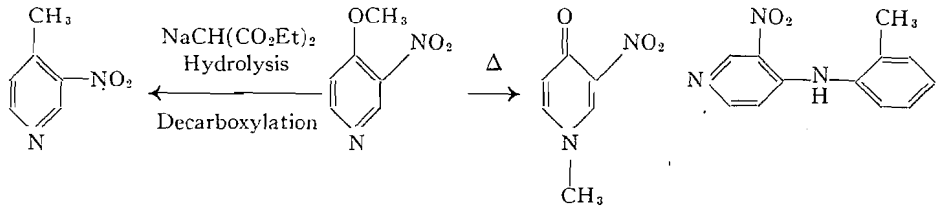
| 5-Hydroxy-2-alkylpyridines VII | M.p., °C. | Analytical figures | |
|---|---|---|---|
| | | Calc., % | Found, % |
| 5-Hydroxy-2-ethylpyridine ($R_1$ = $C_2H_5$, $R_2$ = H) | 129–131 | $C_7H_9NO$ | |
| | | C 68.27 | 68.26 |
| | | H 7.37 | 7.36 |
| | | N 11.37 | 11.35 |
| 5-Hydroxy-2-*n*-propylpyridine ($R_1$ = *n*-$C_3H_7$, $R_2$ = H) (5) | 92–94 | | |
| 5-Hydroxy-2-*n*-butylpyridine ($R_1$ = *n*-$C_4H_9$, $R_2$ = H) | 83–85 | $C_9H_{13}NO$ | |
| | | C 71.49 | 71.39 |
| | | H 8.67 | 8.60 |
| | | N 9.26 | |
| 5-Hydroxy-2-*sec*-butylpyridine ($R_1$ = *sec*-$C_4H_9$, $R_2$ = H) | 96–98 | | 71.27 |
| | | | 8.76 |
| 3,5-Dinitrobenzoate ($R_1$ = *sec*-$C_4H_9$, $R_2$ = 3,5-$(NO_2)_2C_6H_3CO$-) | 133–135 | $C_{16}H_{15}N_3O_6$ | 9.50 |
| | | C 55.65 | 55.44 |
| | | H 4.38 | 4.32 |
| | | N 12.17 | 12.15 |
| 5-Hydroxy-2-*n*-amylpyridine, 3,5-Dinitrobenzoate ($R_1$ = *n*-$C_5H_{11}$, $R_2$ = 3,5-$(NO_2)_2C_6H_3CO$-) | 98–101 | $C_{17}H_{17}N_3O_6$ | |
| | | C 56.82 | 56.75 |
| | | H 4.71 | 4.82 |
| | | N 11.70 | 11.52 |
| 5-Hydroxy-2-phenylethylpyridine ($R_1$ = $CH_2CH_2C_6H_5$, $R_2$ = H) | 148–150 | $C_{13}H_{13}NO$ | |
| | | C 78.36 | 78.20 |
| | | H 6.58 | 6.45 |
| | | N 7.03 | 7.14 |

4-Chloro-3-nitropyridine does not seem to be stable (9) (4-chloropyridine is also unstable according to Wibaut and Broekman (11)). The malonation of "4-chloro-3-nitropyridine hydrochloride with diethyl disodiomalonate" reported by Koenigs and Fulde (7) was almost certainly a malonation of 4-methoxy-3-nitropyridine hydrochloride, in view of a later paper by Bremer (3), who prepared 4-methoxy-3-nitropyridine (VIII) *in situ* by pouring a mixture of 4-hydroxy-3-nitropyridine and phosphorus pentachloride into cooled methanol. The methoxyl group was highly reactive, so that this stable compound could be used as starting material for many reactions instead of the unstable halide. Bremer did perform the malonation of (VIII) with diethyl sodiomalonate, which yielded 4-methyl-3-nitropyridine (IX).

The synthesis of (VIII) was repeated in the hope of establishing a general method for the synthesis of 3-nitro-4-alkylpyridines, but we could not achieve the desired malonation with substituted diethyl malonates. The identity of the starting material was checked by its rearrangement to N-methyl-3-nitro-4-pyridone (X) and by its reaction with *o*-toluidine to yield N-(3-nitropyridyl-4)-*o*-toluidine (XI) quantitatively. Malonation of (VIII) was attempted with diethyl sodiomethylmalonate and diethyl sodio-*i*-propylmalonate using ether,

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ethanol, or benzene as a solvent. After reduction of the supposed nitro-compound, the amine, which was obtained as an oil, was characterized as a picrate which was the same in both cases, but identical neither with that of 3-amino-4-hydroxypyridine nor that of 3-aminopyridine. This picrate (Substance P) is now believed to derive from a base generated during the reaction by decomposition of the pyridine nucleus.



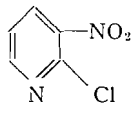

IX VIII X XI

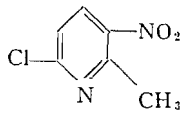
Finally, malonations were tried with 2-chloro-3-nitropyridine (XII). Although the components reacted violently and the reaction mixture gave a positive test for chloride ion, the desired (3-nitropyridyl-2)-alkylmalonate could not be isolated, probably because (XII) decomposed. According to Baumgarten and Chien-Fan Su (1) the reaction of 2-chloro-5-nitropicolin (XIII) with sodium methylate gave 2-methoxy-5-nitropicolin in high yield, whereas the same reaction with the 2,3-isomer (XIV) brought about only decomposition. From these facts it was concluded that all chloro-nitropyridines with substituents in ortho position react in a similar way; however, the reaction of 2-chloro-3-nitropyridine (XII) with sodium methoxide yields the methoxyl compound (m.p. 57–58°C.) almost quantitatively. 2-Methoxy-3-nitropyridine (XV) has been reported in the literature (8) to have a m.p. of 110°C. It was prepared from the silver salt of 2-hydroxy-3-nitropyridine and methyl iodide and it is well known from methylation experiments on 2-hydroxy-5-nitropyridine (2) that this silver salt method gives rise not only to the methyl ethers but also to the N-methyl-nitropyridones. The methylation of 2-hydroxy-3-nitropyridine with methyl iodide via Ag-salt was therefore repeated and 2-methoxy-3-nitropyridine (XV) as well as N-methyl-3-nitro-2-pyridone (XVI) could be separated from the reaction mixture. The methyl ether (XV) from this experiment was identical with the compound prepared by methylation of the halide (XII) with sodium methoxide. The methylation of the potassium salt of 2-hydroxy-3-nitropyridine with methyl sulphate produced mainly the pyridone (XVI), which again was identical with the compound, prepared by methylation of the silver salt.

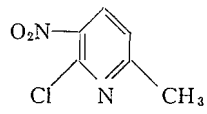
The reaction of (XII) with aliphatic and aromatic amines proceeds normally.

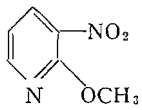
To compare the reactivity of the methoxyl groups in (VIII) and (XV) attempts were made to rearrange 2-methoxy-3-nitropyridine (XV) to N-methyl-3-nitro-2-pyridone by heating *in vacuo* in a sealed tube. Such a rearrangement would be expected by analogy with XVII → XVIII, (10), but the reaction failed. Unlike (VIII) the 2-methoxyl group in (XV) would react

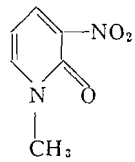
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XII

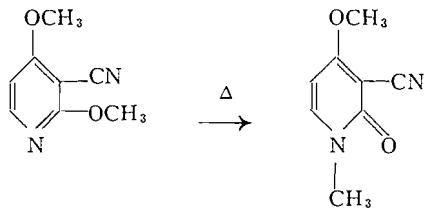

XIII


XIV


XV


XVI

neither with *o*-toluidine nor piperidine at 130°C., but could be hydrolyzed easily even with 0.5 *N* acid at the steam bath for two hours.


XVII XVIII

## EXPERIMENTAL*

The following are a few typical examples of the malonation reaction and of subsequent steps.

*Diethyl (5-nitropyridyl-2)-methylmalonate* (I, $R = CH_3$)

Diethyl sodiomethylmalonate was prepared by refluxing a mixture of 1.2 gm. of finely powdered sodium and 8.7 gm. of diethyl methylmalonate in 100 ml. of absolute ether. After complete dissolution of the sodium sand (10 hr.) the solvent was evaporated, the residue dried overnight in a desiccator, intimately mixed with 8 gm. of 2-chloro-5-nitropyridine, and cautiously heated on the steam bath. At 90°C. (thermometer in the mixture) a violent reaction set in and the content of the flask darkened. After the reaction subsided the mixture was heated to 150°C. (oil bath) for one hour, cooled, and 200 ml. of water added. The solution was extracted exhaustively with ether, the solvent evaporated and the residue distilled at 1 mm. The fraction above 150°C. (air bath temperature) was collected and redistilled; yield: 8.7 gm. (58%). Calc. for $C_{13}H_{16}N_2O_6$: N, 9.46%; Found: N, 9.70%.

*5-Nitro-2-n-amylpyridine* (V, $R_1 = n\text{-}C_5H_{11}$)

Diethyl (5-nitropyridyl-2)-*n*-butylmalonate (I, R = n-$C_4H_9$) (15.5 gm.) was heated to 110–120°C. with 90 ml. of sulphuric acid (1:1) until evolution of gas bubbles ceased (four hours). After cooling, the dark solution was ex-

**Melting points are corrected. Analyses are by A. Bernhardt, MPI, Mühlheim (Ruhr), Germany.*

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tracted with ether and the organic layer discarded. The acid layer was diluted and made alkaline and after exhaustive extraction with ether, the ether was evaporated and the residue distilled *in vacuo* (120–130°C. air bath, 2 mm. Hg); Yield, 7.0 gm., i.e. 68%.

Of this base 380 mgm. was dissolved in 2 ml. of 20% hydrochloric acid and added to 3 ml. of a solution containing 350 mgm. $H_2PtCl_6$. The precipitate was thoroughly washed with very dilute hydrochloric acid and methanol. M.p. 152–155°C. (dec.); Yield, 578 mgm., i.e. 79%. Calc. for $(C_{10}H_{15}N_2O_2)_2$. $PtCl_6$: Pt, 23.89%. Found: Pt, 23.70%.

*5-Nitro-2-n-butylpyridine* (V, $R_1 = n\text{-}C_4H_9$)

This was synthesized as above. Chloroplatinate: m.p. 181–183°C. (dec.). Calc. for $(C_9H_{13}N_2O_2)_2$ $PtCl_6$: C, 28.06; H, 3.40; Pt, 25.34%. Found: C, 28.07; H, 3.27; Pt, 25.34%.

*5-Amino-2-n-butylpyridine* (VI, $R_1 = n\text{-}C_4H_9$)

A solution of 1.98 gm. of (V) ($R_1 = n\text{-}C_4H_9$) in 80 ml. of absolute methanol was shaken in a hydrogen atmosphere in the presence of 0.3 gm. of Adams' catalyst. The required amount of three moles of hydrogen (0°C., 760 mm. Hg, 739.2 ml.) was taken up in 15 min. The amine was isolated by filtering off the catalyst and evaporating the solvent and purified by distillation *in vacuo* (0.005 mm. Hg, 90–100°C. air bath). Yield: 1.64 gm. (almost quantitative). The picrate was prepared in ethereal solution from 300 mgm. of the base and 530 mgm. picric acid. Purification by several recrystallizations from methanol; m.p. 142–143°C.

*5-Amino-2-phenylethylpyridine* (VI, $R_1 = CH_2CH_2C_6H_5$)

A solution of 4.4 gm. of the nitro compound (V) ($R_1 = CH_2CH_2C_6H_5$) in 15 ml. of concentrated hydrochloric acid was added slowly to a cooled solution of 20 gm. of crystalline stannous chloride in 16 ml. of concentrated hydrochloric acid. After standing for one hour a strong sodium hydroxide solution was added in excess and then exhaustively extracted with ether. Purification by recrystallization from ether yielded 3.6 gm., i.e. 95%; m.p. 113–115°C.

*5-Hydroxy-2-sec-butylpyridine* (VII, $R_1 = sec\text{-}C_4H_9$, $R_2 = H$)

A solution of 1.26 gm. of (VII) ($R_1 = sec\text{-}C_4H_9$) in 90 ml. of 1 *N* sulphuric acid was diazotized with 0.8 gm. of sodium nitrite in 12 ml. of water, the yellow mixture was then heated on the steam for one hour and cooled. After the addition of solid sodium bicarbonate in excess, the solution was extracted with ether, the solvent evaporated, and the residue distilled *in vacuo*, giving a crude yield of 1.10 gm., i.e. 86%. This oil crystallized and was purified by several recrystallizations from ether – petroleum ether; m.p. 96–98°C.

The 3,5-dinitrobenzoate of this phenolic base was prepared by heating a mixture of 0.8 gm. of (VII) ($R_1 = sec\text{-}C_4H_9$, $R_2 = H$) and 1.3 gm. of 3,5-dinitrobenzoyl chloride for one hour on the steam bath. The cooled reaction mixture was taken up in ether, washed with 1 *N* sodium hydroxide and with water, then the solvent was evaporated. The residue was recrystallized twice from ether; m.p. 133–135°C.

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*N-(3-Nitropyridyl-4)-o-toluidine* (XI)

4-Methoxy-3-nitropyridine (1.54 gm.) was heated with 1.07 gm. of *o*-toluidine on the steam bath until the mixture solidified completely (two hours). After cooling the mass was triturated with ether, filtered, and the residue recrystallized from dilute methanol; m.p. 85–87°C. Calc. for $C_{12}H_{13}N_3O_2$: C, 62.87; H, 4.84; N, 18.33. Found: C, 62.76; H, 4.84; N, 18.12%.

*2-Methoxy-3-nitropyridine* (XV)

A solution of 1.4 gm. of 2-chloro-3-nitropyridine (XII) in 10 ml. of absolute methanol was shaken with sodium methoxide (from 0.3 gm. sodium and 5 ml. of methanol) for eight hours at room temperature, then refluxed for one hour, the solvent evaporated *in vacuo* and after addition of 100 ml. of water, the precipitate filtered with suction. After purification by vacuum distillation and recrystallization from ether – petroleum ether the m.p. was 57–59°C. Yield, 0.9 gm., i.e. 65%. Calc. for $C_6H_6N_2O_3$: C, 46.75; H, 3.93; N, 18.18; $OCH_3$, 20.13%. Found: C, 46.81; H, 4.05; N, 18.10; $OCH_3$, 20.05%.

*Methylation of 2-Hydroxy-3-nitropyridine* (XX)

(*a*) A solution of 0.60 gm. of (XX) in aqueous potassium hydroxide (0.25 gm. potassium hydroxide in 34 ml. of water) was mixed with aqueous silver nitrate solution (0.73 gm. silver nitrate in 2 ml. of water). The silver salt was isolated and dried; 800 mgm. was suspended in 8 ml. of methanol, 0.3 ml. of methyl iodide added, and the mixture refluxed overnight. The solvent was evaporated and the residue extracted twice with 10 ml. of cooled ether. After evaporation of the solvent and vacuum distillation of the residue, the m.p. was 57–58°C., not depressed by admixture of the methyl ether XV. Yield, 88 mgm., i.e. 18%, based on silver salt. The residue from the ether extraction weighed 286 mgm., i.e. 59%, and had a m.p. of 168–171°C. It was recrystallized several times from methanol–ether; m.p. 171–174°C.

(*b*) A mixture of 737 mgm. of (XX), 645 mgm. of potassium hydroxide, 633 mgm. of freshly distilled dimethyl sulphate, and 6 ml. of water was refluxed for six hours, cooled, the precipitate collected on a Büchner funnel and recrystallized twice from water. Yield, of N-methyl-3-nitro-2-pyridone, almost quantitative; m.p. 171–174°C. The mixed m.p. with the same fraction from (*a*) was not depressed. Calc. for $C_6H_6N_2O_3$: C, 46.75; H, 3.93; N, 18.18%. Found: C, 46.29; H, 3.82; N, 18.02%.

*Acid Hydrolysis of* XV

2-Methoxy-3-nitropyridine (257 mgm.) was heated with 20 ml. of 0.5 *N* hydrochloric acid on the steam bath for three hours. The oil disappeared slowly; cooling precipitated yellow crystals, m.p. 224–226°C.; no depression when mixed with 2-hydroxy-3-nitropyridine.

*N-(3-Nitropyridyl-2)-o-toluidine*

2-Chloro-3-nitropyridine (XII, 0.9 gm.) and *o*-toluidine (1.0 gm.) were heated at 150°C. for one hour. After removal of the excess of *o*-toluidine as hydrochloride, the residue was recrystallized from dilute methanol; m.p.

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124–126°C. Calc. for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84%. Found: C, 62.72; H, 5.00%.

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# THE STABILITY OF RESIN EMULSIONS[1]

By L. A. Munro and F. H. Sexsmith

ABSTRACT

Accelerated settling tests were made on dilute polyvinyl acetate emulsions in the presence of increasing concentrations of electrolyte. Stability–electrolyte concentration curves for five of the six emulsions studied show a marked similarity to the zeta potential or mobility curves, indicating that under such conditions the charge on the latex particle is the most important factor in determining stability. The anomalous behavior of an almost neutral latex formulated with mixed cationic and nonionic emulsifiers is attributed to the preponderance of other factors associated with micellar phenomena.

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In a previous paper (9) the authors have reported the effect of electrolyte concentration on the mobilities of polyvinyl latices prepared with cationic, anionic, and mixed emulsifying agents. With most of the emulsions, marked irregularities were found in the mobility–salt concentration curves. These irregularities were attributed to micellar phenomena. The zeta potentials calculated by the Henry modification of the Smoluchowski equation from the mobilities of a very uniform latex showed the same sharp minimum.

Reference to recent literature indicates that the dependence of the stability of colloidal suspensions or emulsions on particle charge or zeta potential is still being debated. Clayton (1) states that the stability of oil-in-water emulsions is a function of interfacial tension, Brownian movement, and particle charge. Ray and Hutchinson (10) consider that the zeta potential is the principal factor in the suspension stability of carbon particles in a dilute soap solution. Greiner and Vold (3) in their study of the suspending power of various surfactants for fine manganese dioxide powder, attribute stability to the zeta potential rather than to solubilization or to colloidality of the solution, except to the extent that micelle formation affects the concentration of simple ions.

Eilers and Korff (2) have attempted mathematically to relate electrical charge with stability of hydrophobic dispersions. They postulated a stability factor which varies with the square of the zeta potential and inversely as the Debye-Huckel function $\kappa$. The latter is an indication of the thickness of the ionic atmosphere. Concentrations of electrolyte too small to affect this factor may have an appreciable influence on the zeta potential.

Hayek (4) on the other hand reports no correlation between electrophoretic mobility and sol stability. He concludes from his work with dispersions in organic media that in such systems particle charges are incidental to but not responsible for the stability of the sols.

King has maintained that there is a lack of relationship between electrical charge and the stability of oil-in-water emulsions (5, 6). He suggested that there is an optimum degree of dispersion for maximum stability, which in turn is conditioned by the nature of the emulsifying or protective agent.

[1] *Manuscript received August 13, 1953.*
*Contribution from Department of Chemistry, Queens University, Kingston, Ontario.*

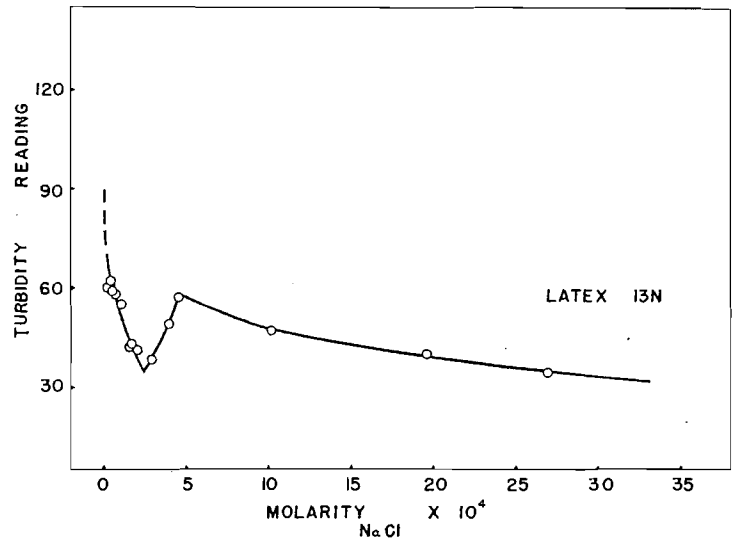



FIG. 1. Stability curve for latex 13N formulated with a nonionic emulsifier, hydroxyethyl cellulose.

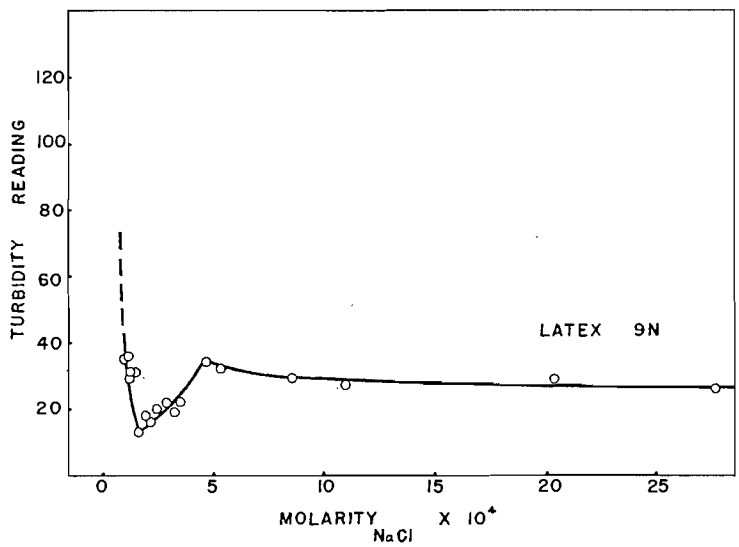



FIG. 2. Stability curve for latex 9N formulated with a nonionic emulsifier, polyvinyl alcohol.

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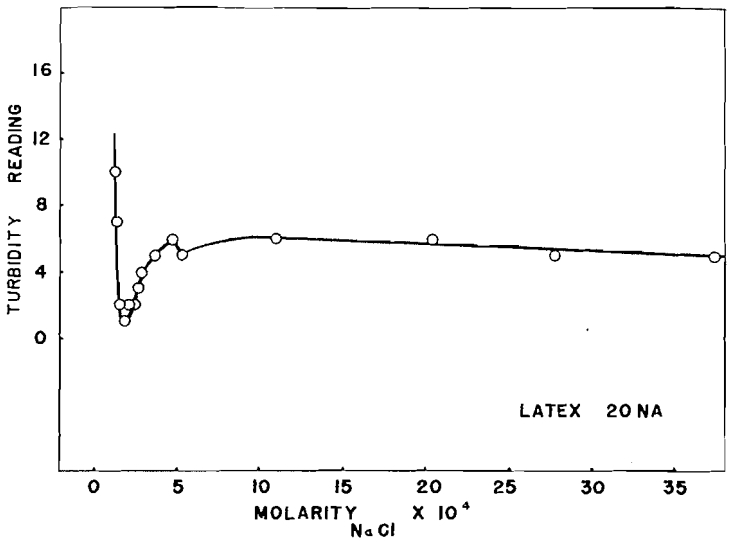



FIG. 3. Stability curve for latex 20NA formulated with mixed emulsifiers, gum tragacanth, and polyvinyl alcohol.

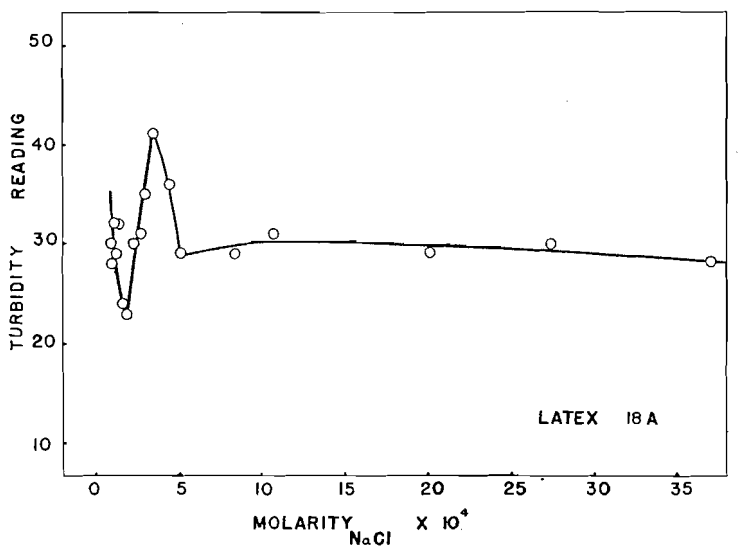



FIG. 4. Stability curve for latex 18A formulated with an anionic emulsifier, gum arabic.

