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SYNTHESIS OF ORGANIC DEUTERIUM COMPOUNDS

X. METHYL-d_3 IODIDE AND DEUTERIUM SUBSTITUTION PRODUCTS OF METHYL ACETATE[1]

By B. Nolin

ABSTRACT

Methyl-d_3 bromide was easily converted by treatment with calcium iodide into methyl-d_3 iodide in 94% yield. The latter was reacted on the 50-millimole scale with silver acetate or silver acetate-d_3 to yield methyl-d_3 acetate or methyl-d_3 acetate-d_3. Methyl iodide and silver acetate-d_3 gave methyl acetate-d_3.

INTRODUCTION

This paper deals with the synthesis of methyl acetate derivatives deuterated specifically in each of the two methyl groups and in both; the preparation of methyl-d_3 iodide required as an intermediate in a number of cases is also described. These esters have been prepared as part of a systematic investigation of the infrared absorption of acyl compounds (3) and their spectra will be discussed in a subsequent publication.

The procedure adopted for the synthesis of the methyl acetates was the reaction between the silver salt of a carboxylic acid and an alkyl iodide, which had previously proved satisfactory for the preparation of a number of deuterated ethyl acetates on the 10-25 millimole scale (2). The desired esters were thus prepared according to the following scheme:

$$RCOOAg + RI \rightarrow RCOOR + AgI,$$

where $R = CH_3$ or CD_3.

Silver acetate-d_3 was prepared as previously described (4). Methyl-d_3 iodide was obtained from the corresponding bromide (4) after prolonged and repeated treatment with calcium iodide hexahydrate. Preparative details are given in the experimental part.

EXPERIMENTAL*

Methyl-d_3 Iodide

Methyl-d_3 bromide (9.1 gm., 93 millimoles) was transferred through a vacuum line into a long necked 50-ml. flask containing calcium iodide hexa-

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**All mass spectrometer analyses are corrected for C_{13}.*

hydrate (22.4 gm., 1.2 equivalents) and cooled in liquid nitrogen. The reaction vessel was sealed off and shaken at about 75°C. for a day. The volatile material was separated and treated with mercury and phosphoric anhydride to remove small amounts of free iodine and water. The vapor pressure at 0°C. was 169 mm. This indicated the presence of about 4% of unchanged methyl-d_3 bromide since the vapor pressures of deuterated methyl iodide and methyl bromide at 0°C. are 148 and 481 mm. respectively (1); mass analyses also showed an incomplete conversion at this stage. Weight, 13.0 gm.

The mixture of methyl-d_3 halides was treated with fresh calcium iodide for two days. The reaction material was worked up as above. Neither methyl-d_3 bromide nor other contaminants were detected in the product, which analyzed 97.8 mole % CD_3I and 2.2 mole % CD_2HI for a total isotopic content of 99.2 atom % deuterium. The vapor pressure at 0°C. was 147.2 mm. n_D^{20} 1.5263. Yield, 12.7 gm., 94%.

The conditions described above for the small-scale conversion of methyl bromide into methyl iodide are convenient, but not necessarily ideal. A larger excess of calcium iodide hexahydrate and a longer period of heating might eliminate the necessity of a second treatment. However, the use of anhydrous calcium iodide which was reported several times in the literature for the conversion of higher bromides is definitely unnecessary in the case of methyl bromide.

Deuterated Methyl Acetates

The iodide (35–55 millimoles) was transferred through a vacuum line into a 25-ml. flask containing the appropriate silver acetate* (1.1 equivalents) and cooled in liquid nitrogen. The flask was removed from the manifold, attached to a reflux condenser, and heated overnight at 65–75°C. The volatile material was separated on the vacuum line and reacted again with fresh silver acetate (0.3 equivalent). Usually no yellow coloration developed overnight during this second treatment and the reaction was then considered complete. In the preparation of methyl-d_3 acetate-d_3 a third treatment appeared desirable.

The ester was treated twice with small amounts of phosphoric anhydride, where some loss necessarily occurred. A small fraction was removed by allowing the material cooled in dry ice – acetone to distill under its own pressure into a receiver cooled in liquid nitrogen. A large middle fraction was then collected in a similar way. It had a practically constant vapor pressure at 0°C.; its refractive index did not differ from that of the removed fractions by more than ±0.0002 unit. The yield of pure product averaged 50%.

The refractive indices, vapor pressures, and deuterium contents of the three deuterated methyl acetates thus obtained are listed in Table I, together with those of the normal compound prepared by the same method. The isotopic purity of the deuterated esters corresponded to 99.0 atom % deuterium or more. The vapor pressure of normal methyl acetate is raised on complete deuteration by 1.6 mm. at 0°C. On the other hand, deuteration lowers the

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The isotopic purity of silver acetate-d_3 corresponded to 99.3 atom % deuterium.

TABLE I

Physical properties of normal and deuterated methyl acetates

Compound	D atoms per molecule		Vapor pressure (mm., 0°C.)	n_D^{20}
	Found	Required		
CH_3COOCH_3	—	—	62.4*	1.3616**
CH_3COOCD_3	2.97	3	63.2	1.3607
CD_3COOCH_3	2.97	3	63.4	1.3603
CD_3COOCD_3	5.95	6	64.0	1.3595

*Literature (6), 62.1 mm.
**Literature (5), 1.36193.

refractive index by 0.0003–0.0004 unit per carbon–deuterium bond. However, the difference observed between the refractive indices of methyl-d_3 acetate and methyl acetate-d_3 may not be due entirely to experimental errors. Part of it could result in the last analysis from a smaller amplitude of the zero-point vibrations of the latter ester.

ACKNOWLEDGMENTS

The author wishes to thank 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.

The mass spectrometer analyses were kindly performed by Miss F. Gauthier and Miss J. Fuller.

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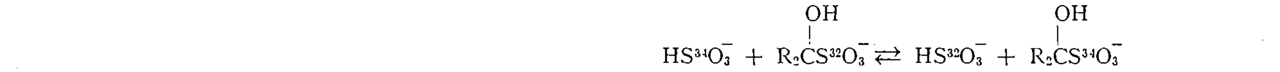
SULPHUR ISOTOPE EFFECTS IN THE BISULPHITE ADDITION REACTION OF ALDEHYDES AND KETONES

I. EQUILIBRIUM EFFECT AND THE STRUCTURE OF THE ADDITION PRODUCT[1]

By W. A. Sheppard[2] and A. N. Bourns

ABSTRACT

Equilibrium constants for the isotopic exchange reaction between bisulphite ion and the addition product of eight aldehydes and ketones have been measured.

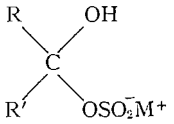


$$HS^{34}O_3^- + R_2\overset{\text{OH}}{\overset{|}{\mathrm{C}}}S^{32}O_3^- \rightleftarrows HS^{32}O_3^- + R_2\overset{\text{OH}}{\overset{|}{\mathrm{C}}}S^{34}O_3^-$$

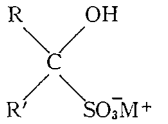
At 25° C., values ranging from 1.021 for acetone to 1.010 for anisaldehyde have been observed. Since constants of this magnitude are to be expected only if the bonding of the sulphur atom is different in the bisulphite ion and the addition product, these results are considered to confirm the carbon–sulphur bond structure of the latter. This conclusion is supported by the small constant, 1.002, obtained for the diethyl sulphate and ethyl hydrogen sulphate isotopic exchange in which the bonding of sulphur is essentially the same in the two reacting species.

INTRODUCTION

The problem of the structure of the bisulphite-addition product of aldehydes and ketones has occupied the attention of chemists for many years. By 1900, however, it had been fairly well established that these compounds are either α-hydroxysulphite ester salts, I, or α-hydroxysulphonic acid salts, II.



I



II

Structure I was originally favored on the basis of Müller's demonstration (8) that a product obtained by the action of sulphuric acid on methanol, and considered by him to be hydroxymethane sulphonic acid, was nonidentical with formaldehyde bisulphite. Raschig and Prahl (10,11,12), however, showed that Müller's product was symmetrical acetone disulphonic acid, formed by the sulphonation of acetone present in the methanol of that time, and, furthermore, that the actual product of the reaction of sulphuric acid and methanol is methyl hydrogen sulphate, an isomer of hydroxymethane sulphonic acid. These workers presented chemical evidence in favor of II, but their results were differently interpreted by Schroeter and Sulzbacher (13),

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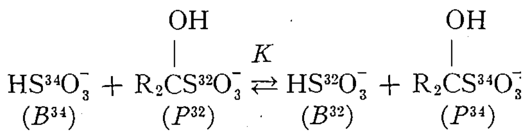
who proposed a stable "trimolecular structure" represented by (R_2CO) (SO_2) (HOH). Backer and Mulder (1, 2), Lauer and Langkammerer (7), and Shriner and Land (14) have each provided strong support for structure II by converting the addition product to a compound considered to contain a carbon–sulphur bond by virtue of its preparation by known reactions from a sulphur compound of established structure. Although this evidence appears conclusive, there is the possibility of unexpected rearrangements, particularly in view of the lability of the carbon–sulphur bond (4).

Physical evidence in support of the hydroxysulphonic acid structure has also been reported. The absorption spectra of the formaldehyde and acetone addition compounds contain a band at 4992.0Å, compared to 4992.2Å found for sulphonic acids and 4996.0Å for metal alkali sulphites (15). Furthermore, Raman data (3), for the addition products of a number of carbonyl compounds suggest a carbon–sulphur bond and clearly eliminate the trimolecular formulation of Schroeter.

The present paper deals with a study of the fractionation of the sulphur isotopes in the exchange reaction between bisulphite ion and the addition product of a number of aldehydes and ketones (Equation 1).



$$\underset{(B^{34})}{HS^{34}O_3^-} + \underset{(P^{32})}{R_2\overset{\overset{\textstyle OH}{|}}{C}S^{32}O_3^-} \overset{K}{\rightleftarrows} \underset{(B^{32})}{HS^{32}O_3^-} + \underset{(P^{34})}{R_2\overset{\overset{\textstyle OH}{|}}{C}S^{34}O_3^-} \qquad [1]$$

The results provide what is considered to be a conclusive proof of the hydroxysulphonic acid structure, II, for the addition compounds.

The equilibrium constant, K, for this exchange reaction is given by:

$$K = \left(\frac{Q_{P^{34}}}{Q_{P^{32}}}\right) \Big/ \left(\frac{Q_{B^{34}}}{Q_{B^{32}}}\right) \qquad [2]$$

where the $Q_{P's}$ are the partition functions for the two isotopic species of addition compounds and the $Q_{B's}$ the corresponding partition functions for bisulphite ion (17). If the addition compounds have the carbon–oxygen–sulphur bond structure, I, the bonding of the sulphur atom is essentially the same as in bisulphite ion. Therefore the change in vibrational frequency of the sulphur bonds resulting from the substitution of S^{34} for S^{32} will be approximately the same in the two chemical species and the quotient of the two partition function ratios (Equation 2) will be very close to unity. If, on the other hand, the addition compounds contain a carbon–sulphur bond (structure II), the partition function ratios for the two chemical species will differ and an appreciable fractionation of the sulphur isotopes will occur. Indeed, this fractionation should be of the order of magnitude observed in the sulphur dioxide – bisulphite ion exchange reaction (Equation 3) in which the heavier isotope concentrates in the bisulphite ion to the extent of 1.9% at 25° C. ($K = 1.019$).

$$S^{34}O_2 + HS^{32}O_3^- \overset{K}{\rightleftarrows} S^{32}O_2 + HS^{34}O_3^- \qquad [3]$$

METHOD

The equilibrium constant for the exchange reaction between bisulphite ion and the addition compound may be expressed in terms of isotopic ratios as follows:

$$K = \frac{[B^{32}][P^{34}]}{[B^{34}][P^{32}]} = \frac{[B^{32}]}{[B^{34}]} \Big/ \frac{[P^{32}]}{[P^{34}]} \qquad [4]$$

where $[B^{32}]/[B^{34}]$ is the ratio of the sulphur isotopes in bisulphite ion at equilibrium and $[P^{32}]/[P^{34}]$ is the corresponding ratio in the addition compound. The equilibrium constant, K, was determined experimentally in the following way. The carbonyl component was shaken with excess saturated sodium bisulphite solution of natural isotopic abundance until equilibrium had been established, and the precipitated addition compound was collected and converted quantitatively to sulphur dioxide. Mass spectrometric measurement of the ratio of the sulphur isotopes in the latter gave the $[P^{32}]/[P^{34}]$ ratio in Equation 4. The ratio, $[B^{32}]/[B^{34}]$, could not be determined directly since the bisulphite ion at equilibrium could not be separated from dissolved addition compound. By using a large excess of sodium bisulphite, however, this ratio is practically identical with the isotopic ratio of the starting material. Furthermore, from a knowledge of the relative amounts of bisulphite ion and carbonyl component, the extent of conversion of the latter to addition product, and the isotopic ratio in the original bisulphite ion and the addition product, $[B^{32}]/[B^{34}]$ may be calculated with considerable accuracy.

RESULTS

In Table I are given the equilibrium constants, K, for the exchange reaction involving the addition product of three aldehydes and five ketones. Although isotopic equilibrium was normally attained within three days, several determinations were made for each compound using equilibration periods ranging from 5 to 24 days. Good agreement was found in every case.

The equilibrium constants differ from the ratios given in the second column from the right by an amount depending upon the sodium bisulphite: carbonyl compound ratio. The low solubility of the addition products of the higher molecular weight compounds permitted the use of a 10: 1 molar ratio, and the isotopic abundance of the bisulphite ion at equilibrium and that of the original bisulphite were therefore nearly the same. With acetone and 2-butanone, the greater solubility of the addition compound necessitated the use of only a small excess (two to three times) of bisulphite and the equilibrium constants are therefore considerably higher than the $\frac{(S^{32}/S^{34})\text{ orig. }HSO_3^-}{(S^{32}/S^{34})\text{ product}}$ ratios. Examination of the K values for 4-methyl-2-pentanone, however, shows that excellent agreement was obtained using widely different ratios of the reactants.

TABLE I

EQUILIBRIUM CONSTANTS FOR S^{32}, S^{34} EXCHANGE IN THE BISULPHITE ADDITION REACTION
(Temp. 25° C.)

Carbonyl component	Mol. wt.	$NaHSO_3$: carbonyl component (molar ratio)	Equil. time (days)	$S^{32}O_2/S^{34}O_2$*	(S^{32}/S^{34}) orig. bisulphite / (S^{32}/S^{34}) prod.	K
Acetone	58.1	1.9	24	22.776 ± 0.014**	1.010	1.021
		2.0	24	22.774 ± 0.015	1.010	1.020
Butanone	72.1	2.5	24	22.713 ± 0.013	1.013	1.022
		2.8	24	22.695 ± 0.015	1.014	1.021
4-Methyl-2-pentanone	100.2	4.7	5	22.678 ± 0.012	1.015	1.019
		8.0	24	22.626 ± 0.015	1.017	1.019
		10.0	24	22.631 ± 0.016	1.017	1.019
Benzaldehyde	106.2	10.0	7	22.748 ± 0.018	1.011	1.013
		10.0	25	22.731 ± 0.012	1.012	1.014
Heptanal	114.2	10.0	8	22.732 ± 0.014	1.012	1.014
		10.0	24	22.761 ± 0.017	1.011	1.013
2-Heptanone	114.2	10.0	14	22.757 ± 0.018	1.011	1.012
		10.0	24	22.765 ± 0.011	1.011	1.012
2-Octanone	128.3	8.0	24	22.746 ± 0.012	1.012	1.013
		10.0	24	22.739 ± 0.018	1.012	1.013
Anisaldehyde	136.1	10.0	17	22.799 ± 0.012	1.009	1.010
		10.0	24	22.799 ± 0.029	1.009	1.010

* *The $S^{32}O_2/S^{34}O_2$ ratios are relative to the $S^{32}O_2/S^{34}O_2$ ratio in the original $NaHSO_3$ arbitrarily chosen as 23.010.*

** *Precisions are expressed as standard deviation.*

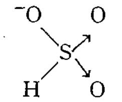
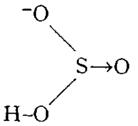
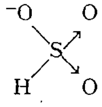
The extent of conversion of the carbonyl component to the addition product was calculated as 100% for the three aldehydes and 99% for acetone and butanone, making use of the equilibrium constants reported by Gubareva (6). The 2-heptanone and 2-octanone addition products were actually isolated in a 98–99% yield, and it seemed reasonable to conclude that a comparable conversion was obtained with 4-methyl-2-pentanone, although the greater solubility of its addition product precluded isolation in high yield. It may be noted that an error of 20% in estimating the yield for the latter ketone introduces an error no greater than 0.1% in the exchange constant.

Validity of the Method and its Assumptions

In addition to the exchange reaction between bisulphite ion and the addition product, a second process which conceivably could contribute to the over-all fractionation observed is an exchange of the sulphur isotopes between solid and dissolved addition product. This effect, however, could only be significant in the case of the more soluble compounds. Furthermore, although the difference in solubility of the two isotopic species could not be measured for the addition products, it has been determined for sodium bisulphite itself. Solid sodium bisulphite was shaken with a saturated sodium bisulphite solution, the solid and solution separated, and sulphur dioxide samples were prepared from each. Mass spectrometric analyses gave the following results:

Sample	64/66 mass abundance ratio
SO_2 from solid bisulphite	21.28 ± 0.02
SO_2 from bisulphite in solution	21.27 ± 0.02

It is apparent that there is no measurable fractionation of the sulphur isotopes between the two phases.

The possibility that bisulphite ion has the structure  rather than  must not be overlooked. If the ion contains a sulphur–hydrogen bond, then the argument, that fractionation of the sulphur isotopes would not be expected in an exchange with an addition product of the sulphite ester structure, might not be valid. However, the change in the bonding of sulphur in going from  to the sulphite ester form of the addition product corresponds to the change in going from this form of bisulphite ion to sulphite ion. If it therefore could be established that there is no fractionation in an exchange involving the two ions, it would seem reasonable to conclude that very little fractionation would occur in a bisulphite ion – sulphite ester addition product system.

The extent of fractionation between the two ions has been determined by taking advantage of the difference in water solubility of barium sulphite and barium bisulphite; the former is quite insoluble whereas the latter is readily soluble and, indeed, is known only in solution. A saturated solution of barium hydroxide was added to an excess of saturated sodium bisulphite and the mixture allowed to equilibrate. Sulphur dioxide samples, prepared from the precipitated barium sulphite and the solution, were analyzed mass spectrometrically with the following results:

Sample	64/66 mass abundance ratio
SO_2 from barium sulphite	20.43 ± 0.01
SO_2 from solution	20.43 ± 0.01

It is apparent that there is no measurable fractionation of the sulphur isotopes between the two ions. This result perhaps could be considered as evidence for the $HOSO_2^-$ structure of bisulphite ion.

Diethyl Sulphate—Ethyl Hydrogen Sulphate Isotopic Exchange Reaction

Further support for the assumption that no appreciable fractionation would occur between bisulphite ion and an addition product of the sulphite ester structure has been provided by a study of sulphur exchange in the equilibrium between diethyl sulphate and ethyl hydrogen sulphate (Equation 5).

$$C_2H_5OS^{34}O_2OH + C_2H_5OS^{32}O_2OC_2H_5 \rightleftarrows C_2H_5OS^{32}O_2OH + C_2H_5OS^{34}O_2OC_2H_5 \qquad [5]$$

Although sulphur is in a higher oxidation state in the compounds involved in this exchange, nevertheless, assuming the $HOSO_2^-$ structure for bisulphite ion, the same bonds are being broken and formed as in a bisulphite ion – sulphite ester equilibrium. Diethyl sulphate was shaken with one-half mole equivalent of water for an extended period. The unconverted ester and ethyl hydrogen sulphate were separated and each converted to barium sulphate and thence to sulphur dioxide for mass spectrometric analysis. From the results given in Table II, it is seen that the equilibrium constant is only slightly greater than unity, confirming the prediction that isotopic fractionation is small in exchange reactions in which the bonding of the isotopic atom remains unchanged.

TABLE II

EQUILIBRIUM CONSTANTS FOR SULPHUR ISOTOPIC EXCHANGE IN THE DIETHYL SULPHATE REACTION

Temp., ° C.	S^{32}/S^{34} ratio*		Equilibrium constant
	Diethyl sulphate	Ethyl hydrogen sulphate	
25	22.095 ± .003	22.119 ± .003	1.001
55	22.080 ± .003	22.123 ± .003	1.002

* *Precisions are expressed as standard deviations.*

DISCUSSION

The equilibrium constants, given in Table I, for isotopic exchange in the eight bisulphite ion – addition product systems have values ranging from 1.010 to 1.021. These values are much larger than would be expected if the addition products were α-hydroxysulphite ester salts, and compare with equilibrium constants for exchange reactions in which the bonding of the isotopic atom is different in the chemical species concerned, e.g., the $SO_2 - HSO_3^-$ system. These results, therefore, are considered to provide a conclusive proof for the sulphonic acid salt structure of the carbonyl–bisulphite addition compounds.

The variation in the constants for the different carbonyl systems is somewhat greater than might have been expected. It is evident from Table I that this variation is in some degree related to the molecular weight of the carbonyl component. This, however, is not the only factor involved. It is seen, for example, that there is a very significant difference in the value of K obtained for 4-methyl-2-pentanone and 2-heptanone but no such difference for 2-heptanone and 2-octanone, although the increment in molecular weight is the same in the two cases.

The present study is the first time, to our knowledge, that equilibrium constants for isotopic exchange reactions of this type have been determined with precision, and the results obtained suggest the value of further study of the effect of substituents on the magnitude of these constants.

EXPERIMENTAL

General

Sodium bisulphite of natural isotopic abundance was used in the investigation. This was possible since the abundance of S^{34} in nature is approximately 4% and, furthermore, it had the advantage over the use of enriched material in that any error of measurement arising from contamination of samples was smaller. Although the fractionation of S^{36} with respect to S^{32} is twice that of S^{34} to S^{32}, only the latter was determined because of the difficulties in the mass spectrometric measurement of the very low abundance of S^{36}.

Reagents

Sodium bisulphite (meta), Baker and Adamson powder, 95.9% assay.

Heptanal, Eastman Kodak White Label.

Benzaldehyde, Eastman Kodak White Label, was shaken with sodium carbonate solution and then with water, dried, and distilled *in vacuo*; b.p. 61–62° C. (10 mm.).

Anisaldehyde, Eastman Kodak White Label, was redistilled; b.p. 106.5–108° C. (5 mm.).

Acetone, Nichols N. F. Grade, was redistilled; b.p. 56° C.

Butanone, Eimer and Amend Technical Grade, was redistilled; b.p. 77–79° C.

4-Methyl-2-pentanone, Eastman Kodak Practical, was redistilled; b.p. 114.5–115° C.

2-Heptanone, Eastman Kodak White Label, was redistilled; b.p. 148–149.5° C.

2-Octanone, Eastman Kodak Practical, was redistilled; b.p. 169.8–170.9° C.

Diethyl sulphate, Eastman Kodak Practical, was redistilled; b.p. 99.5° C. (18 mm.).

Preparation of Bisulphite-Addition Compounds

To an aqueous solution of sodium bisulphite, containing 5.15 moles of bisulphite per liter of solution, was added the carbonyl component in the quantity necessary to give the desired bisulphite to carbonyl ratio. The reaction mixture, contained in a tightly-stoppered flask, was shaken on an agitating machine enclosed in a constant temperature bath maintained at 25 ± 0.5° C. The crystalline addition product was separated by suction filtration, washed with ethanol, and then with ether, and dried.

Preparation of Sulphur Dioxide Samples for Mass Spectrometric Analyses

The apparatus used for the preparation of sulphur dioxide samples is shown in Fig. 1. Solid addition compound, 6×10^{-4} moles, was placed in bulb *B* and

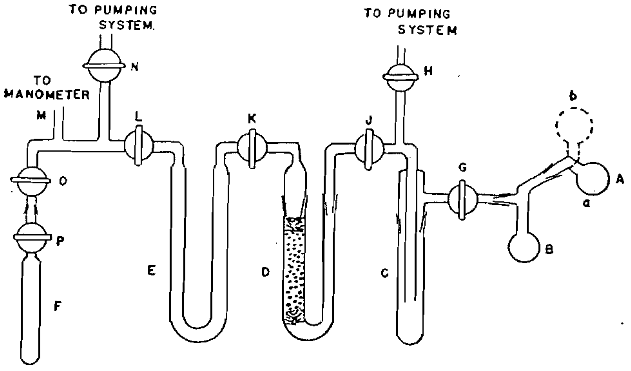


FIG. 1. Apparatus for preparation of sulphur dioxide samples.

0.5 ml. of 85% syrupy phosphoric acid dissolved in 0.5 ml. of distilled water in bulb *A*, which was turned to position "*a*". Both bulbs were surrounded with liquid air and the system evacuated. Stopcocks *H* and *J* were then closed and the liquid air replaced by hot water. Bulb *A* was turned to position "*b*" and the aqueous acid permitted to react with the addition compound. The reaction mixture was allowed to stand for two hours to equilibrate the oxygen isotopes of the sulphur dioxide and water, the latter being in 100-fold excess.* Following equilibration, liquid air was placed around trap *E*, a salt–ice mixture around *C*, and hot water (90–95° C.) around bulb *B*; stopcocks *G*, *J*, and *K* were opened and *L* and *H* closed. As the sulphur dioxide distilled into *E*, the water vapor largely condensed in *C* and was completely removed in the phosphorous pentoxide tower, *D*. To ensure complete recovery of sulphur dioxide, the water condensate was passed back and forth three times between *B* and *C*, using warm water and liquid air baths. Trap *E* was then surrounded by a dry ice – acetone bath, stopcock *N* opened, and carbon dioxide present as impurity removed by pumping on this trap a few seconds;** *N* was then closed. Sample tube *F* was surrounded by liquid air and, with stopcocks *L*, *P*, and *O* open, sulphur dioxide partially distilled into this tube.** Stopcock *L* was closed, *N* opened, and when a pressure of 10^{-6} mm. had been attained, *P* closed.

Samples of sodium bisulphite were decomposed to sulphur dioxide using a similar procedure. An aliquot of the saturated sodium bisulphite solution containing 6×10^{-4} moles of bisulphite (0.12 ml. of solution) was placed in bulb *B* and 0.5 ml. of phosphoric acid dissolved in 0.38 ml. of water used to effect decomposition.

Solid and Dissolved Sodium Bisulphite Equilibration

Twenty grams of sodium bisulphite was shaken with 40 ml. of saturated sodium bisulphite solution for seven days. The solid and liquid phases were

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* *No data were available on the rate of oxygen isotope equilibration in this system. Analyses of sulphur dioxide samples prepared using 1.5, 2.0, and 2.5 hr. equilibration periods gave the same 64/66 mass ratios within the error of measurement. The equilibration time was standardized to 2.0 hr.*

** *It was established that no fractionation of the sulphur isotopes occurs in this process.*

separated and sulphur dioxide samples for mass spectrometric analysis prepared from each using the procedure already described.

Bisulphite–Sulphite Ion Equilibration

Fifteen milliliters of a saturated solution of barium hydroxide was shaken for five days with 30 ml. of saturated sodium bisulphite. The precipitated barium sulphite was filtered, washed with cold water, and dried. Sulphur dioxide samples were prepared from both solid and solution.

Diethyl Sulphate – Ethyl Hydrogen Sulphate Equilibration

Diethyl sulphate (0.04 moles) was shaken with 0.02 moles of water. The equilibration period was five weeks at room temperature in Run 1 and a similar period at this temperature followed by 75 hr. at 55° C. in Run 2. The unconverted ester and ethyl hydrogen sulphate were separated by partition between benzene and water. The aqueous solution, containing the ethyl hydrogen sulphate, was refluxed with 32 gm. of barium chloride and the precipitated barium sulphate removed periodically and ignited. The benzene solution was distilled *in vacuo* to remove solvent and the residual diethyl sulphate refluxed with 32 gm. of barium chloride in 100 ml. of water. Barium sulphate was filtered and ignited. Total recovery of sulphate was 97%.

Conversion of Barium Sulphate to Sulphur Dioxide

Barium sulphate was reduced with a mixture of hydroiodic, hydrochloric, and hypophosphorus acid to hydrogen sulphide (9), which was precipitated as cadmium sulphide from aqueous cadmium acetate and then converted to silver sulphide by addition of silver nitrate. The silver sulphide was oxidized to sulphur dioxide using a standard procedure (16).

Mass Spectrometric Analysis

In the bisulphite ion addition product equilibrium studies the relative isotopic abundance ratios were measured using both a 90° and 180° direction focusing Nier type mass spectrometer equipped with an automatic recorder (16, 5). The same analysis was obtained for a given sample with either instrument. The $S^{32}O_2/S^{34}O_2$ ratio was obtained from the ratio of mass 64 to mass 66 ion currents, the necessary correction being made for the contribution of the molecular species $S^{32}O^{16}O^{18}$ to mass 66. Each sulphur dioxide sample prepared from an addition compound was measured relative to a standard, this being the sulphur dioxide from the saturated sodium bisulphite solution to which was arbitrarily assigned an $S^{32}O_2/S^{34}O_2$ ratio of 23.010. The standard, the sample, and the standard were measured as quickly as possible in that order and the analysis was considered satisfactory if the two sets of results for the standard agreed within 0.1%, the precision of a single analysis. A single analysis consisted of six or seven spectrograms and each spectrogram consisted of masses 64 and 66, and then, by reversing the direction of scan, masses 66 and 64.

The relative abundance ratios for the sulphur dioxide prepared from diethyl sulphate and ethyl hydrogen sulphate were determined using the 90° instrument equipped for simultaneous collection (18). This gave a precision of the order of 0.015%.

ACKNOWLEDGMENTS

We are indebted to Dr. H. G. Thode for helpful discussion, to Mr. E. R. Hayes, Mr. R. F. W. Bader, and Miss Midge Ishii for preparation of samples in the ethyl sulphate studies, and to Mr. R. K. Wanless and Mr. John Warren for mass spectrometer analysis of these samples. We also acknowledge financial assistance from the National Research Council which made this investigation possible.

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NEW COLOR REACTIONS OF SEDOHEPTULOSAN AND ITS DETERMINATION IN MIXTURES OF RIBOSE AND FRUCTOSE[1]

BY L. UJEJSKI[2] AND E. R. WAYGOOD[3]

ABSTRACT

The reagents carbazole – sulphuric acid, cysteine hydrochloride – sulphuric acid, have been applied successfully to the quantitative colorimetric determination of sedoheptulosan in pure solution or in the presence of ribose and/or fructose. Fructose can be determined quantitatively in the presence of sedoheptulosan and/or ribose by using a combination of the two reagents. Results indicate that while sedoheptulose reacts differently to sedoheptulosan with the orcinol reagent, the reactions with carbazole and cysteine are not altered by hydration and these may form a basis for the determination of the naturally occurring seven carbon sugar sedoheptulose.

INTRODUCTION

The only color reaction reported for sedoheptulose to date is the formation of a blue color with orcinol (1, 9). Apparently this reaction is specific for ketoheptoses and the nonreducing anhydride sedoheptulosan only gives the blue color after hydration forming an equilibrium mixture of sedoheptulose and sedoheptulosan (1). Orcinol, however, has not proved to be satisfactory for the determination of carbohydrates in mixture (8).

On the other hand the reactions of carbohydrates with carbazole – sulphuric acid (3) and sulphydryl compounds especially cysteine hydrochloride (4, 6) have opened up new possibilities for their quantitative colorimetric determination. The former reagent has been applied successfully by many investigators (7, 8, 9, 10, 11) to the determination of various sugars and more recently Dische and Borenfreund (5) have used a combination of cysteine hydrochloride and carbazole – sulphuric acid for the determination of ketosugars and trioses.

This paper reports new colorimetric methods for the quantitative determination of sedoheptulosan based upon these reactions. The methods employed permit the determination of sedoheptulosan in pure solution or in the presence of ribose and/or fructose, also the determination of fructose in the presence of sedoheptulosan and/or ribose.

The authors are greatly indebted to Dr. Nelson K. Richtmyer (Federal Security Agency, Public Health Service, National Institute of Health, Bethesda, Md.) for a gift of three grams of sedoheptulosan. While this was sufficient to work out a method for its determination we were unable to obtain any samples of sedoheptulose to make a direct comparison of the methods for this sugar. However, determinations have been made with the equilibrium mixture of sedoheptulosan and sedoheptulose prepared by digestion of the former with 3 N hydrochloric acid at room temperature (12).

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EXPERIMENTAL

Determination of Sedoheptulosan by the Carbazole – Sulphuric Acid Reagent

Twice sublimed carbazole was made up as a 0.5% solution in absolute alcohol. Sulphuric acid was refluxed with 20 mgm. of potassium persulphate per liter and diluted to 84% by weight. The reagent was prepared by making up 8.35 ml. of the carbazole solution to 250 ml. with 84% sulphuric acid. Nine milliliters of the reagent was placed in a test tube and cooled in an ice-water mixture for 10 min. One milliliter water (blank) or sugar solution was carefully layered above the reagent and the contents of the tube were then thoroughly mixed and heated in a boiling water bath for 13 min. During this period a red brown color appears. The tubes were then cooled for a further 10 min. in ice water and the intensity of the coloration measured in a Coleman Universal spectrophotometer (Model 14). Determinations were carried out on solutions containing 10, 20, 25, and 30 μgm. sedoheptulosan per ml. The absorption spectrum of the colored compound is shown in Fig. 1. The solution shows considerable absorption between 400 mμ and 600 mμ with a maximum at 490 mμ.

Over this range of concentration the colored compound obeys Beer's law and it was found that the ratio D490/D400 is characteristically constant (Table I). Equilibrium mixtures of sedoheptulose and sedoheptulosan prepared by hydration of the latter give a similar colored compound with carbazole. The ratio D490/D400 does not change with hydration indicating that both substances react in essentially the same manner. This treatment, however, does result in a positive reaction with the orcinol reagent which indicates the presence of sedoheptulose.

TABLE I
OPTICAL DENSITIES AT 400 mμ AND 490 mμ OF SEDOHEPTULOSAN SOLUTIONS WITH CARBAZOLE – SULPHURIC ACID

Concentration, μgm. per ml.	D400	D490	D490/D400
10	0.075	0.142	1.89
20	0.142	0.270	1.90
25	0.176	0.340	1.93
30	0.225	0.424	1.88

Both ribose and fructose interfere with the determination and make it unsuitable for the determination of sedoheptulosan unless in pure solution.

Determination of Sedoheptulosan in the Presence of Ribose and/or Fructose

The procedure follows essentially the method of Dische (6) for the determination of hexoses. To 0.9 ml. of a solution containing sedoheptulosan alone or in the presence of ribose and/or fructose (for concentrations see Table II) 0.1 ml. of a 3% solution of cysteine hydrochloride and 5 ml. 38.4% sulphuric acid are added. The mixture is heated for 10 min. in a boiling water bath and then cooled in tap water and left at room temperature for 48 hr.

TABLE II
OPTICAL DENSITIES AT 510 mμ OF SEDOHEPTULOSAN SOLUTIONS WITH CYSTEINE HYDROCHLORIDE

Solution	Concentration, μgm. per ml.	D510
a. Sedoheptulosan	20	0.238
b. Sedoheptulosan	40	0.490
c. Sedoheptulosan	60	0.730
d. Sedoheptulosan Ribose	20 10	0.240
e. Sedoheptulosan Ribose	20 20	0.242
f. Sedoheptulosan Fructose	20 10	0.248
g. Sedoheptulosan Fructose	20 20	0.285
h. Sedoheptulosan Ribose Fructose	20 10 10	0.280

Sedoheptulosan gives a yellow orange color appearing at the end of the heating period and becoming more intense after 24–48 hr. changing color to red rose. Ribose under these conditions does not show any color, fructose a slight yellow at the beginning which eventually disappears. Sedoheptulosan shows a sharp absorption between 450 mμ and 550 mμ with a maximum at 500 mμ after one hour (Fig. 2). During the change in color from yellow-orange to red rose the absorption increases and the maximum shifts from 500 mμ to 510 mμ (Fig. 2). The optical densities at 510 mμ are shown in Table II for sedoheptulosan alone and in various mixtures. Table II shows that neither ribose nor fructose interfere with the observance of Beer's law. Furthermore, the optical density increment between 450 mμ and 550 mμ of the sedoheptulosan mixtures (*d*, *g*, *h*, Table II) has the same value as that for sedoheptulosan alone at 20 μgm. per ml. (*a*, Table II). Neither ribose nor fructose interfere at these concentrations. However, we have found that when fructose is raised above this level there is some interference.

After 48 hr. sedoheptulosan, ribose, and fructose all show considerable absorption in the ultraviolet between 270 mμ and 350 mμ with a maximum at 300 mμ for sedoheptulosan and ribose and 320 mμ for fructose (Fig. 3).

Determination of Fructose in the Presence of Sedoheptulosan and/or Ribose

To 1.0 ml. of a solution containing a mixture of the sugars, 0.2 ml. of a 1.5% solution of cysteine hydrochloride are added. Six milliliters 38.4% sulphuric acid was then added immediately followed by 0.2 ml. of 0.12% alcoholic solution of carbazole. The mixture was shaken and left standing at room temperature. The concentrations of the sugar solutions investigated are shown in Table III.

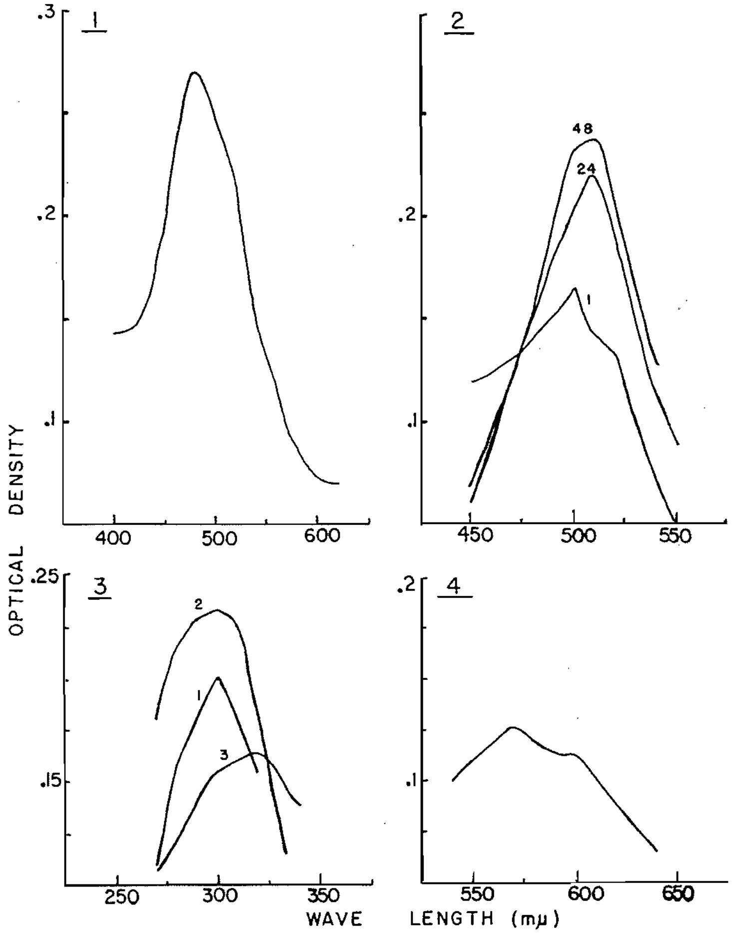

Fig. 1. Absorption spectrum of sedoheptulosan in carbazole reaction.
FIG. 2. Absorption spectrum of sedoheptulosan in cysteine reaction 1, 24, and 48 hr.
FIG. 3. Ultraviolet absorption spectrum of sedoheptulosan (1), ribose (2), and fructose (3) in cysteine reaction.
FIG. 4 Absorption spectrum of sedoheptulosan in cysteine–carbazole reaction after 24 hr.

TABLE III
OPTICAL DENSITIES AT 560 mμ OF FRUCTOSE SOLUTIONS WITH THE CYSTEINE–CARBAZOLE REAGENT

Solution	Concentration, μgm. per ml.	D560
Fructose	10	0.20
Fructose	20	0.41
Fructose	30	0.63
Fructose Sedoheptulosan	20 50	0.43
Fructose Sedoheptulosan Ribose	20 50 50	0.40

Solutions of sedoheptulosan and ribose whether alone or in a mixture produce a weak bluish color after one to two hours. On the other hand solutions of fructose alone or in mixture produce an intense purple color after a few minutes. Fructose absorption is maximum at 560 mμ. and neither sedoheptulosan nor ribose at a concentration of 100 μgm. per ml. interfere up to a period of one hour. After 24 hr. however, both the latter absorb strongly between 500 mμ and 700 mμ (Fig. 4). The determination of fructose in the presence of either or both of these two sugars is accordingly made after one hour duration. Table III shows that the optical densities of the fructose solutions obey Beer's law and there is no interference by either sedoheptulosan or ribose.

DISCUSSION

New color reactions of sedoheptulosan and fructose with carbazole – sulphuric acid and cysteine hydrochloride – sulphuric acid and a combination of the two reagents have been described for the first time. While sedoheptulosan can be determined in pure preparations by the use of the carbazole reagent the method is unsuitable for its determination in the presence of ribose or fructose owing to their interference. However, the use of the reagent cysteine hydrochloride has provided a method by which sedoheptulosan can be determined in the presence of either fructose or ribose. By using a combination of the two reagents fructose can be determined quantitatively in the presence of either sedoheptulosan or ribose. So far we have been unable to discover any colorimetric method by which ribose may be determined in the presence of these two other sugars.

In contrast to sedoheptulose, sedoheptulosan gives no color reaction with orcinol; however, there appears to be no difference between them in their reaction with either carbazole or cysteine. An equilibrium mixture of the two forms gave the same characteristically constant ratio D490/D400 = 1.90 with carbazole as would sedoheptulosan alone, and the same maximum with cysteine.

Owing to the increasing recognition given to the importance of the role played by sedoheptulose and its interrelation with ribose in plant metabolism (2) it was considered appropriate by the authors at this time to make known these new color reactions of sedoheptulosan. Further work on the microdetermination of sedoheptulose isolated from *Sedum spectabile* and *Bryophyllum calycinum* will be reported in a future publication.

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THE ACTION OF HYDROXYLAMINE ON METHYL ALPHA- AND BETA-D-GLUCOPYRANOSIDE TETRANITRATE IN PYRIDINE[1]

BY L. D. HAYWARD[2] and C. B. PURVES

ABSTRACT

The methyl glucoside tetranitrates reacted vigorously at room temperature with an excess of hydroxylamine base dissolved in anhydrous pyridine. Gas consisting of 91% nitrogen and amounting to 1.25 to 1.3 moles per mole was evolved within 20 min. and only a little more during the next 12 hr. Approximately 1.35 moles of nitrate groups in the original tetranitrate had been replaced by hydroxyl groups, for the most part at least without Walden inversions or other change, because hydrogenation of the sirupy product reduced it in more than 80% yield to crystalline methyl glucoside. The product from methyl-β-glucoside tetranitrate consisted of the 2,3,6-trinitrate (28%), the 3,6-dinitrate (17%), and an unidentified trinitrate (8%) which might have been a mixture.

The structures of the first two compounds were confirmed by preparing the fully methylated derivatives, denitrating the latter, and identifying the resulting known, partly methylated methyl-β-glucosides. New syntheses of methyl-β-glucoside-3,6-dinitrate, methyl 2,4-dimethyl-β-glucoside, and methyl-4-methyl-β-glucoside were found.

INTRODUCTION

Segall and Purves (38) found that 1 mole of nitrogen per glucose unit was evolved when cellulose trinitrate was dissolved in anhydrous pyridine containing an excess of hydroxylamine base, and approximately one mole of nitrate group was removed from the nitrocellulose. Apart from a small substitution (0.08) of oxime, the nitrate was replaced by a hydroxyl group which was probably of a secondary rather than a primary nature. Severe technical difficulties, however, caused further attempts to determine the structure of the partly denitrated cellulose to be deferred. It therefore became desirable to apply the hydroxylamine–pyridine reaction to the fully nitrated derivative of a simpler carbohydrate related to cellulose, and to locate the nitrate group or groups removed by the reagent. The present research employed the tetranitrates of methyl α- and β-glucopyranoside for this purpose, because data were available concerning their well-characterized, partly denitrated derivatives (13, 14, 15, 16, 35) which could also be converted, by methylation and subsequent denitration, to one or other of the known methyl ethers of methyl α- or β-glucoside (7, 13, 14, 15). Gladding and Purves (16) and Ansell, Honeyman, and Williams (4, 5) described the action of aqueous and alcoholic alkali on monosaccharide nitrates, but reports concerning organic bases seemed to be restricted to one by Wigner (40), who found in 1903 that pyridine alone removed one nitrate group selectively from mannitol hexanitrate. Hayward (18) recently showed that the group removed was in the third (or fourth) position.

Preliminary experiments on the stability of the methyl glucoside tetranitrates to anhydrous pyridine showed that, although highly colored substances

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were formed, no gas was evolved at room temperature. About 60% of the unchanged tetranitrates could be recovered after 16 hr. by pouring the solutions into water. In a similar experiment with an alcohol solution of hydroxylamine, at least 75% of the β-tetranitrate could be recovered after 12 hr. Although gas was steadily evolved from the colorless solution, a blank containing no tetranitrate behaved in the same way and the observation was attributed to a slow decomposition of the base. The conjunction of either α- or β-tetranitrate with free hydroxylamine plus pyridine almost immediately produced a vigorous exothermic reaction; large volumes of a colorless gas were evolved, no unchanged tetranitrate could be isolated after 10 min., and the solution became only slightly yellow after 14 days.

Pure methyl-α-glucoside tetranitrate, which was more readily available than the β-isomer, was used to prepare a series of eight partly denitrated products isolated after reaction times extending from 10 min. to 12 hr. All these products proved to have refractive indices, methoxyl contents, and nitrogen contents that were practically the same. The partial denitration was therefore rapid, and the resulting pale yellow glass was stable or nearly so to the reagent. The fact that analyses for nitrate nitrogen were about 0.7% less than those for total nitrogen suggested that not all of the nitrogen was present as nitrate groups. By analogy with the behavior of cellulose trinitrate, the difference was tentatively attributed to an oxime substitution of about 0.18. On this basis the calculated average substitutions were methoxyl 0.85, nitrate 2.34, and oxime 0.18 moles per methyl glucoside unit, and the yield was about 80% of theory. Since the methoxyl substitution should obviously be unity, the above assumption was unsatisfactory, although no better one was found.

The partly denitrated methyl glucoside tetranitrate was submitted to catalytic hydrogenolysis over a palladized charcoal catalyst by Kuhn's method (26), and pure crystalline methyl-α-glucoside was recovered in a yield of only 82% of theory, whereas the recoveries from the original α- and β-tetranitrates were 95% to 96%. This decrease in yield provided another reason for the view that perhaps 15% of the product from the partial denitration had failed to retain the basic methyl glucoside structure. All attempts to isolate crystalline di- or tri-nitrates from the product failed, and the same lack of success was encountered when the methylated, benzoylated, or acetylated derivatives were examined, either before or after the removal of the remaining nitrate groups by hydrogenolysis. The α-series of products was therefore abandoned in favor of the β-series derived from methyl-β-glucoside, derivatives of which were often more readily crystallized (34). After two hours in the pyridine–hydroxylamine, the β-tetranitrate gave an 84% yield of a golden-yellow, extremely viscous sirup from which 90% of pure methyl-β-glucoside was recovered by hydrogenolysis.

The volume of gas evolved from the β-tetranitrate during the above reaction was measured at intervals, and was corrected for a rapid initial increase in temperature to about 70°C. The latter, nearly linear portion of the rate plot (Fig. 1), when extrapolated to zero time, corresponded to a production of

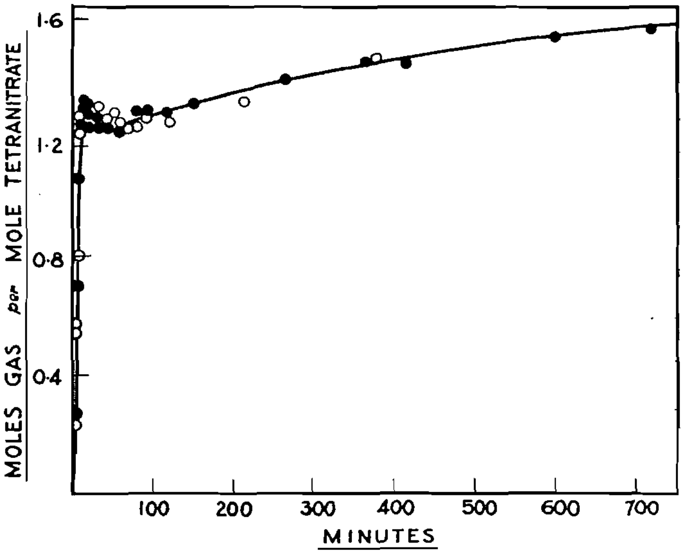
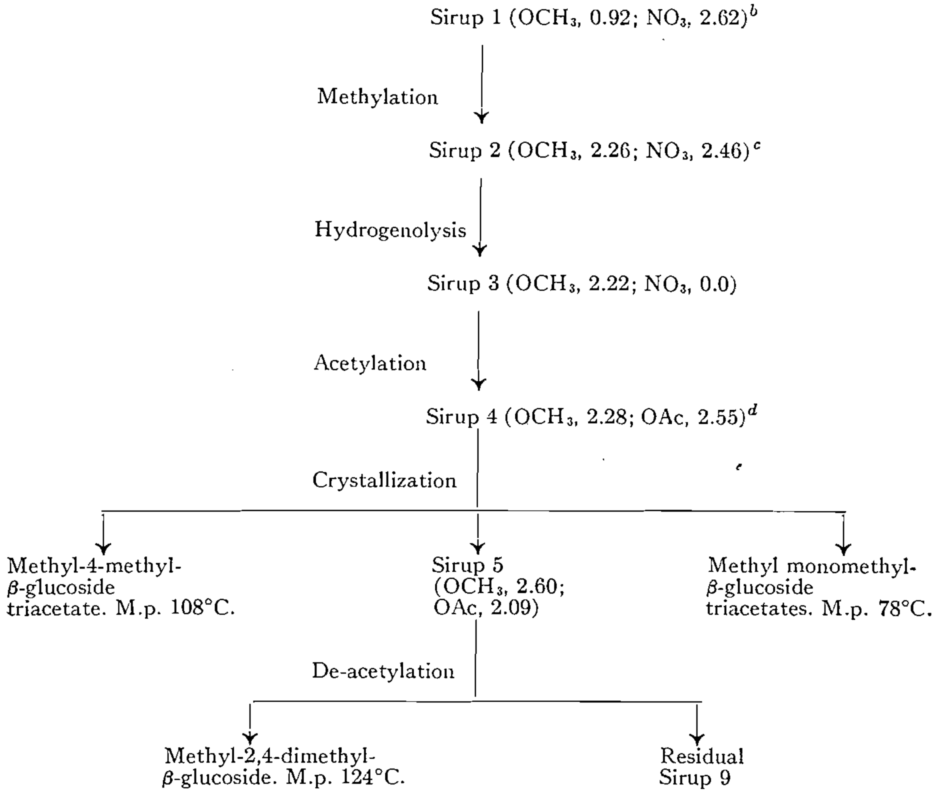


FIG. 1. The rate of gas evolution from 1 gm. of methyl-β-glucoside tetranitrate dissolved in 10 ml. of 12.5% hydroxylamine–pyridine. Corrected for temperature change and for the vapor pressure of pyridine (duplicate experiments).

about 1.25 moles per mole of tetranitrate in the initial rapid reaction. No good explanation was found for the slower reaction represented by the linear portion of the plot, because neither the yield nor the analyses of the partly denitrated product varied substantially with the reaction time, and because no gas was evolved in blank determinations with the pyridine–hydroxylamine reagent. Hydroxylamine, however, was known not to be stable in alkaline solution (30), and its breakdown might have been catalyzed by the sugar nitrate or its decomposition products, as well as by silver, mercury, and other ions (23, 33). The gas evolved during 12 hr. was shown by analysis in an Orsat apparatus and by its density to be nitrogen of 91.4% purity. An absorption of 8.6% in acid cuprous sulphate-β-naphthol solution was attributed to the pyridine vapor known to be present, rather than to carbon monoxide, and the solubility of nitrous oxide in pyridine made it possible that small amounts were formed but escaped detection. The presence of nitrous oxide was associated with oxime formation in the parallel research with cellulose trinitrate (38).