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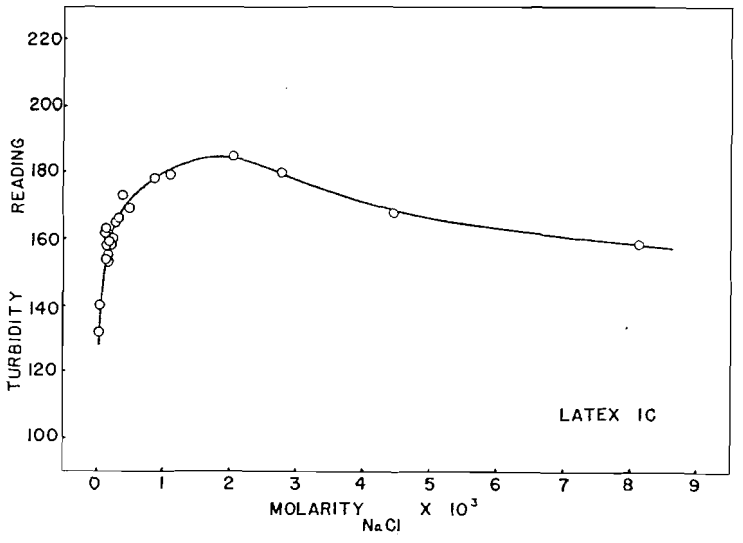



FIG. 5. Stability curve for latex 1C a commercial preparation (8).

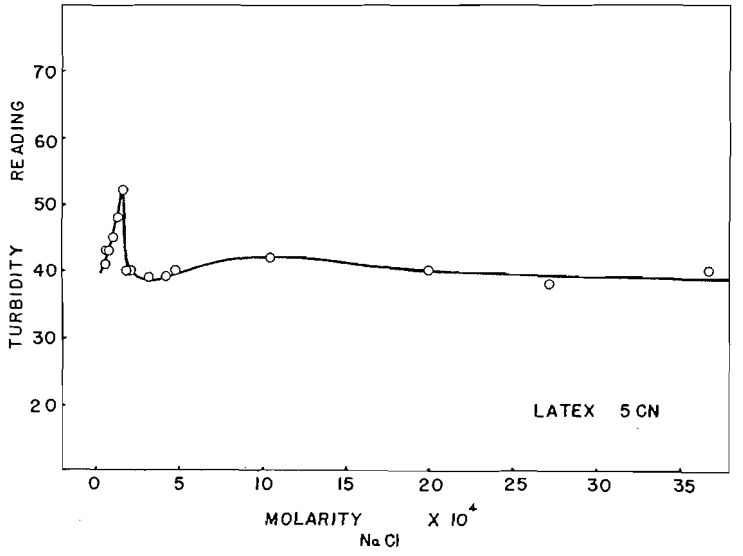



FIG. 6. Stability curve for latex 5CN a commercial preparation with mixed cationic and nonionic emulsifiers.

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With the polyvinyl acetate latices used in our previous studies it was observed that there was a great divergence in primary stability. Some of the concentrated emulsions settled appreciably in a few hours while others showed very little settling after a week. Accelerated settling tests were set up with separate portions of the diluted emulsions used for the electrophoretic studies, or with samples of similar total resin content and identical electrolyte concentrations. It was felt that in addition to being of general interest, the peculiar shape of the mobility and zeta potential curves would facilitate the observation of any correlation between these quantities and the stability in such tests.

## EXPERIMENTAL

Portions of the same samples used for electrophoresis or samples with similar resin content and the same electrolyte concentration were centrifuged for 30 min. in an Adams angle head centrifuge at 2070 r.p.m. The supernatant suspension was then decanted into fresh tubes and centrifuged for a further 10 min. Turbidity readings were made in a photoelectric colorimeter using a 342 blue filter. The scale reading was proportional to the total solids content for any given emulsion except for very dilute suspensions of polydisperse samples, where, as indicated by Morse (7) irregularities of particle size have a pronounced effect on turbidity. Initial concentrations of latex varied from 0.03 to 0.20%. Stability curves were obtained by plotting turbidity scale readings against salt concentration. These are shown in Figs. 1–6.

## DISCUSSION

Reference to the previous paper (9) will show the remarkable similarity between the mobility curves and the curves for stability as indicated by the accelerated settling. In the case of latex 13N which was of very uniform particle size, the sharp minimum for turbidity occurs at $2.7 \times 10^{-4}$ molar NaCl, for the zeta potential at $2.9 \times 10^{-4}$, and for the mobility at $2.5 \times 10^{-4}$ $M$ NaCl. While the other curves are subject to some error due to the variation in particle size, each of the emulsions 9N (Fig. 2), 20NA (Fig. 3), and 18A (Fig. 4) shows minimum turbidity at essentially the same concentration of electrolyte as that which gave minimum mobility. A comparison of the minima is given in Table I.

TABLE I

CONCENTRATION OF SODIUM CHLORIDE ($M \times 10^{-4}$) AT MINIMA FOR DIFFERENT EMULSIONS

| Latex* | 13N | 9N | 20NA | 18A |
|---|---|---|---|---|
| Mobility | 2.5 | 1.9 | 2.0 | 1.3 |
| Stability | 2.7 | 1.7 | 1.9 | 1.9 |

*13N *Nonionic emulsifying agent: hydroxyethyl cellulose.*
9N *Nonionic emulsifying agent: polyvinyl alcohol.*
20NA *Mixed nonionic and anionic: gum tragacanth and PVA.*
18A *Anionic emulsifying agent: gum arabic.*

The stability curve for latex 1C (Fig. 5) is also similar to its mobility curve. Each shows no minimum but a steep rise at low electrolyte concentration

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reaching a broad maximum at salt concentration of approximately $20 \times 10^{-4}$ molar (NaCl).

Latex 5CN (Fig. 6) formulated with mixed cationic and nonionic emulsifiers exhibited anomalous behavior in that the mobility and stability curves are entirely dissimilar. This emulsion had a very low standard mobility (8), and the stock emulsion (containing 55% solids) was the least stable of the 20 latices studied, giving a copious sediment in 24 hr. In contrast latex 1C showed no settling even after standing one week. The latter had the highest standard mobility of all the emulsions (8).

In the case of the initially unstable and almost neutral latex 5CN, the anomalous behavior is probably due to the preponderance of factors associated with micellar phenomena. One is inclined to agree with King's conclusion (6) that when no reaction takes place between electrolyte and emulsifying agent, the electrical charge on the dispersed globules does not determine stability. Under such conditions the initial settling depends more on size distribution, concentration of the latex, interfacial tensions, and the mechanical properties of the interfacial films than on particle charge.

While in the majority of cases the primary stability of concentrated emulsions of polyvinyl acetate can not be predicted from the mobilities at one standard salt concentration, the foregoing curves indicate that for dilute emulsions in the presence of electrolyte, the charge on the particle is the most important factor in determining stability.

ACKNOWLEDGMENT

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# THE BIOGENESIS OF ALKALOIDS

## IX. FURTHER INVESTIGATIONS ON THE FORMATION OF GRAMINE FROM TRYPTOPHAN[1]

By Edward Leete[2] and Léo Marion

ABSTRACT

A mixture of *dl*-tryptophan-2-$C^{14}$ and *dl*-tryptophan-$\beta$-$C^{14}$ with a known ratio of activity in the 2 and $\beta$ positions was prepared. Feeding it to sprouting barley produced radioactive gramine which was isolated from the leaves. Systematic degradation of the alkaloid showed the activity to be present only in the 2 position of the nucleus and the methylene group of the side chain. The ratio of the activity in the two positions was the same as in the administered tryptophan. These results thus indicate that tryptophan is converted to gramine in the plant without cleavage of the indole–alanine linkage.

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It was previously known that sprouting barley synthesized gramine, and it was shown (2) that feeding *dl*-tryptophan-$\beta$-$C^{14}$ to the sprouting plant resulted in the formation of radioactive gramine in which the activity resided entirely in one position corresponding to that in which the $C^{14}$ was located in the administered tryptophan. This result, strongly suggesting that tryptophan was the precursor of gramine, was somewhat surprising since gramine was formerly regarded as the only indole alkaloid that could not be derived from tryptophan by a simple biogenetic scheme, it being assumed that the alkaloid was produced in the plant by a method analogous to its *in vitro* synthesis from formaldehyde, indole, and dimethylamine (9). The experiment with *dl*-tryptophan-$\beta$-$C^{14}$ did not exclude the possibility that the tryptophan might have been hydrolyzed to indole and serine, a reversal of its accepted biosynthesis (15, 16, 19). The serine could then have given rise to a one-carbon fragment which could conceivably have been utilized by the plant for a synthesis of gramine similar to the *in vitro* one.

This problem could be settled by feeding to the barley tryptophan labelled both in the indole nucleus and in the $\beta$-position of the side chain. Then, if any fission of the tryptophan occurred at the 3-position, one would not expect to obtain radioactive gramine in which the ratio between the activity in the indole nucleus and in the $\beta$-position was the same as in the administered tryptophan. The synthesis of *dl*-tryptophan-3-$C^{14}$ has been described (7), the indole-3-$C^{14}$ required for this synthesis being obtained in very poor yield from carbonyl-labelled benzoic acid. For the present work indole-2-$C^{14}$ was prepared in two steps from radioactive sodium formate in 25% yield. The $C^{14}$-sodium formate was heated at 100° for 12 hr. with *o*-toluidine hydrochloride, *o*-toluidine, and inactive formic acid to give formyl-$C^{14}$-*o*-toluidine which was converted to indole-2-$C^{14}$ by heating with potassium tertiary butoxide according to the method of Tyson (17, 18). A sample of the radioactive indole, diluted with

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*Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3109.*
[2] *National Research Council of Canada Postdoctoral Fellow.*

inactive indole, was converted to N-benzoylindole (20). This was oxidized with potassium permanganate to benzoylanthranilic acid (21) which was inactive, thus showing that all the activity in the indole resided in the 2-position. Tryptophan-2-$C^{14}$ was prepared from this indole by established methods (1, 7, 13). Tryptophan-$\beta$-$C^{14}$ was also prepared by the same methods using inactive indole and $C^{14}$-formaldehyde (2). A mixture of definite quantities of these two tryptophans constituted the doubly labelled tryptophan that was fed to the barley.

The initial feeding experiments were carried out by the previously described method (2), the tracer being added to the plant on the sixth day of sprouting and the leaves harvested on the 11th day. When the gramine was isolated it was found to be only weakly radioactive, the activity being too low to allow dilution with inactive gramine in order to make degradations possible. The only apparent differences between this experiment and that previously reported (2) were the state of development of the sprouting barley and the presence of much mold. Whereas in the former experiment the shoots were 5–6 cm. long on the sixth day of germination, they were 10–12 cm. long at the same time of growth in the present experiment, presumably owing to the higher temperature and humidity prevailing in the greenhouse. From these results it appears that the number of days after germination is probably not really significant, and that gramine is only synthesized in the plant during the initial growth of the leaves. It has been reported (3) that the quantity of gramine remains constant during the first 10 days, but that the alkaloid has disappeared after one month. That the more advanced development of the plant due to more rapid growth was indeed the reason for the lower activity in the isolated gramine was established by an experiment in which doubly labelled tryptophan was fed to the barley on the third day of germination, when the shoots were 1–1.5 cm. long, and the leaves were harvested on the ninth day of germination. From this experiment gramine of a high activity was obtained. The comparative results are summarized in Table I.

TABLE I
COMPARATIVE RESULTS

| Experiment | Total activity of tryptophan fed to plant (disintegrations per min.) | Temperature of germination cabinet | Time of feeding tracer | Length of leaves at feeding time, cm. | Harvesting time | Activity of gramine (disintegrations per min. per millimole) |
|---|---|---|---|---|---|---|
| A | $\beta$-$C^{14}$ $6.36 \times 10^7$ | 21–2° (March) | 6th day of germination | 5–6 | 11th day | $1.02 \times 10^5$ |
| B | 2: $\beta$-$C^{14}$ $5.67 \times 10^7$ | 27–32° (June) | 6th day | 10–12 | 11th day | $7.9 \times 10^3$ |
| C | 2: $\beta$-$C^{14}$ $3.59 \times 10^7$ | 27–32° (July) | 3rd day | 1–1.5 | 9th day | $9.8 \times 10^4$ |

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The gramine of high activity thus obtained was diluted with inactive gramine and degraded by essentially the same methods as those previously described (2) and by additional methods rendered necessary because of the labelling of the indole nucleus. The degradations carried out are illustrated in Fig. 1. The

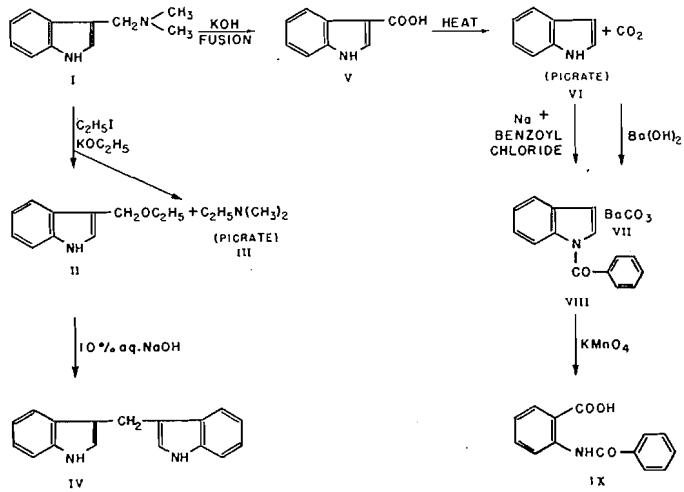



FIG. 1. Degradation of the gramine to determine the location of the radioactivity.

fusion of the gramine with potassium hydroxide gave rise to indolyl-3-carboxylic acid (V) which was decarboxylated to radioactive indole (VI) and radioactive carbon dioxide. The benzoyl derivative of this indole (VIII) when oxidized with potassium permanganate produced inactive benzoylanthranilic acid (IX) thus showing that the radioactivity of the indole nucleus resided entirely in $C_2$. The radioactive carbon dioxide indicated that the $C_\beta$-activity of the tryptophan was to be found in the methylene carbon of the gramine side chain. Degradation of gramine to active 3-ethoxymethylindole and inactive ethyldimethylamine proved that no radioactive carbon was involved in the N-methyl groups. The conversion of 3-ethoxymethylindole (II) to 3,3′-di-indolylmethane (IV) by refluxing with aqueous sodium hydroxide was a convenient way of checking the activity in the 2-position and in the methylene group of the gramine since the product contained two indole nuclei and therefore two $C_2$ but only one methylene group. This self condensation of 3-ethoxymethylindole was expected since it had previously been discovered (10) that the related 3-hydroxymethylindole underwent the same condensation to 3,3′-di-indolylmethane.

The determination of the radioactivity of each of the degradation fragments (results shown in Table II) indicated that there had been no randomization of the activity in the gramine from feeding experiments (C), and that the ratio of activity in $C_2$ and $C_\beta$ in the gramine was the same as in the administered tryptophan. It can therefore be concluded that tryptophan is indeed the precursor of gramine in sprouting barley and that the amino acid involved in the synthesis does not undergo scission to indole.

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Although the activity of the gramine obtained from the initial experiment (B) was very low, it was possible to carry out the reaction with ethyl iodide

TABLE II
ACTIVITIES OF GRAMINE AND DEGRADATION PRODUCTS

| Experiment | Compound | Activity[3] | Labelled atoms |
|---|---|---|---|
| C | *dl*-Tryptophan fed | | |
| | -2-$C^{14}$ | $1.68 \times 10^7$ disintegrations per min. (total activity) (1.0005 gm.) | $C_2$ |
| | -$\beta$-$C^{14}$ | $1.91 \times 10^7$ disintegrations per min. (total activity) (0.0761 gm.) | $C_\beta$ |
| | | $C_2/C_\beta = 0.88$ | |
| C | Gramine (I) | $9.80 \times 10^4$ disintegrations per min. per millimole | $C_2 + C_\beta$ |
| | Gramine picrate | $9.25 \times 10^4$ disintegrations per min. per millimole | $C_2 + C_\beta$ |
| | 3-Ethoxymethylindole (II) | $9.45 \times 10^4$ disintegrations per min. per millimole | $C_2 + C_\beta$ |
| | Ethyldimethylamine picrate (III) | 0 | — |
| | 3,3′Di-indolylmethane (IV) | $13.80 \times 10^4$ disintegrations per min. per millimole | $2C_2 + C_\beta$ |
| | Indole-3-carboxylic acid (V) | $9.02 \times 10^4$ disintegrations per min. per millimole | $C_2 + C_\beta$ |
| | S-Benzyl-iso-thiouronium salt of (V) | $9.56 \times 10^4$ disintegrations per min. per millimole | $C_2 + C_\beta$ |
| | Indole picrate (VI) | $4.30 \times 10^4$ disintegrations per min. per millimole | $C_2$ |
| | Barium carbonate (VII) | $4.63 \times 10^4$ disintegrations per min. per millimole | $C_\beta$ |
| | N-Benzoylindole (VIII) | $4.38 \times 10^4$ disintegrations per min. per millimole | $C_2$ |
| | Benzoylanthranilic acid (IX) | 0 | — |
| | (IV)–(II) | $4.35 \times 10^4$ disintegrations per min. per millimole | $C_2$ |
| | 2(II)–(IV) | $5.10 \times 10^4$ disintegrations per min. per millimole | $C_\beta$ |
| | Mean value of $C_2$ | $4.34 \times 10^4$ disintegrations per min. per millimole | |
| | Mean value of $C_\beta$ | $4.87 \times 10^4$ disintegrations per min. per millimole | |
| | | $C_2/C_\beta = 0.89$ | |

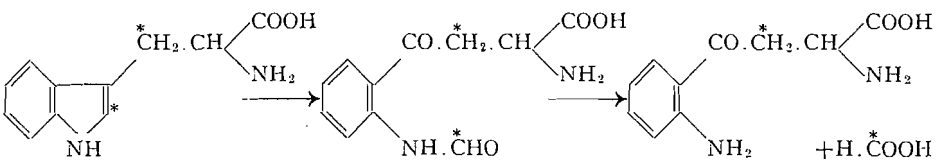
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TABLE II (continued)

| Experiment | Compound | Activity[3] | Labelled atoms |
|---|---|---|---|
| B | *dl*-Tryptophan fed | | |
| | -2-$C^{14}$ | $1.71 \times 10^7$ disintegrations per min. (total activity) (1.0203 gm.) | $C_2$ |
| | -$\beta$-$C^{14}$ | $3.96 \times 10^7$ disintegrations per min. (0.1562 gm.) | $C_\beta$ |
| B | Gramine (I) | $7.9 \times 10^3$ disintegrations per min. per millimole | |
| | 3-Ethoxymethylindole (II) | $4.8 \times 10^3$ disintegrations per min. per millimole | |
| | Ethyldimethylamine picrate (III) | $3.1 \times 10^3$ disintegrations per min. per millimole | |

[3] *All specific activities are for carrier free material and were determined on thin samples, making the usual corrections for self absorption, etc.*

and potassium ethoxide (11) to give 3-ethoxymethylindole and ethyldimethylamine isolated as the picrate. The results shown in Table II indicate that the N-methyl groups in this gramine were appreciably active. From what is known about the methylation of alkaloids in plants (4, 6, 8, 12, 14) this would seem to indicate that radioactive formate or other one-carbon compound has been produced in some way. In the feeding experiment (B) the high temperature and humidity in the germination cabinet produced considerable mold on the roots of the germinating barley and it is very probable that the mold degraded some of the radioactive tryptophan to formyl kynurenine (X) which would serve as a source of radioactive formate (cf. 5 for review of this degradation). Work is at present being carried out in order to determine whether formate is utilized by the sprouting barley for the production of the N-methyl groups of




X

gramine. In the feeding experiments (C) the seeds were dusted with a mercury fungicide which delayed the formation of mold on the seed envelopes.

## EXPERIMENTAL[4]

*Indole-2-$C^{14}$*

$C^{14}$-Sodium formate (total activity $2.75 \times 10^8$ disintegrations per min., 4.92 mgm.) was shaken in a 50 ml. flask with *o*-toluidine hydrochloride (10.0

[4] *All melting points are corrected.*

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mgm.) and freshly distilled *o*-toluidine (2.40 gm., 2.22 millimoles) on a steam bath. After about one minute, inactive 99% formic acid (0.92 gm., 2.00 millimoles) was added and the mixture heated at 100° in an atmosphere of dry nitrogen for 12 hr. The amber colored liquid was then cooled and treated with 1% hydrochloric acid which caused the crystallization of formyl-*o*-toluidine. It was washed with water and dried *in vacuo* (2.2225 gm., yield 82.5%). Potassium (1.1 gm.) was added to tertiary butyl alcohol (20 ml.) in a 3-necked 100 ml. flask and the mixture warmed in an atmosphere of dry nitrogen until the potassium had all dissolved. The formyl-*o*-toluidine was then added and the excess tertiary butyl alcohol distilled off and the residue heated slowly in a metal bath to 350–360°. After 15 min. all effervescence had ceased and the reaction mixture was cooled. Water was added and steam passed in to steam distil the indole-2-$C^{14}$ which was collected in a cooled receiver as silvery white leaflets (0.6081 gm., yield 31.4%). It had a specific activity of $1.37 \times 10^7$ disintegrations per minute per millimole.

*Degradation of Indole-2-$C^{14}$*

A small quantity of active indole was diluted with inactive indole (2.0 gm.) to give a sample with a specific activity of $2.30 \times 10^5$ disintegrations per minute per millimole. This sample was dissolved in dry 1-methylnaphthalene (20 ml.) and sodium (0.8 gm.) was added to the solution which was stirred in an atmosphere of dry nitrogen for five hours at 190–200° (metal bath). The mixture was allowed to cool and the brown sodio-indole filtered off and washed with dry benzene. The sodio-indole was then suspended in dry cooled benzene (20 ml.) and benzoyl chloride (2.0 ml.) added to the suspension which was refluxed for two hours. The resulting pale brown solution was filtered and methanol added to the filtrate to destroy the excess benzoyl chloride. The solution was distilled under diminished pressure and the fraction, b.p. 200–230° at 20 mm., collected (1.30 gm.). This fraction, a pale yellow viscous oil, was dissolved in an equal volume of ethanol and the resulting solution on cooling deposited N-benzoylindole as colorless microscopic prisms, m.p. 66–68° (0.580 gm.). The literature records m.p. 67–68° (20). It had a specific activity of $2.23 \times 10^5$ disintegrations per minute per millimole.

This N-benzoylindole (0.400 gm.) was dissolved in acetone (50 ml.) and finely powdered potassium permanganate (1.00 gm.) was added to the stirred solution at room temperature. After five hours the acetone was removed *in vacuo* and the residue dissolved in warm water, the solution filtered, and the pale yellow filtrate treated with hydrochloric acid when a white precipitate of benzoylanthranilic acid was obtained. Crystallization from aqueous ethanol gave fine colorless needles, m.p. 181–182° (0.086 gm.), not depressed by admixture with authentic benzoylanthranilic acid obtained from anthranilic acid and benzoyl chloride. On assay for radioactivity it was found to be completely inactive.

*dl-Tryptophan-2-$C^{14}$ and dl-Tryptophan-β-$C^{14}$*

These labelled amino acids were obtained by known methods for the synthesis of tryptophan on a small scale (1, 7, 13). Use of indole-2-$C^{14}$ in the syn-

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thesis gave tryptophan-2-$C^{14}$ while $C^{14}$-formaldehyde gave tryptophan-$\beta$-$C^{14}$ (2).

*Growth of the Barley and Administration of the Tracer*

In each of the feeding experiments (B) and (C) 720 gm. of barley (Charlottetown No. 80) was grown as previously described (2). In experiment C the barley seeds were dusted with a commercial fungicide, Semesan (manufactured by Bayer Co. Inc., New York), the active principle of which is hydroxymercurichlorophenol. This delayed the formation of mold on the seed envelopes. Before administering the tracer, the germinating barley which was matted together at the roots was taken out of the glass tray in which it was growing, shaken slightly to remove ungerminated barley seeds, and then placed in a clean tray containing a solution of the radioactive tryptophan. Details of the quantities of tryptophan fed to the plant are given in Table II. The procedure was to dissolve the active tryptophans in separate solutions, assay them, and then mix them in order to obtain accurately the ratio between the activities in the 2- and $\beta$-positions of the tryptophan actually fed to the barley[5]. The tryptophan (as the acetate with one molecule of acetic acid of crystallization) was fed to the barley as a solution in 600 ml. of distilled water.

*Isolation of the Gramine from the Plant*

The gramine was isolated from the dried leaves as previously described (2), and the weights and activities of the various fractions are summarized in Table III.

TABLE III
WEIGHTS AND ACTIVITIES OF EXTRACTS

| Fraction (from 720 gm. of barley) | Experiment B | | Experiment C | |
|---|---|---|---|---|
| | Wt., gm. | Activity, disintegration per min. per mgm. | Wt., gm. | Activity, disintegration per min. per mgm. |
| Dried leaves | 68.8 | — | 54.6 | — |
| Methanol extract of leaves | 26.2 | 3.8 | 23.0 | 35 |
| Crude gramine | 0.3925 | 18.6 | 0.3293 | 425 |
| Gramine (distilled and crystallized from benzene) | 0.1721 | 45 | 0.1276 | 563 |

*Degradation of the Gramine from the Plant*

The number of degradations that could be carried out with the gramine from experiment B was limited by the low activity and the alkaloid was not

[5] *It was deemed advisable to use a mixture of tryptophan labelled in the 2-position and tryptophan labelled in the β-position rather than tryptophan-2-β-$C^{14}$. In such a mixture the ratio of $C^{14}$ in the 2-position to $C^{14}$ in the β-position is much more accurately known than the same ratio in the doubly labelled tryptophan-2-β-$C^{14}$.*

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diluted. It was degraded to 3-ethoxymethylindole and ethyldimethylamine according to known procedures (2) (see Table II). The gramine from experiment C was diluted with 0.400 gm. of inactive gramine and degradations were carried out with this material.