Five-gram portions of methyl-β-glucoside tetranitrate were then partially denitrated in pyridine–hydroxylamine for two hours with control of temperature (25° to 35°C.), and the products were combined, dried to constant weight, and identified as Sirup 1. If it was assumed that one-half of the gas evolved, in this case 1.3 moles per mole of tetranitrate, came from the hydroxylamine, the loss of the other half from the tetranitrate indicated that Sirup 1 should contain 12.0% of nitrogen and 9.84% of methoxyl groups. The values found were N, 11.8; OCH_3, 9.1%, the methoxyl content again being definitely low. Efforts were then directed to separating and identifying the chemical constituents of the sirup by chromatographic methods, but the methods tried proved unsatisfactory because the literature yielded no information as to suitable conditions, and because reference compounds were inaccessible. Sirup 1 was then subjected to the series of reactions summarized in Table I.

TABLE I
CRYSTALLINE DERIVATIVES FROM PARTLY DENITRATED METHYL-β-GLUCOPYRANOSIDE TETRANITRATE (SIRUP 1)[a]



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[a] *Five grams of the tetranitrate, 50 ml. of pyridine, and 6.25 gm. of hydroxylamine near 30°C. for two hours.*

[b] *Substitutions per glucose unit; nitrate substitution might include a little oxime.*

[c] *Substitutions per glucose unit.*

[d] *Calc. from yields and substitutions of the three components (next line of table).*

Methylation with silver oxide and methyl iodide gave Sirup 2 in practically quantitative yield and with little loss of nitrate groups. When these groups were removed by hydrogenolysis, the yield was again close to theory (Sirup 3) but was only 74% when this mixture of partly methylated methyl glucosides was acetylated with pyridine and acetic anhydride. The product, Sirup 4, crystallized in part, and systematic fractional recrystallization separated crude methyl-4-methyl-β-glucopyranoside triacetate (48%), an isomeric triacetate (11%), and a very viscous, uncrystallized residue (Sirup 5). After purification, the identity of the 4-methyl glucopyranoside triacetate was unequivocally established by means of its melting point and specific rotation (8, 27, 31) and by de-acetylation to methyl 4-methyl-β-glucoside. This glucoside was obtained in the crystalline state, m.p. 101°C., in agreement with the recent independent work of McGilvray (29). The substance had the expected behavior toward aqueous sodium periodate, reducing 0.99 mole without the liberation of formic acid or formaldehyde. Acid hydrolysis yielded 4-methyl glucose (32) and its crystalline phenylosazone (13).

The melting point, 76° to 78°C., and the specific levorotation of −38° in chloroform found for the isomeric methyl monomethyl-β-glucoside triacetate did not agree with the values recorded for the 2-methyl (9), the 3-methyl (21), or the 6-methyl (19, 20) derivatives. De-acetylation resulted in a glass that could not be crystallized, either as such or as the benzoate. The glass had the methoxyl content of a methyl monomethyl hexoside, but when oxidized with aqueous sodium periodate consumed only 0.6 mole with the liberation of a little formic acid and no formaldehyde. These fractional amounts suggested that the glass was a mixture of various methyl monomethyl glucosides and that the homogeneity observed in the crystalline triacetate was spurious.

The residual Sirup 5 (Table I) was first de-acetylated with methanolic barium methylate, and the uncrystallized product did not change in specific rotation when dissolved for 48 hr. at 0°C. in anhydrous methanol–chloroform containing sodium methylate. Although de-acetylation appeared to be complete, a portion of the product could not be methylated with silver oxide and methyl iodide beyond OCH_3, 50.1, 49.6%, and no methyl tetramethyl β-glucoside (OCH_3, 62%) was recovered by fractional distillation of the methylated sample. It was assumed that Sirup 5 contained an acetyl group resistant to saponification by sodium or barium methylate, or of the type encountered by Helferich and Lang (21) and Dewar and Fort (13). The remainder of Sirup 5 was again submitted to de-acetylation, this time with aqueous sodium hydroxide (21), and 55% was recovered as crystalline methyl 2,4-dimethyl-β-glucoside with the correct melting point and rotation (13). The structure of this substance was confirmed by its failure to react with aqueous sodium periodate, by its hydrolysis to 2,4-dimethyl glucose, and by the capacity of the latter to yield the crystalline 4-methyl glucose phenylosazone (1,13) with elimination of a methyl group.

The above results clearly showed that the partial denitration of methyl-β-glucoside tetranitrate led to a mixture of nitrates which included the 2,3,6- and 3,6-derivatives. After standing for two months in a desiccator over phosphorus pentoxide, a sample of Sirup 1 (Table I) deposited in 5% yield the crystalline 3,6-dinitrate, which was identified by its rotation and melting point. This identity was confirmed by a quantitative methylation to the uncrystallized methyl 2,4-dimethyl-β-glucoside-3,6-dinitrate (13), and by hydrogenolysis of the latter in 93% yield to crystalline methyl 2,4-dimethyl-β-glucoside (1, 13). Methyl-β-glucoside-3,6-dinitrate was more conveniently isolated by extracting a chloroform solution of Sirup 1 with water, in which the dinitrate was rather soluble (15). The yield was 11.9% by weight, but the extract also contained 20% of a yellow sirup that could not be crystallized. Evaporation of the chloroform solution left a sirup which on methylation yielded another with the approximate composition of a methyl monomethyl glucoside trinitrate. Found: OCH_3, 17.1, 17.5%. Calc. OCH_3, 18.1%. A series of experiments, analogous to those already described, recovered the 4-methyl, and the acetylated, unidentified monomethyl, derivatives of methyl glucoside from this trinitrate, but no other substances were identified. Sirup 1, after the partial removal of the 3,6-dinitrate by crystallization, was also acetylated, but fractional crystallization of the mixed acetate nitrates did not yield chemical individuals. These two series of experiments have not been described in detail because they merely confirmed, but did not extend, the results already reported.

Throughout the work noted in Table I and supported by other results, there was no indication that methylation produced an additional substitution of more than two in Sirup 1. The partial denitration of the methyl glucoside tetranitrate therefore appeared to remove only one or two nitrate groups from each molecule, and to give a mixture consisting exclusively of di- and tri-nitrates, perhaps contaminated with minor amounts of oximes and other substances. When this possibility was neglected, the production of tri- and di-nitrates was in a molar ratio of about 70:30 from the amount of gas evolved (Fig. 1), about 62:38 from the substitution of nitrate groups in Sirup 1 (Table I), and about 64:36 from the separation effected by extracting a chloroform solution of Sirup 1 with water. The 2,3,6-trinitrate and the 3,6-dinitrate preponderated, because about 28% of the original tetranitrate was recovered as crude methyl-4-methyl-β-glucoside triacetate, and about 18% as methyl-2,4-dimethyl β-glucoside, from Sirup 4. These yields might actually be greater, because losses of an undetermined nature reduced the yield of Sirup 4 to about 68% of theory.

The isolation of the unidentified methyl monomethyl glucoside triacetate, and of numerous intractable sirups with reasonable analyses, showed that the removal of nitrate groups from the tetranitrate by hydroxylamine in pyridine was to some extent of a random nature. Methyl-β-glucoside tetranitrate, moreover, failed to serve as a model of cellulose trinitrate, because the group most affected was in the fourth position of the former substance, and the fourth positions of the glucose residues of the latter were not nitrated. In both cases the partial denitration probably depended upon the superior reactivity of some nitrate groups, whose elimination stabilized the remainder. The elimination might involve the formation of nitrohydroxamic acid, NO_2NHOH, and its decomposition to nitrogen when in the presence of excess hydroxylamine (3), as previously discussed (38).

EXPERIMENTAL

Materials and Methods

Pure methyl-β-D-glucoside hemihydrate (24, 25, 28, or 36), when nitrated with acetic anhydride–acetic acid–100% nitric acid as described by Brissaud

(10), gave an 80 to 85% yield of the crystalline 2, 3, 4, 6-tetranitrate with the correct physical constants (6). Pure methyl-α-D-glucoside was nitrated with a phosphoric anhydride – 100% nitric acid mixture (38). The 2,3,4,6 tetranitrate, isolated in 86% yield, showed a marked tendency to remain as a supercooled liquid, but was recrystallized repeatedly by the slow cooling of its solution in ethanol. The analyses and physical constants (10, 26) of the product showed it to be quite pure. Since the two tetranitrates and also their partially nitrated derivatives were explosives, the scale of the preparations was restricted to 5 gm. or less, and all evaporations were under reduced pressure with bath temperatures below 50°C. Samples for analysis were dried to constant weight *in vacuo*. Vacuum distillation of the nitrates was not attempted.

Free crystalline hydroxylamine, prepared as required by a published method (38), was sensitive to moisture, heat, metals, and traces of alkali. The substance was immediately dissolved in pyridine which had been dried over barium oxide and which boiled at 115° to 115.5°C. The solution was stored at 0°C. for not more than 48 hr. before use.

Commercial electrolytic hydrogen and an Adams Low Pressure apparatus were employed in the hydrogenolyses. The palladized charcoal catalyst was prepared by the method of Hartung (17) and when thoroughly dry was pyrophoric. Two-gram-samples of methyl α- or β-glucoside tetranitrate, when hydrogenated in dioxane–ethanol at 30 to 40 p.s.i. and room temperature for 30 min. over 2 gm. of the catalyst, absorbed 7.6 and 7.8 moles of hydrogen per mole. Theory, 8 moles. The crystalline methyl glucosides were recovered from the filtered hydrogenated liquors in 96 to 98% yield, as Kuhn reported (26). Other hydrogenolyses of nitrate groups were carried out in the same manner.

Total nitrogen, nitrate nitrogen, and methoxyl groups were determined by methods previously indicated (38), and acetyl groups by saponification with alcoholic sodium hydroxide (11). In the oxidations with aqueous sodium periodate, the procedures described by several authors (2,22,37) were adapted and combined so that a single 100 mgm. to 200 mgm. sample revealed the change in optical rotation, the moles of periodate consumed, and of formic acid and formaldehyde produced.

Degrees of substitution were calculated by solving simultaneous equations of the type, $\% \ \mathrm{OCH_3} = 3100\ x/(180 + 14x + 45y + 13z + 42w)$, where x, y, z, and w were the molar substitutions of methoxyl, nitrate, oxime, and acetyl groups, respectively. One or more of the unknowns was usually zero in practice, and the small, doubtful oxime substitution z was usually ignored.

Action of Hydroxylamine–Pyridine on Methyl Glucoside Tetranitrates (Sirup 1)

In a typical experiment, 5 gm. of the β-tetranitrate was mixed with 50 ml. of an ice-cold 12.5% solution of pure hydroxylamine in pyridine contained in a flask fitted with a thermometer and calcium chloride drying tube. The nitrate dissolved readily to give a clear, colorless solution which almost immediately commenced to evolve gas, and to become hot. The final temperature was restricted to 25° to 35°C. by external cooling. After two hours, the solution, now pale yellow and still evolving gas, was poured into 500 ml.

of water, the aqueous mixture was rendered just acid to Congo red by adding 4 *N* sulphuric acid and was extracted with one 200 ml. and four 100 ml. volumes of ether. Continuous extraction of the aqueous residue with ether for seven days removed only 0.17 gm. of a brown liquid that soon changed to a black tar. The washed and dried ether extracts on evaporation gave the golden yellow glass denoted as Sirup 1 (Table I), which was very soluble in acetone, ether, and chloroform, and soluble in methanol, ethanol, and benzene. Found: OCH_3, 9.11, 9.19; total N (micro-Kjeldahl), 11.7, 11.9%. Calc. for glucose substituted with 0.92 methoxyl and 2.62 nitrate groups (mol. wt. 311): OCH_3, 9.18; total N, 11.8%. The average yield of 3.5 gm. was 84% of theory according to these substitutions.

One-gram samples of methyl-α-glucoside tetranitrate were separately dissolved in 10 ml. volumes of the pyridine–hydroxylamine reagent, but the solutions were precipitated into water after 10, 20, 30, 60, 120, 240, 360, and 720 min. at room temperature. The aqueous mixtures when extracted with chloroform gave uniform yields of pale yellow glasses with refractive indices within the range n_D^{20}, 1.4925 ± 0.0015, and of constant composition. Found for all samples: OCH_3, 8.72 ± 0.07; total N (micro-Kjeldahl) 11.65 ± 0.25%; for samples after 10 min. and 120 min., nitrate N (nitrometer) 10.93, 10.95%. Calc. for glucose substituted by 0.846 methoxyl, 2.34 nitrate, and 0.18 oxime groups (mol. wt. 300); OCH_3, 8.7; total N, 11.7; nitrate N, 10.09%. The yields, 0.65 gm., were about 80% of theory.

Gas Evolved from Methyl-β-glucoside Tetranitrate – Hydroxylamine–Pyridine

The tetranitrate, 1.00 gm., was placed in a 125 ml. round-bottomed flask fitted with a thermometer and dropping funnel, and connected to two 100 ml. gas burettes by a 3-way stopcock, substantially as described by Segall and Purves (38). A 12.5% solution of hydroxylamine in pyridine (10 ml.), was run into the flask and the volume and temperature of the gas evolved was noted at two to four minute intervals. The results (Fig. 1) were closely reproducible and were corrected for the vapor pressure of pyridine (31).

To determine the nature of the gas, samples were collected in the absence of air by carrying out the partial denitration for 12 hr. in the Toricellian vacuum of a Lunge nitrometer (38). The samples were then analyzed in an Orsat apparatus fitted with pipettes containing potassium hydroxide, potassium pyrogallate, and acidified cuprous sulphate-β-naphthol reagents (39) for the absorption of carbon dioxide, oxygen, and carbon monoxide, respectively. Found: CO_2, 0.0, 0.0; O_2, 0.0, 0.0; CO (apparent), 8.6, 8.6; residual gas, 91.4, 91.4%. The residual gas, when dried with anhydrous calcium chloride, was found to have a molecular weight of 28.8 by the method of Daniels, Mathews, and Williams (12). A control determination with commercial nitrogen of 98.4% purity gave the correct molecular weight of 28.02.

Methylation, Denitration, and Acetylation of Sirup 1 (Table I)

In a typical experiment, Sirup 1, 3 gm., dissolved in 75 ml. of methyl iodide, was heated under reflux with 10 gm. of silver oxide and 4 gm. of powdered Drierite for eight hours. Filtration and evaporation yielded 3.38 gm. of

Sirup 2, which gave a positive diphenylamine test for nitrate groups. Found: OCH_3, 21.8, 21.5; N, 10.7, 10.7%. Calc. for glucose substituted with 2.26 methoxyl and 2.46 nitrate groups (mol. wt. 322): OCH_3, 21.75; N, 10.7%. Remethylation did not alter the methoxyl content.

Hydrogenolysis of 6.78 gm. of Sirup 2 yielded 4.41 gm. (98%) of Sirup 3, a colorless, nitrate-free glass. Found: OCH_3, 32.5, 32.7%. Calc. for glucose substituted with 2.22 methoxyl groups (mol. wt. 211): OCH_3, 32.6%. A 7.15 gm. sample of Sirup 3 was acetylated overnight at room temperature with pyridine (196 ml.) and acetic anhydride (19.6 ml.) and 8.0 gm. (72%) of the acetate was recovered in a clear, colorless state (Sirup 4).

A solution of all of this product in 55 ml. of anhydrous ether was cooled to 0°C. and was diluted until just turbid with about 5 ml. of pentane. The long needles that separated were removed, and six further crops of crystals were recovered from the mother liquors over a period of four weeks. Evaporation of the mother liquors yielded 3.86 gm. of a tough, viscous sirup which was retained as Sirup 5. The first three crops of crystals, 3.06 gm., all melting between 105° and 108°C., and also the fourth, 0.17 gm., m.p. 96° to 99°C., were crude methyl-4-methyl-β-glucoside triacetate. The remaining three fractions, 0.88 gm., each melting rather sharply between 76° and 81°C., contained the crystalline isomer.

Methyl-4-methyl-β-glucopyranoside and its Triacetate

After recrystallization from ether, the crude triacetate, 3.23 gm., yielded 2.51 gm. of pure material as long, colorless needles, with the proper methoxyl content. The melting point, 107.5° to 108.5°C., and the specific rotation in chloroform, −34.8°, agreed closely with the published values (8,27,32).

A solution of 2.11 gm. in 50 ml. of anhydrous methanol was deacetylated according to Levene and Tipson (28) by adding 2.7 ml. of 0.2 *N* barium methylate in methanol. After standing overnight at 0°C., barium was removed as the carbonate, and the filtrate yielded 1.3 gm. of long needles. Repeated crystallization from ethyl acetate established the melting point of methyl-4-methyl-β-glucoside at 101° to 101.5°C., and the compound had specific levorotations of $[\alpha]_D^{20} - 21.0°$ in water (c, 2), $- 17.4°$ in methanol (c, 3.44). McGilvray (29) found m.p. 102° to 103°C., and $[\alpha]_D^{20} - 17.6°$ in water.

A 200 mgm. sample of the glucoside was dissolved at 20°C. in water, 15 ml. of 0.1458 *M* sodium metaperiodate, $NaIO_4$, was added and the final volume was adjusted to 25 ml. The specific rotation changed from − 21° to − 126° in 80 min.; no formic acid or formaldehyde was formed and 0.99 moles of periodate per mole of glucoside was consumed.

Hydrolysis of the glucoside, 1.105 gm., with *N* sulphuric acid near 100°C. caused the specific rotation to assume the constant value of 51.0° in 11 hr., and 1.04 gm. of 4-methyl glucose was isolated as a colorless, copper reducing glass with the correct methoxyl content. A 3.846% solution of the sugar in water mutarotated from $[\alpha]_D^{20} + 62.1°$ (19 min.) to a constant value of + 56.2° (330 min.). Munro and Percival (32) reported the final value as + 53° (c, 2.1). The phenylosazone of the sugar was prepared in 58% yield, and after recrystallization from aqueous acetone the fine yellow needles melted at 157.5° to 159°C., in agreement with the published value (32).

Methyl-monomethyl-hexoside Triacetate

Fractions 5 to 7 of Sirup 4, 0.88 gm., were recrystallized from alcohol-*n*-pentane until the melting point became constant at 76° to 77.5°C. and the rotation in chloroform was −34.6° (*c*, 16.4). Found: OCH_3, 18.7, 18.5; acetyl, 36.7, 37.7; N, 0.0, 0.0%. Calc. for $C_6H_7O_4(OCH_3)_2(CH_3CO)_3$: OCH_3, 18.6; acetyl, 38.6%.

An accumulation of 1.64 gm. of the triacetate was dissolved in 10.0 ml. of chloroform and was de-acetylated by adding 0.0165 gm. of sodium dissolved in 16.0 ml. of methanol to the solution. The observed rotation was $[\alpha]_D^{20}$ − 3.36° after four minutes and attained constancy at − 1.96° after 96 min. The product, 1.025 gm. (101%) could not be crystallized, and 4% solutions in water and methanol at 20°C. had specific rotations (D line) of − 22.1° and − 22.9°, respectively. Found: OCH_3, 28.3, 28.4%. Calc. for $C_8H_{16}O_6$: OCH_3: 29.8%.

A solution of 0.933 millimoles (0.194 gm.) of the monomethyl methyl hexoside in 25 ml. of 0.15 *M* sodium periodate changed in rotation from − 0.54° (3 min.) to constancy at − 1.14° (60 min.). No formaldehyde was detected in the liquor, but 0.012 millimoles of formic acid was produced and 0.556 millimoles (60%) of periodate was consumed.

Methyl-2,4-dimethyl-β-glucopyranoside and 2,4-Dimethyl Glucose

Sirup 5 (Table I), 3.725 gm., was de-acetylated with alcoholic barium methylate at 0°C. (28), and the uncrystallized product (Sirup 6), 2.95 gm., was dissolved in 40 ml. of water. When this solution was shaken with three 10 ml. volumes of chloroform, the portion extracted and the portion remaining in the aqueous residue had the same properties. Found in each: OCH_3, 32.9, 32.7%; n_D1.4668; $[\alpha]_D^{20}$ − 19.7° in water.

A second sample of Sirup 6, 0.55 gm., was again de-acetylated by solution for 20 hr. at room temperature in 15 ml. of 0.05 *N* sodium hydroxide (21). The alkali was exactly neutralized with sulphuric acid and the crystalline residue from the evaporation of the liquor was extracted with boiling acetone. The colorless crystals, 0.55 gm., recovered from the acetone melted at 99° to 113°C., and recrystallization from alcohol–petroleum ether gave 0.22 gm. of Sirup 9, which was not further examined, and 0.28 gm. of pure methyl-2,4-dimethyl-β-glucoside. Yield, 55% of theory from Sirup 5.

Pure methyl-2,4-dimethyl-β-glucoside, which could also be recrystallized from carbon tetrachloride, melted at 123.5° to 124°C. and had specific rotations of $[\alpha]_D^{20}$ − 17.7° in acetone (*c*, 3.3), and − 26.5° in water (*c*, 3.26). Dewar and Fort (13) found m.p. 124°C. and a rotation of − 16.3° in acetone; while the values quoted by Adams, Reeves, and Goebel (1) were m.p. 122° to 124°C. and $[\alpha]_D^{29}$ − 18.6°. A second m.p. of 107° to 108°C. was found for the freshly remelted substance, as Adams and his co-workers reported. No change in rotation or pH occurred when the glucoside was dissolved in aqueous sodium periodate at 20°C. for four hours. No periodate was consumed and no formaldehyde could be detected in the final solution.

A 0.81 gm. sample of the pure glucoside, when hydrolyzed with boiling *N* sulphuric acid, gave 0.77 gm. of 2,4-dimethyl glucose as a sirup that did not crystallize. Found: OCH_3, 29.3, 29.0%. Calc. for $C_6H_{10}O_6(OCH_3)_2$: OCH_3, 29.8%. The product readily reduced Fehling's solution, and its specific rotation in water changed from $[\alpha]_D^{20} + 59.2°$ (*c*, 2.88) after 11 min. to a constant value of 62.2° after two hours. When heated near 100°C. for 2.5 hr. with 10 ml. of water, 3 gm. of sodium acetate, 2 gm. of phenylhydrazine, and 3 drops of saturated sodium bisulphite solution, 0.72 gm. of the dimethyl glucose yielded a red oil that was extracted with ether. After being washed with 4 *N* acetic acid, cooling of the ether solution and the addition of *n*-pentane caused the crystallization of 0.05 gm. of 4-methyl glucose phenylosazone. Recrystallization from aqueous acetone caused the product to melt correctly at 157° to 158°C., and a mixed m.p. with an authentic sample was not depressed.

Methyl-β-glucopyranoside-3,6-dinitrate

This dinitrate was conveniently isolated by dissolving 26.5 gm. of Sirup 1 (Table I) in 500 ml. of chloroform and extracting the solution four times with 200 ml. volumes of water. The combined aqueous extracts were then continuously re-extracted with ether for 24 hr., or until a fresh ether extract gave no color in the diphenylamine test for the nitrate group. Evaporation of the ether then left 8.56 gm. of a semicrystalline mass which on recrystallization from chloroform gave 3.14 gm. (11.9% by weight) of the dinitrate.

The large colorless prisms of methyl-β-glucoside-3,6-dinitrate when recrystallized from cold chloroform melted at 144° to 145°C. and had a specific rotation of $[\alpha]_D^{20} - 7.2°$ in acetone (*c*, 1.52), in agreement with the observations of Dewar and Fort (13). Found: OCH_3, 10.9, 10.3; N, 9.85, 9.84%. Calc. for $C_6H_9O_5(OCH_3)(NO_2)_2$: OCH_3, 10.9; N, 9.86%.

Two grams of the pure dinitrate, when twice methylated with silver oxide and methyl iodide, yielded 2.15 gm. of an uncrystallized product with the methoxyl and nitrogen contents of methyl-2,4-dimethyl-β-glucoside-3,6-dinitrate. The refractive index, n_D^{20}, 1.4623, and the specific rotation in chloroform, $[\alpha]_D^{20} - 7.9°$, (*c*, 5.36) were close to those reported (13). A 1.34 gm. sample of this methylated dinitrate on hydrogenolysis gave 0.89 gm. (93%) of crystalline, nitrate-free methyl-2,4-dimethyl-β-glucoside with the proper rotation, m.p., and mixed m.p. (13).

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A NEW GENERAL SYNTHESIS OF 2-AMINO ALCOHOLS[1, 2]

By Louis Berlinguet[3]

RÉSUMÉ

Une nouvelle synthèse permet d'obtenir les 2-amino alcools à partir de l'acétamidomalonate d'éthyle. La méthode consiste à condenser un dérivé halogéné approprié avec le sel de sodium de l'acétamidomalonate d'éthyle. Par monosaponification de ce di-ester suivie de décarboxylation, on obtient un ester éthylique *N*-acétamidé qu'on réduit par l'hydrure de lithium et d'aluminium en alcool *N*-acétamidé. Par hydrolyse, on obtient le chlorhydrate du 2-amino alcool correspondant. Le D,L-phénylalaninol, le D,L-tyrosinol et le D,L-leucinol ont ainsi été préparés avec d'excellents rendements. La méthode semble être d'application générale et les produits intermédiaires sont faciles à isoler.

INTRODUCTION

2-Amino alcohols are an important class of compounds owing mainly to their pharmalogical and physiological properties (14). With the development of new techniques for the degradation of proteins (6, 9, 12), amino alcohols related to natural amino acids have assumed a new importance. In these stepwise degradations, reduction of an esterified protein at a free carboxyl end gives an amino alcohol which is separated from the amino acids and identified by a suitable analytical method (4, 8).

In order to investigate a new method for the determination of 2-amino alcohols, it became of interest to develop a new general synthesis that would allow these compounds to be prepared in substantial quantities and in analytically pure form. Some of these 2-amino alcohols have been prepared by the reduction of the corresponding natural amino acids or their derivatives. Karrer and his co-workers (15, 17) and Enz and Leuenberger (11) have reduced the ethyl esters of some amino acids with sodium in alcohol. Some years later, Karrer *et al.* (16) and Barrow and Ferguson (3) acetylated the amino acid esters, thus improving the yields in the reduction.

Some workers have tried a catalytic reduction with hydrogen of the amino acid esters (7, 20, 21) and of the α-benzylamino acids (23), but in all cases the yields were poor.

With the availability of powerful reducing agents such as lithium aluminum hydride, Karrer, Portmann, and Suter (18, 19) have used them for the reduction of amino acid esters and have obtained yields between 50% and 85% in the corresponding amino alcohols. Dornow, Messwarb, and Frey (10) have reduced amino acid esters with lithium aluminum hydride in boiling tetrahydrofuran. Fromageot and his collaborators (12) have applied the same reduction to esterified proteins and to different amino acid esters in order to determine the chromatographic behavior of the amino alcohols thus obtained.

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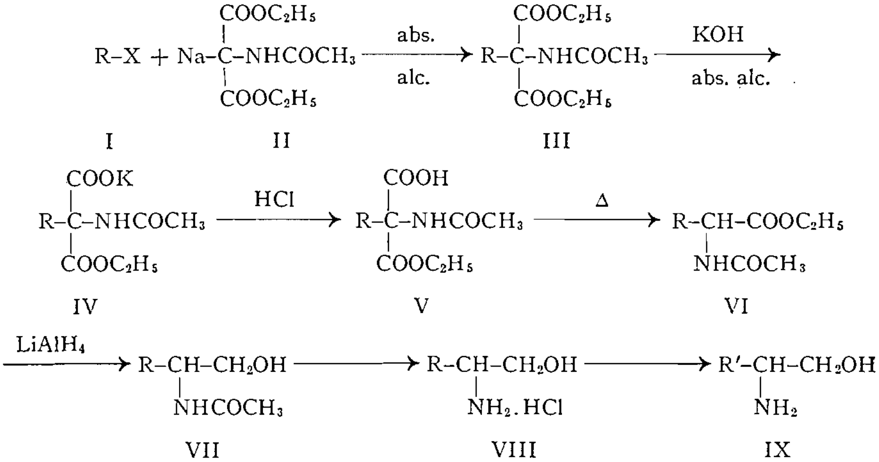
Finally in 1952, Vogl and Pöhm (24) have reduced directly the free amino acids, in suspension in boiling tetrahydrofuran, to the amino alcohols with yields of 75% to 85%. The quantities used in this case were less than one gram.

If small quantities of optically active amino alcohols are required, they can be obtained by simple procedures from L-amino acids. If, however, optical activity is not a consideration it was felt that a new direct synthesis of the amino alcohols, without the use of the amino acids, would be more economical.

Ethyl acetamidomalonate has been widely used in the synthesis of amino acids (1, 2, 22), and it has become the starting material in one of the classical methods in that field. It consists in condensing an alkyl halide with the ester and degrading by hydrolysis the resulting compound to the desired amino acid.



$R = R' = C_6H_5\text{-}CH_2\text{-}$ for phenylalaninol
$R' = p\text{-}OH\text{-}(C_6H_4)\text{-}CH_2\text{-}$ for tyrosinol
$R' = CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}$ for leucinol

In order to obtain amino alcohols by modifying this method, it was necessary to proceed stepwise in the hydrolysis of the condensation product of ethyl acetamido malonate (II) with the alkyl halide (I) (the average yield in this condensation is 80%). The di-ester (III) was monosaponified in absolute alcohol with slightly more than one equivalent of potassium hydroxide. The potassic salt (IV) was then acidified and the half ester (V) was isolated with yields around 80%.

By heating the *N*-acetamido half ester (V) at 150°C., decarboxylation took place smoothly and the resulting *N*-acetamido ethyl ester (VI) was recrystallized from ligroin (yield 90%). It was reduced in the cold with lithium aluminum hydride in absolute ether or tetrahydrofuran to give the *N*-acetamido alcohol (VII).

Reduction was always carried out in the cold in order to minimize reduction at the *N*-acetamido link (8).

In the case of *o*-methyl-D,L-tyrosinol, the *N*-acetamido derivative (VII) has been isolated from ether. But the other *N*-acetamido alcohols, being liquids, were directly hydrolyzed to give the corresponding 2-amino alcohol hydrochlorides (VIII) with 70–80% yield.

The free amino alcohols (IX), except D,L-tyrosinol, were obtained by passing the hydrochloride solutions through a column of Permutit S-1.

In the case of *o*-methyl-*N*-acetyl-D,L-tyrosinol the hydrolysis with hydrochloric acid did not split the ether link, and *o*-methyl-D,L-tyrosinol was obtained. This amino alcohol when refluxed for 12 hr. with a mixture of glacial acetic acid and hydrochloric acid did not yield any D,L-tyrosinol.

o-Methyl-tyrosinol was then refluxed with a mixture of glacial acetic acid and hydrobromic acid (48%) for 12 hr. The hydrobromide was passed through a column of Permutit S-1, but the expected free D,L-tyrosinol did not come out and was adsorbed. Elution with hydrochloric acid gave D,L-tyrosinol hydrochloride.

To obviate this adsorption on the column, D,L-tyrosinol hydrobromide was neutralized with sodium carbonate and the free amino alcohol was extracted with alcohol. Free D,L-tyrosinol (70%) was recrystallized from alcohol–ether mixture.

This general method of synthesis is presently applied in this laboratory for other amino alcohols.

Results of the physiological tests will be published elsewhere.

EXPERIMENTAL PART

2-Acetamido-2-carbethoxy-3-phenylpropionic Acid

To a solution of 30.7 gm. (0.1 mole) of ethyl 2-acetamido-2-carbethoxy-3-phenylpropionate (prepared by the method of Albertson and Archer) (2) in 100 ml. of absolute alcohol was added 110 ml. of 1.0 *N* potassium hydroxide solution in absolute alcohol. The mixture was stirred and allowed to stand at room temperature overnight. It was then filtered to yield 1 gm. of inorganic salt and possibly some dipotassic salt of 2-acetamido-2-carboxy-3-phenylpropionic acid. The filtrate was concentrated *in vacuo* on the water bath, and cold water was added. Most of the residue dissolved with the exception of unreacted ethyl 2-acetamido-2-carbethoxy-3-phenylpropionate, which was filtered and dried, giving 3.0 gm. (9.8%) of the starting material.

The clear filtrate was then acidified to Congo red with hydrochloric acid. The heavy precipitate thus formed was allowed to solidify in the cold, filtered, and dried. The yield of 2-acetamido-2-carbethoxy-3-phenylpropionic acid was 23.8 gm. (85.4%). Melting point: 129–130°C.* with evolution of gas. Calc. for $C_{14}H_{17}O_5N$: N, 5.02%. Found: N, 5.04%.

Ethyl 2-Acetamido-3-phenylpropionate

In a dried flask connected to a vacuum pump there were placed 19.5 gm. of 2-acetamido-2-carbethoxy-3-phenylpropionic acid. The flask was immersed

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*Melting points are not corrected.

in a metal bath at 150°C. for 15 min. and decarboxylation took place vigorously. The resulting oil was recrystallized from ligroin yielding 14.5 gm. (88.3%) of ethyl 2-acetamido-3-phenylpropionate. Melting point: 69–70°C. Calc. for $C_{13}H_{17}O_3N$: N, 5.96%. Found: N, 5.98%.

N-Acetyl- D, L*-phenylalaninol*

In an Erlenmyer surrounded with ice and containing 12.15 gm. of ethyl 2-acetamido-3-phenylpropionate in solution in absolute ether, there were added drop by drop, by means of a separatory funnel fitted with a calcium chloride tube, 3.0 gm. of lithium aluminum hydride in 100 ml. of absolute ether. During the addition and for two more hours, the mixture was shaken with a magnetic stirrer. Excess of lithium aluminum hydride was decomposed with small lumps of ice until there was no more evolution of gas. The mixture was heated and filtered on a Büchner funnel. The inorganic solid was extracted twice with boiling alcohol and the combined extracts were evaporated *in vacuo*. The oily residue weighing 9.0 gm. did not crystallize in the cold and was then hydrolyzed.

In a subsequent run, 2.8 gm. were distilled at 160–170°C. at 6 mm. giving a viscous liquid which did not crystallize.

D, L*-Phenylalaninol Hydrochloride*

N-acetyl- D, L-phenylalaninol obtained from the preceding reduction was refluxed for three hours with 100 ml. of 2 *N* hydrochloric acid. The solution was then evaporated *in vacuo*, dissolved in water, and purified with Norit. The clear solution was again evaporated *in vacuo* and the residue was redissolved in 30 ml. of boiling alcohol. Ether was added until turbidity appeared and D, L-phenylalaninol hydrochloride crystallized out rapidly. It was collected by filtration and dried, yielding 8.1 gm. (81%) of pure product. Melting point: 154–155°C. Karrer and collaborators (17) gave a melting point of 128°C. for L-phenylalaninol hydrochloride. Calc. for $C_9H_{14}ONCl$: N, 7.48%, Cl, 18.92%. Found: N, 7.57%, Cl, 18.90%.

D, L*-Phenylalaninol*

D, L-Phenylalaninol hydrochloride (7.01 gm.) was dissolved in 50 ml. of distilled water. The solution was passed through a column of Permutit S-1. The resulting solution was free from chloride ions and had a pH above 11.0. It was evaporated to dryness and dissolved in a minimum of boiling alcohol. Ether was then added until faintly turbid and upon cooling, 4.7 gm. (83%) of pure D, L-phenylalaninol was obtained. Melting point: 73–75°C. An analytical sample, recrystallized from ether, had a melting point of 75–77°C. Litt.: 67–68°C. (18,21). The R_f value in water–phenol solution is 0.74. Calc. for $C_9H_{13}ON$: N, 9.28%. Found: N, 9.30%.

D, L*-Phenylalaninol Acid Oxalate*

D, L-Phenylalaninol (0.6 gm.) was dissolved in 5 ml. of ethanol and 3.0 gm. of oxalic acid in solution in 5 ml. of ethanol were added. The mixture was warmed a little and chilled with some scratching. D, L-Phenylalaninol acid oxalate thus obtained weighed 0.95 gm. (98%). Melting point: 176°C. Calc. for $C_{11}H_{15}O_5N$: N, 5.81%. Found: N, 5.93%.

D,L-*Phenylalaninol Neutral Oxalate*

A solution of 0.2 gm. of D,L-phenylalaninol in 5 ml. of ethanol was slowly neutralized by the addition of 1.0 gm. of oxalic acid in 5 ml. of water until phenolphthalein was discolored. Upon cooling, the neutral oxalate crystallized. It was recrystallized in dilute alcohol. Yield: 2.2 gm. (81%). Melting point: 225°C. Calc. for $C_{20}H_{28}O_6N_2$: N, 7.14%. Found N, 7.20%.

N-Benzoyl- D,L-*phenylalaninol*

A solution containing 0.8 gm. of sodium hydroxide and 1.87 gm. of D,L-phenylalaninol hydrochloride was vigorously shaken with 1.16 ml. of benzoyl chloride. After a few minutes, the solid was filtered and dried. It was recrystallized from water and alcohol, yielding 1.7 gm. (69%) of *N*-benzoyl-D,L-phenylalaninol. Melting point: 140–142°C. Calc. for $C_{16}H_{17}O_2N$: N, 5.50%. Found: N, 5.61%.

A small quantity of another product, possibly *N*-benzoyl-*O*-benzoyl-D,L-phenylalaninol, was also collected. Melting point: 150–152°C. Calc. for $C_{23}H_{21}O_3N$: N, 3.91%. Found: N, 3.95%.

Ethyl 2-Acetamido-2-carbethoxy-3-(p-methoxyphenyl)propionate

To a stirred, boiling solution of 43.4 gm. of ethyl acetamidomalonate and 4.6 gm. of sodium in 200 ml. of absolute ethanol was added 33.0 gm. of anisyl chloride. The anisyl chloride was prepared with 85% yield from thionyl chloride, anisyl alcohol, and dimethylaniline in chloroform according to Gaudry's method (13). Refluxing was continued for four hours after which the sodium chloride was filtered. The resulting alcoholic solution was concentrated *in vacuo* and 500 ml. of ether added. Upon cooling, 53.8 gm. (80%) of crystalline ethyl 2-acetamido-2-carbethoxy-3-(*p*-methoxyphenyl)propionate were obtained. The melting point was 101°C. Litt.: 96°C. (5). Calc. for $C_{17}H_{23}O_6N$: N, 4.16%. Found: N, 4.12%.

2-Acetamido-2-carbethoxy-3-(p-methoxyphenyl)propionic Acid

In a flask containing 370 ml. of 0.3 *N* alcoholic potassium hydroxide was added 33.7 gm. (0.1 mole) of ethyl 2-acetamido-2-carbethoxy-3-(*p*-methoxyphenyl)propionate. The mixture was agitated with a magnetic stirrer overnight. It was then treated according to the procedure described for 2-acetamido-2-carbethoxy-3-phenylpropionic acid. Yield of 2-acetamido-2-carbethoxy-3-(*p*-methoxyphenyl) propionic acid: 27.2 gm. (88%). Melting point: 132–133°C. with evolution of gas. It was recrystallized by solution in a minimum of boiling alcohol which was then rapidly poured over cracked ice. Calc. for $C_{15}H_{19}O_6N$: N, 4.54%. Found: N, 4.59%.

If the amount of added potassium hydroxide is less than the theoretical quantity, unreacted starting material is recovered without any loss or contamination. If the alcohol contains an appreciable amount of water, some spontaneous decarboxylation might occur during or before acidification, in which case the decarboxylated ester is recovered by ethereal extraction of the acidified water.

Ethyl 3-(p-Methoxyphenyl)-2-acetamido Propionate

The decarboxylation was carried out in the same way as for ethyl 2-acetamido-3-phenylpropionate. The 2-acetamido-2-carbethoxy-3-(*p*-methoxyphenyl)-propionic acid (21.3 gm.) was decarboxylated to yield 17.4 gm. (95%) of 3-(*p*-methoxyphenyl)-2-acetamido propionate. When recrystallized from ligroin, it had a melting point of 72–73°C. Calc. for $C_{14}H_{19}O_4N$: N, 5.29%. Found, 5.30%.

o-Methyl-N-acetyl- D,L*-tyrosinol*

The reduction was carried out as for *N*-acetyl-D,L-phenylalaninol. Ethyl 3-(*p*-methoxyphenyl)-2-acetamido propionate (15.5 gm.) was reduced in cold absolute ether with 3.0 gm. of lithium aluminum hydride. The *o*-methyl-*N*-acetyl-D,L-tyrosinol thus obtained weighed 13.1 gm. (88%). An analytical sample was recrystallized from ether and had a melting point of 110–111°C. Calc. for $C_{12}H_{17}O_3N$: N, 6.28%. Found: N, 6.28%.

o-Methyl- D,L*-tyrosinol Hydrochloride*

o-Methyl-*N*-acetyl-D,L-tyrosinol (9.5 gm.) was hydrolyzed as described for D,L-phenylalaninol hydrochloride. *o*-Methyl-D,L-tyrosinol hydrochloride crystallized from alcohol–ether mixture. It was collected and dried. Yield: 7.92 gm. (85.6%). Melting point: 195–197°C. Calc. for $C_{10}H_{16}O_2NCl$, 16.3%. N, 6.47%. Found: Cl, 16.2%. N, 6.44%.

o-Methyl- D,L*-tyrosinol*

A solution containing 3.0 gm. of *o*-methyl-D,L-tyrosinol hydrochloride in 50 ml. of water was passed through a column of Permutit S-1. The resulting solution, which was free from chloride ions, was evaporated to dryness. The residue was recrystallized from ether yielding 2.1 gm. (84%) of *o*-methyl-D,L-tyrosinol. Melting point: 80–82°C. Calc. for $C_{10}H_{15}O_2N$: N, 7.74%. Found: N, 7.83%.

o-Methyl- D,L*-tyrosinol Neutral Oxalate*

The *o*-methyl-D,L-tyrosinol neutral oxalate, recrystallized from water and alcohol, had a melting point of 220°C. Calc. for $C_{22}H_{32}O_8N_2$: N, 6.20%. Found: N, 6.21%.

o-Methyl- D,L*-tyrosinol Acid Oxalate*

o-Methyl-D,L-tyrosinol acid oxalate recrystallized from alcohol had a melting point of 160°C. Calc. for $C_{12}H_{17}O_6N$: N, 5.17%. Found: N, 5.10%.

D,L*-Tyrosinol*

A solution of 1.18 gm. of *o*-methyl-D,L-tyrosinol in 50 ml. of glacial acetic acid and 50 ml. of hydrochloric acid was refluxed for 12 hr. The starting material was recovered. It did not give the Millon test for phenolic group.

A solution containing 6.35 gm. of *o*-methyl-D,L-tyrosinol in 50 ml. of glacial acetic acid and 50 ml. of 48% hydrobromic acid was refluxed for 12 hr. The mixture was evaporated to dryness, and dissolved in water.

Half of the solution was passed through a column of Permutit S-1. The filtrate did not give the ninhydrin or the Millon tests. Alcohol was then passed through the column and this alcoholic filtrate was also negative to the previous tests. Both filtrates were combined and evaporated to dryness. No residue was obtained. 2 *N* Hydrochloric acid was then passed through the column and the acid eluate was evaporated to dryness yielding 2.6 gm. of a viscous oil which gave a positive ninhydrin and Millon test.

The other half of the solution was evaporated to dryness and then dissolved in a minimum of water. A solution of sodium carbonate was then added until pH 9.0 was obtained. The mixture was evaporated to dryness and the residue was dissolved in 20 ml. of boiling alcohol. Insoluble salts were filtered and the alcoholic filtrate was again evaporated. The residue was recrystallized by solution in boiling alcohol and addition of ether until turbidity appeared. D,L-Tyrosinol crystallized yielding 2.0 gm. (70%). Melting point: 128–129°C. Litt.: 94°C. for L-tyrosinol (11, 18). Calc. for $C_9H_{13}O_2N$: N, 5.40%. Found: N, 5.50%.

D,L-*Tyrosinol Hydrochloride*

D,L-Tyrosinol was neutralized by addition of hydrochloric acid. The D,L-tyrosinol hydrochloride thus obtained was recrystallized from alcohol–ether mixture. Melting point: 186°C. Calc. for $C_9H_{14}O_2NCl$: N, 6.88%. Cl, 17.42%. Found: N, 6.78%. Cl, 17.32%.

D,L-*Tyrosinol Neutral Oxalate*

D,L-Tyrosinol neutral oxalate, recrystallized from methanol, had a melting point of 231°C.

D,L-*Tyrosinol Acid Oxalate*

The melting point of D,L-tyrosinol acid oxalate recrystallized from alcohol–ether mixture was 166°C.

2-Acetamido-2-carbethoxy-4-methyl-pentanoic Acid

A solution containing 27.3 gm. of ethyl 2-acetamido-2-carbethoxy-4-methylpentanoate (prepared according to the method of Albertson and Archer (2)) in 370 ml. of 0.3 *N* alcoholic potassium hydroxide was agitated overnight in a closed flask by means of a magnetic stirrer.

The solution was then treated as described for 2-acetamido-2-carbethoxy-3-phenyl propionic acid. Yield of 2-acetamido-2-carbethoxy-4-methylpentanoic acid: 19.6 gm. (80%).

An analytical sample was recrystallized from water. Melting point: 130–132°C. with evolution of gas. Calc. for $C_{11}H_{19}O_5N$: N, 5.72%. Found: 5.73%.

Ethyl 2-Acetamido-4-methyl-pentanoate

In a flask connected to a vacuum pump, 10.8 gm. of 2-acetamido-2-carbethoxy-4-methyl-pentanoic acid were heated at 150°C. *in vacuo* for 15 min. Decarboxylation proceeded smoothly and the resulting oil was distilled; 8.0 gm. (90.3%) of ethyl 2-acetamido-4-methylpentanoate passed at 148–

152°C. at 7 mm. The clear oil did not crystallize after a prolonged period in the cold.

N-acetyl D,L-*Leucinol*

The reduction was carried out as for *N*-acetyl-D,L-phenylalaninol. Ethyl 2-acetamido-4-methyl-pentanoate (8.0 gm.) was reduced with 3.0 gm. of lithium aluminum hydride. *N*-acetyl-D,L-leucinol was isolated as an oil, weighing 4.6 gm. (72.8%), and distilling at 172–175°C. at 9 mm. It did not crystallize in the cold.

D,L-*Leucinol Hydrochloride*

A solution containing 4.6 gm. of *N*-acetyl-D,L-leucinol was treated according to the procedure described for D,L-phenylalaninol hydrochloride. The recrystallized D,L-leucinol hydrochloride weighing 3.9 gm. (88%) had a melting point of 161–162°C. Calc. for $C_6H_{16}ONCl$: N, 9.13%. Cl, 23.8%. Found: N, 9.22%. Cl, 24.3%.

D,L-*Leucinol Neutral Oxalate*

A solution of free D,L-leucinol was obtained by passing 1.0 gm. of D,L-leucinol hydrochloride through a column of Permutit S-1. From this solution D,L-leucinol neutral oxalate was prepared. Recrystallized from alcohol, it had a melting point of 206°C. Calc. for $C_{14}H_{32}O_6N_2$: N, 8.64%. Found: N, 8.61%.

D,L-*Leucinol Acid Oxalate*

In the same way, D,L-leucinol acid oxalate was prepared. Melting point: 179°C. Calc. for $C_8H_{17}O_5N$: N, 6.77%. Found: N, 6.70%.

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THE PHOTOLYSIS OF MERCURY DIMETHYL WITH 3-ETHYL PENTANE[1]

By Richard E. Rebbert[2] and E. W. R. Steacie

ABSTRACT

Mercury dimethyl was photolyzed in the presence of 3-ethyl pentane in the temperature range from 76°C. to 238°C. The activation energy for the reaction

$$CH_3 + C_7H_{16} \rightarrow CH_4 + C_7H_{15}$$

was found to be 6.8 ± 0.3 kcal. per mole.

INTRODUCTION

In a previous paper (1) the activation energies and the rate constants for a number of reactions of the type

$$CH_3 + RH \rightarrow CH_4 + R$$

were determined. To these we can now add the present hydrocarbon, 3-ethyl pentane. So far as the authors know, this reaction has not been investigated before by any method.

EXPERIMENTAL

The experimental set-up was exactly the same as that reported previously (1). No filters were used. The mercury dimethyl was the same as before and was better than 99% pure. The 3-ethyl pentane was a standard sample from the American Petroleum Institute, 225–5S. The stated impurity was 0.13 ±0.03 mole per cent.

Results

The results are given in Table I and are plotted in Fig. 1. The method of calculating the results is exactly the same as before.