(a) *Self Condensation of 3-Ethoxymethylindole*

3-Ethoxymethylindole (0.100 gm.) obtained from the gramine as described previously (2) was refluxed with 10% sodium hydroxide (20 ml.) for one hour. After cooling, the reaction mixture was filtered and the insoluble material crystallized from benzene. The product consisted of small colorless prisms, m.p. 161–162° (0.055 gm.) not depressed in admixture with 3,3′-di-indolylmethane (10).

(b) *Degradation to N-Benzoylanthranilic Acid*

The gramine was fused with potassium hydroxide as previously described (2) and the indolyl-3-carboxylic (m.p. 209°, S-benzyl-iso-thiouronium salt, m.p. 157.5°) decarboxylated to indole which was converted to the picrate (m.p. 187°, undepressed in admixture with an authentic specimen) and carbon dioxide which was absorbed in barium hydroxide. The indole recovered from the picrate was converted to N-benzoylindole and oxidized to benzoylanthranilic acid as described above. Whereas both the indole and barium carbonate were active, the last product was inactive showing that all the activity in the indole nucleus resided in the 2-position.

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# BETATRON IRRADIATION OF AQUEOUS CERIC SULPHATE SOLUTION[1]

By R. W. Hummel[2], A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

Ceric ions, from ceric ammonium sulphate dissolved in aerated 0.8 *N* sulphuric acid solution, are reduced by $Co^{60}$ $\gamma$-rays and betatron X-rays of 23 Mev. peak energy. *G* values were calculated on the basis of calculated electron distributions.

## INTRODUCTION

Solutions of ceric ammonium sulphate in 0.8 *N* sulphuric acid have been recommended as chemical dosimeters for ionizing radiations (18), in particular for radiations of high intensity. In such cases the ferrous sulphate dosimeter is unsuitable owing to the decreased rate of ferrous ion oxidation after the oxygen concentration of the solution has been depleted (about 60 kiloroentgens). For ceric sulphate solutions the *G* value (the number of ceric ions reduced per 100 ev. absorbed) is independent of the oxygen concentration and of the rate of energy absorption from 0.37 to 2170 kiloroentgens per hour (8). The yield appears to be energy dependent at X-ray energies below about 300 KVP, but is energy independent from there up to the energy of $Co^{60}$ $\gamma$-rays (9). The energy dependence at low energies has been related (9) to an increased specific ionization per unit of energy dissipated by secondary electrons.

The present investigation was carried out to study the usefulness of the system for chemical dosimetry and to extend the maximum of the energy range over which it has been studied.

## EXPERIMENTAL PROCEDURE

Ceric ammonium sulphate (G. Frederick Smith) was dissolved in 0.8 *N* sulphuric acid to make an approximately $1.9 \times 10^{-4}$ *M* solution. (It has been shown (8) that the yield is independent of concentration from $10^{-2}$ *M* to $2 \times 10^{-5}$ *M*). The water was prepared by distilling tap water, first in an all-Pyrex apparatus from alkaline permanganate solution, then in an all-Pyrex apparatus from alkaline manganous hydroxide suspension, and finally from a Pyrex still into a silica condenser and receiver. The c.p. sulphuric acid was distilled from a dichromate solution (1). Fresh ceric ion solutions were prepared for each run the day before they were to be used. All glassware was Pyrex and was cleaned before use with hot chromic acid solution, followed by multiple rinses with tap water and triple-distilled water. In order to forestall any erratic results due to chemical effects by the radiations on untreated tubes, and also as an aid in removing oxidizable impurities, the tubes used for the irradiations were, in addition, filled with distilled water the day before use and placed around a 1-curie $Co^{60}$ source in a lead castle. After removal from the castle they were cleaned with hot chromic acid solution, rinsed, and dried in an air

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oven. For irradiations with $Co^{60}$ $\gamma$-rays, 3-ml. aliquots of ceric ion solution were used; for irradiations with betatron X-rays, 2-ml. aliquots were used.

Optical density measurements were made on a Beckman Model DU spectrophotometer, using silica cells and a hydrogen lamp. The molar extinction coefficient of ceric ammonium sulphate in 0.8 *N* sulphuric acid at 3300 Å was found to be $5314 \pm 22$, where the latter figure is the standard deviation. Measurement of the ceric ion concentration prior to an extinction coefficient determination was carried out by adding varying aliquots of ceric ammonium sulphate solution to constant aliquots of a ferrous sulphate solution and finding the optical density at 3040 Å where only ferric ions absorb. The molar extinction coefficient for ferric ion in 0.8 *N* sulphuric acid at $24 \pm 2$°C. was $2213 \pm 9$. This was checked by irradiating a ferrous ammonium sulphate solution to complete oxidation, determining the ferric ion concentration using the coefficient, and comparing it with the initial ferrous ion concentration found using orthophenanthroline (extinction coefficient $11550 \pm 30$ at 5100 Å). The difference was less than 1%.

The optical densities of irradiated ceric ion solutions were found using the original solution as the 'blank'. For ferric ion measurements 0.8 *N* sulphuric acid was the blank.

Irradiations with the 1-curie $Co^{60}$ source were carried out in a lead castle. The source could be withdrawn into the top of the castle so that the samples, in $13 \times 100$ mm. Pyrex tubes, could be inserted. The tubes were placed in holes in a ring-shaped Lucite block. The block was located on a brass disc, short pegs on the disc coinciding with small holes in the bottom of the block. A shallow brass cup was soldered onto the center of the disc. After inserting the Lucite–brass assembly an aluminum source-holder could be lowered to fit snugly into the brass cup. The $Co^{60}$ was then above the rim of the cup with its center at the same height above the disc as the centers of the 3-ml. aliquots of solution. The details are shown in Fig. 1. Two Lucite blocks with different radii permitted measurements at dose rates of about 1.05 and 0.3 kiloroentgens per hour. Dose rates were determined initially with a Victoreen thimble chamber modified by replacing the Bakelite thimble by a Lucite thimble whose outer dimensions corresponded to 3.0 ml. of solution in a $13 \times 100$ mm. tube, and by replacing the central aluminum electrode by a longer one. This chamber was calibrated against recently calibrated* 25 r. and 100 r. Victoreen chambers using a 1100-curie $Co^{60}$ source with about 3 m. between source and chamber. Irradiation of ferrous ammonium sulphate solutions using the 1100-curie and 1-curie sources and the 100 r. Victoreen and modified Victoreen, respectively, gave the same *G* values. Thus, the geometry of the modified Victoreen appeared to be such as to give reasonably accurate dose rate values at 3 cm. from the 1-curie $Co^{60}$ source. Subsequent dose rate calculations were made using the decay constant for $Co^{60}$.

Irradiations with betatron X-rays were carried out in a rotating Lucite block described previously (12). A 100 r. Victoreen thimble chamber was used for dosimetry.

**Calibrations were checked at the National Research Council, Ottawa.*

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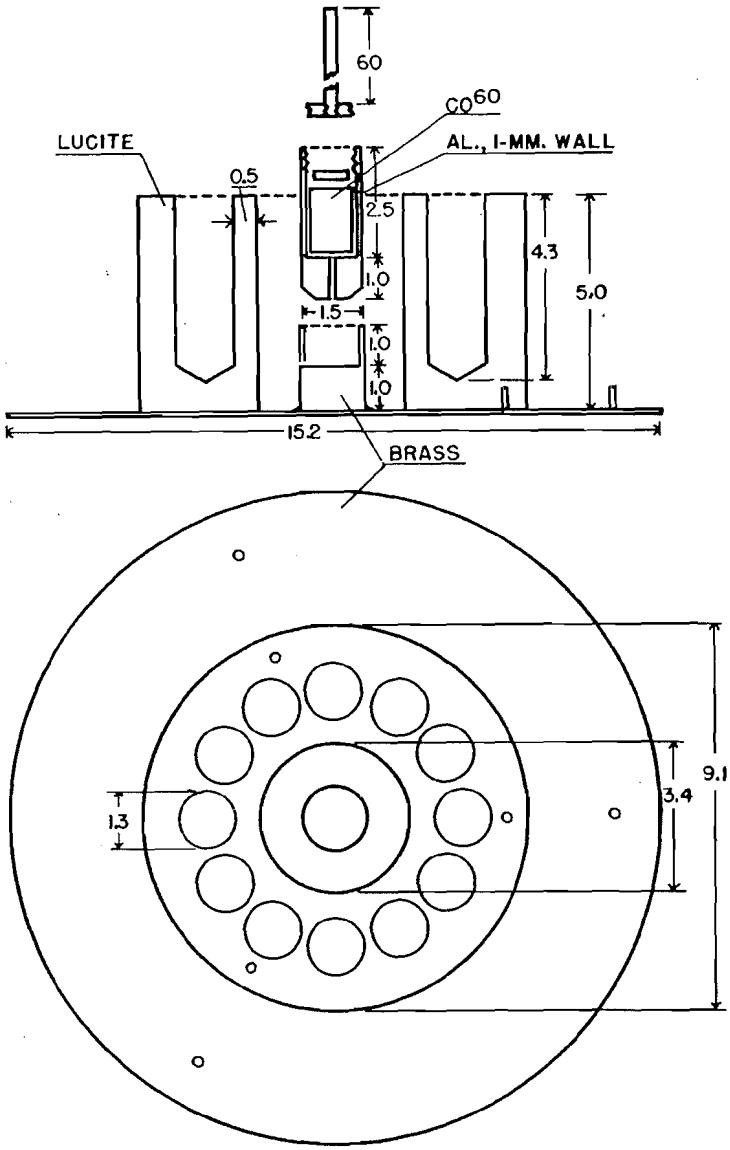



FIG. 1. Lucite block for irradiation with 1 curie $Co^{60}$ source (dimensions in cm.).

The construction of the Lucite block was such that the minimum thicknesses of Lucite between ionization chamber (or solution) and X-ray source were, for the outer and inner circles of holes, 1.5 and 3.0 cm., respectively. These thicknesses give about 75% and 92%, respectively, of the ionization obtained with the equilibrium thickness (about 4 cm.). Thus for part of the time electronic equilibrium did not exist at the points of measurement. However, experiments with ferrous sulphate solutions, in which the results obtained in the inner and outer circles were compared (12), indicated that the intermittent

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departure from electronic equilibrium was not of sufficient magnitude to be detectable by the techniques employed.

## ENERGY ABSORPTION CALCULATIONS

The energy absorbed per unit volume of a medium irradiated with X- or $\gamma$-rays has often been calculated from an expression due to Bragg (2) and Gray (6), which is: $E_v = J.W.\rho$

where $E_v$ = energy absorbed per unit volume of medium,
$J$ = ion pairs produced per unit volume in an "infinitesimal" air cavity in the medium,
$W$ = energy expended in producing an ion pair in air,
$\rho$ = ratio of stopping powers, of medium with respect to air, for electrons.

The factors $W$ and $\rho$ are usually considered to be energy independent.

In this treatment $W$ will be taken as 32.5 ev. (6) and $\rho$ will be taken as a function of energy, weighted according to a calculated distribution of primary electrons in the medium, so that

$$[1] \qquad E_v = J.W.\frac{n_z}{n_a}.\frac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}$$

where $n_z$ = electron density in the medium, in electrons per cm.$^3$,
$n_a$ = electron density in air, in electrons per cm.$^3$,
${}_eS_z^c(E)$ = stopping power of medium with respect to collisional energy losses by primary electrons, per electron of medium, at primary electron energy $E$ in Mev. cm.$^2$ per electron,
${}_eS_a^c(E)$ = same as ${}_eS_z^c(E)$, but for air,
$N_z(E)$ = number of primary electrons, with energies in a small interval about $E$, at a point in the medium.

Stopping powers were calculated from the Bethe-Bloch expression for the rate of energy loss by collisions by electrons passing through a medium. Account was also taken of the polarization properties of a medium, whereby the rate of energy loss by collisions is decreased, by multiplying the stopping powers of 0.8 $N$ sulphuric acid, calculated from the Bethe-Bloch equation, by the ratio of the modified stopping power of water to the unmodified value, at various energies, as taken from Fig. 3 of a paper by Halpern and Hall (7). The stopping powers of air were calculated from the Bethe-Bloch equation. There is no polarization effect in air at these energies.

The average excitation potential $\bar{I}$, which appears in the Bethe-Bloch equation, was taken as 45 ev. in 0.8 $N$ sulphuric acid and 97.6 ev. in air. The former value is the mean of two recent determinations, as quoted by Platzman (17). The latter was calculated as follows:

$$\bar{I} = k\bar{Z} = 13.5\bar{Z} \text{ ev.},$$

where $\bar{Z}$ is given by

$$\ln \bar{Z} = a_1 \ln Z_1 + a_2 \ln Z_2 + \ldots$$

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where $a_1$, $a_2$, etc., are the fractions of the total number of electrons which belong to atoms with atomic numbers $Z_1$, $Z_2$, etc.

For $Co^{60}$ $\gamma$-rays the number of primary electrons produced per unit energy interval per electron of material per photon per cm.$^2$ was calculated using the differential Klein-Nishina coefficient and the method given by Johns *et al.* (13). The number existing per unit volume at a given instant was obtained by multiplying by the electron density, and adding to those produced in a given energy interval the number degraded from high energy intervals. The number of primary electrons in a given energy interval occurring at a point in the medium was assumed proportional to the distance travelled by the electrons as they were degraded through that energy interval. These distances, $\Delta R$, were calculated by plotting the reciprocal of the total rate of energy loss, $(-dE/dx)^t$, in Mev. per cm., against the energy, $E$. The total rate of energy loss is the sum of the collisional and radiational losses, i.e.,

$$\left(-\frac{dE}{dx}\right)^t = \left(-\frac{dE}{dx}\right)^c + \left(-\frac{dE}{dx}\right)^r.$$

The collisional contribution was calculated from the Bethe-Bloch equation, modified as required by the polarization factors, while the radiational contribution was obtained from expressions given by Heitler (10). The range, $\Delta R$, was the area under the curve between the energies involved. For $Co^{60}$ radiations the energy interval was 0.1 Mev. while for betatron radiations the interval taken was 1 Mev.

For betatron X-rays of 24 Mev. peak energy, the number of primary electrons produced per cm.$^3$ of water per photon per cm.$^2$ for a range of initial electron energies and for photon energies from 0–25 Mev. have been tabulated by Cormack and Johns (4, Tables I and III). To find the number of primary electrons produced by the Compton process in a cm.$^3$ of 0.8 $N$ sulphuric acid, the values for water were multiplied by the ratio of electron densities. To find the number produced by the pair process in this material, the values for water were multiplied by the ratios of effective atomic numbers and electron densities. The effective atomic number of a material, for the pair production process, is found from the equation:

$$Z_{\text{eff.}} = a_1Z_1 + a_2Z_2 + \ldots + a_nZ_n,$$

where $a_1$ and $Z_1$, etc., have the same meanings as before. The numbers of Compton and pair electrons so obtained were on the basis of one photon per cm$^2$. They were multiplied by the photon flux obtained from Fig. 3 of a paper by Johns *et al.* (14), by dividing the values of the ordinates of the modified Schiff curve, in ergs per cm.$^2$, at given photon energies, by the photon energies. Tables were constructed giving the relative number of electrons produced per Mev. interval per cm.$^3$ of material at various photon energies. The relative numbers of electrons existing in any energy interval were then obtained by adding the contributions due to the various photon energies. The relative numbers of primary electrons occurring at a point were obtained as described above in the case of $Co^{60}$ radiations.

Having calculated ${}_eS^c(E)$ and $N_z(E)$ at all electron energies, the ratio in equation [1] could be calculated. It should be noted that $N_z(E)$ is the number of electrons in an energy interval, that $\Delta R$ is the range in that interval, and that ${}_eS^c(E)$ is taken at the middle of the interval.

The results of the calculations are given in Table I, where B.–B. refers to calculations based on the Bethe-Bloch equation, and H.-H. refers to those calculations modified by the factors taken from Halpern and Hall.

TABLE I
RESULTS OF ENERGY ABSORPTION CALCULATIONS

| Radiation source | Basis of calculation | $\dfrac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}$ | Relationship between energy absorption and Victoreen reading |
|---|---|---|---|
| Cobalt | B.-B. | 1.092 | $E_v = 6.50 \times 10^{13}\cdot V_r$ |
| Betatron | B.-B. | 1.075 | $E_v = 6.40 \times 10^{13}\cdot V_r$ |
| | H.-H. | 1.042 | $E_v = 6.20 \times 10^{13}\cdot V_r$ |

The relationships in Column 3 of Table I were obtained by taking $J = 2.082 \times 10^9$ ion pairs/cm.$^3$/r. $\times V_r$, where $V_r$ is the Victoreen meter reading in r. (roentgens), corrected for temperature and pressure, so that Equation [1] becomes:

$$E_v = 2.082 \times 10^9 \cdot V_r \cdot 32.5 \cdot \frac{3.42 \times 10^{23}}{3.888 \times 10^{20}} \cdot \frac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}$$

$$= 5.952 \times 10^{13} \cdot V_r \cdot \frac{\sum_E {}_eS_z^c(E)\cdot N_z(E)}{\sum_E {}_eS_a^c(E)\cdot N_z(E)}.$$

## RESULTS

The results of irradiations of $1.9 \times 10^{-4}\,M$ ceric ammonium sulphate solutions are given in Table II. Values of $G$, the number of ceric ions reduced per 100 ev. absorbed in the solution, are given on the basis of the two sets of calculations described above. Yields are also given in terms of the number of micromoles reduced per liter of solution per kiloroentgen as measured with the Victoreen.

Application of the equations in Table I to experimental results obtained with ferrous ammonium sulphate solutions in 0.8 $N$ sulphuric acid gave, for $Co^{60}$ $\gamma$-rays, $G(Fe) = 15.8 \pm 0.2$, and for betatron X-rays $G(Fe) = 15.5 \pm 0.4$ (B.-B.) or $15.9 \pm 0.4$ (H.-H.). The ratios of these results to the results of ceric solution irradiations are given in Table III, together with recent results reported in the literature.

The deviations from the means in Table II and III are, for the present work, in terms of the standard deviations, $(\sigma)(n - 1$ degrees of freedom). The devi-

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TABLE II
RESULTS OF IRRADIATIONS OF CERIC AMMONIUM SULPHATE SOLUTIONS

| Radiation | Expt. No. | Yield | | |
|---|---|---|---|---|
| | | $G$ | | $\mu$M./l./1000 $V_r$ |
| | | B.-B. | H.-H. | |
| $Co^{60}$ $\gamma$-rays | 1 | 2.65 | — | 2.86 |
| | 2 | 2.70 | — | 2.92 |
| | 3 | 2.60 | — | 2.82 |
| | 4 | 2.66 | — | 2.87 |
| | Mean | 2.65 ± 0.04 | — | |
| Betatron X-rays | 1 | 2.69 | 2.77 | 2.84 |
| | 2 | 2.51 | 2.59 | 2.67 |
| | 3 | 2.50 | 2.58 | 2.66 |
| | 4 | 2.49 | 2.57 | 2.65 |
| | Mean | 2.55 ± 0.09 | 2.63 ± 0.09 | |

TABLE III
RATIOS OF RESULTS WITH FERROUS AND CERIC SOLUTIONS

| | $G$(Fe)/$G$(Ce)* |
|---|---|
| Present work, $Co^{60}$ | 15.8 ± 0.2/2.65 ± 0.04 = 5.96 ± 0.12 |
| Present work, betatron (B.-B.) | 15.5 ± 0.4/2.55 ± 0.09 = 6.08 ± 0.27 |
| Present work, betatron (H.-H.) | 15.9 ± 0.4/2.63 ± 0.09 = 6.05 ± 0.25 |
| Hardwick (8), $Co^{60}$ | 20.8 ± 0.3/3.30 ± 0.03 = 6.30 ± 0.11 |
| Hochanadel and Ghormley (11), $Co^{60}$ | 15.6 ± 0.3/2.52 ± 0.05 = 6.19 ± 0.17 |
| Weiss (18) | 5.96 ± 0.03 |

**All G values in Table III were calculated on the basis of 32.5 ev. expended per ion pair formed in air except those of Hardwick which were based on 31.9 ev.*

ations of the $G$ value ratios, except for Weiss's, were obtained from the expression (5):

$$\rho = \pm 1/G(\mathrm{Ce}) \sqrt{\sigma^2(\mathrm{Fe}) + \left\{\frac{G(\mathrm{Fe}) \cdot \sigma(\mathrm{Ce})}{G(\mathrm{Ce})}\right\}^2}.$$

## DISCUSSION

Ceric ammonium sulphate solutions are not suitable as dosimeters for low intensity $\gamma$-ray and X-ray beams owing to the relatively low yield. For beams of high intensity the low yield may be an advantage, but this has to be balanced against the precautions which must be taken if consistent results are to be obtained. The details concerning the preparation of ceric sulphate solutions as given under *Experimental Procedure* are only an indication of the difficulties involved. Miller and Wilkinson (16) have commented recently on this disadvantage.

Application of the "Student's $t$" test (19) to the mean values given in Table II shows that, based only on the Bethe-Bloch equation, the means obtained with $Co^{60}$ and betatron radiations are not significantly different at the 95% level of significance (6 degrees of freedom), and that the means based on application of the correction factors from Halpern and Hall are essentially the same.

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It may, therefore, be inferred that energy yields ($G$) for ceric sulphate in 0.8 $N$ sulphuric acid solutions are energy-independent in the range covered, and that the pulsed nature of the betatron beam (a 4 $\mu$sec. pulse 180 times per second) is not an important factor.

It should be kept in mind that the calculations carried out here are based on the primary electron distribution in 0.8 $N$ sulphuric acid and on the distribution in an infinitesimal air cavity in the solution such that the distribution is unaltered. Actually, the ionization measurements were done with Victoreen thimble chambers. Experiments reported elsewhere (3) indicate that the error involved probably does not exceed 2 or 3%. Our results (Table III) are therefore much more in accord with those of Hochanadel and Ghormley (11), $G(Fe) = 15.6$, $G(Ce) = 2.52$, than with those of Miller (15), $G(Fe) = 20.3$, and Hardwick (8), $G(Fe) = 20.4$, $G(Ce) = 3.2$. All these $G$ values are based on 32.5 ev. expended per ion pair formed in air.

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# THE STRUCTURE AND GRIGNARD REACTION OF THE β-AMINOCROTONONITRILE[1]

By Jaspar J. Conn[2] and Alfred Taurins

ABSTRACT

The ultraviolet absorption spectra of the low and high melting forms of β-aminocrotononitrile (I) provide evidence that both of them possess the same enamine structure. Since the existence of the polymorphic modifications of I must be excluded on the basis of the thermochemical behavior of I, the difference of the two modifications is capable of accounting for *cis* and *trans* isomerism, the low melting modification being the *cis* form, and the high melting modification being the *trans* form.

In the reaction of I with aromatic Grignard reagents β-amino ketones of the type $CH_3-CO-CH=C(NH_2)-R$ are formed as the main reaction products.

The free radical mechanism of the formation of I is postulated.

## INTRODUCTION

The treatment of acetonitrile (3) and propionitrile (7) with sodium in the absence of a solvent gives aminopyrimidine derivatives. However, in benzene solution sodium produces with acetonitrile the β-aminocrotononitrile (I) (9), and propionitrile gives 3-amino-2-methyl-2-pentenenitrile (II) (10, 11). The same type of condensation occurs between acetonitrile and aromatic nitriles (11, 13, 14, 16), or higher aliphatic nitriles (15, 18).

von Meyer (13) obtained I in the form of two crystalline modifications: the low melting (52–53°) modification having the higher solubility in benzene, and the high melting (79–83°) modification having the lower solubility in benzene. von Meyer postulated the ketimine–enamine tautomerism of this substance. However, he did not give any proof of this idea. Although I is a versatile reagent in organic synthesis, the structure of the two modifications of I is not known as yet.

The objective of this work was twofold: firstly, to study the properties of I to elucidate the nature of the two modifications, and secondly, to find out whether the Grignard reaction of I could serve as a preparative method for the synthesis of β-amino ketones.