TABLE I

The photolysis of mercury dimethyl with 3-ethyl pentane

Temp., °K.	Pressure of $Hg(CH_3)_2$ (mm.)	Pressure of $CH(C_2H_5)_3$ (mm.)	Time (sec.)	Products (μM.)		$k_1/k_2^{\frac{1}{2}} \times 10^{13}$
				CH_4	C_2H_6	
349	29.8	34.6	3600	1.23	15.66	3.47
378	38.0	32.0	2700	1.99	13.65	6.77
394	40.2	33.1	2700	3.06	13.91	10.2
420	42.0	35.1	1800	3.40	9.13	16.6
446	44.2	36.9	1500	4.65	7.02	27.6
470	48.0	39.3	1200	5.58	5.23	40.7
497	50.1	41.1	1200	8.21	5.35	56.0
511	50.1	41.1	900	8.24	3.84	81.3

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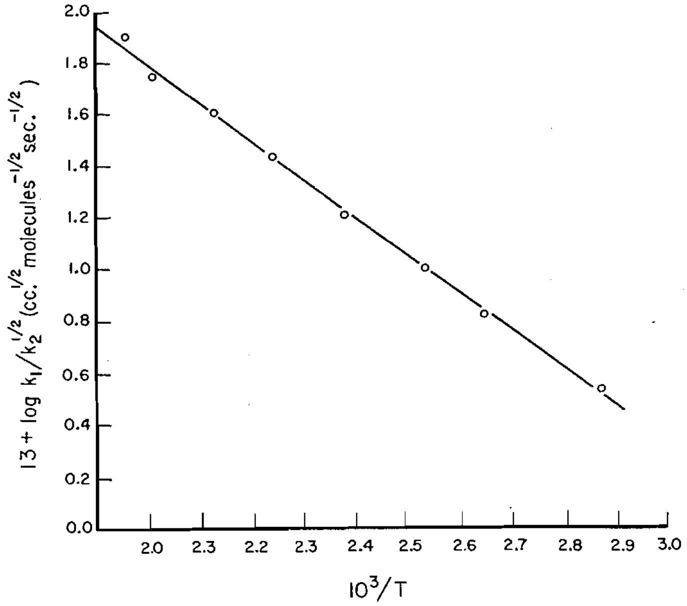

FIG. 1. Arrhenius plot for reaction of methyl radicals with 3-ethyl pentane.

Discussion

The main steps of the over-all reaction are the following

$$Hg(CH_3)_2 + h\nu \rightarrow Hg + 2CH_3 \qquad [0]$$

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + CH_3HgCH_2 \qquad [1']$$

$$CH_3 + C_7H_{16} \rightarrow CH_4 + C_7H_{15} \qquad [1]$$

$$2CH_3 \rightarrow C_2H_6. \qquad [2]$$

We assume that methane and ethane are not formed by any other reaction than those postulated above. The fate of CH_3HgCH_2 and C_7H_{15} may be dimerization, reaction with each other, or reaction with a methyl radical.

The above mechanism leads to an activation energy for reaction [1] of 6.8 kcal. per mole. The best line through all points has been found by the method of least squares to be $13 + \log k_1/k_2^{\frac{1}{2}} = 4.76 - (1478/T)$. If P_2 is assumed to be unity, the steric factor, P_1, is 1.2×10^{-4}.

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THE HYDROLYSIS OF THE CONDENSED PHOSPHATES

I. SODIUM PYROPHOSPHATE AND SODIUM TRIPHOSPHATE[1]

BY JOAN PEDLEY CROWTHER AND A. E. R. WESTMAN

ABSTRACT

The rates of hydrolysis of sodium pyrophosphate and triphosphate in solution have been measured at 65.5°C. over the pH range 2.0 to 12.0 and the phosphorus concentration range 0.10 to 0.25 atomic weights per liter. The reactions were found to be first order providing a constant concentration of hydrogen ion was maintained in the reaction flask. Both reactions are acid catalyzed but only the hydrolysis of triphosphate was found to be base catalyzed. Pyrophosphate and triphosphate apparently hydrolyze independently of each other.

INTRODUCTION

The hydrolysis of condensed phosphates is of interest commercially because the complexing properties of these materials are not possessed by the ultimate reversion product, orthophosphate. It is not surprising then that many workers have investigated the hydrolysis of sodium pyrophosphate and triphosphate. The value of the work, however, is frequently diminished by the failure to control the hydrogen ion concentration during the course of the reaction (the hydrolysis produces weaker acids resulting in an increase in pH), and because good analytical procedures were not available.

The inadequacies of analytical methods for phosphates are not so apparent in the studies of the hydrolysis of pyrophosphate since pyrophosphate reverts directly to orthophosphate, and orthophosphate can be determined in the presence of other phosphates. By such a procedure Green (3) and Muus (6) investigated the hydrolysis of pyrophosphate.

When the investigations of the hydrolysis of triphosphate are examined, however, it becomes very obvious that these studies have been handicapped by poor analytical procedures. The fact that one mole of triphosphate anion reverts to one mole of pyrophosphate and one mole of orthophosphate anion was established by Bell (1) as recently as 1947. Bell (1) employed an analytical method (2) which he had developed and which permitted the direct determination of triphosphate. However, most workers studied the hydrolysis of the triphosphate anion indirectly. Thus Green (3) followed the course of the reaction by measuring the amount of orthophosphate formed. Morgan and Swoope (5) could not measure directly the triphosphate, and thus could not study effectively the hydrolysis of commercial sodium 'tetraphosphate'. Similarly Watzel (8) could not directly determine the triphosphate.

The analytical method (9) used by the authors permits a direct determination of each component with adequate accuracy and provides qualitative as well as quantitative information on the system.

The study of the hydrolysis of pyrophosphate and triphosphate has also been complicated by the failure to recognize the importance of the hydrogen ion

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[1] *Manuscript received September 28, 1953.*
Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto, Ontario.

concentration. Even when the initial hydrogen ion concentration and its subsequent changes are measured (the procedure followed by Muus(6)), the worker must deal with the additional variable, the hydrogen ion concentration. Green (3) avoided this by measuring the rate of reaction at a series of hydrogen ion concentrations. From his data the dependence of the rate of hydrolysis on the hydrogen ion and phosphate ion concentration could be evaluated. In the present investigation the experimental design was similar to that of Green (3). However, a more efficient analytical procedure (9) was employed and the effect of the hydrogen ion concentration was investigated over a wider range.

EXPERIMENTAL

Materials

The preparation of pure sodium triphosphate is very difficult, and in the present investigation a commercial grade was used. The sodium pyrophosphate used was initially believed to be pure. When the analytical procedure was improved, however, it was found that one per cent of the phosphorus was present as orthophosphate.

A stock solution of sodium pyrophosphate (0.245 atomic weights phosphorus per liter) was used in the experiments. This concentration was selected because it was suitable for the analysis.

The sodium triphosphate was 87.3 mole per cent sodium triphosphate and 12.7 mole per cent sodium pyrophosphate. The concentration of the stock solution used was 0.190 atomic weights phosphorus per liter—this value being suitable for analysis.

Procedure

Samples (100 ml.) prepared from the stock phosphate solutions were placed in a long narrow tube fitted with a stirring rod and a reflux condenser. The solutions were heated by suspending the tube in a water bath maintained at 65.5 ± 0.1°C. This temperature was selected so that the experimental results could be compared with Green's (3) results obtained at 150°F. Since the pH values of sodium pyrophosphate and triphosphate solutions are approximately 9.5, and since their rates of hydrolysis in this region are very small, it was assumed that the solutions did not undergo reversion while they were being heated to 65.5°C. To adjust the phosphate solution approximately to the desired pH value, either 10 N sulphuric acid or sodium hydroxide pellets was added. The time at which either was added was considered to be the time at which the hydrolysis reaction began. The pH was finally adjusted and maintained within ±0.1 units of the desired value by adding known volumes of $N/10$ ammonium hydroxide and $N/10$ sulphuric acid. The pH values were measured with a glass electrode and a Leeds and Northrup pH meter (Cat. No. 7663) which had a sensitivity of 0.02 pH units. After each pH measurement the sample was returned to the reaction flask. At measured time intervals samples were withdrawn and spotted on the filter paper chromatogram within one minute. Further hydrolysis during the analysis was negligible.

Analysis

The analyses were made using a procedure (9) developed in this laboratory. This method involves the separation of the phosphate components by filter paper chromatography and the subsequent colorimetric determination of the phosphorus content of each component. The accuracy of the method is an absolute figure ± 1.0%.

Data

The hydrolysis of sodium pyrophosphate in solution was studied at 65.5°C. over the pH range 2.0 to 10.8. At pH 2.0, the solution concentrations were 0.082, 0.123, and 0.245 atomic weights phosphorus per liter. In the remainder of the experiments the solution concentration was 0.245 atomic weights phosphorus per liter. The compositions of these solutions, after various time periods, are given in Table I.

TABLE I
HYDROLYSIS OF PYROPHOSPHATE

pH	Concentration (moles phosphorus per liter)	Reaction time (min.)	% Distribution of phosphorus		k (First order rate constant)(min.$^{-1}$)	Average k (min.$^{-1}$)
			Pyrophosphate	Orthophosphate		
—	—	0	99.0	1.0		
2.0	0.245	60	95.6	4.3	5.76×10^{-4}	
		120	92.4	7.6	5.76×10^{-4}	
		180	90.1	9.9	5.25×10^{-4}	
		240	87.0	13.0	5.37×10^{-4}	5.53×10^{-4}
2.0	0.123	120	92.2	7.8	5.76×10^{-4}	
		180	90.0	10.0	5.12×10^{-4}	
		240	87.4	12.6	5.19×10^{-4}	5.36×10^{-4}
2.0	0.082	120	92.4	7.7	5.76×10^{-4}	
		240	86.4	13.6	5.66×10^{-4}	
		360	82.8	17.2	4.99×10^{-4}	
		420	80.0	20.0	5.04×10^{-4}	5.36×10^{-4}
3.0	0.245	242	92.1	7.9	2.94×10^{-4}	
		425	86.1	13.9	3.25×10^{-4}	
		1344	61.0	39.0	3.59×10^{-4}	
		1655	55.0	45.0	3.54×10^{-4}	
		1840	54.4	45.6	3.25×10^{-4}	3.31×10^{-4}
6.0	0.245	128	96.7	3.3	1.45×10^{-4}	
		260	95.0	5.0	1.24×10^{-4}	
		368	95.0	5.0	0.88×10^{-4}	
		418	91.4	8.6	1.43×10^{-4}	1.25×10^{-4}
9.3	0.245	425	98.6	1.4	1.1×10^{-5}	
		1380	97.5	2.5	1.0×10^{-5}	
		1865	97.4	2.6	0.9×10^{-5}	1.0×10^{-5}
10.9	0.245	2820	98.4	1.6	1.6×10^{-6}	
		3250	97.4	2.6	4.9×10^{-6}	
		4250	95.5	4.5	7.9×10^{-6}	4.8×10^{-6}

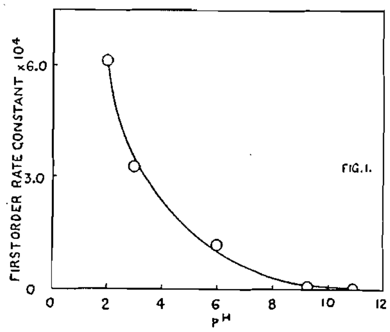
Similarly the hydrolysis of sodium triphosphate in solution was studied at 65.5°C. over the pH range 2.0 to 12.0. At pH 2.0, the solution concentrations were 0.190 and 0.0951 atomic weights phosphorus per liter. In the remainder of the experiments the solution concentration was 0.0951 atomic weights phosphorus per liter. The compositions of these solutions after various time periods are given in Table II.

TABLE II
HYDROLYSIS OF TRIPHOSPHATE

pH	Concentration (moles phosphorus per liter)	Reaction time (min.)	% Distribution of phosphorus			*k* (First order rate constant) (min.$^{-1}$)	Average *k* (min.$^{-1}$)
			Triphosphate	Pyrophosphate	Orthophosphate		
—	—	0	91.2	8.8	0		
2.0	0.0951	60	77.9	17.0	5.0	2.58×10^{-3}	
		135	70.5	20.4	9.2	1.89×10^{-3}	
		295	49.7	31.6	18.7	2.04×10^{-3}	
		425	33.8	40.0	26.3	2.32×10^{-3}	
		1395	4.7	35.1	60.3	2.11×10^{-3}	2.19×10^{-3}
2.0	0.190	96	74.6	18.0	7.4	2.06×10^{-3}	
		225	47.8	27.7	14.5	2.02×10^{-3}	
		345	44.6	35.5	19.9	2.06×10^{-3}	2.05×10^{-3}
3.0	0.0951	238	73.5	20.6	6.0	9.08×10^{-4}	
		400	61.5	25.4	13.0	9.76×10^{-4}	
		1360	24.9	42.5	32.6	9.52×10^{-4}	9.4×10^{-4}
5.0	0.0951	120	87.7	11.0	1.3	3.26×10^{-4}	
		240	85.2	12.6	2.3	2.78×10^{-4}	
		360	83.6	13.9	2.4	2.36×10^{-4}	
		420	79.8	14.6	5.7	3.17×10^{-4}	2.89×10^{-4}
9.3	0.0951	317	90.8	9.2	0	1.1×10^{-5}	
		2818	86.6	12.2	1.2	1.8×10^{-5}	
		3202	86.4	12.4	1.2	1.7×10^{-5}	1.5×10^{-5}
12.0	0.0951	1360	76.5	17.5	6.0	1.29×10^{-4}	
		1635	71.6	19.9	8.7	1.51×10^{-4}	
		1820	70.4	20.6	8.9	1.43×10^{-4}	1.41×10^{-4}

Calculations

When the data in Tables I and II were substituted in the general equation for a first order reaction, the rate constants (calculated for each hydrogen ion



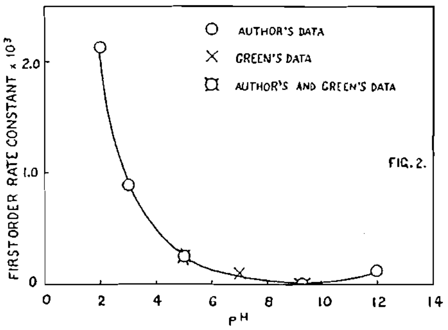


FIG. 1. Effect of pH on rate of hydrolysis of sodium pyrophosphate in solution.
FIG. 2. Effect of pH on rate of hydrolysis of sodium triphosphate in solution.

concentration studied) were found to be constant within the experimental accuracy, even when the initial phosphorus concentration was varied. The values of these rate constants, for the hydrolysis of pyrophosphate and triphosphate, are included in Tables I and II respectively. Figs. 1 and 2 are the curves obtained by plotting the first order rate constants, for pyrophosphate and triphosphate solutions respectively, against the pH of the solutions.

DISCUSSION

Order of Reaction

The above results are in agreement with Muus' (6) theory that the hydrolysis of the pyrophosphate anion is a first order reaction at constant hydrogen ion concentration. Muus (6) was unable to establish this theory experimentally since he did not maintain a constant hydrogen ion concentration in his experimental work, and only studied the reaction over the pH range 0.91 to 1.3, but he deduced the concept from his results.

On the other hand, Green (3) found that the first order rate constants for the hydrolysis of the triphosphate anion depended upon its initial concentration. Green's (3) first order rate constants for a 0.005% sodium triphosphate solution are included in Fig. 2. The concentration of the sodium triphosphate solution, which we studied, was 1.17%. Different analytical procedures were used, and Green (3) determined the rate of reaction by the amount of orthophosphate formed. Under these circumstances, the agreement between the two sets of data is quite acceptable. However, Green (3) found that the rate constants which he determined for a 0.0005% sodium triphosphate solution disagreed with those determined for the 0.005% solution. Possibly in very dilute solutions the reaction may not be first order with respect to the triphosphate concentration, but certainly it appears to be so over the concentration range 0.005 to 1.17%.

In conclusion, the results indicate that the hydrolysis of triphosphate anion or pyrophosphate anion is first order at constant hydrogen ion concentration over the pH range 2.0 to 12.0.

Acid–Base Catalysis

An examination of Figs. 1 and 2 indicates that the hydrolyses of pyrophosphate and triphosphate in solution are both acid catalyzed while only the triphosphate hydrolysis is base catalyzed over the pH range studied. Triphosphate solutions are most stable in the pH range 9 to 10, and this finding is in accordance with Watzel's (8) results. Van Wazer, Griffith, and McCullough (7) have suggested that this apparent base catalysis of triphosphate is due to the formation of complexes with sodium ion. The discussion of the effect of the hydrogen ion concentration on the hydrolysis of pyrophosphate solutions has been reserved for a second paper by McGilvery and Crowther (4).

Hydrolysis of Solutions Containing Both Pyrophosphate and Triphosphate Anions

Whether or not triphosphate and pyrophosphate hydrolyze independently of each other can be ascertained from an examination of the course of hydrolysis of sodium triphosphate and the corresponding first order rate constants for pyrophosphate and triphosphate. That is, the proportion of pyrophosphate was measured at various times as the hydrolysis of triphosphate solutions proceeded, and this proportion can be calculated from the following relationship if pyrophosphate and triphosphate hydrolyze independently:

$$P = b\left(\frac{a-x}{a}\right)^{k_2/k_1} + \frac{2}{3}\left(\frac{k_1 a}{k_2 - k_1}\right)\left\{\left(\frac{a-x}{a}\right) - \left(\frac{a-x}{a}\right)^{k_2/k_1}\right\}$$

where P is the percentage phosphorus as pyrophosphate at time t
b is the initial percentage phosphorus as pyrophosphate
x is the percentage phosphorus as triphosphate which has decomposed at time t
a is the initial percentage phosphorus as triphosphate
k_1 is the first order rate constant for the hydrolysis of triphosphate anion at a specified hydrogen ion concentration
k_2 is the first order rate constant for the hydrolysis of pyrophosphate anion at the same hydrogen ion concentration

The calculated and measured percentages of phosphorus as pyrophosphate are shown in Table III. These values are in satisfactory agreement indicating that pyrophosphate and triphosphate hydrolyze independently.

TABLE III
TEST OF INDEPENDENCE OF THE HYDROLYSIS OF TRIPHOSPHATE AND PYROPHOSPHATE

pH	Reaction time	% Phosphorus as pyrophosphate (measured)	% Phosphorus as pyrophosphate (calculated)
—	0	8.8	—
2.0	60	17.0	17.1
	96	18.0	19.1
	135	20.4	21.6
	225	27.7	28.8
	295	31.6	33.0
	345	35.5	35.4
	425	40.0	39.9
	1395	35.1	38.2
3.0	238	20.6	19.5
	400	25.4	26.1
	1360	42.5	39.4
5.0	120	11.0	11.1
	240	12.6	12.6
	360	13.9	13.6
	420	14.6	15.5
9.3	317	9.2	9.0
	2818	12.2	11.5
	3202	12.4	11.6
12.0	1360	17.5	18.5
	1635	19.9	21.8
	1820	20.6	22.6

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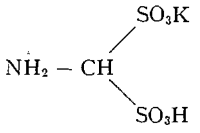
NOTE

MONO- AND DIPOTASSIUM AMINOMETHIONATE

By R. A. B. Bannard[1] and J. H. Ross

In 1895, von Pechmann and Manck (3) isolated monopotassium aminomethionate (I) and dipotassium aminomethionate (II) from the solution which resulted on addition of crystalline potassium cyanide to a potassium bisulphite solution. When prepared according to the directions given by these workers (3) monopotassium aminomethionate was obtained in yields of approximately 40% rather than the 58–72% range claimed, and a more reliable method of preparation was sought.



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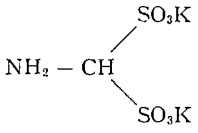

II

Recently, Arnold and Perry (1, 2) have patented a process for the preparation of sodium and potassium salts of aminomethionic acid. In their method, a solution of an alkali-metal cyanide is added to an alkali-metal bisulphite solution at 40 to 45°C. over a prolonged period, with addition of sulphur dioxide to neutralize the alkalinity developed by the reaction and to precipitate the salts at the conclusion of the process. Arnold and Perry (1, 2) obtained a 30% yield of the disubstituted salts or a 40% yield of the monosubstituted salts, and found that the yield of the latter increased to 80% on addition of fresh cyanide to the liquor after the monosubstituted salt was removed.

Not wishing to resort to a recycling operation for laboratory preparation we have modified Arnold and Perry's (1, 2) method by (i) using more concentrated bisulphite solutions (3.5 molar), (ii) increasing the reaction temperature to 55–80°C., (iii) holding the pH of the solution at 7.85 during heating, and (iv) precipitating monopotassium aminomethionate at pH 2.5. These modifications have increased the yield of monopotassium aminomethionate to 68.0% and shortened the reaction time from 12 hr. to 35 min.

Dipotassium aminomethionate was prepared in 68.5% yield simply by neutralization of the monopotassium salt with potassium hydroxide in aqueous solution.

EXPERIMENTAL

Monopotassium Aminomethionate

A 400-ml. Berzelius beaker was equipped with glass and calomel electrodes, a thermometer, mechanical stirrer, burette, and fritted-glass gas disperser

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connected to a sulphur dioxide cylinder. A potassium bisulphite – sulphite solution was prepared from 14.6 gm. (equivalent to 0.125 mole $KHSO_3$) of potassium metabisulphite, 93.9 gm. (0.581 mole) of potassium sulphite and 140 ml. of water, and placed in the reaction vessel. The burette was filled with a solution of 23.2 gm. (0.349 mole) of potassium cyanide in 35 ml. of water. The bisulphite – sulphite solution was heated to 55°C.; simultaneous addition of cyanide solution and sulphur dioxide was begun and continued in order to maintain the pH at 7.85, while the temperature was raised at a rate of approximately 1°C. per minute until a maximum of 80°C. was reached (20 min.). At this point all the cyanide solution had been added but addition of sulphur dioxide was continued for a further 15 min. at 80°C. to hold the pH at 7.85. The solution was cooled to 20°C. over a period of 20 min. and acidified to pH 2.50 by addition of sulphur dioxide. After standing for 30 min. at 10°C. the precipitated salts were collected on a fritted-glass funnel by suction filtration and washed with two 100-ml. portions of water to remove coprecipitated potassium bisulphite. The colorless microcrystalline powder was air-dried yielding 54.4 gm. (68.0%) of pure monopotassium aminomethionate.

Dipotassium Aminomethionate

Monopotassium aminomethionate, 45.8 gm. (0.200 mole) was suspended in 100 ml. of water and the mechanically stirred suspension treated with 10% potassium hydroxide solution until a clear solution was obtained. The pH of the solution was adjusted to 8.00 by addition of concentrated hydrochloric acid. The solution was filtered, diluted to a volume of 300 ml., and allowed to stand at 0°C. for 12 hr. The colorless crystals of dipotassium aminomethionate monohydrate which separated were collected by suction-filtration and weighed 39.0 gm. (68.5%) after air-drying.

We wish to gratefully acknowledge the award of a National Research Council Studentship to one of us (R.A.B.B.) and financial assistance from the Defence Research Board of Canada.

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VISCOSITY AND MOLECULAR WEIGHT OF DEGRADED CARRAGEENIN[1]

BY C. R. MASSON AND G. W. CAINES

ABSTRACT

Viscosities and number average molecular weights of various carrageenin preparations, including thermally and photochemically degraded samples, have been measured. Aqueous solutions of carrageenin of low molecular weight are shown to exhibit viscosity characteristics which are entirely similar to those of other natural and synthetic polyelectrolytes. Solutions of carrageenin of high molecular weight exhibit plastic flow. The relationship between viscosity and molecular weight for the degraded polymer indicates that the molecular configuration in solution is that of a fairly stiff rod, even in the presence of salts.

INTRODUCTION

Carrageenin, the water-soluble polysaccharide obtained from the red alga *Chondrus crispus*, is of importance commercially as a gelling and suspending agent. The useful properties of this substance are undoubtedly due, in part, to the high viscosities which its solutions possess. Chemically, the polymer consists largely of D-galactose residues linked through positions 1 and 3 and carrying a negatively charged sulphate group on position 4. Solutions of carrageenin should therefore exhibit physical properties similar to those of other natural and synthetic polyelectrolytes.

In the course of an investigation of the kinetics of the degradation of carrageenin (9), the viscosities of various preparations in aqueous solution have been measured both in the presence and absence of salts. These measurements, along with corresponding molecular weight determinations, are described below.

EXPERIMENTAL

Details regarding the extraction of the carrageenin used in this study are given elsewhere (9). The sodium salt, prepared by means of ion-exchange techniques (9), was used in all experiments.

For most of the viscosity measurements Ostwald viscometers of similar dimensions were employed. The characteristics of these viscometers were as follows: capillary diameter 0.0515 cm.; volume of bulbs approx. 2 ml.; flow times for water 75 to 90 sec.; mean shear gradient for water 1100 to 1300 sec. $^{-1}$; kinetic energy correction less than 1%. The temperature of measure-

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ment was 25 ± 0.1°C. A few experiments were also performed using a commercial Stormer viscometer (A. H. Thomas Co.) equipped with a cylindrical rotor.

Molecular weights were determined osmotically at 25°C. using 0.1 *M* sodium chloride as solvent. The osmometer used here has been described elsewhere (10). Cellophane, grade P.T. 600 (kindly supplied by Canadian Industries Ltd., Montreal) was used as membrane. To avoid 'sticking' of the liquids in the osmometer capillaries, toluene was introduced into the capillaries after filling the osmometer cells, and the osmotic pressures were recorded as a head of this solvent using a cathetometer. A preservative consisting of a mixture of 1 part chlorobenzene plus 1 part dichloroethane plus 2 parts chlorobutane was added in small amounts to both solution and solvent. Osmotic equilibrium was generally attained overnight.

In the osmotic pressure measurements, a slight 'cell constant' or 'cell zero' was often observed with solvent in both half-cells, and corrections were applied for this effect. The cell constant was generally zero when a fresh membrane was used, or when solutions of high molecular weight polymer were measured. On prolonged use of the same membrane, however, or when degraded polymers of low molecular weight were employed, a small cell constant did develop.* If the necessary correction became greater than 0.05 cm., the membrane was discarded.

Concentrations were determined by weight, known portions of the solutions being evaporated to constant weight in an oven at 55°C. Further heating *in vacuo* at this temperature in an apparatus similar to that described by Grassie (7) did not lead to a significant decrease in weight of the residual polymer. Dilutions of highly viscous solutions were made by weight.

RESULTS

Fig. 1 shows the results of viscosity measurements on a relatively low molecular weight sample of carrageenin ($M = 120{,}000$) in three solvents. In aqueous solution, the reduced specific viscosity η_{sp}/c increases markedly with dilution. In the presence of a very low concentration of added salt (0.000231 *M* sodium bisulphate) the plot of η_{sp}/c against c passes through a maximum at a carrageenin concentration of approximately 0.03 gm. per 100 cc. At higher salt concentrations (0.1 *M* sodium chloride) the plot becomes linear.

These curves are entirely similar to those observed for other polyelectrolytes (4) and may be interpreted in terms of changes in molecular shape resulting from changes in the degree of ionization of the macromolecule. In dilute aqueous solution the molecule becomes rigidly extended as a result of the repulsive forces between neighboring charged groups, and the reduced viscosity increases accordingly. By analogy with the results of Fuoss and Strauss (4), the maximum observed in Fig. 1 at a low salt concentration

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These observations are in accordance with the idea that the cause of the cell constant is adsorption of polymer molecules on the membrane. It has recently been shown (S. Rothman, A. Schwebel, and S. G. Weissberg. J. Polymer Sci. 11: 381. 1953) that such adsorption does, in fact, take place on collodion membranes by radioactive dextran.

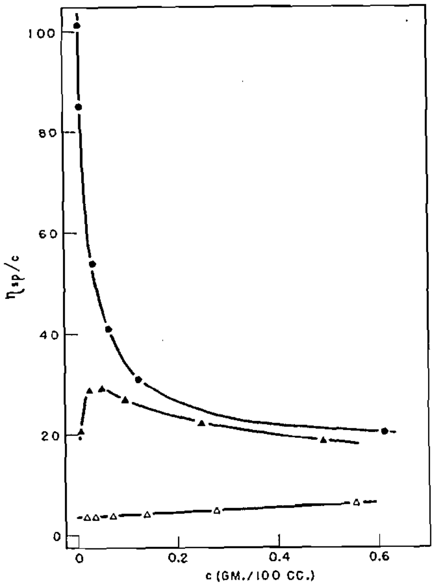

FIG. 1. η_{sp}/c vs. c for extract D in various solvents. ● water; ▲ 0.000231 M NaHSO$_4$; △ 0.1 M NaCl.

should occur when the concentration of sodium ions from the polyelectrolyte is of the same order of magnitude as the concentration of cations from the

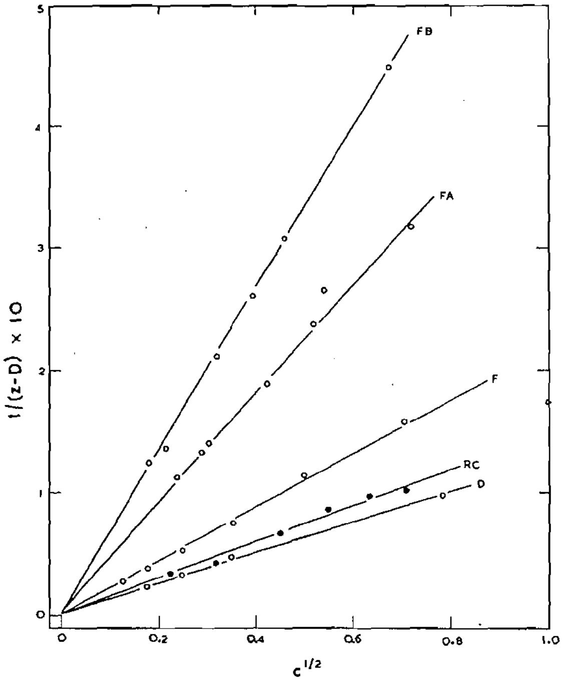

FIG. 2(*a*). $1/(z - D)$ vs. $c^{\frac{1}{2}}$ for various polymers in aqueous solution. ● Polymer of Rose and Cook.

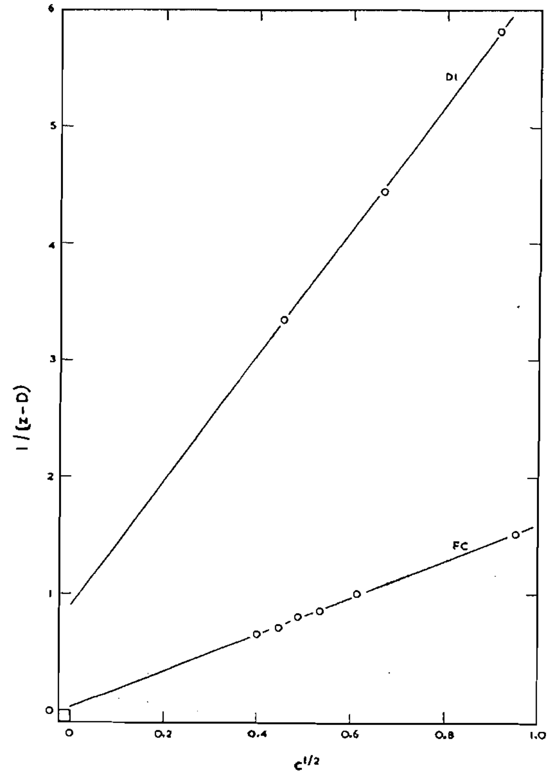

FIG. 2(*b*). $1/(z-D)$ vs. $c^{\frac{1}{2}}$ for two polymers in aqueous solution.

added salt. Assuming complete ionization of the salt, this implies that carrageenin is approximately 40% ionized at a concentration of 0.03 gm. per 100 cc. in this solvent.

The viscosities of aqueous solutions of carrageenin of low molecular weight may be adequately represented by the Fuoss (2, 3) equation

$$\eta_{sp}/c = z = A/(1 + Bc^{\frac{1}{2}}) + D, \quad [1]$$

where A, B, and D are constants. This equation has been shown to represent the viscosity behavior of a wide variety of polyelectrolytes. Figs. 2(*a*) and 2(*b*) show plots of $1/(z-D)$ against $c^{\frac{1}{2}}$ for various samples of carrageenin. Included in Fig. 2(*a*) are points calculated from the experimental viscosity–concentration curve published by Rose and Cook (12) for an aqueous solution of a carrageen extract. Linear plots are obtained for all the polymers.

The samples designated FA, FB, and FC in these figures were prepared from the parent material F by heating a 1% solution, buffered at pH 7.0, at 90°C. for 14.3, 38.6, and 141.4 hr. respectively. The polymers were then precipitated with ethanol, washed with freshly distilled ether, and dried *in vacuo*. Solutions of these polymers were dialyzed under pressure to remove any low molecular-weight products of degradation before the viscosity and molecular weight measurements were performed. As shown elsewhere (9), the sulphate content of the dialyzed polymer increases slightly (from 25.8% to 31.7%) as a result of this degradation.

Sample D1 was a photochemically degraded preparation, obtained by irradiating a 1% solution of extract D for 57 min. by means of a mercury resonance lamp immersed in the solution. Nitrogen was passed through the solution during this treatment to prevent possible photo-oxidation reactions. The polymer was precipitated with ethanol and sodium chloride, and dried as before. The solution of the degraded polymer was passed through ion-exchange columns before use, but was not dialyzed. The sulphate content of the degraded polymer was 25.7%.

The values of the constants A, B, and D in equation [1] have been determined for the polymers represented in Figs. 2(a) and 2(b). The slopes of the lines give the value of B/A for each polymer. The intercepts at $c^{\frac{1}{2}} = 0$ give the values of $1/A$. On account of the extremely small intercepts in Fig. 2(a), the values of A (and hence also of B) could not be determined directly for the polymers of highest molecular weight. For polymers FC and D1, however, measurable intercepts were obtained, from which values of B equal to 63 (± 10) and 71 (± 7) respectively were calculated. The fact that the value of B remains constant, within experimental error, for these two polymers is in accordance with the idea (3) that this constant is an electrostatic term whose value depends on the charge density along the polymer chain and is independent of molecular weight. Taking a mean value of $B = 67$, the values of A shown in Table I have been calculated for all the polymers. Included in this table are the values of D (obtained by extrapolating plots of η_{sp}/c against $c^{-\frac{1}{2}}$ to $c^{-\frac{1}{2}} = 0$) and, where measured, the intrinsic viscosities of the polymers in $M/30$ sodium phosphate buffer at pH 7.0. In this solvent, plots of η_{sp}/c against c were linear.

TABLE I

VISCOSITY CONSTANTS AND MOLECULAR WEIGHTS OF VARIOUS CARRAGEENIN PREPARATIONS

Polymer	$[\eta]$ in $M/30$ phosphate buffer (pH 7.0)	D	B/A	A	Osmotic molecular weight
D		10	0.12	558	120,000
RC*		14	0.15	446	
F	(2.48)	3.4	0.22	304	74,500
FA	1.75	2.2	0.45	149	42,900
FB	1.23	1.1	0.66	101	30,100
FC	0.74	0.75	1.57	42.6	21,800
D1		0.22	6.40	10.5	9,000

Polymer of Rose and Cook.

The results of the osmotic pressure measurements are shown in Fig. 3 where the reduced osmotic pressure π/c (π in cm. water) is plotted against concentration c (in gm. per 100 cc. solution). Molecular weights were calculated from the intercepts at zero concentration using the relationship

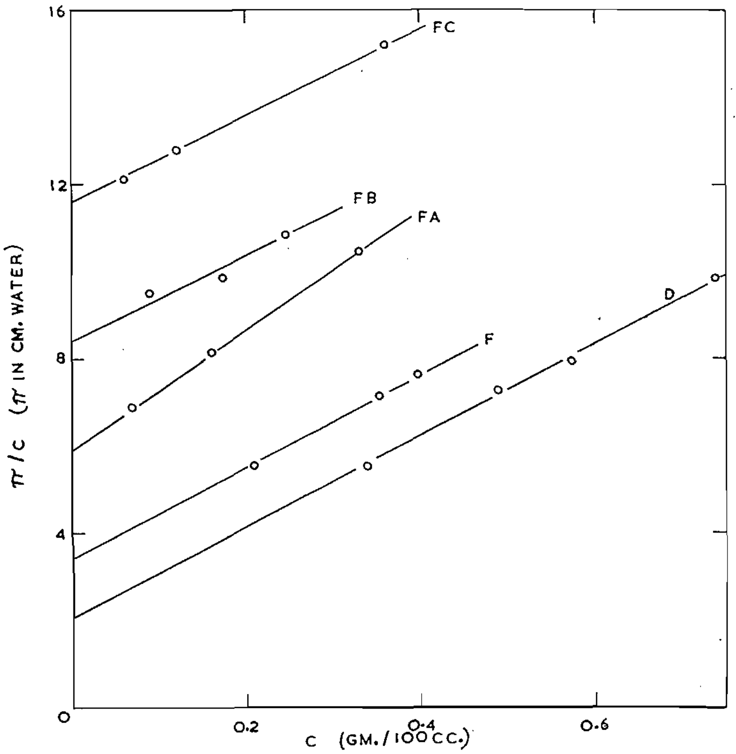

FIG. 3. π/c vs. c for various polymers in 0.1 M NaCl solution at 25°C.

$(\pi/c)_0 = 10330\ RT/M$. The values of M are given in Table I. The molecular weight of fraction D1 was so low that some diffusion of polymer through the membrane occurred, as witnessed by a slow downward drift in the osmotic pressure on standing. The approximate value of 9000 listed for the molecular weight of this fraction was obtained by using a dilute solution in the osmometer and extrapolating the osmotic pressure values back to the time of filling the osmometer.

DISCUSSION

On account of the low molecular weights observed, all the polymers described above must be considered as having been degraded to some extent. Degradation can occur either during extraction of the polymer from the seaweed (11), or upon subsequent storage of the solid extract (5). Both of these factors are believed to be responsible for the low molecular weights of extracts D and F. The molecular weight may also depend on the time of storage of the dried seaweed before extraction, although data are not yet available to test this point. Certain extracts of fresh seaweed have been found (8) to have an osmotic molecular weight of the order of 2×10^6, which is at the limit of the range of osmometric techniques.

For the low molecular weight extracts described above, viscosity measurements in the Stormer viscometer have shown that the solutions exhibit Newtonian flow, at least in the range of concentration and shear rate studied.

This is illustrated in Fig. 4(*a*) where the rate of rotation of the cylinder is plotted against the driving weight for various concentrations of extract F. The curves are essentially linear through the origin, characteristic of a Newtonian fluid. For an extract of higher viscosity, however, the curves shown in Fig. 4(*b*) were found. A 'yield point' is observed for these solutions, indicating that the flow is structual in nature, the curves being characteristic of a 'plastic' substance. Measurements in capillary viscometers at different rates of shear (6) confirm this behavior.

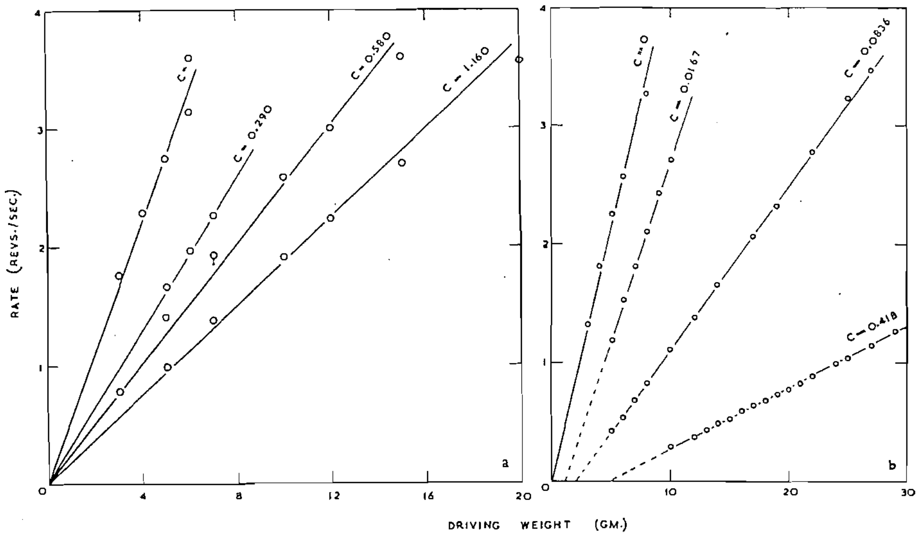

FIG. 4. Stormer viscosities. Rate of rotation of inner cylinder vs. driving weight for various concentrations of polymer. (*a*) Extract F (25°C.); (*b*) Extract A. (0°C.).

From the data in Table I an approximate value can be obtained for the constant α in the modified Staudinger equation $[\eta] = KM\alpha$ relating the intrinsic viscosity to the molecular weight. Unfortunately, the intrinsic viscosity of extract F in $M/30$ buffer was measured about two months after the other measurements had been performed. Subsequent measurements showed that degradation of the extract had taken place during storage, so that the viscosity and molecular weight values for this polymer are not exactly comparable. On the basis of the three measurements for the thermally degraded polymers, an approximate value of $\alpha = 1.28$ is obtained.

In assigning this value of α, the assumption is made that the samples have the same degree of polydisperity. Since these samples were prepared from the same parent material, and since, as shown elsewhere (9), the degradation proceeds mainly by a random process under the conditions employed, this assumption is probably justified. The high value of α should therefore have some significance, and indicates that, even in the presence of salt, the degraded carrageenin molecules exist in solution as fairly stiff rods. Since it is unlikely that this rigidity is due to the presence of ionized groups in the molecule at the salt concentration employed, the result must be interpreted in terms of restricted rotation at the glycosidic linkage, and, possibly, an unbranched configuration for the degraded fragments. A similar conclusion concerning the structure of carrageenin of moderately low molecular weight has been reached by other workers (1).

According to equation [1], the quantity $(A + D)$ should be the value of the intrinsic viscosity of the polyelectrolyte in aqueous solution. Since the polymer molecules will be even more rigidly extended in aqueous solution than in the presence of salts, substitution of $(A + D)$ for $[\eta]$ in the Staudinger equation should result in an even higher value of α. Fig. 5 shows the plot of log $(A + D)$ vs. log M for all the polymers, from which a value of $\alpha = 1.58$ is obtained, in agreement with this consideration.

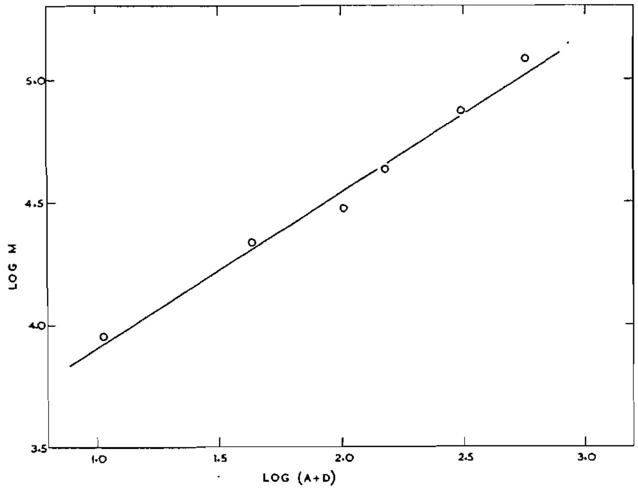

FIG. 5. Log $(A + D)$ vs. log M for degraded carrageenin.

ACKNOWLEDGMENTS

The authors are greatly indebted to Dr. L. A. McLeod of Polymer Corporation, Sarnia, Ont., for lending the osmometer used in this study. We wish to thank Dr. A. N. O'Neill of these laboratories for the extraction and purification of most of the carrageenin samples employed, and for performing the sulphate analyses. We wish also to thank Dr. E. Gordon Young for his interest and encouragement during this work.

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CYCLIC THIOUREAS[1]

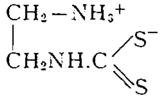
By A. F. McKay and G. R. Vavasour

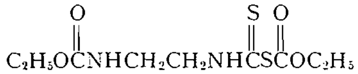
ABSTRACT

1-β-Hydroxyethylimidazolidine-2-thione was prepared from 1-amino-5-hydroxy-3-azapentane and carbon disulphide. Since its properties differ from those claimed by Sergeyev and Kolychev (7) for this compound prepared from ethylene oxide and thiocyanic acid, its structure was confirmed by conversion to 1-β-hydroxyethyl-2-benzylamino-2-imidazoline. The latter compound was prepared for comparison from the known 1-β-hydroxyethyl-2-nitramino-2-imidazoline.

INTRODUCTION

Hofmann (4) found that ethylenediamine combined with carbon disulphide to give an intermediate addition product, which, on being boiled with water, evolved hydrogen sulphide to give ethylene urea. This intermediate was considered to be a dithiocarbamic acid inner salt (I). Later Yakubovich and Klimova (9) proved this assumption to be correct by obtaining compound II from the treatment of the addition product I with alkali and ethylchloroformate.


I



$$C_2H_5O\overset{O}{\overset{\|}{C}}NHCH_2CH_2NH\overset{S}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}OC_2H_5$$

II

On the other hand Goldenring (3) found that two mole equivalents of N-phenyltrimethylenediamine combined with one mole of carbon disulphide. This was also observed (2) with N-*p*-tolyltrimethylenediamine. In the present studies 1,3-diaminobutane with carbon disulphide gave an inner salt analogous to that obtained by Hofmann with ethylenediamine. This inner salt was converted by thermal decomposition into 4-methyl-hexahydropyrimidine-2-thione in good yield. Also 1-amino-5-hydroxy-3-azapentane was observed to combine with carbon disulphide to yield a solid addition product. This intermediate when heated in the dry state evolved hydrogen sulphide to give a new product. This new compound melted at 136.5–137.5°C. and gave analytical values in good agreement with the expected 1-β-hydroxyethylimidazolidine-2-thione (III). However, Sergeyev and Kolychev (7) previously had claimed to have prepared this compound from ethylene oxide and thiocyanic acid. Their product melted at 168.5°C. with decomposition. Because of this discrepancy in melting points it was considered necessary to confirm

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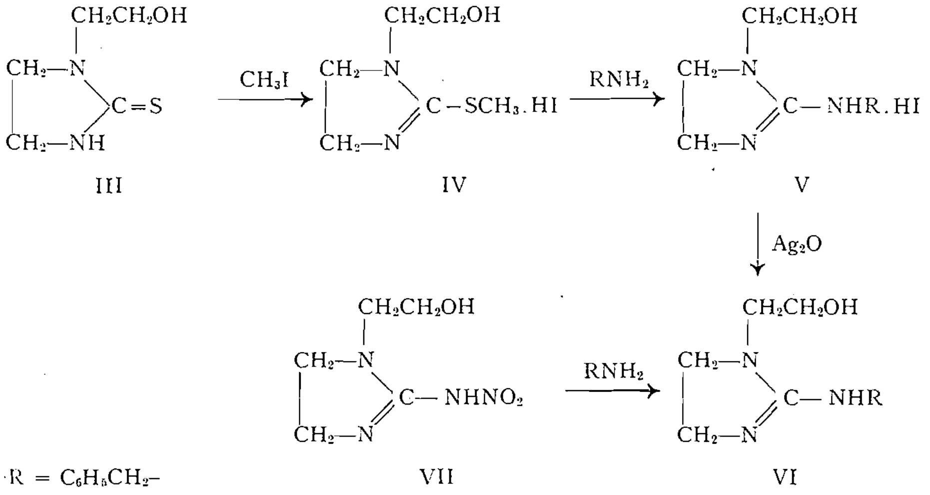
the identity of the compound prepared from 1-amino-5-hydroxy-3-azapentane and carbon disulphide.

1-β-Hydroxyethylimidazolidine-2-thione was converted to 1-β-hydroxyethyl-2-methylmercapto-2-imidazolinium iodide with methyl iodide.



The iodide (IV) on treatment with benzylamine by the method of Aspinall and Bianco (1) gave the hydrogen iodide salt of 1-β-hydroxyethyl-2-benzylamino-2-imidazoline (V) which was isolated as its picrate. The same compound (VI) was obtained from the known 1-β-hydroxyethyl-2-nitramino-2-imidazoline (VII) (5) and benzylamine. The identity of these two products was established by a mixed melting point determination. The structure of 1-β-hydroxyethyl-2-nitramino-2-imidazoline was established previously (5,6) by nitration and hydrolysis to 1-β-nitroxyethyl-3-nitro-2-imidazolidone which was prepared also by the nitration of the known 1-β-hydroxyethyl-2-imidazolidone (6,8). These chemical reactions confirm the assignment of structure III to the cyclic thiourea from the reaction between aminoethylethanolamine and carbon disulphide.

EXPERIMENTAL[2]

4-Methyl-hexahydropyrimidine-2-thione

A solution of 8.8 gm. (0.1 mole) of 1,3-diaminobutane in 50 cc. of 95% ethanol was added dropwise to a solution of 25 cc. of carbon disulphide in 50 cc. of 95% ethanol. During the addition period the temperature was held below 40°C. with an ice–salt bath. The reaction mixture was allowed to stand at room temperature overnight in an open Erlenmeyer. At this time the viscous white oil had solidified, yield 12.65 gm. (77.2%). One gram of this γ-aminobutyldithiocarbamic acid inner salt was purified by solution in aqueous ammonia. On slow evaporation of ammonia from the solution white crystals separated. These crystals decomposed from 125–160°C. leaving a

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[2] *All melting points were determined on a Kofler block. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois.*

residue which then melted at 175–178°C. Calc. for $C_5H_{12}N_2S_2$: C, 36.57; H, 7.32; N, 17.06; S, 39.02%. Found: C, 36.86; H, 7.55; N, 17.00; S, 38.72%.

The remaining inner salt (11.65 gm., 0.088 mole) was placed in an Erlenmeyer and heated in an oil-bath at 130–145°C. until the evolution of hydrogen sulphide ceased. The tan residue was crystallized from ethanol using charcoal for decolorizing the product, yield 8 gm. (87.4%). The melting point of 182–183°C. was increased to 183–184.5°C. after one further crystallization from ethanol. Calc. for $C_5H_{10}N_2S$: C, 46.15; H, 7.69; N, 21.52; S, 24.62%. Found: C, 46.35; H, 7.85; N, 21.88; S, 25.02%.

1-β-Hydroxyethylimidazolidine-2-thione

1-Amino-5-hydroxy-3-azapentane (40.0 gm., 0.38 mole) in 95% ethanol (100 cc.) was added dropwise with stirring into a solution of 100 cc. of carbon disulphide in 100 cc. of 95% ethanol. During the addition period, which required 30 min., the temperature was held below 15°C. The stirring was continued for one half hour after the addition period after which the solid was recovered by filtration, yield 67.0 gm. (96.9% based on formation of inner salt). This solid was heated in an oil bath at 145 ± 5°C. until the evolution of hydrogen sulphide had ceased. The residue was crystallized from 95% ethanol (250 cc.) to give 46.0 gm. (86.3% yield from inner salt) of crystals which melted at 136.5–137.5°C. Calc. for $C_5H_{10}N_2OS$: C, 41.10; H, 6.85; N, 19.16; S, 21.93%. Found: C, 41.34; H, 6.49; N, 19.16; S, 22.30%.