## DISCUSSION

### *Mechanism of Formation*

The chemical equations of the formation of I from acetonitrile and sodium, as they were given by von Meyer (10) and Holtzwart (9) did not represent a detailed mechanism of the reaction. Therefore we propose a new mechanism of formation of β-aminocrotononitrile involving free radical intermediates (Chart I). In the primary interaction a free methyl radical is formed. The free methyl radical extracts a hydrogen atom from the second molecule of aceto-

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*Presented before the 35th Annual Conference of the Chemical Institute of Canada, June 3, 1952, Montreal, Que.*

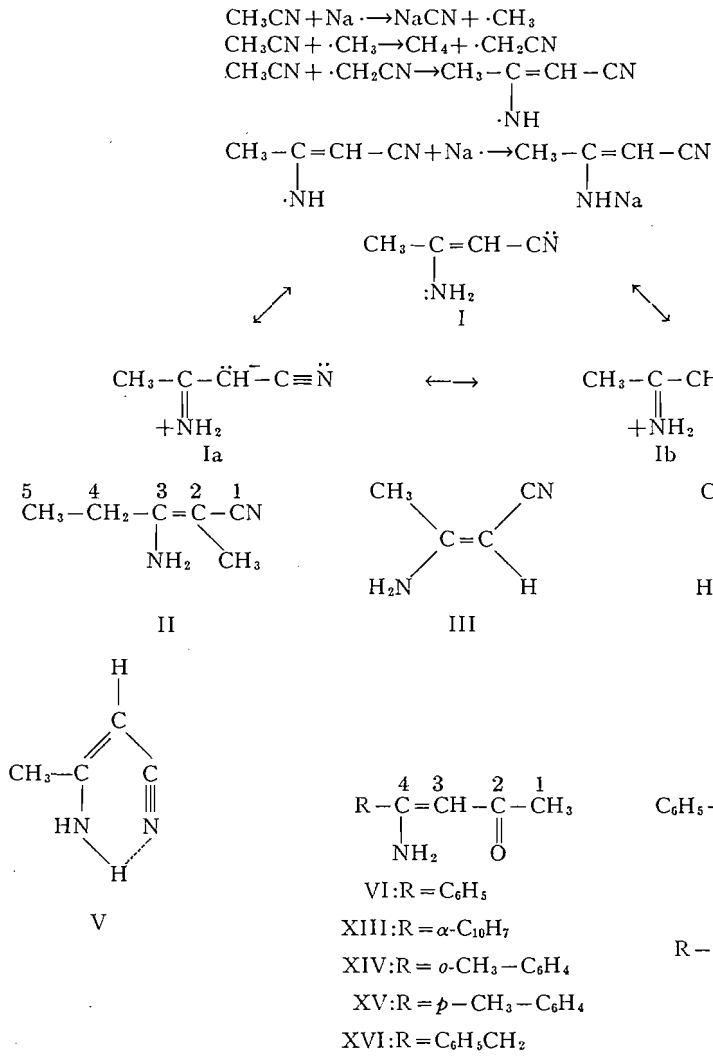
[2] *Holder of a National Research Council Fellowship 1950–1951.*



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CHART I

FREE RADICAL MECHANISM OF FORMATION OF I



nitrile, forming methane and the free $\cdot CH_2CN$ radical. This radical attacks the third molecule of acetonitrile to form the free $\beta$-aminocrotononitrile radical, which reacts with the second atom of sodium to produce the sodium salt of $\beta$-aminocrotononitrile. This mechanism could apply equally well to the reaction of other aliphatic nitriles with sodium in benzene solution.

*The Ultraviolet Absorption*

The ultraviolet absorption spectra of both the modifications of I were determined in absolute ethanol and acetonitrile in the region from 220 to 295 m$\mu$. In both solvents, the absorption curves were symmetrical with only

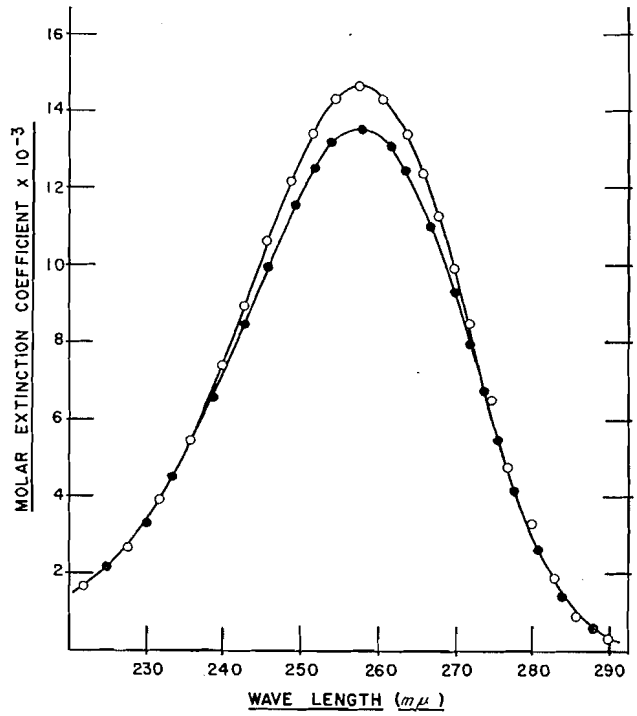
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one well defined maximum at almost the same wave length for both modifications (Table I), (Figs. 1 and 2).

The observed ultraviolet absorption indicates that both the modifications of I have identical electronic configuration when dissolved in polar solvents, and therefore the existence of the tautomeric forms of I must be excluded. The spectra are in accordance with the enamine structure of I, in which the

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA OF β-AMINOCROTONONITRILE

| | Absolute ethanol | | Acetonitrile | |
|---|---|---|---|---|
| | $\lambda_{max}$ | $\epsilon_{max}$ | $\lambda_{max}$ | $\epsilon_{max}$ |
| Low melting modification | 258 mμ | 13600 | 254.5 mμ | 12430 |
| High melting modification | 256 mμ | 14700 | 254.5 mμ | 13650 |




ULTRAVIOLET ABSORPTION SPECTRA

FIG.— 1

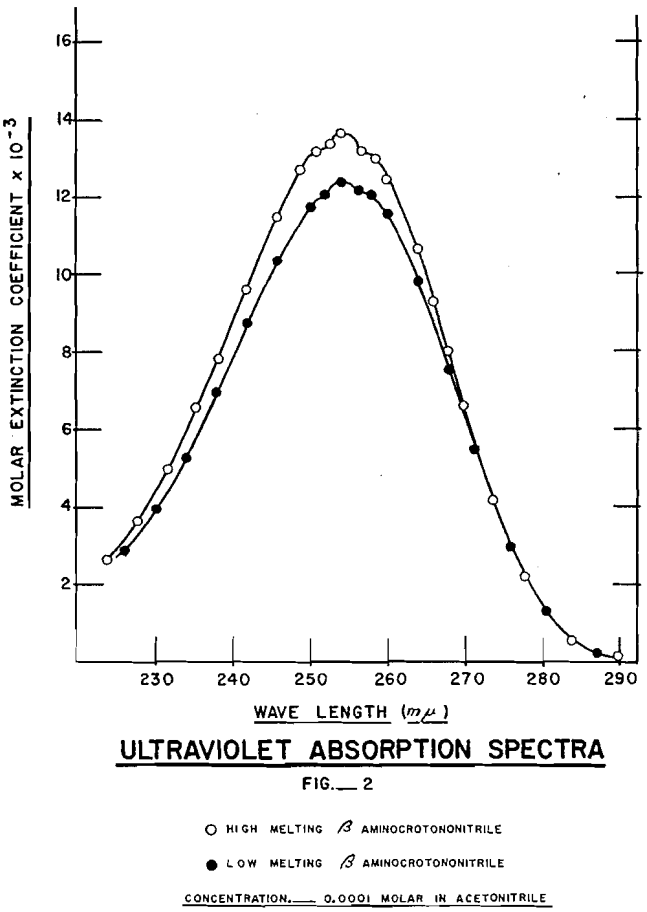
○ HIGH MELTING β AMINOCROTONONITRILE

● LOW MELTING β AMINOCROTONONITRILE

CONCENTRATION.— 0.0001 MOLAR IN ABSOLUTE ETHANOL

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conjugation of the carbon–carbon double bond and cyano group, and the interaction of the amino group gives rise to the molar extinction coefficients and the shift of the $\lambda_{max}$ towards the longer wave lengths, comparing the ultraviolet absorption of I with that of butyronitrile ($\lambda_{max}$ 180 m$\mu$) and acrylonitrile ($\lambda_{max}$ 250 m$\mu$) (4). The enamine form of I can exist as a resonance hybrid of three resonating structures I $\leftrightarrow$ I*a* $\leftrightarrow$ I*b*, two of them being ionic (I*a*, I*b*).

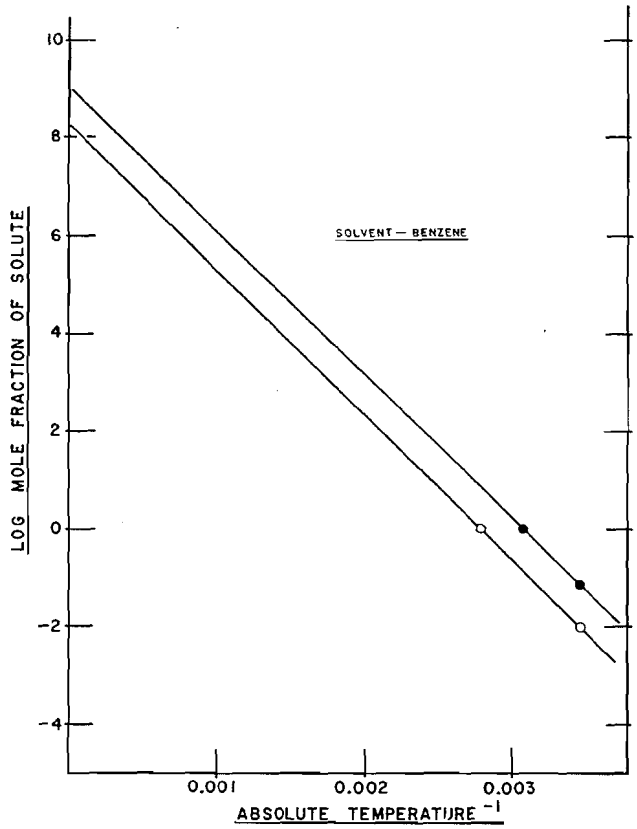



*Heats of Melting and Solution*

It is known that in an ideal solution, the heat of solution of a solid is identical with its heat of melting at the same temperature (17).

Rough values for the heats of melting of the two modifications of I are therefore given by the heats of solution of the two modifications in benzene, assuming ideal conditions for the solutions. Knowing the melting points of the two modifications, and their solubilities at 16.5°, it is possible to obtain the solubility curves for the two modifications. The plot of the mole fraction versus the inverse of the absolute temperature is a straight line (Fig. 3). The

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**SOLUBILITY RELATIONSHIP**

FIG. 3

○ HIGH MELTING β AMINOCROTONONITRILE

● LOW MELTING β AMINOCROTONONITRILE

heats of solution are obtained by multiplying the intercept by the term 2.303 *RT*. It is found that the values of the heats of solution of the two modifications, at the melting point, are identical within experimental limits of error (Chart III). It is quite safe to assume that the heats of melting of the two modifications will be of the same order of magnitude, and almost identical to each other.

CHART III

CALCULATION OF HEATS OF SOLUTION AND HEATS OF FUSION OF β-AMINOCROTONONITRILE MODIFICATIONS

Data for solubility curves of benzene solutions of β-aminocrotononitrile

Low Melting Modification:

Solubility at 289.5°A. = 8.57 gm./100 gm. of benzene.
Mole fraction of solute = 0.0755.
Log mole fraction = −1.122.
Inverse of absolute temperature = 0.00346.
Melting point = 325°A.
Inverse of absolute temperature = 0.00308.
Log mole fraction = 0.0.

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High Melting Modification:

Solubility at 289.5°A. = 1.22 gm./100 gm. of benzene.
Mole fraction of solute = 0.0115.
Log mole fraction = −1.939.
Inverse of absolute temperature = 0.00346.

Melting point = 352–357°A.
Inverse of absolute temperature = 0.00280.
Log mole fraction = 0.0.

Intercept for *High Melting Modification* = 9.10.
Heat of solution = 9.10 × 4.576 × 325 = 13,500 cal./mole.

Intercept for *Low Melting Modification* = 8.22.
Heat of solution = 8.22 × 4.576 × 357 = 13,600 cal./mole.

The heats of melting of enamine and ketimine tautomers would not be identical, with the result that such tautomers are ruled out as possible structures for the two modifications of I.

*Polymorphic Modifications*

The possibility of the two modifications of I being polymorphic modifications has been considered.

Enantiotropic polymorphism demands the existence of a transition temperature, above which one modification would be stable and the other modification would be reversed (8). That means that the two forms should be entirely interconvertible at some temperature below their melting points. Also, there should be only one melting point for the compound. No such transition temperature has been found for I, the lower melting modification being the stable modification at all temperatures. Both forms have definite melting points. These lines of evidence rule out the existence of enantiotropic polymorphism of I.

Monotropic polymorphism appears to be a likely possibility at first. Such polymorphism demands the existence of an imaginary transition temperature, that is, one which is above the melting points of the two modifications (8). One modification would be stable, and the other would be metastable at all times. There would be two melting points, one for each modification. Such stability and the two melting points were found in the case of I. However, the order of stability is the reverse of the expected one. The lower melting modification, if it is a polymorph of the monotropic type, should be the metastable form and should spontaneously transform into the higher melting modification. Investigation of the I has shown that the low melting modification is the more stable of the two modifications, and that the direction of transformation is from the high melting form to the low melting form. In addition, the heats of fusion of polymorphic modifications have been found to differ greatly. Because the heats of fusion of the two modifications of I were found to be nearly identical, the existence of monotropic polymorphism has been ruled out.

*Cis and Trans Isomerism of I*

Since the two possibilities to explain the existence of two modifications of I were excluded as a result of the present investigation, we propose that these

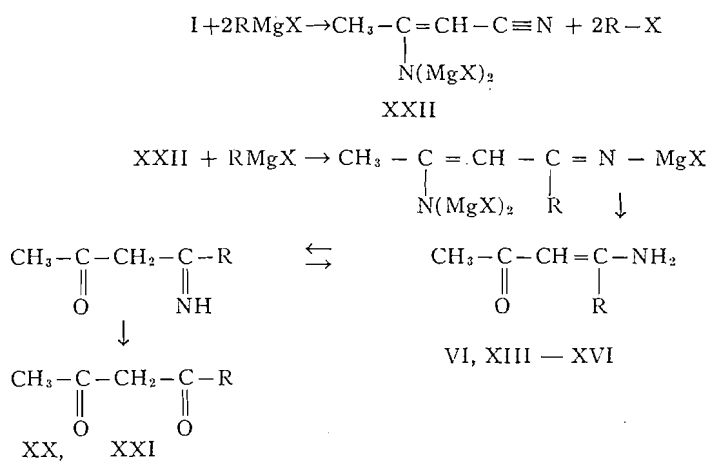
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modifications are *cis* and *trans* isomers. The high melting form (79–83°) has been given the *trans* structure (III) by virtue of its higher melting point and lower solubility. The low melting form (52–53°) has been given the *cis* structure (IV) on the basis of its lower melting point and higher solubility. In the *cis* form, the amino and cyano groups are in adjacent positions, and can form an internal hydrogen bond (V), which would make the *cis* form more stable than the *trans* isomer. This means that irradiation of the lower melting form with ultraviolet light would not cause any transformation of the molecule into the higher melting form. The additional ionic structures I*a* and I*b* could influence the crystallization of I from organic solvents. From a nonpolar solvent, like benzene, both modifications can be easily crystallized without any changes. However, crystallization of these modifications from a polar solvent, like ethanol, produce only the low melting form. The explanation of this behavior is that in polar solvents, the contribution of the ionic structures I*a* and I*b* to the resonance hybrid would be greater than in a nonpolar solvent. The structures I*a* and I*b* do not possess the double bond of the enamine system, permitting the free rotation about the single bond between the $\alpha$- and $\beta$-carbon atoms, and consequently, the change of the unstable modification into the stable one.

*The Grignard Reaction*

The Grignard reaction of I starts in the amino group by substituting both

GRIGNARD REACTION OF I

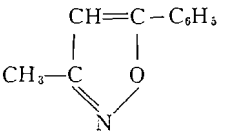



of the hydrogen atoms by the MgX groups and the formation of two hydrocarbon molecules (15). Only if the threefold excess of the Grignard reagent is used the nitrile group is also attacked. In the reaction of I with aromatic Grignard reagents substituted $\beta$-amino ketones (VI, XIII–XVI), and $\beta$-diketones were isolated as the final reaction products in varying yields.

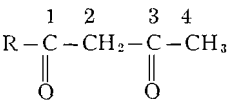
Phenylmagnesium bromide and I gave the 4-amino-4-phenyl-3-butene-2-one (VI). The structure of VI was evidenced by the fact that it gave with hydroxylamine hydrochloride 3-methyl-5-phenylisoxazole (IX) (6). The latter

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CHART II

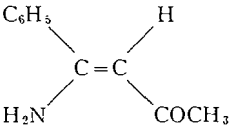


IX

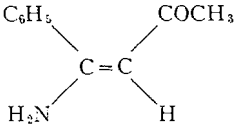


XX: R = $C_6H_5$

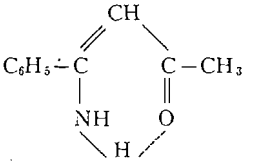
XXI: R = $\alpha$-$C_{10}H_7$



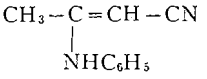
X



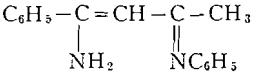
XI



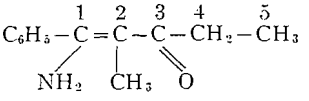
XII



XVII



XVIII



XIX

compound could only be formed if the N=OH group, and therefore the carbonyl group of the $\beta$-amino ketone, was adjacent to the methyl group. As further proof of the position of the carbonyl group in VI, the $\beta$-phenylaminocrotononitrile (XVII) was reacted with phenylmagnesium bromide. The main reaction product was 1-amino-1-phenyl-3-phenylimino-1-butene (XVIII) which on hydrolysis with 75% sulphuric acid produced 4-amino-4-phenyl-3-butene-2-one (VI).

The VI isolated in this investigation was an oil, boiling at 70–80° at 1 mm. of pressure. The boiling point of VI was not in agreement with physical properties of the two isomer amino ketones prepared by Claisen (5). The latter compounds were 4-amino-4-phenyl-3-butene-2-one, melting point 86–87°, and 3-amino-1-phenyl-2-butene-1-one, melting point 143° (VIII).

The fact that two compounds have been identified as having the structure VI is believed to be due to the *cis–trans* isomerism, as shown by the formulae X and XI. The amino ketone, boiling point 70–80° at 1 mm., is assumed to be the *cis* form, because it has the lower melting point of the two known isomers. The substance, isolated by Claisen (5), is given the *trans* configuration. The *cis* isomer can be stabilized by the hydrogen bond (XII), as in the case of the enol forms of $\beta$-diketones.

The presence of the carbon–carbon double bond and exclusion of other possible structures for the obtained substance VI is evident from the following

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considerations. The failure of the VI to give a positive test with ferric chloride solution indicates that there is no enol formation. The β-ketimino ketone structure (VII) was also excluded, since this structure cannot form any resonance forms, contrary to β-amino ketone structure which is stabilized by resonating ionic forms (VI*a* and VI*b*).

In the reactions of aromatic Grignard reagents with I, 1-phenyl-1,3-butanedione (XX) and 1-α-naphthyl-1,3-butanedione (1) (XXI) were isolated in yields of 5–10%. It is evident that these β-diketones were formed by hydrolysis of the corresponding β-amino ketones, VI and XIII respectively.

The reaction of β-amino nitriles with Grignard reagents was extended to include the 3-amino-2-methyl-2-pentenenitrile (II). This substance gave with phenylmagnesium bromide 1-amino-2-methyl-1-phenylpentene-3-one (XIX).

## EXPERIMENTAL*

*Preparation of β-Aminocrotononitrile* (I) (13).

The main feature of the preparation of the two modifications of I is the decomposition of the sodium salt of I with water at different temperatures. The low melting modification is obtained if the decomposition of the salt is carried out at 30°. The preparation of the high melting modification requires the use of ice-cold water. In both cases I is extracted from the reaction mixture with ether. After the evaporation of ether at reduced pressure the crystalline residues are recrystallized from benzene.

Since both modifications of I did not show any difference in reactions with other substances, the low melting modification was only used in the study of the Grignard reaction of I.

*Ultraviolet Absorption Spectra*

Ultraviolet absorption spectra were obtained using a Beckman quartz spectrophotometer model DU. The solvents, ethanol and acetonitrile, were purified by the standard methods.

*Reaction of I with Phenylmagnesium Bromide*

Ten grams (0.15 mole) of I dissolved in 100 ml. of ether were added with stirring to a solution of 0.5 mole of phenylmagnesium bromide in 300 ml. ether over a period of 10 min. A dark oil separated from solution. The mixture was then refluxed for six hours.

(*a*) *4-Amino-4-phenyl-3-butene-2-one* (VI)

The Grignard complex was decomposed by the gradual addition of an ice-cold saturated aqueous ammonium chloride solution. The ether layer was separated and the aqueous solution was extracted with ether. The combined ether extract was dried and distilled under reduced pressure to yield VI as a light colorless oil, boiling at 70–80° at 1 mm. pressure. The yield was 5.0 gm. (20%).

*The 2,4-dinitrophenylhydrazone* of VI, crystallized from benzene as orange needles, melting point 241–242°.

* Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

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Anal. calc. for $C_{16}H_{15}N_5O_4$: C, 56.30; H, 4.40; N, 20.53%. Found: C, 56.28; H, 4.29; N, 20.40%.

*3-Methyl-5-phenylisoxazole* (IX).—A mixture of 0.5 gm. of VI, 0.5 gm. of hydroxylamine hydrochloride, and 2.0 gm. of potassium hydroxide in 5 ml. of water were refluxed for two hours. The reaction product IX was recrystallized from alcohol as white needles, melting at 67°, lit. (6) m.p. 67–68°.

Anal. calc. for $C_{10}H_9NO$: N, 8.81%. Found: N, 8.70%.

(*b*) *1-Phenyl-1,3-butanedione* (XX)

(*α*).—Following decomposition of the Grignard complex and extraction with ether, the alkaline aqueous solution was neutralized with hydrochloric acid and cooled. A precipitate of XX was removed by filtration and recrystallized from ethanol as white needles, melting at 60–61°; lit. (6). The yield was 1 gm. (5%).

(*β*).—The ether solution of the decomposed Grignard complex was repeatedly extracted with 20 ml. portions of saturated sodium bicarbonate solution until the aqueous portion was colorless. The bicarbonate solution was acidified with hydrochloric acid, and cooled in ice. The crystalline precipitate was recrystallized from ethanol as white needles, m.p. 60–61°. The yield was 2.0 gm. (10%).

*Reaction of hydroxylamine with XX.*—The XX was treated with hydroxylamine hydrochloride in a procedure similar to that described previously, and IX was obtained as white needles, m.p. 66–67°.

Anal. calc. for $C_{10}H_9NO$: N, 8.81%. Found: N, 8.72%.

*Reaction of I with α-Naphthylmagnesium Bromide*

Ten grams (0.15 mole) of I and 0.5 mole of α-naphthylmagnesium bromide were reacted in a procedure similar to that described in the reaction of phenylmagnesium bromide. The residue which was obtained by the evaporation of the ether extract was steam-distilled to remove naphthalene produced by the reaction of the Grignard reagent with the active hydrogen of I. Following the steam distillation, the residue was extracted with ether.

(*a*) *4-Amino-4-α-naphthyl-3-butene-2-one* (XIII)

The dried ether extract was distilled under reduced pressure, yielding 6.5 gm. (25.2%) of a light oil, boiling at 130–135° at 1 mm.

Anal. calc. for $C_{14}H_{13}NO$: N, 6.48%. Found: N, 6.30%.

*The 2,4-dinitrophenylhydrazone* of XIII was recrystallized from benzene as fine orange needles, m.p. 216–217°.

Anal. calc. for $C_{20}H_{17}N_3O_4$: C, 61.38; H, 4.35; N, 17.90%. Found: C, 61.44; H, 4.14; N, 17.61%.

*The semicarbazone* of XIII had the m.p. 213–214° (white plates from ethanol).

Anal. calc. for $C_{15}H_{16}N_4O$: N, 20.90%. Found: N, 20.76%.

*Reaction of hydroxylamine with* XIII gave 3-methyl-5-α-naphthylisoxazole (IX) as white plates crystallized from ethanol, m.p. 140–141°.

Anal. calc. for $C_{14}H_{11}NO$: N, 6.70%. Found: 6.82%.

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(*b*) *1-α-Naphthyl-1,3-butanedione* (XXI)

The ether extract of the decomposed Grignard complex was repeatedly extracted with saturated bicarbonate solution. The latter was neutralized with hydrochloric acid, and cooled. The precipitate was recrystallized from ethanol as fine prisms, melting at 107–108°. The yield was 1.5 gm. (5.8%).

Anal. calc. for $C_{14}H_{12}O_2$: C, 79.25; H, 5.66%. Found: C, 79.27; H, 5.60%.

*4-Amino-4-o-tolyl-3-butene-2-one* (XIV).—This substance was prepared from *o*-tolylmagnesium bromide and I. It was a light yellow oil, boiling at 40–50° at 4 mm. The yield was 2.5 gm. (11%).

*The 2,4-dinitrophenylhydrazone of* XIV, orange needles, melting at 162–163°.

Anal. calc. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.79; N, 19.72%. Found: C, 57.81; H, 4.25; N, 19.41%.

*4-Amino-4-p-tolyl-3-butene-2-one* (XV).—It was obtained in the reaction of *p*-tolylmagnesium bromide and I. XV was a yellow oil, distilling at 30–40° at 4 mm. The yield in several preparations varied from 2.5 to 3.2 gm. (11–15%).

*The 2,4-dinitrophenylhydrazone* of XV, fine red needles from benzene, m.p. 259–260°.

Anal. calc. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.79; N, 19.72%. Found: C, 57.62; H, 4.58; N, 19.65%.

*4-Amino-5-phenyl-3-pentene-2-one* (XVI).—This compound was synthesized from I and benzylmagnesium bromide. It was a yellow oil, distilling at 70–75° at 1 mm. The yield was 3.5 gm. (16%).