1-β-Hydroxyethyl-2-methylmercapto-2-imidazolinium Iodide

A mixture of 1-β-hydroxyethylimidazolidine-2-thione (14.6 gm., 0.1 mole) and methyl iodide (15.6 gm., 0.11 mole) in 50 cc. of absolute methanol was shaken at room temperature for 40 min., after which all the solid had dissolved. While the vigorous shaking was continued 200 cc. of anhydrous ether was added gradually. A dense white precipitate (m.p. 119–120°C.) was formed, yield 27.3 gm. (95%). This product was brought to a constant melting point of 120–121°C. after one crystallization from absolute ethanol (3.9 cc./gm.). However purification was unnecessary for further chemical reactions. Calc. for $C_6H_{13}IN_2OS$: C, 25.01; H, 4.55; I, 44.10%. Found: C, 25.35; H, 4.67; I, 43.63.

1-β-Hydroxyethyl-2-nitramino-2-imidazoline

1-β-Hydroxyethyl-2-nitramino-2-imidazoline (m.p. 131.5–132°C.) was prepared in 39% yield as previously described (5).

1-β-Hydroxyethyl-2-benzylamino-2-imidazoline

Method A

1-β-Hydroxyethyl-2-methylmercapto-2-imidazolinium iodide (2.5 gm., 0.0087 mole) and benzylamine (1.8 gm., 0.017 mole) were dissolved in 25 cc. water and allowed to stand overnight. The mixture then was heated on a steam bath for one hour after which it was taken to dryness. The residual oil gave no picrate or picrolonate under the usual conditions. This oil was redissolved in 25 cc. water and this solution shaken for one hour with 1.0

gm. (0.0044 mole) of silver oxide. After filtration to remove silver salts, the solution was taken to dryness *in vacuo*. The oil was dissolved in 25 cc. of water, filtered, and the filtrate treated with 200 cc. of 1% aqueous picric acid solution. A crystalline picrate (m.p. 120.5–122.5°C.) was obtained in 64.8% yield (2.48 gm.). One crystallization from absolute alcohol (25 cc.) gave 2.1 gm. of crystalline picrate with a constant melting point of 124–125°C. Calc. for $C_{18}H_{20}N_6O_8$: C, 48.21; H, 4.50; N, 18.74%. Found: C, 48.54; H, 4.26; N, 18.78%.

Method B

One gram (0.0057 mole) of 1-β-hydroxyethyl-2-nitramino-2-imidazoline and 8 cc. of benzylamine were refluxed for one hour in an apparatus protected from carbon dioxide. The excess benzylamine was distilled off under water pump vacuum at 100°C. The residual light yellow oil was dissolved in 30 cc. of 50% aqueous ethanol. One half of this solution was treated with 200 cc., of 1% aqueous picric acid solution. The crude picrate melted at 118–122°C., yield 0.93 gm. (72.4%). Two crystallizations from ethanol raised the melting point to 124–125°C. This melting point was not depressed on admixture with the picrate of 1-β-hydroxyethyl-2-benzylamino-2-imidazoline prepared above by Method A.

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EFFECT OF FLUCTUATIONS OF FREE RADICAL CONCENTRATIONS ON THE CALCULATION OF RELATIVE RATE CONSTANTS[1]

By R. J. Cvetanovic and E. Whittle[2]

ABSTRACT

The effect of fluctuations in free radical concentrations on the values of relative reaction rate constants calculated from steady state expressions has been evaluated for a number of idealized model cases, representative of various conditions usually encountered in experiments.

INTRODUCTION

In many instances the concentration of free radicals or atoms participating in chemical reactions cannot be determined and it is then only possible to evaluate relative rate constants for two or more reactions competing for the same radical or atom. For mathematical simplicity calculations of the relative rate constants are as a rule carried out on the assumption of stationary concentrations of the free radicals or atoms involved. Time fluctuations, however, are usually inevitable and, as has been pointed out by Szwarc (8), introduce an error in the calculated relative rate constant when one of the two competing reactions is first order while the other is second order in the free radical. There may be some uncertainty (8,4) about the extent to which the error may affect the calculated values of rate constants and activation energies. In view of this, we have attempted to obtain more detailed information than is possible by mere inspection about the magnitude of this error, as well as of the similar error caused by concentration gradients.

Since, in general, the variation with time of the free radical concentration is not known, the treatment comprises a number of idealized model cases, believed to be sufficiently representative of various conditions usually encountered in experiments to allow an estimation of the magnitude of the effect.

Most of the systems for which relative rate data have been obtained in recent years are embraced by the following general reaction scheme, applicable also for radicals produced by other than photochemical methods:

$$\begin{array}{ll}
\mathrm{A} + h\nu \rightarrow m\mathrm{X} + \mathrm{L} & \phi I_a \\
\mathrm{X} + \mathrm{B} \rightarrow \mathrm{M} + \mathrm{K} & k_1 \\
\mathrm{X} + \mathrm{B}' \rightarrow \mathrm{M}' + \mathrm{K}' & k_1' \\
\mathrm{X} + \mathrm{B}'' \rightarrow \mathrm{M}'' + \mathrm{K}'' & k_1'' \\
\dots\dots\dots\dots\dots\dots & \dots \\
\mathrm{X} + \mathrm{X} \rightarrow \mathrm{N} & k_2
\end{array}$$

where m = 1 or 2 and X is a free radical, the concentration of which will be

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denoted by x. The relative rate constant of Reaction (1), $k_1/k_2^{\frac{1}{2}}$, is usually calculated from the mean rates of formation of M and N ($\bar{R}_M$ and $\bar{R}_N$, respectively), and, neglecting concentration gradients, can be expressed in the form

$$[1] \qquad \frac{k_1}{k_2^{\frac{1}{2}}} = \frac{\bar{R}_M}{\bar{R}_N^{\frac{1}{2}}(B)} \cdot \delta \qquad \text{where } \delta = \frac{t^{\frac{1}{2}}\left(\int_0^t x^2\,dt\right)^{\frac{1}{2}}}{\int_0^t x\,dt}.$$

The effect of time fluctuations is, therefore, as was pointed out by Szwarc (8), that $\delta \geqslant 1$.

We have considered the effect on the value of δ of the time fluctuations of the following types: (*a*) steady drift in x, (*b*) sporadic fluctuations, (*c*) intermittent illumination; and of concentration gradients due to: (*i*) removal of radicals on the wall and (*ii*) nonuniform light absorption.

Steady Drift in the Free Radical Concentration

A drift in the free radical concentration may result, for example, from a gradual decline in the amount of light absorbed. The maximum and the minimum values of x will be denoted by x_0 and x_i respectively, so that $x = x_0(1 - \gamma t)$, and $0 \leqslant \gamma t \leqslant 1$. On integration it is found that

$$[2] \qquad \delta_a = \left\{1 + \frac{1}{3[(2/\alpha) - 1]^2}\right\}^{\frac{1}{2}}$$

where $\alpha = (x_0 - x_i)/x_0$, and $0 \leqslant \alpha \leqslant 1$. The values of δ_a for different values of α are shown in Fig. 1. The maximum value of δ_a is 1.15.

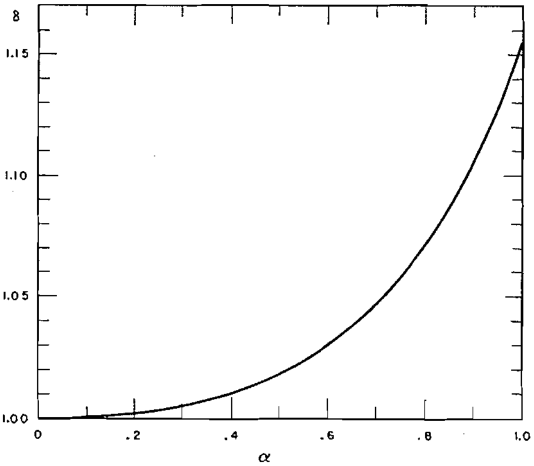

FIG. 1. Variation in the correction factor with relative fluctuation (α).

Sporadic Fluctuations

Sporadic fluctuations may result from technical imperfections in the control of experimental conditions, which are frequently unavoidable. These fluctuations can be expected to be for the most part relatively slow, and the following model case chosen for mathematical simplicity, is probably adequate to give an idea of their possible importance.

The reaction time is divided into a large number of equal intervals and during each interval x is assumed to be constant, but in general varies from one interval to another. The variation in x is confined to a range between a maximum (x_0) and a minimum value (x_i). It is further assumed that, within this range, x can assume with equal probability any of $(n + 1)$ equally spaced discrete values. If $\alpha = (x_0 - x_i)/x_0$, it is found that

$$\delta_b = \left\{1 + \frac{1 + 2/n}{3[(2/\alpha) - 1]^2}\right\}^{\frac{1}{2}}. \tag{3}$$

For large n Equation [3] reduces to the case of a steady drift. When both α and n are unity, δ_b becomes $\sqrt{2}$, which is its maximum value. Usually, however, α will be considerably smaller than unity and, consequently, δ_b will in general be close to unity.

Intermittent Illumination

The theory of the effect of intermittent illumination on the rate of a chain propagation step, has been extensively treated (1,2,3,5,7). The present problem is related to, though it differs in some respects from, the ones treated by Briers and Chapman (1) and by Rice (7). A simplified case, when x describes a linear and symmetrical zigzag curve, should provide a good first approximation (δ_c) for relatively fast light interruptions when the light and dark intervals are of equal duration. If, as before, the maximum and the minimum values of x are x_0 and x_i, respectively, and $\alpha = (x_0 - x_i)/x_0$, it is found, that δ_c also is given by Equation [2] and is, therefore, entirely determined by the relative fluctuation α. Determination of x_0 and x_i, however, requires a more elaborate treatment in which it is assumed that, during light intervals ϕI_a = const. and in dark intervals $\phi I_a = 0$, so that the light pulses are rectangular. Only the case when the light and the dark intervals are of equal duration ($p_l = p_d = p$) need be considered. It is assumed that x_0 and x_i immediately attain steady values, which is justifiable for the usual experimental reaction times.

It is convenient to express the value of x at any instant as a fraction (y) of the stationary value (x_s) corresponding to steady illumination, so that $y = x/x_s$. Introducing the notations

$$\epsilon = \left(1 + \frac{8\ mk_2\phi I_a}{\{k_1(\mathrm{B}) + k_1'(\mathrm{B}') + k_1''(\mathrm{B}'') + \ldots\}^2}\right)^{\frac{1}{2}},$$

$$\lambda = \{k_1(\mathrm{B}) + k_1'(\mathrm{B}') + k_1''(\mathrm{B}'') + \ldots\}\,p,$$

and

$$\eta = \left(y_0 + \frac{2}{\epsilon - 1}\right)\left(y_i + \frac{\epsilon + 1}{\epsilon - 1}\right) \Big/ \left(y_i + \frac{2}{\epsilon - 1}\right)\left(y_0 + \frac{\epsilon + 1}{\epsilon - 1}\right)^*$$

$$* \quad y_0 = \frac{y_i\left(\frac{\epsilon+1}{\epsilon-1} + e^{\lambda\epsilon}\right) + \left(\frac{\epsilon+1}{\epsilon-1}e^{\lambda\epsilon} - 1\right)}{y_i\left(e^{\lambda\epsilon} - 1\right) + \left(\frac{\epsilon+1}{\epsilon-1}e^{\lambda\epsilon} + 1\right)}$$

$$y_i = \frac{2y_0}{y_0\,(\epsilon - 1)\,(e^{\lambda} - 1) + 2e^{\lambda}}$$

it is found that

$$[4] \qquad \delta = \frac{(\delta_N)^{\frac{1}{2}}}{\delta_M} = \left\{\tfrac{1}{2} - \frac{2}{\lambda(\epsilon-1)^2}\ln\eta\right\}^{\frac{1}{2}} \Big/ \left\{\tfrac{1}{2} + \frac{1}{\lambda(\epsilon-1)}\ln\eta\right\}$$

where $\delta_N = \bar{R}_N/k_2x_s^2$ and $\delta_M = \bar{R}_M/k_1(\mathrm{B})x_s$. In general $\delta_M \geqslant \frac{1}{2}$, $\delta_N \leqslant \frac{1}{2}$ and δ lies between unity (for very fast light interruptions) and $\sqrt{2}$ (for slow light interruptions).

The variation of the quantities of interest with duration of light and dark intervals is illustrated for the case when $\epsilon = 126.5$ by calculations given in Table I and presented graphically in Fig. 2. (The calculated quantities are

TABLE I

EFFECT OF VARIATION OF λ

Example	ϵ	λ	y_0	y_i	δ_M	δ_N	δ	δ_c
1	126.5	Large	1	0	.5	.5	1.414	1.155
2	"	4	1.0000	.00029	.5069	.4999	1.395	1.155
3	"	0.4	1.0000	.0309	.5482	.4992	1.289	1.138
4	"	0.04	0.9929	.2771	.6585	.4975	1.071	1.052
5	"	0.004	0.7710	.6438	.7041	.4967	1.001	1.002
6	"	0.0004	0.7110	.6983	.7042	.4967	1.001	1.000
7	"	0	0.7048	.7048	.7048	.4967	1.000	1.000

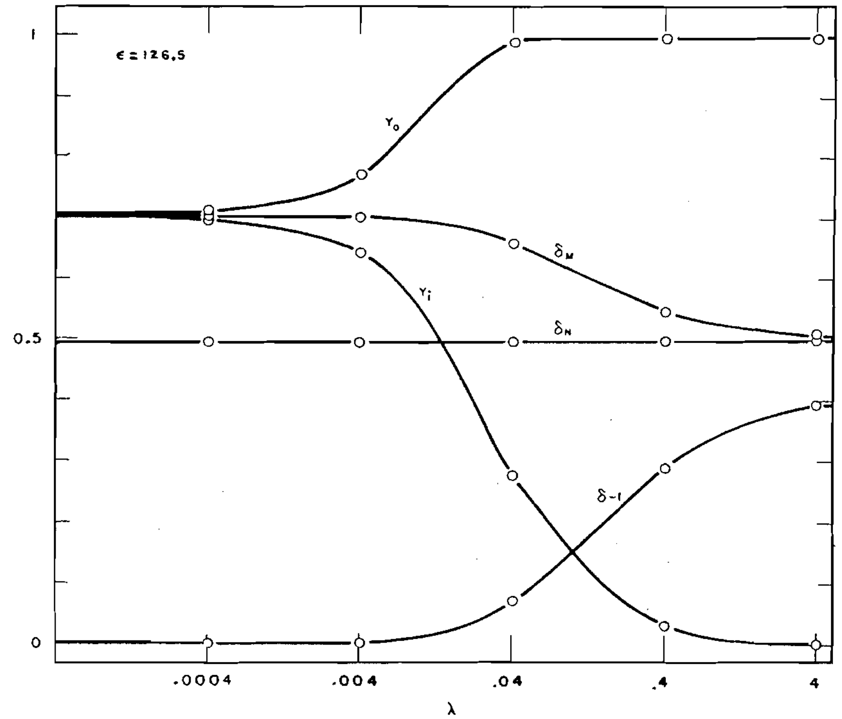

FIG. 2. Variation in the correction factors in the case of intermittent illumination.

indicated in Fig. 2 by circles.) The case corresponds, for example, to the following set of values: $\phi I_a = 10^{15}$ quanta/cc. sec., (B) $= 10^{18}$ molecule/cc. ((B′) = (B″) = . . . = 0), $k_2 = 10^{-10}$ and $k_1 = 10^{-17}$ cc./molecule sec., with p varying from 4×10^{-1} to 4×10^{-5}. The quantities chosen are of magnitudes which may be encountered in experiments. The limiting values for $\lambda \rightarrow \infty$, irrespective of the value of ϵ, are $y_0 = 1$, $y_i = 0$, $\delta_M = \frac{1}{2}$, $\delta_N = \frac{1}{2}$, $\delta = (2)^{\frac{1}{2}}$. When $p \rightarrow 0$, $\delta = 1$, and for this particular case, $y_0 = y_i = \delta_M = .705$, $\delta_N = .497$. If a 60 cycle a.c. is used for the excitation of the light source, the corresponding duration of the light and dark intervals can be taken as $p_l = p_d = 4 \times 10^{-3}$ sec., which for the above set of values leads to $\lambda = 4 \times 10^{-2}$. In this case $\delta = 1.071$, so that an error of 7% is introduced when mean rates are used to calculate $k_1/k_2^{\frac{1}{2}}$ and no fluctuation in the radical concentration is taken into account.

The value of k_2 usually shows only slight or no temperature dependence. The value of k_1, on the other hand, may show a very pronounced temperature dependence. It is, therefore, important to see how the values of δ are affected by the variation in k_1, the other relevant quantities being kept constant. Table II gives calculations for the above set of data with $p = 4 \times 10^{-3}$ sec. and k_1 varying from 10^{-18} to 10^{-15} cc./molecule sec.

TABLE II
EFFECT OF VARIATION OF k_1 (WITH $\phi I_a = 10^{15}$, (B) $= 10^{18}$, (B′) = (B″) = . . . = 0
$k_2 = 10^{-10}$, $p = 4 \times 10^{-3}$; units: molecule (quanta), cc., sec.).

Example	k_1	λ	ϵ	y_0	y_i	δ_M	δ_N	δ	δ_c
1	10^{-18}	0.004	1265	.9930	.2826	.6607	.4997	1.070	1.050
2	10^{-17}	0.04	126.5	.9929	.2771	.6585	.4975	1.071	1.052
3	10^{-16}	0.4	12.69	.9925	.2284	.6354	.4768	1.089	1.063
4	10^{-15}	4	1.612	.9981	.0141	.5226	.4261	1.249	1.147

The last columns in Tables I and II give the values of δ_c calculated from Equation [2]. It is seen that δ_c is a good approximation for small values of p and not too large values of k_1.

DISCUSSION

The various model cases considered show that the effect of fluctuations in radical concentration on the calculated relative rate constant increases in general with increasing magnitude of the fluctuations relative to the average radical concentration. However, it is evident that sporadic fluctuations or drifts in the radical concentration under the usual experimental conditions will not affect the value of the relative rate constant to any appreciable extent. Thus, such fluctuations to the extent of as much as 40% cause an error in $k_1/k_2^{\frac{1}{2}}$ which is not greater than one per cent. Even under the most unfavorable experimental conditions the errors which may occur are not particularly great. In a similar manner, the use of 60 cycle a.c. for excitation of the light source will normally introduce an error of a few per cent only. The error increases for greater k_1(B), and can be estimated to the approximation of rectangular light pulses. The case of rectangular pulses is more unfavorable than the actual conditions with a sinusoidal alternating current, and, therefore, provides an upper limit of the error.

The error in the activation energy (δ_E) obtained from the values of the rate constants at two temperatures is given by

$$\delta_E = R\frac{T_1T_2}{T_1 - T_2}\ln\frac{\delta_{T_1}}{\delta_{T_2}},$$

where δT_1 and δT_2 are the values of the correction factor δ at the temperature T_1 and T_2 respectively. Evidently, the value of δ_E will be largely influenced by the value of $(T_1 - T_2)$. For temperature ranges of the order of 100°, the sporadic fluctuations and drifts in radical concentrations encountered under usual experimental conditions are unlikely to introduce an appreciable error in the calculated value of the activation energy. Sporadic fluctuations, such as may be caused, for example, by instability of the light source, are likely to introduce similar errors at the two temperatures and, consequently, not affect the activation energy. Drifts in the radical concentration would have to be very pronounced and different at the two temperatures in order to affect appreciably the activation energy. In the cases where pronounced drifts with time are encountered, the relative extent of the drift can be estimated from the drift in $\bar{R}_N$ and the error introduced by it can be evaluated from Equation [2]. Both in the case of sporadic fluctuations and drifts in the radical concentration the sign of δ_E is determined by the relative magnitudes of δ_{T_1} and δ_{T_2} and is not predictable *a priori*. It is, therefore, evident that the suggestion that, since in many instances the extent to which the reaction is allowed to proceed is greater at higher temperatures, the estimated activation energy will be slightly lower than its true value, cannot be expected to hold in general, except in the case of a very pronounced increase in the relative fluctuation at the higher temperature.

In the case of intermittent illumination, since k_2 is usually temperature independent and k_1 becomes greater with increasing temperature, a reference to Table II shows that the value of δ will usually be greater at higher temperature, provided ϕI_a, (B), and p remain unchanged, so that δ_E is positive. When k_1 is much smaller than k_2, k_1 will vary appreciably with temperature, but, on the other hand, the value of δ is only slightly affected and δ_E is small. As k_1 approaches k_2 the effect of its variation on δ becomes more pronounced but at the same time its temperature coefficient is reduced and for experimental convenience smaller concentrations of B are usually employed, so that the total effect may still remain relatively small. As an illustration we may consider two hypothetical cases, with $\phi I_a = 10^{15}$, $(B) = 10^{18}$, $(B') = (B'') = \ldots = 0$, $k_2 = 10^{-10}$, $p = 4 \times 10^{-3}$ (the units as given previously). Also it is assumed that $z_1 = 10^{-10}$ and that z_1 and k_2 are temperature independent. *Case 1*: At 400°K., $k_1 = 10^{-17}$, at 500°K., $k_1 = 10^{-16}$, and, therefore, $E = 9.15$ kcal./mole and the steric factor $s = 10^{-2}$. The values of δ for this case are given in Table II, examples 2 and 3 respectively, and it is found that $\delta_E =$ .07 kcal./mole. *Case 2*: At 400°K., $k_1 = 10^{-16}$, at 500°K., $k_1 = 10^{-15}$, and, therefore, $E = 9.15$ kcal./mole and $s = 10^{-1}$. The respective values of δ are given by examples 3 and 4 in Table II, and, in this case $\delta_E = .55$ kcal./mole. It should, however, be borne in mind that the treatment presented here is strictly correct for the case of rectangular light pulses only. When sinusoidal a.c. is used for excitation of the light source, the maximum possible limits of error can be evaluated rather than the error itself.

The model cases considered are evidently highly idealized. They are, however, sufficiently representative of the types usually occurring in experiments to give an insight into the magnitude of the effects which can be expected. It is likely that in most cases the real conditions are much more favorable and the errors due to time fluctuations will normally be very small. More serious errors may arise, under certain circumstances, from space variations in the radical concentration. Such variations may be caused by a rapid consumption of free radicals on the reaction vessel walls or by a high extinction coefficient. The general effect is again that $\delta \geqslant 1$.

In order to evaluate the magnitude of the wall effect Noyes (6) has developed a mathematical solution of the diffusion equation, subject to certain simplifications. The solution is valid for a spherical distribution of the radical, with ϕI_a constant throughout the reaction vessel, and when the radical concentration is not affected by the first order homogeneous reaction or convection currents. It should, however, be applicable, as a first approximation, to the reaction scheme considered here and to a cylindrical reaction vessel of dimensions usually employed in vapor phase photolysis. If $a = (m\phi I_a/2k_2)^{\frac{1}{2}}$, $b = 1.15(m\phi I_a 2k_2/D^2)^{\frac{1}{4}}$, and R is the radius of the reaction vessel, Noyes finds that for $bR > 5.7$, $x = a[1 - \exp(-b(R - r))]$, if all radicals striking the wall are consumed. In the region of validity of this expression, it is found then that $\delta = (1 - 1.5/bR)^{\frac{1}{2}}/(1 - 1/bR)$ or, to a good approximation, $\delta \approx (1 + 0.25/bR)$. In view of the underlying assumptions this value of δ should represent an approximate upper limit. Thus, at a total pressure of 100 mm. the diffusion coefficient (D) may be of the order of 1.5 cm.^{2}/sec., $m\phi I_a$ 10^{12} to 10^{15} quanta/cc. sec., $2k_2$ 10^{-10} cc./molecule sec., and R 2 to 5 cm. For $R = 4$ cm. $\delta \leqslant 1.02$ when $m\phi I_a = 10^{12}$, and $\delta \leqslant 1.01$ when $m\phi I_a = 10^{13}$.