*The 2,4-dinitrophenylhydrazone* of XVI, orange needles from benzene, m.p. 146–147°.

Anal. calc. for $C_{17}H_{17}N_5O_4$: C, 57.46; H, 4.79; N, 19.72%. Found: C, 57.53; H, 4.78; N, 19.62%.

*1-Amino-1-phenyl-3-phenylimino-1-butene* (XVIII).—The reaction between 19.2 gm. of XVII and 0.75 mole of phenylmagnesium bromide in 400 ml. ether was carried out for 48 hr. The reaction mixture was decomposed with ammonium chloride solution and extracted with ether. After evaporation of ether the residue was distilled under reduced pressure. The first fraction, boiling at 50–80° at 3 mm., was aniline (3.5 gm.). Distillation was stopped at this point, and the residue was crystallized from alcohol. The XVIII formed yellow crystals, m.p. 85–86°. The yield was 6.5 gm. (12%).

Anal. calc. for $C_{16}H_{16}N_2$: C, 81.36; H, 6.78; N, 11.86%. Found: C, 81.59; H, 6.70; N, 11.75%.

Acid hydrolysis of XVIII with 75% sulphuric acid at 150–160° for one hour yielded VI, which was identified by its 2,4-dinitrophenylhydrazone, m.p. 241–242°. The hydrazone was also analyzed quantitatively.

Anal calc. for $C_{16}H_{15}N_5O_4$: C, 56.30; H, 4.40; N, 20.53%. Found: C, 56.22; H, 4.16; N, 20.26%.

*1-Amino-2-methyl-1-phenyl-1-pentene-3-one* (XIX).—In the reaction between 20.7 gm. of II and 0.6 mole of phenylmagnesium bromide in 400 ml. ether, 5.2 gm. (15%) of XIX was obtained as a light oil distilling at 80–90° at 8 mm.

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*The 2,4-dinitrophenylhydrazone* of XIX was crystallized from benzene as bright orange needles, m.p. 230–231°.

Anal. calc. for $C_{18}H_{19}N_5O_4$: N, 18.97%. Found: N, 18.68%.

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# INFRARED AND RAMAN SPECTRA OF TETRABROMOETHYLENE[1]

By F. E. Malherbe,[2] G. Allen,[3] and H. J. Bernstein

ABSTRACT

The infrared spectrum of liquid and dissolved tetrabromoethylene has been investigated from 3$\mu$–36$\mu$. The Raman spectrum has been obtained photographically in the liquid state and photoelectrically in solution and depolarizations measured. All of the fundamentals were observed except $\nu_4$, $\nu_7$, $\nu_{10}$, and $\nu_{12}$. The last two vibration frequencies are estimated by calculations from two different potential functions.

The infrared spectrum of dissolved and solid tetrabromoethylene has been obtained previously in the rock salt region of the spectrum (4). The Raman spectrum also has been obtained (9) in solution and as solid. Since it is now possible to investigate the infrared spectrum with CsBr optics and since the depolarizations of the Raman frequencies were not obtained previously reinvestigation of both spectra was considered to be worthwhile.

## EXPERIMENTAL

The tetrabromoethylene used was the product of Matheson, Coleman and Bell Inc., East Rutherford, New Jersey, m.p. 56.5°, b.p. 227° at 760 mm. Hg. The infrared spectra were obtained in solution and as a molten liquid, with CsBr, KBr, NaCl, and LiF optics in a Perkin Elmer 12C Infrared spectrometer. To obtain the spectrum of the liquid a preheated sample was introduced into a liquid cell kept hot in a furnace arrangement (1).

The Raman spectra with depolarizations were obtained photographically (24 hr. exposure) with the instrument previously described (2) and also electronically recorded with a grating Raman spectrometer with photomultiplier detector.* The great advantage in having the electronically recorded spectrum is that the spectrum is obtained in about one-half hour during which the tetrabromoethylene does not undergo photochemical decomposition to any appreciable extent. The spectrum was recorded photoelectrically for a 30% tetrabromoethylene in carbon disulphide solution with slits of 5 $cm^{-1}$. Peak intensities were measured and corrected for the spectral sensitivity of the photomultiplier tube (10). The depolarizations were obtained in a manner described by Stamm (11). In order to obtain the Raman spectrum of the liquid, heated water (60°C.) was circulated through a jacket enclosing the Raman tube. The results are shown in Table I and Fig. 1.

## DISCUSSION

Tetrabromoethylene belongs to the point group $D_{2h}$ for which the symmetry types and selection rules may be found in Herzberg (5). In the Raman spec-

[1] *Manuscript received August 27, 1953.*
*Contribution from the Division of Pure Chemistry, National Research Council, Ottawa. Issued as N.R.C. No. 3118.*
[2] *National Research Council Postdoctoral Research Fellow, 1950–1951.*
[3] *National Research Council Postdoctoral Research Fellow, 1952–1954.*
**This instrument was made by the White Development Co., Stamford, Connecticut.*



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TABLE I

THE VIBRATIONAL SPECTRUM OF TETRABROMOETHYLENE

| Raman | | | | Infrared | | | | | Assignment |
|---|---|---|---|---|---|---|---|---|---|
| Solution[a] | Relative intensity and depolarization[b] | Solid[c] | Liquid[d] | Solution[e] | Liquid[f] | Solid[g] | Solid | Gas[i] | |
| 144 (8) | (P) | 154 (2) | 144 ± 2 | | | | | | $\nu_3$ |
| 211 (8) | 21.5 (D) | 187 (2) | 208 ± 2 | | | | | | $\nu_6$ |
| 266 (16) | 100 (0.2) | 267 (5) | 265 | | | | | | $\nu_2$ |
| | | | | | 366 w. | | | | $\nu_{11} - \nu_2\ (B_{3u})$ |
| | | | | | 420 w. | | | | $\nu_{11} - \nu_6\ (B_{2u})$ |
| | | | | | 463 w. | | $h$ | | |
| 463 (0) | 3 (D) | 478 (00) | 464 | | | | | | $\nu_8$ |
| | | | | 498 w. | 494 w. | | | | 709 − 211 |
| | | | | 552 w. | 552 w. | 527 (10) | | | $\nu_9 - \nu_6\ (B_{3u})$ |
| | | | | 631 s. | 631 s. | 630 (2) | 630 s. | 632 s. | $\nu_{11}$ |
| | | | | 694 w. | 694 sh. | | 690 v.w. | | |
| | | | | 708 w. | 709 m. | 716 (8) | 711 w. | 707 m.s. | 847 − 144 |
| | | | | 747 w. | 745 w. | | | | |
| | | | | 766 s. | 767 s. | 763 (10) | 765 s. | 770 v.s. | $\nu_9$ |
| | | | | 778 sh. | 778 v.v.w. | | | 784 | $\nu_3 + \nu_{11}\ (B_{3u})$ |
| | | | | 817 w. | 817 w. | | 805 m. | 810 v.w. | |
| | | | | 847 w. | 847 m. | 843 (10) | 834 m. | 852 s. | $\begin{cases}709 + \nu_3 \\ \nu_6 + \nu_{11}\ (B_{3u})\end{cases}$ |
| | | | | 881 w. | 883 w. | 896 (6) | | | |
| 886 (5) | 9 (D) | 884 (3) | 880 | | | | | | $\nu_5$ |
| | | | | 904 v. | 903 w. | | | | $\nu_2 + \nu_9\ (B_{3u})$ |
| | 4 (P) | | 927 | | | | | | $2\nu_8$ |
| | | | | 943 w. | 944 w. | 954 (6) | | 943 m.w. | |
| | | | | 974 w. | 974 w. | | $h$ | | $\begin{cases}709 + \nu_2 \\ \nu_6 + \nu_9\ (B_{3u})\end{cases}$ |
| | | | | 998 w. | 997 w. | | | | $847 + \nu_3$ |
| | | | | 1028 w. | 1026 w. | 1012 (8) | | 1028 m. | $\nu_2 + \nu_9\ (B_{3u})$ |
| | | | | 1045 w. | 1045 w. | | | | $847 + \nu_6$ |
| | | | | 1110 v.w. | 1122 w. | 1113 (6) | | | $847 + \nu_2$ |
| | | | | | | 1296 (3) | | | |

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TABLE I (*Concluded*)

| Raman | | | | Infrared | | | | | Assignment |
|---|---|---|---|---|---|---|---|---|---|
| Solution[a] | Relative intensity and depolarization[b] | Solid[c] | Liquid[d] | Solution[e] | Liquid[f] | Solid[g] | Solid | Gas[i] | |
| 1513 (3) | 14 (0.7) | 1517 (3) | 1515 | | | | | | Fermi resonance of $\nu_1$ and $2\nu_9$ |
| | | | | | 1527 w. | | | | $\nu_5 + \nu_{11}$ ($B_{3u}$) |
| 1546 (4) | 21 (0.5) | 1546 (6) | 1547 | | | | | | Fermi resonance of $\nu_1$ and $2\nu_9$ |
| | | | | | 1733 w. | | | | 847 + $\nu_5$ |
| | | | | | 1756 | | [h] | | |
| | 5 (0.56) | | 1764 | | | | | | $2\nu_5$ ($A_{1g}$) |
| | | | | | 1788 | | | | |
| | | | | | 2216 | | | | 709 + $\nu_1$ ($B_{3u}$) |
| | | | | | 2265 | | | | $\nu_1 + \nu_9$ ($B_{3u}$) |
| | | | | | 2326 | | | | |
| | | | | | 2394 | | | | 847 + $\nu_1$ ($B_{3u}$) |

*w = weak, m = medium, s = strong, v = very, sh = shoulder.*

[a] *The results from reference (9).*

[b] *Tetrabromoethylene in carbon disulphide obtained with photoelectric instrument. The line at 266 cm.$^{-1}$ is taken to have intensity 100. The line at 144 cm.$^{-1}$ could not be measured because of grating ghost intensity.*

[c] *Reference (9).*

[d] *Obtained with photographic instrument in six hours.*

[e] *Carbon disulphide solution.*

[f] *Liquids were obtained in cells of different thickness so that the relative intensities have very little quantitative significance.*

[g] *The results from reference (4).*

[h] *Our results but these regions not investigated.*

[i] *Gas phase results obtained only in potassium bromide and sodium chloride regions.*

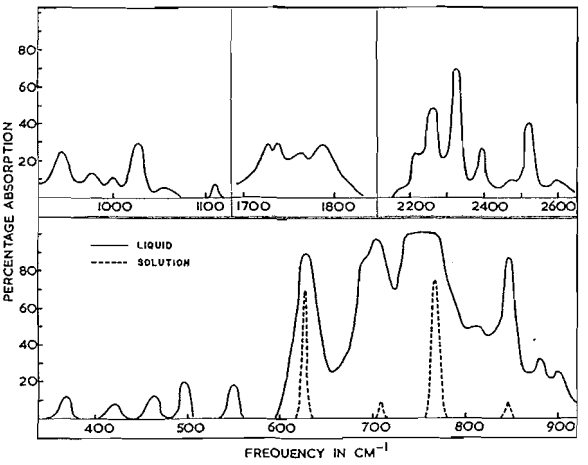



Fig. 1. The infrared spectrum of $C_2Br_4$; ———— liquid, – – – – – solution in $CS_2$.

trum there are six allowed fundamentals, three polarized Raman lines of type $a_{1g}$, two depolarized of type $b_{1g}$, and one depolarized of type $b_{2g}$. In the infrared spectrum there are five allowed fundamentals, two of type $b_{2u}$, two of type $b_{3u}$, and one of type $b_{1u}$. The torsion frequency of type $a_{1u}$ is forbidden in both spectra. The mutual exclusion selection rule for molecules with a center of symmetry is well observed in the case of this molecule as can be seen from the table, no coincidences of frequencies being observed in the infrared and Raman spectra. Since the Raman lines at 1547, 1515, 267, and 144 cm.$^{-1}$ have been found to be polarized it is natural to select them as the $a_{1g}$ vibrations describing approximately the C=C and C–Br stretching vibrations and the C–Br bending vibrations respectively. The doublet at 1547 and 1515 probably arises because of Fermi resonance (6) since the relative intensity of the two lines of the doublet changes from 1.5 in carbon disulphide solution to 2.1 in alcohol solution. It is probable that the energy levels of $2\nu_9$ and $\nu_1$ (see Table I) are sufficiently perturbed in alcohol solution so that the resonance interaction is different, giving rise to intensity changes. Of the other Raman frequencies 885 and 211 cm.$^{-1}$ are chosen as fundamentals because of their intensity; 464 cm.$^{-1}$ is also chosen as the frequency of a fundamental since the vibration is out-of-plane and expected to be lower than either 925 or 1760 cm.$^{-1}$ which are taken as overtones. By analogy with the assignment in tetrachloroethylene and incidentally a confirmation** of this assignment of the $b_{1g}$ frequencies in tetrachloroethylene, $\nu_5$ is chosen as 885 cm.$^{-1}$ and $\nu_6$ as 211 cm$^{-1}$. $\nu_8$, the $b_{2g}$ type frequency is then taken as 464 cm$^{-1}$.

In the infrared spectrum the dilute solution results show unequivocally that two of the fundamentals are at 767 cm.$^{-1}$ and 631 cm$^{-1}$. No other bands of appreciable intensity were observed down as far as 275 cm$^{-1}$. Our choice of

****It has been suggested that $\nu_5$ in tetrachloroethylene is 512 cm.$^{-1}$ (P. Torkington, Trans. Faraday Soc. 45: 445. 1949) rather than 1024 cm.$^{-1}$ (H. J. Bernstein, J. Chem. Phys. 18: 478. 1950). The strong line at 884 cm.$^{-1}$ in tetrabromoethylene indicates that the higher of the two should be taken for $\nu_5$ in tetrachloroethylene.**

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fundamentals for this molecule differs from that of Guy and Lecomte (4) who made their assignment from solid spectra data only, and chose the bands at 767 cm.$^{-1}$ and 840 cm.$^{-1}$ as fundamentals. Our dilute solution data indicate that 840 cm.$^{-1}$ is too weak to be a fundamental. In order to decide whether 767 cm.$^{-1}$ was of type $b_{2u}$ or $b_{3u}$, normal coordinate calculations were invoked using a potential function due to Morino, Kuchitsu, and Shimanouchi (8).

In reference (8) it is established that $\nu_5\nu_6 = 3.393\nu_9\nu_{10}$ if the CC and CBr internuclear distances are taken as 1.38Å and 1.91Å respectively and the BrCBr angle is 125°. Since $\nu_5$ and $\nu_6$ are reasonably well identified $\nu_{10}$ can be calculated if $\nu_9$ is known. So that for

$\nu_5 = 885$ cm.$^{-1}$, $\nu_6 = 211$ cm.$^{-1}$, and $\nu_9 = 767$ cm.$^{-1}$, $\nu_{10} = 72$ cm.$^{-1}$,

whereas for $\nu_9 = 631$ cm.$^{-1}$, $\nu_{10} = 87$ cm.$^{-1}$;

thus $\nu_{10}$ is a very low lying frequency in the vicinity of 80 cm$^{-1}$.

Using $\nu_5 = 885$ cm.$^{-1}$, $\nu_6 = 211$ cm.$^{-1}$, and $\nu_9 = 767$ cm.$^{-1}$

and $H_{CCBr} = H_{BrCBr} = 0.11 \times 10^5$ dynes per cm.,

we find $K_2 = 2.91 \times 10^4$, $B = 2.10 \times 10^4$,

and $A - C = 2.6 \times 10^5$ dynes per cm.

Assuming further that all primed constants $\approx 0$, we find

$F_{CBr} = 0.756 \times 10^5$, $H_{CCBr} = 1.06 \times 10^4$, and $K_{CBr} = 2.02 \times 10^5$ dynes per cm.

Now using $\nu_1 = 1547$ cm.$^{-1}$, $\nu_2 = 267$ cm.$^{-1}$, and $\nu_3 = 144$ cm.$^{-1}$,

we find $F_{BrBr} = 0.350 \times 10^5$ and $K_{CC} = 7.35 \times 10^5$ dynes per cm.

Using these constants in the expressions for the $b_{3u}$ type frequency in reference (8) we calculate

$\nu_{11} = 605$ cm.$^{-1}$ and $\nu_{12} = 185$ cm$^{-1}$.

This is supporting evidence for the assignment of 767 cm.$^{-1}$ for $\nu_9$ and 631 cm.$^{-1}$ for $\nu_{11}$. If the calculation is performed with $\nu_9 = 631$ cm.$^{-1}$ instead of 767 cm.$^{-1}$ we find that the value obtained for $K_{CC}$ is $< 4.0 \times 6^5$ dynes per cm. which seems physically unacceptable in view of the fact that most C=C force constants are $>7 \times 10^5$ dynes per cm. (7).

TABLE II

ASSIGNMENT FOR TETRABROMOETHYLENE

| Type | Mode | Obs. | Calc.[b] | Calc.[c] |
|---|---|---|---|---|
| $a_{1g}$ | $\nu_1$ | 1547[a] / 1517[a] | | |
| | $\nu_2$ | 267 | | |
| | $\nu_3$ | 144 | | |
| $a_{1u}$ | $\nu_4$ | | | |
| $b_{1g}$ | $\nu_5$ | 885 | | 1650 |
| | $\nu_6$ | 211 | | 206 |
| $b_{1u}$ | $\nu_7$ | | | |
| $b_{2g}$ | $\nu_8$ | 464 | | |
| $b_{2u}$ | $\nu_9$ | 767 | | |
| | $\nu_{10}$ | | ~80 | 133 |
| $b_{3u}$ | $\nu_{11}$ | 631 | 605 | |
| | $\nu_{12}$ | | 185 | 243 |

[a] *Fermi doublet.*
[b] *Calculated with potential function of reference (8).*
[c] *Calculated with potential function of reference (3).*

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If the potential function of Bonner (3) is used, $\nu_{10}$ is calculated to be 133 cm.$^{-1}$ and $\nu_{12}$ is calculated to be 243 cm$^{-1}$. However, the constants*** used in this calculation yield values for $\nu_5$ and $\nu_6$ which are 1650 and 206 cm.$^{-1}$ respectively. The agreement with the observed value for $\nu_5$ of 885 cm.$^{-1}$ is very poor.

The final assignment derived from our results is given then in Table II. The bands and frequencies listed in Table I have been tentatively interpreted on the basis of this assignment invoking binary and some ternary combination tones. The unassigned bands are all very weak and could possibly be interpreted on the basis of ternary combinations.

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****The force constants are found to be* $K_1 = 6.99 \times 10^5$, $K + K_2 = 3.51 \times 10^5$, $H + \theta = 1.08 \times 10^5$, $\lambda = 0.04 \times 10^5$ *dynes per cm.* $\theta$ *is assumed to be* $0.16 \times 10^5$ *dynes per cm. so* $K - K_2 = 2.04 \times 10^5$ *dynes per cm., and* $\nu_{10}$ *is found to be 133 cm*$^{-1}$.

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# LIQUID-PHASE OXIDATION OF *p*-CYMENE: NATURE OF INTERMEDIATE HYDROPEROXIDES AND RELATIVE ACTIVITY OF THE ALKYL GROUPS[1]

By G. S. Serif[2], C. F. Hunt[3], and A. N. Bourns

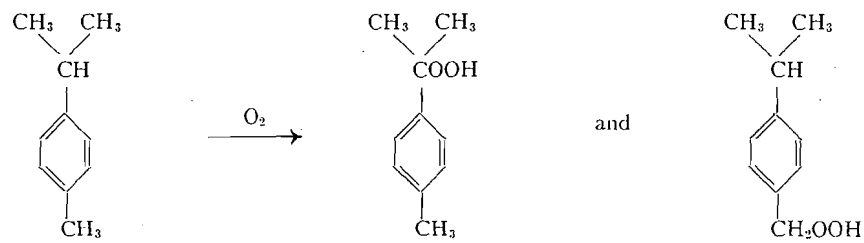
ABSTRACT

A study has been made of the liquid-phase oxidation of *p*-cymene with elemental oxygen using emulsion and photochemical procedures with the object of determining (*a*) the nature of the resulting hydroperoxides and their decomposition products, and (*b*) the relative activity of the methyl and isopropyl side chains.

The following compounds have been shown to be present in the emulsion oxidation product: 2-*p*-tolyl-2-propyl hydroperoxide, 2-*p*-tolyl-2-propanol, *p*-isopropylbenzyl alcohol, *p*-methylacetophenone, cumic acid, *p*-(α-hydroperoxyisopropyl) benzoic acid, *p*-(α-hydroxyisopropyl) benzoic acid, and *p*-acetylbenzoic acid. The two hydroperoxides have been isolated and characterized. By chromatographic separation of the carboxylic acids and fractional distillation of the alcohols formed by lithium aluminum hydride reduction of all other products, the relative susceptibility of the methyl and isopropyl groups to oxidative attack has been shown to be 1:4.

In the photochemical oxidation, hydroperoxide decomposition was very small and the product was shown to consist of 20% *p*-isopropylbenzyl hydroperoxide and 80% of 2-*p*-tolyl-2-propyl hydroperoxide. The relative extent of oxidative attack at the two positions was therefore identical in the two oxidations.

The preferred position of attack by elemental oxygen in the liquid-phase oxidation of alkyl benzenes has been shown to be the side-chain carbon directly attached to the aromatic ring, provided that this carbon is not quaternary (17). The initial products of such oxidations are hydroperoxides and, under appropriate conditions, these may be isolated and characterized. Included among the known hydroperoxides of this type are *p*-xylyl hydroperoxide (8), 1-phenylethyl hydroperoxide (8), and 2-phenyl-2-propyl hydroperoxide (9, 1). The hydrocarbon *p*-cymene, I, provides two centers for attack, the methyl carbon and the tertiary carbon of the isopropyl group, and two isomeric hydroperoxides, 2-*p*-tolyl-2-propyl hydroperoxide, II, and *p*-isopropylbenzyl hydroperoxide, III, may, therefore, be formed.




I II III

[1] *Manuscript received July 2, 1953.*
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Helberger, Rebay, and Fettback (6) studied the oxidation of *p*-cymene with oxygen in the presence of sunlight and isolated the sodium salt of the hydroperoxide by precipitation with aqueous sodium hydroxide. The hydroperoxide was considered to have structure III since cuminaldehyde could be isolated from the products of the decomposition of the salt in boiling water. Lorand (12), on the other hand, has reported that the sodium sulphide reduction of the hydroperoxide formed by oxidation of *p*-cymene with oxygen in the presence of aqueous alkali furnished a product consisting of 90% 2-*p*-tolyl-2-propanol and 10% *p*-methylacetophenone. The apparent absence of *p*-isopropylbenzyl alcohol in the reduction product would suggest that the tertiary hydroperoxide, II, was the only hydroperoxide formed by oxidation under these conditions.

The seemingly contradictory results obtained using the two oxidation methods are indeed surprising since current ideas concerning the mechanism of hydrocarbon oxidation (2) would strongly suggest that a product of similar composition should be obtained in each case. The present paper reports the results of a reinvestigation of the oxidation of *p*-cymene in which an effort has been made to determine quantitatively the composition of the total oxidation product formed using the two oxidation procedures. In addition to establishing the nature of the hydroperoxide product, this study has provided an accurate measure of the relative activity of the methyl and isopropyl groups toward oxidative attack.

*Emulsion Oxidation*

The oxidation in the presence of aqueous alkali was carried out using a procedure recently developed by Armstrong, Hall, and Quinn (1) for the preparation of tertiary hydroperoxides. Oxygen was passed into an emulsion of *p*-cymene and aqueous sodium carbonate in the presence of sodium stearate as the emulsifying agent and a small amount of cymyl hydroperoxide as the initiator. Oxidations were studied at 85 and 60°C. At the higher temperature the reaction was continued until the emulsion had broken, at which point the hydroperoxide concentration of the hydrocarbon had reached 40% by weight. At 60°C., however, the oxidation was very slow and the reaction was interrupted when a 19% hydroperoxide concentration had been attained.

On completion of an oxidation, the aqueous layer of the reaction product was separated and acidified, and the precipitated acids were then analyzed by a column partition chromatographic method. Four compounds were obtained: cumic acid, *p*-acetylbenzoic acid, *p*-(α-hydroxyisopropyl)benzoic acid, and a new hydroperoxide, *p*-(α-hydroperoxyisopropyl)benzoic acid. The structure of the latter was established by (*a*) neutralization equivalent, (b) peroxidic oxygen analysis, (*c*) reduction to the *p*-(α-hydroxyisopropyl)-benzoic acid, and (*d*) metal-catalyzed decomposition to the hydroxy acid and *p*-acetylbenzoic acid.

The organic layer was divided into two portions. *Aliquot I* was reduced with lithium aluminum hydride to furnish a product which was separated into two fractions by fractional distillation. The lower-boiling fraction was a

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mixture of the tertiary and secondary alcohols, 2-*p*-tolyl-2-propanol and 1-*p*-tolylethanol, respectively, with the former predominating. The greater part of the tertiary alcohol resulted from the reduction of the tertiary hydroperoxide, II, although some was formed by decomposition of this hydroperoxide during the oxidation. The secondary alcohol was formed by reduction of *p*-methylacetophenone, a second decomposition product of the tertiary hydroperoxide. The smaller second fraction was the primary alcohol, *p*-isopropylbenzyl alcohol, formed from the primary hydroperoxide, III, by decomposition during the oxidation and by reduction with lithium aluminum hydride. The results of this fractionation, combined with those of the chromatographic analysis of the acids and the ketone analysis on Aliquot II, permitted the calculation of the relative extent of oxidative attack at the two available positions.

In order to obtain additional information on the composition of the oxidation product as well as to determine the nature of the hydroperoxide isolated by the sodium salt precipitation, the second portion of the organic layer, *Aliquot II*, was treated with a concentrated solution of sodium hydroxide. The insoluble hydroperoxide salt was filtered, the hydroperoxide liberated with carbon dioxide and reduced with lithium aluminum hydride to yield 2-*p*-tolyl-2-propanol in high yield. The absence of *p*-isopropylbenzyl alcohol in the reduction product established that the hydroperoxide actually *isolated* as the sodium salt from the products of the emulsion oxidation was the tertiary compound, II, uncontaminated with the primary isomer, III. The small organic layer of the filtrate from the sodium salt filtration was analyzed for its ketone (*p*-methylacetophenone) content and was then fractionated. A single fraction consisting of the tertiary alcohol, 2-*p*-tolyl-2-propanol plus a small amount of *p*-methylacetophenone was obtained.

The composition of the product from emulsion oxidations at 85 and 60°C., expressed as mole %, is shown in Table I.

TABLE I
COMPOSITION OF THE PRODUCTS OF THE EMULSION OXIDATION

| Product | Mole % | |
|---|---|---|
| | 85°C. Run | 60°C. Run |
| 2-*p*-Tolyl-2-propyl hydroperoxide | 49.4 | 59.2 |
| 2-*p*-Tolyl-2-propanol | 22.3 | 12.1 |
| *p*-Isopropylbenzyl hydroperoxide plus *p*-isopropylbenzyl alcohol | 7.5 | 10.3 |
| *p*-Methylacetophenone | 3.4 | 7.0 |
| Cumic acid | 11.7 | 9.6 |
| *p*-(α-Hydroperoxyisopropyl)benzoic acid | 2.9 | 1.2 |
| *p*-(α-Hydroxyisopropyl)benzoic acid | 1.7 | 0.4 |
| *p*-Acetylbenzoic acid | 1.1 | 0.2 |

*Photochemical Oxidation*

The procedure used in the so-called photochemical oxidation of *p*-cymene was similar to that described by Helberger *et al.* except that a mercury-vapor lamp was used as a source of illumination rather than sunlight. The reaction,

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which was carried out at 60°C. only, was much slower than the emulsion oxidation and therefore was stopped when the hydroperoxide concentration was 5.5%.

Preliminary work had shown that carboxylic acids were present in the oxidation product to only a very small extent (less than 0.6% of the oxidized hydrocarbon) and consisted mainly of cumic acid. For this reason, the total reaction mixture was reduced directly with lithium aluminum hydride without making a preliminary alkaline extraction. Fractionation of the reduction product furnished the tertiary and primary alcohols, 2-*p*-tolyl-2-propanol and *p*-isopropylbenzyl alcohol, respectively. The total weight of the reduction product was almost identical with the weight expected from the reduction of the known amount of hydroperoxide in the oxidation mixture. Since such reductions are practically quantitative it was concluded that the photochemical oxidation product was almost entirely in the form of hydroperoxides. The composition of the product calculated on the basis that the total tertiary alcohol was formed by reduction of the tertiary hydroperoxide, II, and the primary alcohol by reduction of the primary hydroperoxide, III, was 79.5% II and 20.5% III.

*Relative Activity of the Methyl and Isopropyl Groups*

The extent of oxidative attack at the primary and tertiary α-carbon atoms *p*-cymene in the emulsion and photochemical oxidation is shown in Table II.

TABLE II
PER CENT ATTACK AT PRIMARY AND TERTIARY α-CARBON ATOMS

| Position of attack | Emulsion oxidation | | Photochemical oxidation |
|---|---|---|---|
| | 85°C. | 60°C. | 60°C. |
| Primary carbon | 22.0 | 20.8 | 20.5 |
| Tertiary carbon | 78.0 | 79.2 | 79.5 |

For the emulsion oxidation the per cent attack at the primary position has been calculated as the sum of the mole % of primary alcohol and hydroperoxide, the mole % of cumic acid, and one-half the mole % of the oxy-acids. Similarly, the extent of attack at the tertiary carbon has been calculated by summing the mole % of tertiary hydroperoxide, tertiary alcohol, and ketone, and one-half of the mole % of the oxy-acids. The per cent attack at the two positions in the photochemical oxidation has been based on the composition of the product as determined by reduction with lithium aluminum hydride and separation of the resulting alcohols.

## DISCUSSION

The results presented in Table II indicate that within experimental error the *relative* activity of the methyl and isopropyl groups toward oxidative attack is the same in the emulsion and photochemical reactions. This, of course, is not surprising. The nature of the major proportion of the product

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will be determined by the identity of the propagation steps and these are the same for oxidation under the two conditions, namely,

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$
$$RO_2\cdot + RH \longrightarrow RO_2H + R\cdot,$$

where R· is either the primary or tertiary cymyl radical and $RO_2H$ is the corresponding hydroperoxide (2). Some product may be attributed to the initiation and termination steps of the oxidation, but since the reaction chains are probably fairly long, this will constitute a very minor proportion of the total. Furthermore, the relative activity of different radicals toward the primary and tertiary carbon atoms will be approximately the same regardless of their nature. Thus, some reaction chains in the emulsion oxidation may be initiated by RO· and HO· radicals formed by thermal decomposition of the hydroperoxide (18). The relative activity of these radicals towards the two reaction sites, however, should correspond closely to that of the $RO_2$· radicals acting in the propagation step.

It is of interest to compare the results of the present study with those reported by Kooyman (11) who obtained a measure of hydrocarbon activity in radical reactions by comparing the inhibiting action of different hydrocarbons in the propagation step of the peroxide-catalyzed addition of carbon tetrachloride to olefins. He has found that the ratio of the $\alpha$-methylenic activity of the isopropyl group of cumene to that of the methyl group of toluene is 4.2:1 at 91.5°C. This corresponds fairly closely to the 3.5:1 ratio for the two groups obtained at 85°C. in the present study*.

As stated earlier, the isolation of cuminaldehyde from the products of the decomposition of the sodium salt of the hydroperoxide formed in a photochemical oxidation was considered by Helberger to characterize the hydroperoxide as the primary compound, III. This experimental result, confirmed in the present study, is not in conflict, however, with the fact that the oxidation product actually contains only 20% of III, the remainder being the tertiary hydroperoxide, II. It has been well established that primary hydroperoxides decompose very readily in the presence of alkali to form aldehydes. Hock and Lang (8), for example, obtained *p*-tolualdehyde in good yield by warming *p*-xylyl hydroperoxide with an equivalent of alkali for a few minutes. Tertiary hydroperoxides, on the other hand, are considerably more stable toward alkali, particularly when sufficient is present to convert the hydroperoxide to its salt. Thus, Kharasch (10) has shown that in the presence of excess alkali $\alpha$-cumyl hydroperoxide is decomposed only to the extent of 70% at 90°C. in six hours and the main product is 2-phenyl-2-propanol. In the present investigation the treatment of the cymyl hydroperoxide salts for 15 min. with boiling water would be expected to completely decompose the

**Kooyman has also shown that whereas the activity of m-xylene is exactly twice that of toluene the activity of o- and p-xylene is significantly greater than twice. Because of this mutual interaction of groups in ortho and para positions the relative activity of the two alkyl groups of p-cymene, as determined in the present study, is not a true measure of the activity of methyl and isopropyl groups attached to the benzene ring. This could be determined, however, from a similar study of the oxidation of m-cymene.*

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primary component to cuminaldehyde and partially decompose the tertiary component to the tertiary alcohol.

## EXPERIMENTAL*

### *Purification of p-Cymene*

Eastman Kodak "White Label" *p*-cymene was dried over Drierite and distilled over sodium through a 30 plate column. A mid-fraction, b.p. 62.5°C. (12 mm.), $n_D^{20}$ 1.4908, was used in the oxidation studies.

### *Emulsion Oxidation*

#### *Apparatus*

A train consisting of an activated charcoal tower, solid sodium hydroxide tower, back-splash trap, sulphuric acid trap, and glass wool tower was used to purify cylinder oxygen. Gas-flow rate was regulated by a needle valve and measured with a mercury flowmeter. The reaction vessel consisted of a three-neck five-liter flask provided with a fritted-glass gas dispersion tube, mercury-seal stirrer, thermometer, and condenser. The top of the condenser was connected through a dry-ice trap to a wet-test gasmeter.

#### *Oxidation Procedure*

The reaction vessel was charged with a reaction mixture of the following composition:

| | |
|---|---|
| water | 2000.0 gm. |
| *p*-cymene | 340.0 gm. |
| stearic acid | 3.0 gm. |
| sodium carbonate | 27.0 gm. |
| cymyl hydroperoxide | 0.4 gm. |

The stirred mixture was brought to the desired temperature and the oxygen flow adjusted to seven liters per hour. The oxidation was followed using an iodometric procedure (7) for hydroperoxide analysis of samples periodically removed from the reaction flask. The reaction at 85°C. was stopped when the hydroperoxide content of the cymene had reached 40% by weight. This required 35.5 hr. The reaction at 60°C. was interrupted after 197 hr. at which time the hydroperoxide concentration was 19%. Two layers separated on cooling. The aqueous layer was separated and washed with petroleum ether (b.p. 30-60°C.), care being taken to retain the flocculent sodium stearate with the water. The ether washings were combined with the organic layer. The greater part of the ether was removed *in vacuo* and the residue divided into two aliquots for further treatment. The aqueous layer was acidified with dilute hydrochloric acid, the precipitated acids taken up in ethyl ether, the ether removed, and the acids separated by a chromatographic procedure.

### *Lithium Aluminum Hydride Reduction of Aliquot I*

Aliquot I from each oxidation (three-quarters of the organic layer from the 85°C. reaction and one-half from the 60°C. reaction) was diluted with

**All melting and boiling points are corrected.*

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500 ml. of ether and the solution added dropwise with stirring to a 25% excess of a 2 *N* ethereal solution of lithium aluminum hydride. The mixture was decomposed with water followed by sufficient 10% sulphuric acid to just barely dissolve the basic aluminum salts. The ether layer was separated and washed with 10% sodium bicarbonate. The ether was removed and the product fractionated in a 35 plate column (13) using benzhydrol as the chaser. Two fractions were obtained in addition to unreacted cymene. Fraction I, b.p. 105-106°C. (12 mm.) was a mixture of 2-*p*-tolyl-2-propanol and 1-*p*-tolylethanol. Fraction II, b.p. 125.5-126.5°C. (12 mm.) was *p*-isopropylbenzyl alcohol.* A phenylurethan derivative of this fraction melted at 62.0-62.5°C., reported 62.5°C. (14).

*Treatment of Aliquot II*

Aliquot II of each oxidation product was added slowly to twice its volume of an ice-cooled 25% solution of sodium hydroxide. The hydroperoxide salt separated in about two hours.** It was filtered rapidly using an ice cooled, fritted-glass funnel, washed with petroleum ether and dried. The salt was crushed to a fine powder, stirred with 150 ml. of petroleum ether, filtered and again dried. This product was suspended in water and the hydroperoxide liberated by passing in carbon dioxide until a pH of 8 had been reached. The hydroperoxide was taken up in petroleum ether and the ether removed *in vacuo*. The colorless oily residue analyzed for 98—99% cymyl hydroperoxide. It was diluted with ether and reduced with lithium aluminum hydride using the procedure already described. Fractionation of the reduction product in the 35 plate column using benzhydrol as the chaser furnished 2-*p*-tolyl-2-propanol, b.p. 105—106°C. (12 mm.), $n_D^{20}$ 1.5174.† The yield was 93 and 91% based on the isolated hydroperoxide and 78 and 71% based on the hydroperoxide content of the original oxidation mixture for the 85 and 60°C. oxidations, respectively. There was no evidence of a *p*-isopropylbenzyl alcohol fraction boiling between the tertiary alcohol and the chaser.

The organic layer of the filtrate from the hydroperoxide salt filtration was separated and the petroleum ether distilled off. The residue was heated under reflux for three hours to decompose hydroperoxides and a sample was then removed for ketone analysis (16). The remainder on fractionation furnished a single fraction consisting mainly of 2-*p*-tolyl-2-propanol and *p*-methylacetophenone.‡ The primary alcohol, *p*-isopropylbenzyl alcohol, could not be isolated at this stage. Reduction with lithium aluminum hydride of the product of this distillation followed by a fractionation of the reduction product,

**Fractionation of a synthetic mixture of these alcohols demonstrated that the primary alcohol does not form an azeotrope with the other alcohol components.*

***Seeding of the alkaline mixture with a small amount of the hydroperoxide salt induced immediate precipitation. This method was used in the treatment of the 85°C. oxidation product and resulted in higher hydroperoxide recovery.*

*†The slightly high refractive index of this product was attributed to the presence of a small amount of α, p-dimethylstyrene ($n_D^{20}$ 1.5283) formed by dehydration of the alcohol. When the column was maintained at total reflux for a short period droplets of water appeared in the head and the refractive index of subsequent distillate increased.*

*‡The ketone was identified by means of its 2,4-dinitrophenylhydrazone, m.p. 259.8-260.6°C., which gave no melting point depression when mixed with an authentic sample of this derivative.*

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however, furnished a very small fraction boiling between the main product and the chaser. This was identified by its phenylurethan derivative as the primary alcohol.

*Separation and Identification of the Carboxylic Acid Oxidation Products*

The acids were separated by column partition chromatography using methanol on silicic acid as the stationary phase and benzene saturated with aqueous methanol as the mobile phase. The packing was prepared by grinding 150 gm. of Mallinckrodt A. R., 100 mesh, silicic acid with 200 ml. of methanol, 7.5 ml. of a 1% methanolic bromocresol green solution, and 2 ml. of 1 *N* ammonium hydroxide until a homogeneous powder was produced (15). The powder was slurried with 300 ml. of benzene and poured into 49 × 3.5 cm. (diam.) column. Benzene, equilibrated with 90% aqueous methanol, was forced through the column to remove excess indicator and, using this solvent as eluent, 0.5 gm. of cumic acid was then passed through to remove excess ammonium hydroxide. Elution with 'equilibrated' benzene of two grams of the acid oxidation product, placed on the column in 25 ml. of this solvent, produced four distinct bands. The eluent corresponding to each band was collected and the solvent removed *in vacuo* to give separated acids in a total recovery of 95—98%.

The first band emerging from the column comprised a mixture of cumic and stearic acids, which could not be separated adequately by the above described chromatographic procedure. Recrystallization of this mixture from aqueous ethanol, however, furnished a product which gave no melting point depression when mixed with an authentic sample of cumic acid and gave a neut. equiv. of 164.7, calc. 164.2. Since care had been taken to retain precipitated sodium stearate with the aqueous layer of the oxidation product a fairly accurate correction for the stearic acid present in the first band could be made.

The second acid, recrystallized from benzene–ethanol, was *p*-acetylbenzoic acid: m.p. found 209.2–209.8°C., reported (5) 208.6–209.4°C.; neut. equiv. found 168.2, calc. 164.2; phenylhydrazone m.p. found 234–235°C., reported 234°C.

The fourth acid to pass from the column was recrystallized from ethanol–benzene and identified as *p*-(α-hydroxyisopropyl)benzoic acid: m.p. found 159.2—159.6°C., reported (4) 156°C.; neut. equiv. found 180.5, calc. 180.2.

The third acid after recrystallization from benzene–ethanol gave a melting point of 151.5—151.8°C. Its neut. equiv. and peroxidic oxygen content agreed with the calculated values for *p*-(α-hydroperoxyisopropyl)benzoic acid: neut. equiv. 196.9, calc. 196.2; peroxidic oxygen found 16.34, 16.28, calc. 16.31%.

The hydroperoxy acid was further identified by sodium sulphide reduction to *p*-(α-hydroxyisopropyl)benzoic acid. The acid, 0.085 gm., was refluxed overnight with 10 ml. of water, 0.05 gm. of sodium carbonate and 0.10 gm. sodium sulphide hydrate. The product was acidified and the precipitated acids separated chromatographically by the method already described.

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There was obtained 0.069 gm. (88%) of *p*-(α-hydroxyisopropyl)benzoic acid and 0.003 gm. (4%) of *p*-acetylbenzoic acid.

Finally, the hydroperoxy acid was decomposed in the presence of cobalt ion. The acid, 0.150 gm., was refluxed for three hours with 45 ml. of benzene and six drops of cobalt napthenate solution (Nuodex Cobalt 6%). The product was taken up in 10% sodium carbonate, and the acids precipitated with dilute hydrochloric acid. Using crystallization and chromatographic procedures, 0.059 gm. (43%) of *p*-(α-hydroxyisopropyl)benzoic acid and 0.0465 gm. (37%) of *p*-acetylbenzoic acid was obtained.

*Preparation and Properties of 2-p-Tolyl-2-propyl Hydroperoxide, II*

The sodium salt of the hydroperoxide, isolated from the products of a separate 85°C. oxidation in the manner already described, was converted to the free hydroperoxide by treatment with carbon dioxide and then reprecipitated. The salt (97.4% pure) was treated with carbon dioxide and the liberated hydroperoxide extracted with petroleum ether. Removal of the ether left a colorless oily liquid which analyzed for 98.9% hydroperoxide. Distillation *in vacuo* furnished a colorless liquid: b.p. 88—91°C. (1 mm.); $n_D^{20}$ 1.5207; $d_4^{25}$ 1.0403; peroxidic oxygen found 19.04, 19.12%, calc. 19.25%. On the basis of the results obtained from the reduction of the hydroperoxide described above, this product was considered to be essentially pure tertiary hydroperoxide, II.

*Photochemical Oxidation*

*Apparatus and Procedure*

The apparatus was identical with that used for the emulsion oxidations except that the reactor was a two-liter flask surrounded by a box lined with aluminum foil. The box was fitted with a 100 watt bulb connected to a Variac to provide a variable heat source and across an open end was aligned an 18 in. long quartz d-c. mercury-vapor lamp. The flask was charged with 850 gm. of *p*-cymene, the temperature raised to 60°C., and the oxygen flow started and adjusted to seven liters per hour. After 118 hr., a hydroperoxide concentration of 5.5% by weight had been reached and the reaction was then stopped.

*Lithium Aluminum Hydride Reduction*

The total oxidation product was reduced with lithium aluminum hydride using the procedure already described. The reduction product was fractionally distilled using benzhydrol as the chaser. Two fractions were obtained in addition to unchanged *p*-cymene. Fraction 1, b.p. 105—106°C. (12 mm.), $n_D^{20}$ 1.5172, wt. 34.1 gm. was 2-*p*-tolyl-2-propanol, and Fraction 2, b.p. 125.0—126.5°C. (12 mm.) $n_D^{20}$ 1.5204, wt. 8.8 gm. was *p*-isopropylbenzyl alcohol. The total weight of 42.9 gm. compared with a theoretical yield of 42.4 gm. based on the hydroperoxide content of the oxidation product.

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# THE EFFECT OF PHYSICAL ADSORPTION ON THE ELECTRICAL RESISTANCE OF ACTIVE CARBON[1]

By W. W. Smeltzer[2] and R. McIntosh[3]

ABSTRACT

The change of the electrical resistance of active carbon rods due to the reversible adsorption of vapors is described. The effects of six saturated hydrocarbons and ethyl chloride were studied. An interesting regularity in the results obtained with the hydrocarbons was found, namely that the extent of the resistance change at a given temperature and volume adsorbed is proportional to the number of carbon atoms in the adsorbate molecule. The alteration of the electrical conductivity of the active carbon by the physically adsorbed vapors and the adsorption isotherms are not modified by small quantities of chemisorbed oxygen. Ethyl chloride exhibits a more complex behavior than the hydrocarbons. It is argued that the resistance measurements may be utilized to support the viewpoint that physically adsorbed saturated hydrocarbon molecules tend to lie flat on the adsorbent surface. Several possible explanations of the findings are examined and proved to be inadequate.

## INTRODUCTION

In an earlier publication McIntosh, Haines, and Benson (12) reported variations of the electrical resistance of active carbon rods when vapors, usually considered to be physically adsorbed, were taken up by the adsorbent. The extent and direction of the resistance changes at a fixed temperature were found to be dependent upon the chemical nature of the adsorbate molecules. The effect of physical adsorption on the change of the linear dimension of the rods was also examined (9). It was concluded that the mechanical alteration of contact resistances between the granules forming the rod could not be the explanation of the phenomena, because no correlation between dimensional and resistance variations was found. An example leading to this conclusion was the comparison of effects caused by butane and ethyl chloride. Both of these adsorbates bring about a marked increase in the length of the rod. The dimensional change per unit quantity of adsorbed vapor is greatest near saturation of the surface. In this region a negligible change of resistance was observed in the case of butane, whereas a marked change was found with ethyl chloride. On the basis of such evidence it was suggested that the adsorbates alter either the mobility or the number of conducting electrons in the semiconductor (12).

Somewhat similar observations have been reported for other systems. Baxter (3) has explained the effect of adsorbed water on the electrical resistance of wool fibers by assuming that the water molecules act as impurity donors. Conduction was postulated to occur by transfer of electrons from one adsorbed water molecule to another. The conductivity was assumed to depend upon the width and height of the potential barrier and thus increased with moisture

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*Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario. Based on a thesis submitted to the School of Graduate Studies, University of Toronto, in partial fulfillment of the requirements for the Ph.D. degree.*
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content. More recently the examination of very thin metallic films (13, 14), which exhibit a temperature coefficient of resistance characteristic of semiconductors, has revealed that their resistance is diminished by adsorbed gases. The effect was found to be reversible at pressures below $10^{-4}$ mm. The resistance alteration was explained by assuming a lowering of potential barriers between the metallic aggregates of the films by adsorbed gases.

Further experiments have been completed with active carbon because adsorption is readily measured, and because this adsorbent should be suitable for study if the effect is dependent upon a large surface to volume ratio. The obvious difficulty is that the conduction mechanism in polycrystalline carbons is not well understood. Mrowzowski (15) has discussed this subject in some detail. In this investigation the adsorption isotherms and the concomitant resistance changes have been determined at several temperatures. Because hydrocarbon vapors produced the simplest type of change, the investigation was largely directed to a study of the effect of saturated hydrocarbons on a carefully evacuated rod, or on one which, after evacuation, was allowed to chemisorb oxygen. Certain regularities in the results obtained with these adsorbates are apparent, but no adequate explanation of the effects has been achieved. The polar adsorbate ethyl chloride was also examined, and the complexity of the phenomena is well illustrated by the results obtained.

## EXPERIMENTAL

The procedures and methods of measurement were identical with those described in the earlier publication (12). Four rods were used in investigating the temperature variation of resistance. The lengths between the potential measuring electrodes of rods 4, 6, 8, 9 were 7.1, 6.9, 8.1, and 7.0 cm. respectively. Rod 4 was evacuated to a reproducible resistance at 120°C., rods 6 and 8 at 160°C., and rod 9 at 240°C. Two rods were utilized for adsorption experiments but as the same characteristic effects were exhibited by each rod, only experiments are recorded in which rod 8 was used. A tubular air oven was employed for the resistance measurements as a function of temperature. It was also used as the thermostat at temperatures above 30°C. The temperature in the oven was uniform to within 0.2°C. over a length greater than the length of the glass envelopes containing the rods, and was controlled manually to within ±0.1°C. whenever equilibrium measurements were taken. Temperatures were measured by means of a thermocouple fastened to the glass envelope. Adsorption isotherms at temperatures lower than 30°C. were determined in a large Dewar vessel thermostat. The bath temperature was established by means of a refrigerator coil and an automatically controlled heater. Fluctuations of the bath temperature did not exceed ±0.05°C. Adequate precautions were taken to eliminate any conduction paths between electrodes or to ground.

## RESULTS

### *Variation of Electrical Resistance with Temperature*

The temperature variation of resistance of the active carbon rods is shown in Fig. 1, and obeys the relation $\log_{10} R = A - BT$, where $R$ is the resistance

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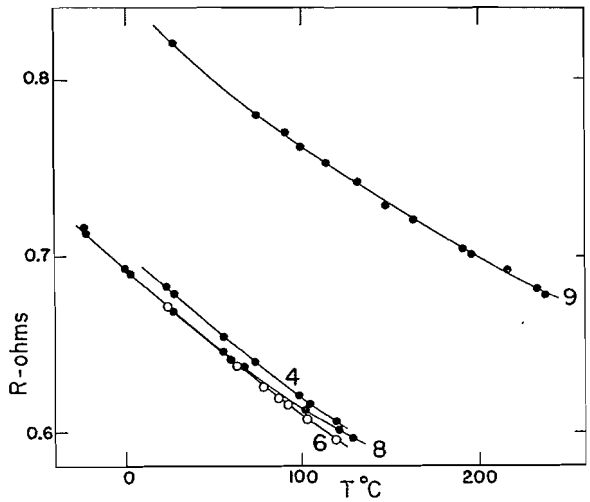



FIG. 1. Variation with temperature of electrical resistance of active carbon rods 4, 6, 8, and 9.

in ohms, $A$ and $B$ are constants, which was reported previously (12). It may be interpreted according to the views put forward by Mrowzowski when discussing baked carbons (15). For baked carbons of similar specific resistance to the active carbon rods, and prepared by baking at about 750°C., Mrowzowski suggested a minimal energy gap between valence and conduction bands of 0.2 ev. This value is supported by reference to measurements of infrared absorption. Thermoelectric effects revealed that an essentially constant number of conduction electrons exists in the temperature range wherein the resistance of the baked carbons was determined, and these two facts were interpreted as showing that the variation of resistance is due to diminished scattering. The specific resistances of the active carbon rods 4, 6, 8, and 9, calculated using a cross sectional diameter of 8 mm., are 0.05, 0.05, 0.04, and 0.06 ohm cm., respectively. The rods were prepared by the zinc chloride process of activation involving carbonization at about 750°C. On the basis of these similarities, the variation with temperature of the resistance of the active carbon rods may be accounted for by a decreased scattering of electrons in the polycrystalline structure with increasing temperature. The large electrical conductivity is presumed to arise from the presence of a large and nearly constant number of excess electrons in the conduction band. The electrons are assumed to be associated with the peripheral carbon atoms, and their unsaturated valence bonds at the surface discontinuities of the solid. They are mobile and contribute to the conductivity. A decrease of resistance caused by the presence of adsorbate molecules would thus necessarily be due to a change in the mobility or scattering of the electrons. Such a postulate would be extremely difficult to formulate quantitatively, and we have adopted other descriptions of the nature of the carbon surface in the attempts made to explain the results observed with the physically adsorbed vapors.

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*Effect of Hydrocarbons*

The resistance effects of six hydrocarbon adsorbates were studied. The vapors used were methane, ethane, propane, *n*-butane, cyclopropane, and isobutane. All the hydrocarbons were investigated over a range of temperature except methane, for which the temperature of −21.3°C. was employed so that the amount adsorbed would be appreciable. The results obtained for

TABLE I
DATA FOR CYCLOPROPANE ON ROD 8

| Temperature, °C. | Volume adsorbed, cc. vapor N.T.P. | Equilibrium pressure, mm. Hg | Resistance, ohms |
|---|---|---|---|
| −22.0 | 0.00 | 0.00 | 0.7128 |
| | 34.9 | 0.13 | 0.7086 |
| | 72.2 | 0.61 | 0.7055 |
| | 117 | 1.69 | 0.7023 |
| | 162 | 4.76 | 0.6996 |
| | 220 | 6.90 | 0.6967 |
| | 272 | 12.0 | 0.6943 |
| | 330 | 23.2 | 0.6917 |
| | 387 | 44.0 | 0.6895 |
| | 445 | 81.9 | 0.6879 |
| | 502 | 132 | 0.6867 |
| | 570 | 227 | 0.6856 |
| −5.6 | 0.00 | 0.00 | 0.6967 |
| | 40.4 | 0.53 | 0.6925 |
| | 80.7 | 2.07 | 0.6894 |
| | 134 | 6.30 | 0.6858 |
| | 189 | 14.9 | 0.6829 |
| | 249 | 24.8 | 0.6800 |
| | 307 | 44.4 | 0.6777 |
| | 364 | 82.7 | 0.6754 |
| | 415 | 144 | 0.6739 |
| | 473 | 251 | 0.6727 |
| | 537 | 403 | 0.6716 |
| | 604 | 603 | 0.6707 |
| 12.4 | 0.00 | 0.00 | 0.6797 |
| | 38.5 | 1.27 | 0.6759 |
| | 76.8 | 5.40 | 0.6728 |
| | 121 | 13.2 | 0.6702 |
| | 171 | 25.6 | 0.6675 |
| | 222 | 46.8 | 0.6650 |
| | 272 | 76.1 | 0.6629 |
| | 329 | 136 | 0.6609 |
| | 388 | 253 | 0.6588 |
| | 442 | 430 | 0.6577 |
| | 485 | 609 | 0.6568 |
| 27.9 | 0.00 | 0.00 | 0.6662 |
| | 37.3 | 3.02 | 0.6628 |
| | 79.6 | 12.2 | 0.6596 |
| | 127 | 29.0 | 0.6568 |
| | 176 | 55.1 | 0.6544 |
| | 222 | 91.8 | 0.6523 |
| | 276 | 160 | 0.6501 |
| | 333 | 284 | 0.6482 |
| | 378 | 450 | 0.6468 |
| | 419 | 666 | 0.6459 |
| | 379 | 448 | 0.6470 |
| | 306 | 211 | 0.6494 |

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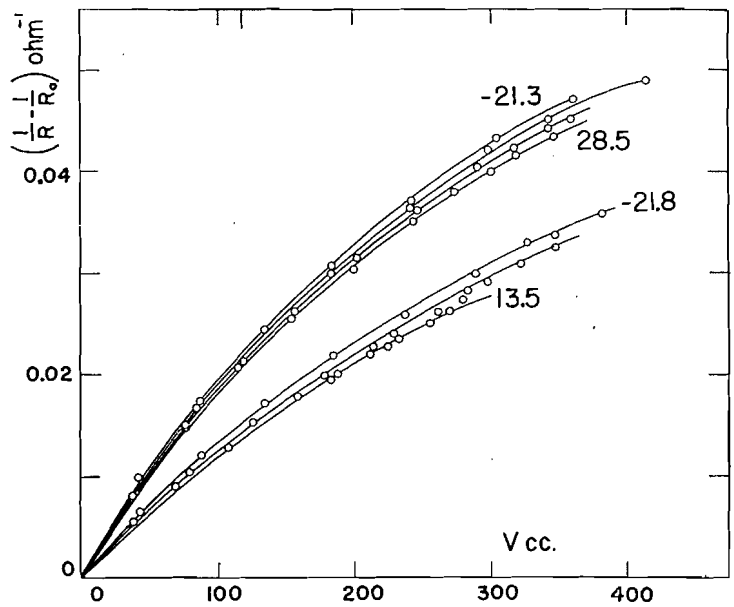



FIG. 2. Conductivity changes versus volumes adsorbed for hydrocarbons, rod 8.
Ethane adsorption—lower curves
Propane adsorption—upper curves

cyclopropane on rod 8 at four temperatures are recorded in Table I. The resistance effects of ethane and propane are illustrated in Fig. 2.

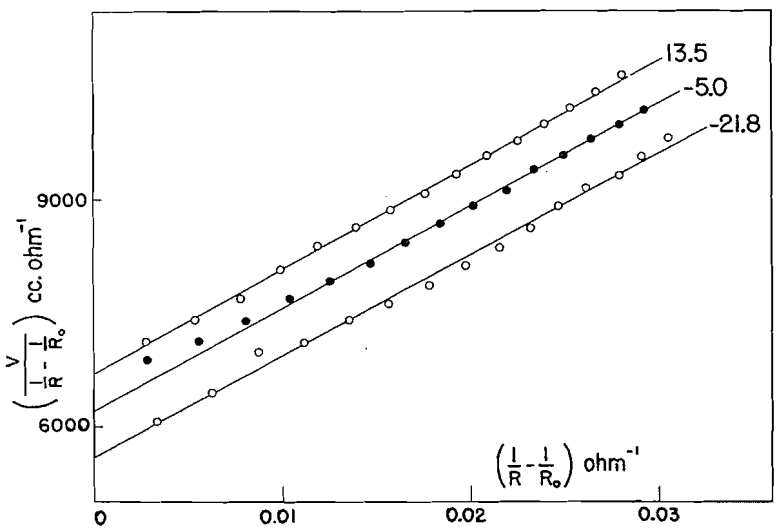



FIG. 3. Representation of the analytical equation

$$V \Big/ \left(\frac{1}{R}-\frac{1}{R_0}\right) = C + D\left(\frac{1}{R}-\frac{1}{R_0}\right)$$

for ethane adsorption on carbon rod 8.

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The results may be summarized as follows. A decrease in the resistance is observed on the adsorption of the hydrocarbons, the magnitude of which increases with increasing amount of adsorbate on the surface, and appears to approach a limit asymptotically. The effect of the hydrocarbons increases with decreasing temperature.

Certain common features are apparent for all the hydrocarbons. The variation of resistance as a function of quantity adsorbed may be expressed empirically by the equation

$$V \Big/ \left(\frac{1}{R} - \frac{1}{R_0}\right) = C + D\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

where $V$ designates the volume of adsorbed vapor in cc. at N.T.P., $R$ is the measured resistance of the rod, $R_0$ is the resistance of the evacuated rod, and $C$ and $D$ are constants at the particular temperature. The range of validity of this relation, illustrated in Fig. 3 for ethane at three temperatures, was up to two thirds of the maximum volume adsorbed. From the intercepts $C$ of this type of plot, the values of the tangents to the curves of Fig. 2 relating change of conductivity to volume adsorbed at zero adsorption were readily obtained. The values of these limiting tangents and these values, divided by $N$, the number of carbon atoms in the adsorbate molecules, are recorded in Table II.

TABLE II

LIMITING TANGENTS, $k_1$, TO CURVES FOR ALTERATION OF CONDUCTIVITY VERSUS ADSORBED VOLUME ON ROD 8

| Temp., °C. | $k_1 \times 10^4$, ohm$^{-1}$ per cc. | $(k_1/N) \times 10^4$, ohm$^{-1}$ per cc. |
|---|---|---|
| *Methane* | | |
| −21.8 | 1.05 | 1.05 |
| *Ethane* | | |
| −21.8 | 1.79 | 0.90 |
| −5.0 | 1.62 | 0.81 |
| +13.5 | 1.49 | 0.75 |
| *Propane* | | |
| −21.3 | 2.89 | 0.96 |
| −5.0 | 2.75 | 0. 2 |
| 13.5 | 2.65 | 0.88 |
| 28.5 | 2.56 | 0.85 |
| *Cyclopropane* | | |
| −22.0 | 2.92 | 0.97 |
| −5.6 | 2.79 | 0.93 |
| 12.4 | 2.73 | 0.91 |
| 27.9 | 2.65 | 0.88 |
| *n-Butane* | | |
| −22.0 | 3.66 | 0.92 |
| 1.4 | 3.57 | 0.89 |
| 26.2 | 3.31 | 0.83 |
| 54.3 | 3.05 | 0.76 |
| *Isobutane* | | |
| −21.3 | 3.85 | 0.96 |
| 3.0 | 3.75 | 0.94 |
| 27.9 | 3.55 | 0.89 |

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It is evident that the values of the tangents divided by $N$ are common for all the hydrocarbons at a given temperature within about 10%. On the basis of this finding it was shown that either the conductivity or resistance alterations for all the hydrocarbons can be represented by a common curve as in Fig. 4,

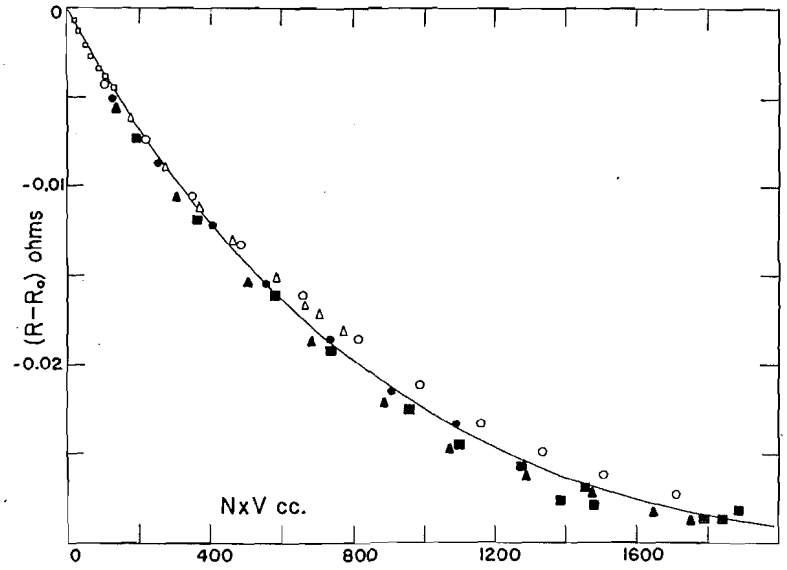



FIG. 4. Resistance changes versus adsorbed volumes of hydrocarbons multiplied by factor $N$. Temp. −21.5°C.

□ Methane ○ Cyclopropane ■ *n*-Butane
△ Ethane ● Propane ▲ Isobutane

where the change of resistance is plotted against the product of the volume adsorbed and the number of carbon atoms in the adsorbate molecules using data obtained at $-21.5 \pm 0.5$°C. The generalization attempted by this treatment is clearly not exact, but departures from it are comparatively small, and do not correlate immediately with the structure of the adsorbate molecule. As some of the discrepancies may be due to experimental error, it seems best to regard the observation as a good first approximation. Some discussion of the results is useful at this point.

It could be postulated that the change of resistance is directly proportional to the amount of hydrocarbon which is adsorbed in the first layer, and that the decreasing extent of the effect per unit quantity adsorbed may be accounted for by a greater proportion of the adsorbate being adsorbed into higher layers as the quantity on the surface is increased. If this view is adopted, the quantity of vapor required to complete the monolayer may be evaluated by an extrapolation of the tangent to the curve relating resistance change to volume adsorbed at zero adsorption, until it meets the limit of the change of resistance. The volume of vapor adsorbed corresponding to this point would then give the quantity required to complete the monolayer. The value deduced for *n*-butane by this method was found to be 165 cc. The B.E.T. (7) determination

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of the monolayer volume, on the other hand, was 321 cc. This method of obtaining the monolayer volume is generally accepted (8, 10). However, Pierce, Wiley, and Smith (17) contest this view, and argue that the generally accepted values of surface areas of active carbons are much too large. In the case of porous glass, Amberg and McIntosh (1) found that the surface area determined by the B.E.T. method agreed with an estimate made on the basis of capillary condensation theory. Because of this controversy, a final decision cannot presently be reached, but it may be noted that the electrical effect might be employed to measure the monolayer volume for active carbons if the gas adsorption method based on the B.E.T. equation is inadequate. For the present the view is adopted that adsorption of the vapors is occurring into the first layer, since the B.E.T. C value is large, and that some other explanation of the experimental results is required. The varying effect of the conductivity alteration with increasing coverage cannot be due to a difference of orientation of the adsorbed molecules on the surface. This view is untenable because methane, a spherical molecule, shows the same characteristic behavior as the other molecules. The electrical data suggest that the hydrocarbon molecules lie with their major axis in the plane of the adsorbent surface, because the electrical effect is found to be proportional to the number of carbon atoms in the adsorbate molecules. This conclusion has been arrived at on the evidence of heats of adsorption (4, 6) and surface area evaluations (16) with hydrocarbon vapors. The isosteric heats of adsorption of the hydrocarbons are shown in Fig. 5 to an accuracy of about ±300 cal./mole. The branched chain methyl

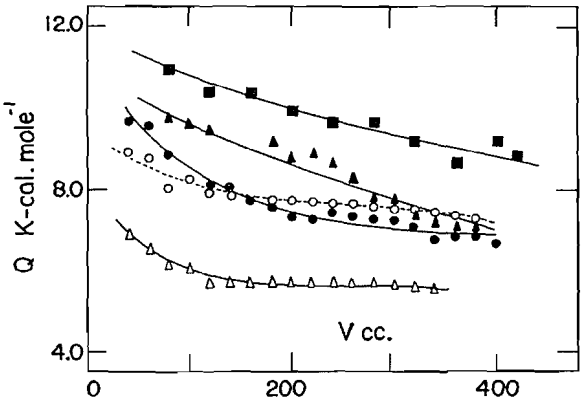



FIG. 5. Isosteric heats of adsorption of hydrocarbons.

△ Ethane ● Propane ▲ Isobutane
○ Cyclopropane ■ *n*-Butane

group of the isobutane molecule should be at a greater distance from the surface than the rest of the molecule if the molecule lies flat on the adsorbing surface. The isosteric heat of adsorption for isobutane, which is intermediate between that of *n*-butane and the heats of adsorption of the propanes, tends to substantiate this viewpoint. As shown in Fig. 4, however, the resistance variations caused by the two butanes are essentially the same. Consequently,

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the resistance effect is much less sensitive to the value of the equilibrium distance from the surface than is the heat of adsorption.

It becomes necessary to account for the form of the conductivity versus volume adsorbed curves by other means if the conclusions are accepted that the molecules tend to lie flat on the surface of the solid and are adsorbed into the first layer. It is possible that the number of electrons in the conduction band of the semiconductor is altered by the adsorbate. It was postulated that the electrons of the free valencies at the surface discontinuity were bound to the surface carbon atoms in contradiction to the concept put forward by Mrowzowski. Since the resistance effect was found to be proportional to the number of methyl or methylene groups in the adsorbate molecule, it was further assumed that the surface atoms may form complexes with these groups. The complexes then act as donors of conduction electrons. That is, the reaction,

$$\text{surface complex} \rightleftharpoons \text{ionized surface complex} + \text{free electron},$$

is assumed. The total number of complexed surface atoms was taken as the number of adsorbed molecules multiplied by the number, $N$, of carbon atoms per molecule. The conductivity $1/R_0$ of the evacuated carbon rod was regarded as proportional to the number and mobility of electronic carriers. The conductivity change is directly proportional to the increased number of carriers if it is assumed that their mobility is not altered when adsorbate is *in situ*. The equilibrium constant of the assumed reaction may then be expressed in terms of the measured resistance and volume of adsorbed vapor by means of the usual type of equilibrium equation. Such a treatment is valid if the semiconductor is nondegenerate (18). The resulting relation is identical in form to the empirical equation (1) given above. However, its use leads to absurd results, since the proportionality constant between number of additional carriers created by the adsorption process and the conductivity is negative in value. The same analytical form may also be obtained, if, in conjunction with the reaction suggested, the postulate is made that the electrons originally present in the conduction band of the solid do not enter into the equilibrium reaction. This treatment is also not valid, since it leads to the result that the number of conduction electrons produced by the reaction is in excess of $10^{21}$ for a solid containing about $5 \times 10^{22}$ carbon atoms. Classical equilibrium equations would thus not be applicable for such a large number of electrons.

*Experiments with Chemisorbed Oxygen*

The resistance of carbon rod 8 was altered by the chemisorption of oxygen to determine whether the number of electrons originally in the conduction band of the solid modifies the effect of the hydrocarbon adsorbates. The surface of the active carbon was therefore exposed to oxygen at 600 mm. pressure at three temperatures, 12.4°C., 120°C., and 130°C. After each exposure the rod was evacuated at room temperature until a 'stick' vacuum was obtained. An adsorption isotherm using cyclopropane was determined at 12.4°C. after each evacuation. In addition one isotherm using ethane was determined after the final treatment of the rod with oxygen. Both of these

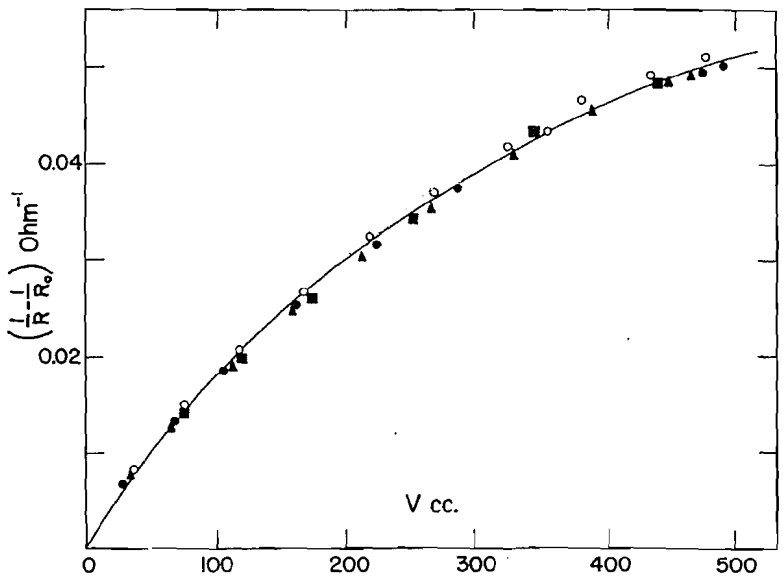



FIG. 6. Conductivity changes versus volumes adsorbed cyclopropane on rod 8 with oxygen at 12.4°C.

○ Bare rod
Resistance alteration with oxygen
■ 0.0028 ohm
● 0.0223 ohm
▲ 0.0520 ohm.

adsorbates gave the usual conductivity effect. It is shown in Fig. 6 that within experimental accuracy the conductivity effect is not modified although successive changes of the original resistance of the rod to the extent of 0.0028, 0.0233, and 0.0320 ohm were obtained by the treatment with oxygen. It is reasonable to postulate that the electronegative oxygen causes an increase of resistance because it is chemisorbed on peripheral carbon atoms which act as donors, with a resulting localization of conduction electrons. A reduction of the number of mobile electrons to an extent of about 7% does not, therefore, alter the effect of the hydrocarbon. This observation supported the treatment of the equilibrium process in which only the electronic carriers formed by the adsorption of the vapor were taken into account. However, as the assumed reaction does not rationalize the observed results, the effect of oxygen must be regarded merely as an additional fact which a postulated mechanism must explain. It is believed that peripheral foreign atoms such as oxygen form high resistance barriers in baked carbons (15). It might be assumed that some of these barriers are sufficiently opaque to reduce the number of conduction paths in a porous solid. If one attempts to explain the conductivity effect of hydrocarbons on such a premise, it would follow that its magnitude should be different for the bare rod and the oxygenated one. The experimental results however lead to the conclusion that this effect of chemisorbed oxygen is negligible.

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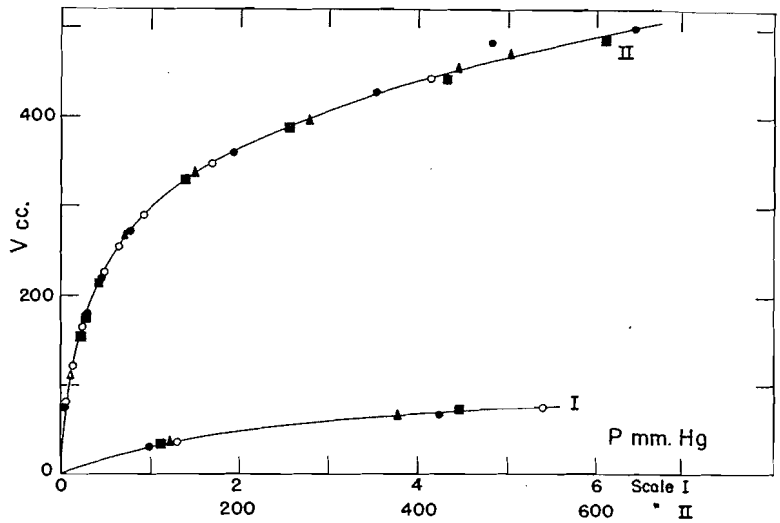



FIG. 7. Adsorption isotherms of cyclopropane on rod 8 at 12.4°C. (points designated as in Fig. 6).

The adsorption isotherms of cyclopropane and ethane were unaltered by the small addition of chemisorbed oxygen to the active carbon. The graphical representation of the cyclopropane results in Fig. 7 illustrates this. All the adsorbates displayed Type I adsorption isotherms. The equation

[2] $$\log (V/P) = A - BV$$

where $A$ and $B$ are constants for a specified temperature gave the best analytical representation of the adsorption isotherm at surface coverages greater than 100 cc. of adsorbed vapor.

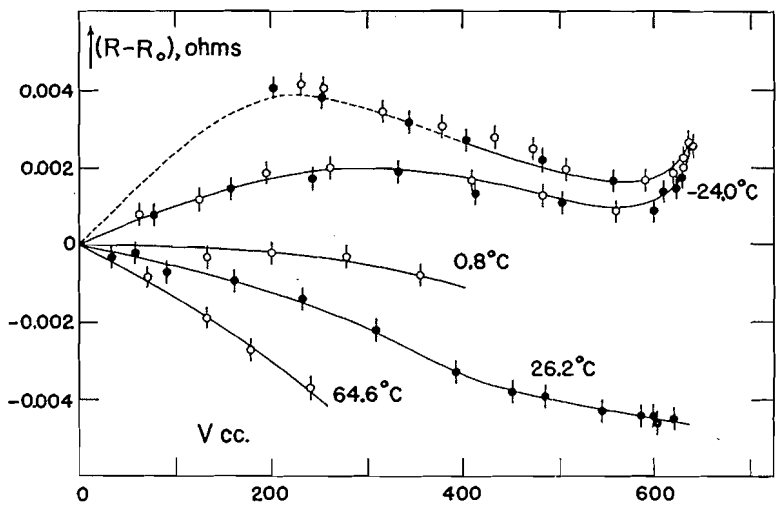



FIG. 8. Resistance versus volumes adsorbed for ethyl chloride, rod 8.

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*Effect of Ethyl Chloride*

The alteration of resistance due to ethyl chloride is shown in Fig. 8. The direction and magnitude of this alteration is dependent upon the volume of adsorbed vapor and the temperature. The resistance is diminished by this adsorbate at 64.6°C. whereas at −24.0°C. the resistance increases appreciably on adsorption of vapor. Again, such behavior is not specific to a given rod as similar results were obtained with rod No. 4. The abrupt increase of the change of resistance near saturation of the surface referred to in the introduction is well illustrated. The resistance variation was not reversible, although the adsorption isotherm was. The latter statement could not be demonstrated in the low pressure region; that is, below the pressure corresponding with the volumes indicated on the solid curve of Fig. 8. Volumes indicated on the dotted portion of the curve were taken from the adsorption isotherm and a knowledge of the equilibrium pressures. It was demonstrated that prolonged pumping at the temperature of the isotherm caused the resistance to return to its original ($R_0$) value. On readsorption after partial desorption, the resistance followed the desorption branch. The findings are too complex to permit interpretation. The hysteresis of the resistance change may be due to a small number of ethyl chloride molecules, not easily removed in desorption, bound interstitially in the expanded graphitic crystallites. It is known that bromine is bound in this manner in graphite (11). It should be noted, however, that the resistance alteration, at a specified temperature, is characteristic of the adsorbate, and that the temperature coefficient of the effect may vary from one adsorbate to adsorbate.

## GENERAL DISCUSSION

The attempts made to account for the observed phenomena have involved the postulate that the presence of physically adsorbed molecules on the surface of the carbon semiconductor alters the number of conduction electrons rather than their mobility. Direct evidence of this is lacking, but could perhaps be obtained by measurements of the thermoelectric effect of the semiconductor in gaseous environments. Bardeen (2) has introduced the concept of surface states on the free surface of a semiconductor. A total surface dipole exists because of a space charge region which extends from the surface into the bulk of the solid. An alteration of the number of electrons trapped in surface states can be brought about by the application of an external electric field. The alteration of the contact potential between an N-type germanium semiconductor and platinum, in the presence of polar vapors, has been treated quantitatively on the basis of the theory of surface states by Brittain and Bardeen (5). Stuetzer (19) has shown that the electrical conductivity of an N-type germanium semiconductor is increased if a polar liquid such as nitrobenzene is present at the surface. It is suggested that excess holes are formed in the valence band owing to the repelling field of the oriented polar molecules. In the case of active carbon, donor traps at the surface appear indicated because peripheral carbon atoms are the source of electrons in the conduction band. The conductivity effect due to physically adsorbed vapors may thus be due to

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shifts of the equilibrium among electrons in surface states and in the conductivity and valence bands of the solid. This effect would be especially noted for active carbon because of its large surface to volume ratio. A demonstration that the effects are due to changing number of carriers is not possible by resistance measurements alone.

ACKNOWLEDGMENT

We should like to acknowledge the award of a studentship to W. W. Smeltzer, and a grant in aid of this research, from the National Research Council, Ottawa. Financial support was also given by the Advisory Committee on Research, University of Toronto.

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# ION EXCHANGE SEPARATION OF AMMONIUM AND GUANIDINE SALTS[1]

By Marcel Bertrand and J. L. Myers

ABSTRACT

A procedure for the determination of mixtures of guanidine and ammonium salts which employs an ion exchange separation prior to analysis is described. Details of the ion exchange and the results obtained with synthetic mixtures are presented. The recommended procedure permits estimation of guanidine in the presence of up to ten times its weight of ammonium salt.

## INTRODUCTION

The ion exchange mechanism has attracted widespread attention in recent years and the method of separation described herein is an application of this principle.

In analysis of guanidine by picrate precipitation erroneous results are obtained in the presence of large concentrations of ammonium ions (1). If the ammonium ion could be removed by ion exchange, it would be possible to determine mixtures of guanidine and ammonium salts irrespective of their composition.

The behavior of guanidine and ammonium ions on the cation resin exchanger Nalcite was studied and it was established that these ions could be quantitatively separated by this means.

## (A) DISTRIBUTION CURVE

After considerable experimentation, a pyrex glass tube, 3.50 sq. cm. in cross sectional area and 35 cm. in length, was selected. It contained 25.3 gm. of oven dried Nalcite HCR (Canadian trade name for Dowex 50). The Nalcite rested on a sintered glass filter of medium porosity and filled the tube to a height of 14.2 cm., giving a bed volume of 50 ml.

Nalcite resin of regular size was placed in the tube and prepared for use by backwashing with water until the liquid above the resin was clear. This procedure is necessary to prevent subsequent clogging of the glass filter by minute resin particles. To ensure complete conversion to the hydrogen form, the resin was then washed with approximately normal hydrochloric acid until the effluent and influent concentrations were the same.

The exchanger was then saturated with approximately 1.7 *N* sulphuric acid which was prepared by diluting 50 ml. of concentrated sulphuric acid to one liter. One gram samples containing a mixture of ammonium sulphate and guanidine nitrate were dissolved in 10 ml. of 1.7 *N* sulphuric acid. After introduction of the sample and before starting the elution, the column was drained until the level of liquid was one millimeter above the level of the exchanger. The column was then eluted with 1.7 *N* sulphuric acid at the rate of 6.5 ml./

[1] *Manuscript received April 1, 1953.*
*Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec.*



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min. Elutions were performed at room temperature. Fifty-milliliter fractions of eluate were collected in volumetric flasks. Under these conditions the ammonium sulphate appeared in the first 15 fractions and guanidine in the 30 following.

*Determination of Ammonia*

The eluted fractions containing ammonium ions were analyzed by the micro-Kjeldahl method (3). An aliquot of 20 ml. was transferred to a Parnas and Wagner micro-Kjeldahl apparatus, 15 ml. of 30% sodium hydroxide solution were added, and the ammonia was steam distilled into 5 ml. of 2% boric acid solution for three minutes. The solution was then titrated with 0.01 *N* hydrochloric acid, using four drops of 5 : 1 bromocresol green/methyl red mixed indicator.

*Determination of Guanidine*

Guanidine was analyzed by Sullivan's colorimetric method (4), using a Fisher Electrophotometer AC model with a 525 mμ green filter. One milliliter of aliquot of the eluate was transferred into a 50 ml. volumetric flask and 2 ml. of freshly prepared 1% solution of 1,2-naphthoquinone-4-sodium sulphonate were added, followed by 0.5 ml. of 4 *N* sodium hydroxide. This solution was allowed to stand in a boiling water bath for two minutes; then cooled under running water. Three milliliters of 2.5% urea solution were added, followed by 1 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid (density 1.42). The solution was mixed and diluted to the mark with 50–50 ethanol–water solution. The contents were transferred to the cell and compared to distilled water by means of the electrophotometer.

The above method offered the following advantages:

(*a*) Rapidity with which analyses can be performed.

(*b*) High accuracy attained at the low concentrations of guanidine encountered in this work.

The calibration curve obtained with the Sullivan's method using a standard solution of guanidine nitrate in 1.7 normal sulphuric acid solution is shown

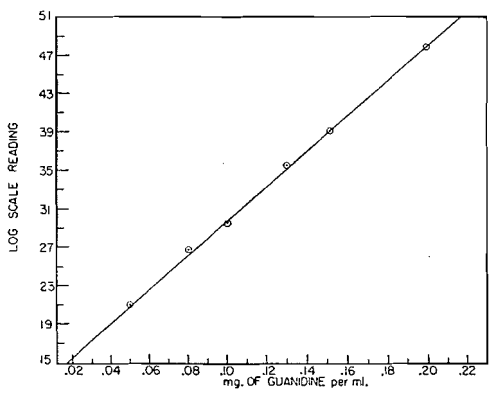



FIG. 1. Calibration curve for colorimetric analysis of guanidine with 1,2-naphthoquinone-4-sodium sulphonate.

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in Fig. 1. This curve illustrates the accuracy and reproducibility achieved by strict adherence to the specified procedure.

*Results*

A typical graph for the separation and recovery of ammonium and guanidine salts (Fig. 2) shows that a good, clear separation was attained. This curve is

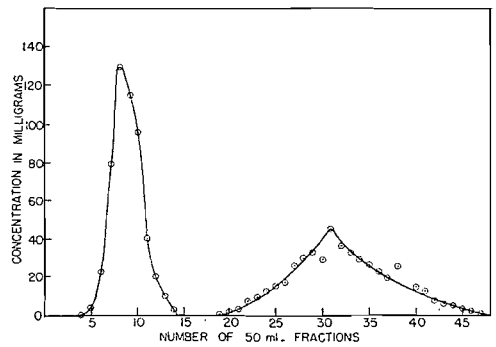



FIG. 2. Elution of ammonium and guanidine salts. Conditions: Column, 3.50 sq. cm. × 14.2 cm.
Exchanger, 25.3 gm. of HCR Nalcite (oven-dried basis).
Elutrient solution, 1.7 $N$ $H_2SO_4$.
Flow rate, 6.5 ml./min.
Temperature, 27°C.

obtained by plotting the concentration of the ammonium or guanidine salts in milligrams in the eluate as ordinate and the number of 50 ml. fractions of eluate as abscissa.

From this curve, it is apparent that the ammonium ions are less strongly absorbed and are eluted in the first 15 fractions. Several fractions are free of cations and then the more strongly bound guanidine ions are slowly eluted in the next 30 fractions.

## (B) ANALYTICAL PROCEDURE

Although the study of the distribution curve showed that guanidine and ammonium ions could be separated on a cation exchange column the procedure was too long and tedious for analytical use. Accordingly a more rapid procedure was investigated.

A pyrex glass tube 3.14 sq. cm. in cross sectional area and 42 cm. long was selected. It contained 45.1 gm. of oven dried Nalcite which filled the tube to a height of 28 cm. giving a bed volume of 85 ml. Nalcite resin was conditioned in the same manner as in Section (*A*) and converted to the hydrogen form. Elutions were performed at room temperature, first with approximately 1 $N$ and later with 6 $N$ hydrochloric acid.

One gram samples containing a mixture of ammonium sulphate and guanidine nitrate were dissolved in 10 ml. of 1 $N$ hydrochloric acid. The exchanger was previously saturated with normal hydrochloric acid. After introduction of the sample, the column was drained until the level of the liquid was one millimeter above the level of the exchanger. The ammonium ion was then

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eluted with 1000 ml. of 1 *N* hydrochloric acid at a rate of 6–6.5 ml./min. The eluate was collected in a 1000 ml. volumetric flask and adjusted to the mark with distilled water at 20°C. The elution acid was replaced by 6 *N* hydrochloric acid and an additional 300 ml. were collected at the same rate of flow.

*Determination of Ammonia*

The analysis of ammonia was carried out in triplicate on suitable aliquots, using the procedure described in Section (*A*).

*Determination of Guanidine*

The 300 ml. eluate was evaporated to near dryness on a steam plate to remove the hydrochloric acid. To assure complete evaporation of the hydrochloric acid, 25 ml. of distilled water was added and the mixture re-evaporated to dryness. The residue was taken up with 25 ml. of distilled water and the solution heated until concentrated to 15 ml. The determination was then completed using the calcium picrate method (2).

*Results*

It was found that the use of different acid concentrations in (*B*) gave a more rapid separation since the two salts were separated and eluted in 1300 ml. of eluate instead of 2500 ml. The time was reduced to $3\frac{1}{2}$ hr. compared to $6\frac{1}{2}$ hr. in the previous experiment. Hydrochloric acid was used instead of sulphuric acid in the final procedure because of its greater ease of evaporation from the solution.

It was found that with 6 *N* hydrochloric acid, all guanidine was eluted from the column in six fractions instead of the 30 fractions obtained with 1.7 *N* sulphuric acid (see Table I). Typical data of the separation and recovery of ammonium and guanidine are given in Table II.

TABLE I
ELUTION OF GUANIDINE WITH 6 *N* HYDROCHLORIC ACID IN SIX FRACTIONS

| Guanidine nitrate | | |
|---|---|---|
| Added, gm. | Found, gm. | Recovery, % |
| 0.5060 | 0.5049 | 99.8 |
| 0.5010 | 0.5002 | 99.8 |
| 0.5025 | 0.5012 | 99.7 |

TABLE II
SEPARATION OF AMMONIUM AND GUANIDINE SALT

| Ammonium sulphate eluted with 1000 ml. of *N* HCl | | | Guanidine nitrate eluted with 6 × 50 ml. of 6 *N* HCl | | |
|---|---|---|---|---|---|
| Added, gm. | Found, gm. | Recovery, % | Added, gm. | Found, gm. | Recovery, % |
| 0.5013 | 0.4988 | 99.5 | 0.5017 | 0.4942 | 98.5 |
| 0.5023 | 0.4987 | 99.3 | 0.5107 | 0.5035 | 98.6 |

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Fainer and Myers (2) claim that their calcium picrate method for the determination of guanidine tolerates large amounts of ammonium salts as impurities. The results in Table III show that this is true up to a ratio of 1 : 2 of ammonium to guanidine salt. Above this ratio accurate results are not obtainable.

TABLE III
DETERMINATION OF GUANIDINE IN PRESENCE OF AMMONIUM IONS USING THE CALCIUM PICRATE METHOD

| Ratio* of mixture | Guanidine nitrate | | | Ammonium sulphate added, gm. |
|---|---|---|---|---|
| | Added, gm. | Found, gm. | Recovery, % | |
| 1 : 1 | 0.5022 | 0.4994 | 99.4 | 0.5034 |
| 1 : 1 | 0.5007 | 0.4986 | 99.6 | 0.5012 |
| 1 : 2 | 0.3548 | 0.3556 | 100.2 | 0.6674 |
| 1 : 5 | 0.1549 | 0.4451 | 287.3 | 0.8878 |
| 1 : 7 | 0.1215 | 0.4122 | 339.2 | 0.8864 |
| 1 : 10 | 0.0912 | 0.2184 | 239.5 | 0.9104 |

**Approximate ratio of guanidine to ammonium salts.*

By the use of the ion exchange column, even a 1 : 10 ratio mixture can be analyzed. Table IV shows the results of a series of experiments with ratios similar to those in Table III.

TABLE IV
ANALYSIS OF MIXTURES OF GUANIDINE AND AMMONIUM SALTS BY ION EXCHANGE COLUMN

| Ratio* of mixture | Guanidine nitrate by calcium picrate method | | | Ammonium sulphate by Kjeldahl distillation | | |
|---|---|---|---|---|---|---|
| | Added, gm. | Found, gm. | Recovery, % | Added, gm. | Found, gm. | Recovery, % |
| 1 : 1 | 0.5017 | 0.4942 | 98.5 | 0.5013 | 0.4988 | 99.5 |
| 1 : 2 | 0.3570 | 0.3488 | 97.7 | 0.6655 | 0.6560 | 98.6 |
| 1 : 5 | 0.1525 | 0.1448 | 95.0 | 0.8692 | 0.8524 | 98.1 |
| 1 : 7 | 0.1217 | 0.1176 | 96.6 | 0.8833 | 0.8865 | 100.3 |
| 1 : 10 | 0.0890 | 0.0837 | 94.0 | 0.9165 | 0.9175 | 100.1 |

**Approximate ratio of guanidine to ammonium salts.*

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## SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
## VIII. DEUTERIUM SUBSTITUTION PRODUCTS OF ETHYL ACETATE[1]

By B. Nolin

The deuterium labelling technique was used recently in the study of the infrared absorption spectrum of pentanone-3 (5). To extend this method of investigation to ethyl acetate, several deuterium substitution products were required in which one or more of the hydrogen containing groups are completely deuterated. This paper deals with the synthesis of seven deuterated ethyl acetates. The results of the spectroscopic investigation will be reported in a subsequent publication.

Several routes to the desired compounds were considered. On the 10–25 millimole scale, the reaction between the silver salt of acetic acid and ethyl iodide (4) proved the most suitable, because the corresponding deuterated materials could be obtained in high purity and no by-products are formed in the reaction. The esters were thus prepared by the following scheme:

$$RCOOAg + R'I \longrightarrow RCOOR' + AgI,$$

where R = $CH_3$ or $CD_3$, and R′ = $CH_3CH_2$,$CH_3CD_2$, $CD_3CH_2$, or $CD_3CD_2$.

Deuterated silver acetate of high isotropic purity was prepared as described in a previous paper (6); the isotopic determination was carried out by mass spectrometer analysis of samples of deuterated methyl bromide prepared by brominative degradation of the silver salt essentially as reported in the above-mentioned paper. This analytical procedure is now recommended for the accurate determination of the deuterium content of the alkyl groups of lower fatty acids, whatever the isotopic purity may be. For such an analysis, no special purification of the silver salt is required. The decarboxylation is readily carried out in a straight sealed tube with less than a gram of material and the deuterated bromide is merely freed from carbon dioxide and excess bromine by passing the reaction product through Ascarite.

The deuterated ethyl iodides were obtained from the corresponding bromides by an extension and modification of Spindler's method (7) which consists in treating an alkyl bromide with calcium iodide in a sealed tube. According to this author, who investigated bromides higher than ethyl, the conversion was incomplete. In the present work the conversion of ethyl bromide was carried nearly to completion by a second treatment with calcium iodide.

Ethyl-2-$d_3$ bromide was prepared through this sequence of reactions: alkylation of ethyl malonate with methyl-$d_3$ bromide (6) essentially as reported in (9) for the preparation of the normal compound, hydrolysis of the reaction product to methyl-$d_3$ malonic acid, decarboxylation of the dibasic acid to propionic-3-$d_3$ acid, and finally brominative decarboxylation of silver propionate-3-$d_3$ as described in a previous paper for silver acetate-$d_3$ (6). Höle-

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mann and Clusius had prepared propionic-3-$d_3$ acid but by a different method (2).

Ethyl-1-$d_2$ bromide was prepared by the brominative degradation of silver propionate-2-$d_2$. The preparation of propionic acid labelled in the methylene group (95.0 atom % deuterium) had been reported (2).

## EXPERIMENTAL*

### *Deuterated Ethyl Acetates*

The preparation of ethyl-$d_5$ acetate-$d_3$ is given as a typical procedure. Ethyl-$d_5$ iodide** (4.4 gm.) was transferred through a vacuum line to a small flask containing silver acetate-$d_3$*** (4.6 gm.). The flask was removed from the manifold, attached to a reflux condenser, and heated overnight at 95°C. The volatile material was separated from the inorganic residue and found by mass spectrometer analysis to contain a small amount of unreacted ethyl-$d_5$ iodide. The mixture was therefore treated as before with fresh silver acetate-$d_3$ (2.3 gm.). The ester, now free from ethyl iodide, was treated three times with small amounts of phosphoric anhydride, that is until the latter was not discolored within five minutes. The material was degassed in the usual way and a very small fraction was removed. The bulk had a practically constant vapor pressure at 0°C. Yield, 2.0 gm., 75%.

The refractive index, vapor pressure at 20°C., and isotopic purity expressed in deuterium atoms per molecule of ethyl-$d_5$ acetate-$d_3$ are listed in Table I,

TABLE I
PHYSICAL PROPERTIES OF NORMAL AND DEUTERATED ETHYL ACETATES

| Compound | D atoms per molecule | | $n_D^{20}$ | Vapor pressure (mm., 20°C.) |
|---|---|---|---|---|
| | Found | Required | | |
| $CH_3COOCH_2CH_3$ | — | — | 1.3723* | 72.9** |
| $CH_3COOCD_2CH_3$ | 1.98 | 2 | 1.3718 | 74.2 |
| $CH_3COOCH_2CD_3$ | 2.97 | 3 | 1.3716 | 74.0 |
| $CD_3COOCH_2CH_3$ | 2.97 | 3 | 1.3712 | 74.8 |
| $CH_3COOCD_2CD_3$ | 4.97 | 5 | 1.3710 | 75.0 |
| $CD_3COOCD_2CH_3$ | 4.97 | 5 | 1.3707 | 75.3 |
| $CD_3COOCH_2CD_3$ | 5.92 | 6 | 1.3704 | 75.9 |
| $CD_3COOCD_2CD_3$ | 7.94 | 8 | 1.3700 | 76.3 |

*Literature (8), 1.37233.*
**Literature (10), 72.8 mm.*

together with those of six partially deuterated ethyl acetates and normal ethyl acetate prepared in the same way. The isotopic purity of the deuterated esters was determined by mass spectrometry and corresponded to 98.8–99.4 atom % deuterium. The vapor pressures were measured with an apparatus similar to that described by Booth and Swinehart (1); they are higher than

*All mass spectrometer analyses are corrected for $C_{13}$.
**The isotopic purity of this iodide, ethyl-$d_3$ iodide, and ethyl-$d_2$ iodide corresponded to 99.2 atom % deuterium or more.
***99.3 atom % deuterium.

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the vapor pressure of normal ethyl acetate, which is raised on complete deuteration by 1.0 and 3.4 mm. at 0°C. and 20°C. respectively. The refractive index of ethyl acetate is lowered on deuteration, the average difference being 0.0003 unit per carbon–deuterium bond.

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The author is very grateful to Dr. L. C. Leitch who has initiated the present series of papers on the synthesis of organic deuterium compounds and in whose section this work has been done. Thanks are also due to Miss F. Gauthier and Miss J. Fuller for the mass spectrometer analyses.

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## SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS
## IX. BISTRIDEUTEROMETHYL MERCURY*

By E. E. Bevege, R. Renaud, and L. C. Leitch

Although several methods have been reported for the preparation of dimethyl mercury (5) which is widely used in photochemical work as a source of methyl radicals, none of them is suitable for the synthesis of the deuterated analogue where economy of deuterated reactants is of paramount importance. It appeared to us that bistrideuteromethyl mercury would be readily prepared by the method employed by Emeléus and Haszeldine (1) for the synthesis of organo fluorine compounds. The methyl-$d_3$ iodide required in the present work was prepared as recently reported by Nolin and one of us (3, 4). When it was heated in a sealed tube for several days at 125°C. with cadmium amalgam a 75% yield of bistrideuteromethyl mercury was obtained. Its deuterium content was essentially the same as that of the methyl-$d_3$ iodide. The vapor pressure of deuterated dimethyl mercury, measured as described in an earlier paper (2), is 17.9 mm. at 0°C. compared with 17.4 mm. for the normal compound.

The synthesis described in detail below could probably be used in preparing deuterated diethyl mercury from the corresponding deuterated ethyl iodide.

*Bistrideuteromethyl Mercury*

Cadmium amalgam was prepared by shaking 13.0 gm. of cadmium turnings and 20 ml. of redistilled mercury in a bottle. The amalgam was poured into a

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the vapor pressure of normal ethyl acetate, which is raised on complete deuteration by 1.0 and 3.4 mm. at 0°C. and 20°C. respectively. The refractive index of ethyl acetate is lowered on deuteration, the average difference being 0.0003 unit per carbon–deuterium bond.

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tube (12 in. × 1 in.) with a constriction and a joint for attaching it to a vacuum line. Methyl-$d_3$ iodide (12.5 gm.) was distilled into the evacuated tube which was then carefully sealed off at the constriction. The reactants were heated for a day at 100°C. and three days at 125°C. There was no pressure in the cold tube when it was opened. The volatile material was distilled off on the vacuum line into a trap and fractionally distilled at 0°C. into other traps on the line. After collecting 0.1 ml. (vapor pressure 19.5 mm. at 0°C.), the main fraction (2.2 ml.) had a constant vapor pressure of 17.9 mm. at 0°C. Analysis by mass spectrometry indicated the compound contained no methyl-$d_3$ iodide.

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## THE PHOTOGRAPHIC RECORDING OF PAPER CHROMATOGRAMS OF CARBOHYDRATES AND A NEW SPRAY REAGENT*

BY G. L. KILGOUR AND G. G. S. DUTTON

The standard method of spraying paper chromatograms of sugars with various reagents to give colored spots (1) is in many cases satisfactory but the method has certain disadvantages. The most important one is that the colored spots produced are not stable indefinitely and hence such chromatograms are not satisfactory for reference purposes. It has been noted that the colored spots absorb strongly in the ultraviolet and we have been able to utilize this fact in making photographic copies of chromatograms.

A paper chromatogram is run in the normal way and after removal from the tank or cabinet is thoroughly air-dried to remove solvent, sprayed with any of the recommended reagents (1), and again dried. When dry, the chromatogram is laid on the emulsion side of a piece of photographic paper** and the two sheets are then stretched over a gently curved surface. This is important in order to get maximum contact between the chromatogram and the photographic paper, otherwise the spots will be very diffuse. The photographic paper is now exposed by holding a small ultraviolet source, e.g. a Mineralight, about twelve inches above the paper for one or two seconds. The photographic paper is then processed in the normal way.

*This work was undertaken while one of us (G.L.K.) was the holder of a Powell River Company Limited Scholarship, and we also wish to acknowledge financial assistance from the National Research Council.

**We have used Kodabromide A5 obtainable in rolls of 200 ft. and 4¼ in. wide from Air Photo Supply Corp., 555 East Tremont Avenue, New York 57, N.Y.

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This method has the advantage that the chromatogram is unharmed and as many copies as may be required can readily be made from the same chromatogram. In addition, the photographic print gives a clear indication of the size and exact shape of the spots which facilitates $R_f$ measurements and permits of rough quantitative estimations. Further, very often spots will show up under ultraviolet illumination, and hence on the photographic copy, which would not have been rendered visible by the ordinary spraying technique and inspection in visible light. This applies particularly to uronic and biuronic acids.

In this connection we have noted that all spray reagents do not give the same response with different sugars. In an attempt to find a spray not suffering from such a defect a new reagent was created, aniline hydrogen malonate. This was found to be decidedly superior to any other reagent used for the simple sugars, especially when dissolved in glacial acetic acid (2%) instead of butanol. This spray reacts equally with pentoses and hexoses giving pink and green colors respectively. However, it is not satisfactory for uronic acids and we found that aniline trichloroacetate was the best spray for general work (1), although the malonate reagent causes less discoloration of the paper.

It would seem wise to draw attention to the inadvisability of relying only on one spray reagent in any initial investigation of a carbohydrate material by means of paper chromatography especially if use is not made of ultraviolet light photographs.

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