When wall effects, time fluctuations, and convection currents can be neglected, and if $s = 8\ m\phi k_2 q(\mathrm{A}) I_0/(\lambda/p)^2$ and $\beta = q(\mathrm{A})L$, the correction factor δ for the decreasing x along the length of the vessel (of total length L) due to an appreciable extinction coefficient (q) is

$$\delta = \frac{\beta^{\frac{1}{2}}\{s(1-e^{-\beta})/4-(1+s)^{\frac{1}{2}}+(1+se^{-\beta})^{\frac{1}{2}}+\ln\{[(1+s)^{\frac{1}{2}}+1]/[(1+se^{-\beta})^{\frac{1}{2}}+1]\}\}^{\frac{1}{2}}}{(1+s)^{\frac{1}{2}}-(1+se^{-\beta})^{\frac{1}{2}}-\ln\{[(1+s)^{\frac{1}{2}}+1]/[(1+se^{-\beta})^{\frac{1}{2}}+1]\}}.$$

In the limiting case when $k_2 \ll \lambda/p$, $\delta = (\frac{1}{2}\beta)^{\frac{1}{2}}[(e^\beta + 1)/(e^\beta - 1)]^{\frac{1}{2}}$ and when $k_2 \gg \lambda/p$, $\delta = (\frac{1}{2}\beta/2)^{\frac{1}{2}}[(e^{\beta/2} + 1)/(e^{\beta/2} - 1)]^{\frac{1}{2}}$. The limiting curves and the curves for $s = 1$, 10, 100 are plotted against $(1 - e^{-\beta})$ in Fig. 3. For $s = 10^{-2}$ δ already practically coincides with curve I (Fig. 3), which gives an upper limit of the error. The error remains small to quite appreciable

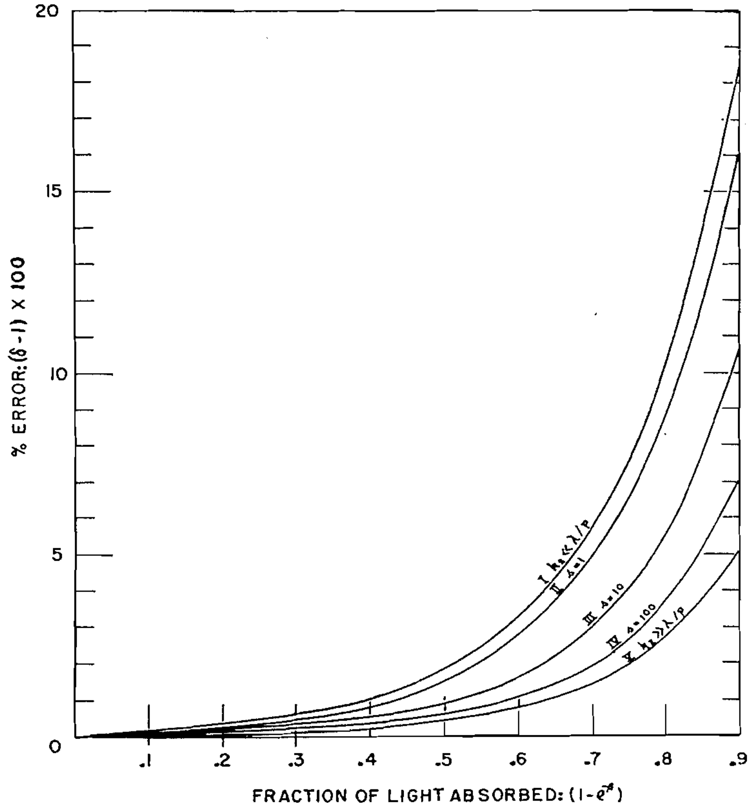

FIG. 3. Variation in the correction factor with the fraction of light absorbed.

absorptions and in actual experiments is further decreased by convection currents.

It is evident that while concentration gradients may under certain conditions have a serious effect, in many instances the limits of the errors can be evaluated and the experimental conditions adjusted so that the errors remain very small. Such conditions do prevail in many experimental determinations of relative rate constants.

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TEMPERATURE COEFFICIENTS FOR SELF-DIFFUSION IN SOLUTION[1]

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

ABSTRACT

Coefficients of self-diffusion have been measured for aqueous solutions of sodium dihydrogen phosphates from 1 molar to 10^{-4} molar and at temperatures of 15, 25, 35, and 45°C. The activation energy of self-diffusion has been calculated for various concentrations. It decreases from 5.4 kcal./mole at 0.9 M to 4.3 kcal./mole. at infinite dilution.

INTRODUCTION

Self-diffusion has been described as "the diffusion of something into its exact counterpart" (13), and in the past few years isotopic tracers have often been used in studies of self-diffusion. While isotopes are obviously not exactly alike, the isotope effect in diffusion studies in solution is often small. For example, Adamson, Cobble, and Nielsen (1) found no detectable difference in the rates of diffusion of Na^{22} and Na^{24} ions in aqueous solutions of sodium chloride.

Various methods for measuring self-diffusion using tracer techniques have been developed. The diaphragm cell technique developed by McBain and Dawson (10) has been used extensively, and more recently Mysels and Stigter (11) have developed a method involving two fritted glass diaphragms. Anderson and Saddington developed a capillary cell method for studying self-diffusion in solution (2,4).

The capillary cell method was used in the present work for the determination of temperature coefficients for self-diffusion in aqueous solutions of sodium dihydrogen phosphate.

The equation for the diffusion coefficient for the capillary cell method is

$$D = \frac{4L^2}{\pi^2 t}(\ln 8/\pi^2 - \ln R) \tag{1}$$

where D is the diffusion coefficient, L is the length of the capillary, t is the time, and R is the ratio of the activity (activity is used here in the sense of radioactivity) in the cell after diffusion to that in the cell before diffusion (4).

Various equations have been used to relate the diffusion coefficient to the temperature. One such equation is that of Stokes-Einstein:

$$D = kT/6\pi\eta r \tag{2}$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity, and r is the radius of the diffusing particle. Another equation frequently used is

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Contribution from Department of Chemistry, University of Saskatchewan, Saskatoon, Sask.
Paper is based on a thesis written in partial fulfillment of the requirements for the degree of Master of Arts, University of Saskatchewan, Saskatoon.

$$D = Ae^{-E_D/RT} \tag{3}$$

where A is a constant, R is the gas constant, T is the absolute temperature, and E_D is the activation energy for self-diffusion.

The activation energy can be calculated from equation [3] and also from viscosity data (14) using equation [4].

$$E_\eta = R\left(T - \frac{d \ln (1/\eta)}{d(1/T)}\right) \tag{4}$$

Wang and co-workers (14, 15, 19) have published a series of papers on "Self-diffusion and structure of liquid water." They used the capillary cell method and calculated the activation energy for self-diffusion in liquid water from a plot of log D vs. $1/T$. In another series of papers in which activation energies for self-diffusion were calculated from conductance data (16, 18, 17), Wang showed that diffusion data, viscosity data, and conductance data should yield the same activation energy.

Graupner and Winter (6) measured the self-diffusion coefficients for water, benzene, bromoethane, and ethanol using the diaphragm cell method and calculated activation energies for self-diffusion in each liquid.

Partington, Hudson, and Bagnall (12) determined self-diffusion coefficients and activation energies for self-diffusion for water and several aliphatic alcohols using the diaphragm cell method.

Hoffman (7) has determined the activation energy for self-diffusion in liquid mercury using the capillary cell method.

Table I lists the values from the literature cited, for the activation energy for self-diffusion calculated from diffusion data and from viscosity data.

TABLE I
ACTIVATION ENERGIES FOR SELF-DIFFUSION

Ref. No.	Ion or molecule	(kcal./mole) E_D	(kcal./mole) E_η	Temperature range, °C.
14	HDO	4.6	4.59	10–50
15	HHO^{18}	4.4		10–50
19	HTO	4.6		10–50
6	DDO and HHO^{18}	4.6	3.28	15–45
12	DDO	3.93	3.80	15–45
8	$H_2PO_4^-$ (∞ dilution)	4.3	4.6	15–45
12	Methanol	2.77	2.33	15–35
12	Ethanol	4.62	3.30	15–35
6	Ethanol	4.5	3.85	15–45
12	*n*-Propanol	4.25	4.31	15–45
12	*n*-Propanol	5.30	5.19	15–45
12	*n*-Butanol	4.60	4.57	25–45
12	*t*-Butanol	7.50	8.20	35–55
6	Benzene	2.1	2.4	15–45
6	Bromoethane	1.2	1.75	15–45
7	Mercury	1.16	1.25	0–90

The object of the present work was to determine self-diffusion coefficients for the $H_2PO_4^-$ ion in aqueous solutions of sodium dihydrogen phosphate at different concentrations and at different temperatures. The value of the activation energy for self-diffusion of $H_2PO_4^-$ determined in the present work is included in Table I for purposes of comparison.

EXPERIMENTAL

Materials and Methods

Capillary cells about 3 cm. long and 0.1 cm. in diameter were made from glass capillary tubing of uniform bore. The uniformity of the bore was determined by accurately measuring the length of a mercury thread at overlapping intervals along the capillary tube. For a mercury thread of average length, 2.499 cm., the standard deviation of the length was 0.003 cm., indicating that the tubing was quite uniform (standard deviation in the radius is 0.07%). The cells contained 0.0250 ml. of solution when full.

The capillary cells were mounted vertically in a lucite holder (for details see (4, 8). The bottom ends of the capillaries were sealed. Three cells were used in each experiment. The cells were filled with radioactive solution of known concentration and then gently immersed in an inactive solution of the same concentration. The experiments were carried out at constant temperature. The time of diffusion, from two to six days, was measured to the nearest minute.

At the end of the diffusion period the cells were emptied and rinsed onto aluminum dishes and the solution evaporated to dryness. Five 0.0250 ml. samples of the undiffused radioactive solution were prepared as standards for each experiment. Fine pipettes were used to fill and empty the cells. The samples were analyzed for radioactivity using an end window Geiger-Mueller counter. The ratio of the activity of the diffused sample to the activity of the standard sample is equal to R in equation [1]. The experimental method for determining the self-diffusion coefficients was described in detail by Burkell and Spinks (4).

The diffusion apparatus was completely immersed in a constant temperature water bath. Measurements of temperature variation indicated that the temperature along the diffusion path did not fluctuate by more than 0.02°C. Experiments were carried out at 15, 25, 35, and 45°C.

Analyzed reagent grade $NaH_2PO_4 \cdot H_2O$ and distilled water were used to prepare a series of solutions of concentrations from 1 to 10^{-4} molar.

P^{32} in the form of $PO_4^{\equiv}$ in aqueous solution was obtained from the Atomic Energy Project at Chalk River. The radiochemical purity of the P^{32} was established by its half-life, 14.3 days, and its half-thickness, 117 cm./cm.^{2} The P^{32} solution was analyzed for $PO_4^{\equiv}$ and 1 ml. of solution containing originally 1 mc. of P^{32} was found to contain 28 mgm. of phosphorus. Radioactive solutions were prepared by adding sufficient radioactive phosphate to the inactive solution to give the 0.025 ml. standard sample an activity of about 2000 counts per minute. The weight of phosphorus introduced with the P^{32} was thus negligible even for the most dilute solution used (10^{-4} M).

All counting measurements were made with an end window Geiger-Mueller counter. Background corrections and resolving time corrections were applied to all the measurements. Since the same weight of material was present in all the samples counted for individual experiments, and constant end-on geometry was maintained, and since only the ratio of the activities was used in the calculations, no corrections for back-scatter and self-absorption were necessary.

Viscosity Measurements

The viscosities of the sodium dihydrogen phosphate solutions were determined using an Ostwald viscometer. The results are plotted in Fig. 1. (The necessary densities at 15, 35, and 45°C. were determined, using the pyknometer method (8).) The densities of the solutions at 25°C. were obtained from Mason and Culvern (9).

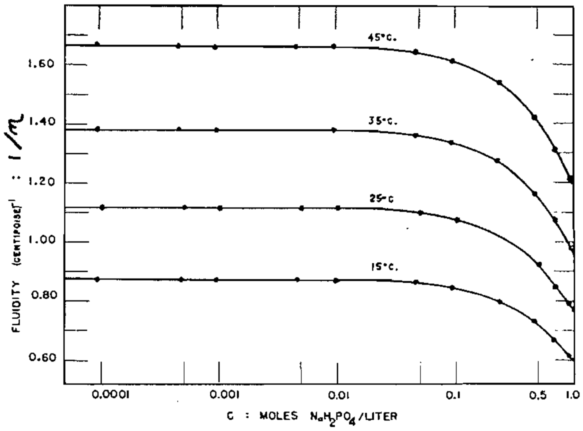

FIG. 1. Plot of fluidity ($1/\eta$) vs. log C for sodium dihydrogen phosphate solutions.

pH Measurements

Measurements of pH on the sodium dihydrogen phosphate solutions were made using a Beckman pH meter. In solution, the $H_2PO_4^-$ ion dissociates, $H_2PO_4^- \rightleftarrows H^+ + HPO_4^=$, and it was of interest to know which ion was present in larger amount.

The ratio, X, of concentrations of the ions present is given by

$$X = \frac{(H_2PO_4^-)}{(HPO_4^=)} = \frac{(H^+)}{K_2} = \frac{(H^+)}{7.5 \times 10^{-8}}$$

where K_2 is the second ionization constant for phosphoric acid. Calculations from the pH measurements indicated that above 0.005 molar the diffusion measured was essentially that of the $H_2PO_4^-$ ion, while below 0.005 molar, both ions contributed appreciably (See Table II).

Effect of Stirring

One of the boundary conditions for the capillary cell method of determining diffusion coefficients was that the concentration of tracer at the upper end of the capillary be zero at all times during the experiment. To determine whether this condition was being fulfilled, the outer inactive solution was

TABLE II
DETERMINATIONS OF pH FOR SODIUM DIHYDROGEN PHOSPHATE SOLUTIONS AND VALUES OF $X = (H_2PO_4^-)/(HPO_4^=)$

Conc. (moles/liter)	15°C.		25°C.		35°C.		45°C.	
	pH	X	pH	X	pH	X	pH	X
0.9256	4.02	1270	4.03	1240	4.10	1060	4.13	988
0.694	4.12	1010	4.12	1010	4.19	861	4.22	804
0.463	4.20	841	4.22	802	4.27	716	4.31	653
0.231	4.32	639	4.37	568	4.40	530	4.44	484
0.0926	4.48	441	4.51	412	4.51	412	4.55	376
0.0463	4.57	358	4.59	343	4.61	327	4.65	299
0.00926	4.78	221	4.84	192	4.86	184	4.89	172
0.00463	5.08	111	5.10	106	5.10	106	5.15	95
0.000926	5.60	33	5.63	31	5.65	30	5.68	28
0.000463	5.88	18	5.90	17	5.86	18	5.90	17
0.0000926	6.15	9	6.22	8	6.35	6	6.46	5

stirred at 60 r.p.m. The diffusion coefficients obtained in these experiments were the same, within the expected standard deviation, as those obtained in parallel runs without stirring.

Effect of Immersion

The immersion error due to the lowering of the capillary cells into the inactive solution was estimated in diffusion experiments in which the time of diffusion was about one minute. The loss of activity by the cells in this operation was less than 0.5%. Thus, the actual immersion error in R was probably less than 0.5%.

RESULTS

The mean diffusion coefficients are plotted against the log of the concentration in Fig. 2. (Each point is the mean value of five determinations.)

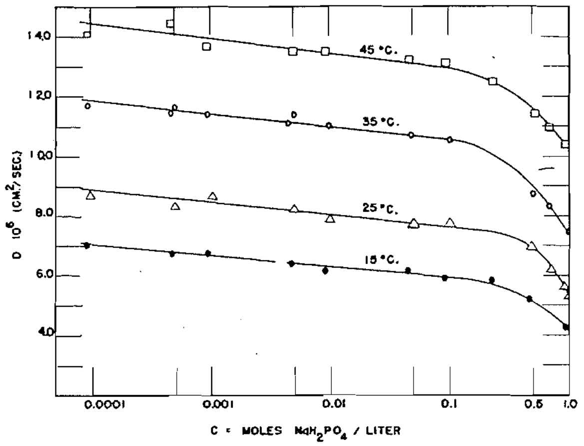

FIG. 2. Plot of $D \cdot 10^6$ vs. log C for sodium dihydrogen phosphate solutions.

For concentrations between 10^{-1} and 10^{-4} molar NaH_2PO_4 the variation of D with log C was found to be linear. The best fitting straight line for the data at each temperature was determined by the method of least squares.

S_D is the standard error of the estimate.
For 15°C., $D \cdot 10^6 = 5.60 - 0.364 \log C$; $S_D = 0.11$.
For 25°C., $D \cdot 10^6 = 7.22 - 0.412 \log C$; $S_D = 0.16$.
For 35°C., $D \cdot 10^6 = 10.14 - 0.450 \log C$; $S_D = 0.15$.
For 45°C., $D \cdot 10^6 = 12.49 - 0.492 \log C$; $S_D = 0.26$.
For the 25°C. curve, the results of Burkell (3) and the results obtained in the present work were used. The diffusion coefficient at infinite dilution was obtained by extrapolating the curves in the plot D vs. $\sqrt{C}$ (Fig. 3).

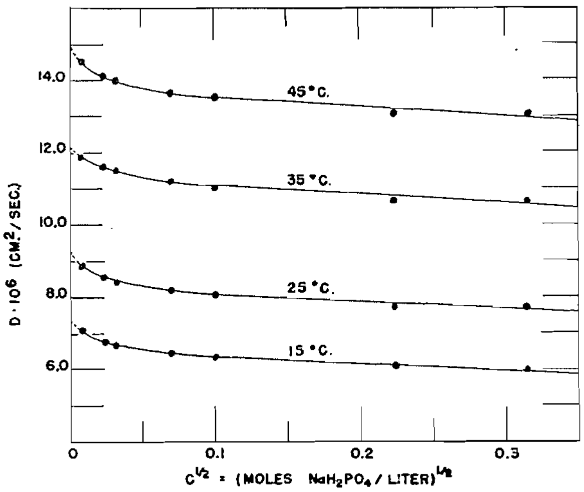

FIG. 3. Plot of $D \cdot 10^6$ vs. $\sqrt{C}$ for sodium dihydrogen phosphate solutions.

In order to obtain activation energies for self-diffusion, log D was plotted against $1/T$ for various concentrations (Fig. 4) and the best fitting straight

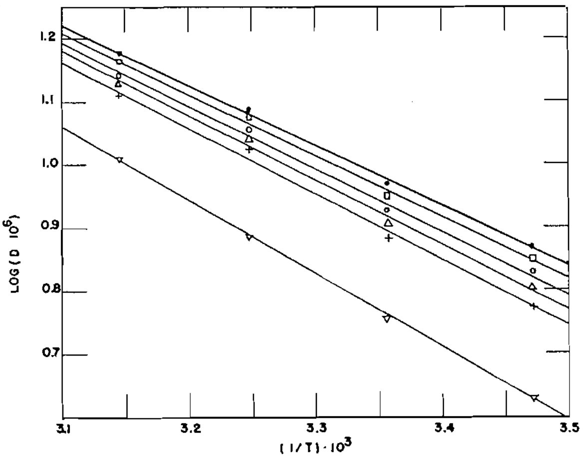

FIG. 4. Plot of log $(D \cdot 10^6)$ vs. $(1/T) \cdot 10^3$ for sodium dihydrogen phosphate solutions:
● ∞ Dilution
□ 0.0001 molar
○ 0.001 molar
△ 0.01 molar
+ 0.1 molar
▽ 0.926 molar

lines determined using the method of least squares. The values of E_D were calculated from: $E_D = -2.3R\ (d(\log D/d(1/T))$. The slopes of the lines are recorded in Table III together with the activation energies calculated from viscosity data using the equation:

$$E_\eta = R\left(T - \frac{d \ln (1/\eta)}{d(1/T)}\right).$$

TABLE III
ACTIVATION ENERGIES FOR SELF-DIFFUSION IN AQUEOUS SOLUTIONS OF SODIUM DIHYDROGEN PHOSPHATE

Concentration (moles/liter)	$-\frac{d \log D}{d(1/T)}$	E_D (kcal./mole.)	$-\frac{d \log (1/\eta)}{d(1/T)}$	E_η (kcal./mole)
0.926	1.178	5.4	0.921	4.8
0.1	1.051	4.8	0.870	4.6
0.01	1.024	4.7	0.870	4.6
0.001	0.996	4.6	0.870	4.6
0.0001	0.974	4.5	0.870	4.6
∞ Dilution	0.946	4.3	0.870	4.6

The plot of activation energy from diffusion data, E_D vs. log C is given in Fig. 5.

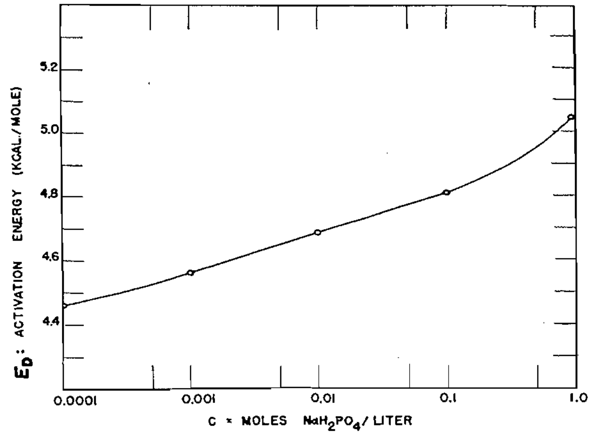

FIG. 5. Plot of E_D vs. log C.

DISCUSSION

From Table III it is seen that, for solutions of moderate concentration, the activation energy of self-diffusion for the $H_2PO_4^-$ ion is about 4.8 kcal./mole and that it decreases somewhat with increasing dilution. The extrapolated value for infinite dilution is 4.3 kcal./mole, not very different from the value for HHO^{18}(4.4 kcal./mole, Table I). The fact that the activation energy for the dilute solution of $H_2PO_4^-$ is close to that for water is not surprising in view of the fact that ions are commonly hydrated in aqueous solution. It has been suggested that the activation energy for the diffusion of water is due to the breaking of the hydrogen bond for which the approximate energy is 4.5 kcal./mole (5).

ACKNOWLEDGMENTS

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METHYL ETHYL KETONE IN THE PHOTOLYSIS OF ACETONE VAPOR[1]

By L. Mandelcorn[2] and E. W. R. Steacie

ABSTRACT

By mass spectrometric analyses, methyl ethyl ketone was determined as a product of the photolysis of acetone between 100 and 284°C. According to the postulated mechanism, methyl ethyl ketone together with methane and ethane accounted for approximately 95% of the methyl radicals produced.

INTRODUCTION

It is now accepted that the mechanism for the photolysis of acetone vapor between 100°C. and 250°C. is (6,7)

$$CH_3COCH_3 + h\nu \rightarrow 2CH_3 + CO \qquad [1]$$
$$2CH_3 \rightarrow C_2H_6 \qquad [2]$$
$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2 \qquad [3]$$
$$CH_3 + CH_3COCH_2 \rightarrow CH_3COC_2H_5 \qquad [4]$$
$$2CH_3COCH_2 \rightarrow (CH_3COCH_2)_2 \qquad [5]$$

Reaction [1] was shown to proceed with a quantum yield of unity in this temperature range (4). The kinetics of reactions [2] and [3] have been investigated (3,6,7) in some detail. Methyl ethyl ketone was identified as a product but was not studied quantitatively (1). Ketene was also found at temperatures above 200°C., presumably resulting from the decomposition of acetonyl radicals (2)

$$CH_3COCH_2 \rightarrow CH_3 + CH_2CO \qquad [6]$$

Considering reaction [1] as the only source of methyl radicals, it can be seen from the results of Trotman-Dickenson and Steacie (7) that reactions [2] and [3] account for from 70 to 100% of the methyl radicals produced, the percentage depending on temperature and concentration. Therefore, the inclusion of reaction [4] should account for all the methyl radicals, and the material balance

$$[2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5}]/R_{CO}$$

where $R_{C_2H_6}$ is the rate of production of ethane etc., should be equal to 2 under all conditions in this temperature range. If reaction [6] is significant, then the above ratio should increase with temperature above 200°C.

The purpose of this work was to study the material balances in the acetone photolysis when methyl ethyl ketone is included. It serves as the basis of an investigation of the kinetics of addition of methyl radicals to unsaturated hydrocarbons, the loss of methyl radicals by addition being related to a decrease in the material balance.

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[2] *National Research Council of Canada Postdoctorate Fellow 1951-53.*

EXPERIMENTAL

The reaction cell consisted of a cylindrical quartz vessel with plane polished ends and 195 cc. in volume, 10 cm. long, and 5 cm. in diameter. It was kept in an aluminum block furnace which had a quartz window at each end. Three thermocouples were fastened to different points on the cell. Two tubes extended from the cell through the furnace, one serving as a cold finger and the other connected to a stopcock located one inch from the top of the furnace. The total volume of the cell and connecting tube was 205 cc.

The analytical system consisted of two traps, a modified Ward still (5), a small mercury diffusion pump, a combination gas burette and Toepler pump, and a copper oxide tube heated to 240°C., all in series. The cell, analytical system, and reagent reservoirs were suitably connected to a two-stage mercury diffusion pump.

A Hanovia S-100 lamp served as the light source and proved to be fairly constant over long periods of use. The light was collimated by a stop and a series of lenses, thereby filling over 90% of the cell and, for greater efficiency, was reflected back by an aluminum mirror on the rear window of the furnace. The light was filtered with a Corning No. 9863 filter. Different light intensities were obtained by adding neutral density filters. In a few experiments the full arc was used.

The acetone was Merck Reagent Grade. It was dried over "Drierite", degassed by bulb to bulb distillation, and separated from the system by a mercury cutoff.

For an experiment, acetone was introduced into the cell to the desired pressure. After condensing in the cold finger and pumping to remove any traces of noncondensible gases, the acetone was photolysed to about seven per cent decomposition.

The products of main interest were carbon monoxide, methane, ethane, and methyl ethyl ketone. Methane and carbon monoxide were separated at −196°C. and the carbon monoxide was combusted and separated in the copper oxide tube. Ethane was separated at −175°C. and various samples were analyzed with the mass spectrometer. The remainder, consisting mainly of acetone, was collected into 150 cc. sample bulbs and analyzed for methyl ethyl ketone with the mass spectrometer.

The analyses for methyl ethyl ketone were based on the height of peak 72. Two synthetic samples containing amounts of acetone used in most experiments and 2.5 and 1.0% methyl ethyl ketone were subjected to the same procedure as after photolysis. Mass spectroscopic analyses of these gave 2.2 and 0.85% methyl ethyl ketone respectively, and therefore all the results for methyl ethyl ketone, obtained by this method, are reported 15% higher than those obtained in the analyses.

Since it is possible that some of the heavier methyl ethyl ketone was absorbed by the stopcock grease in the apparatus and in the sample bulbs, it was felt necessary to check on the validity of applying the 15% correction factor. The apparatus was altered so that the methyl ethyl ketone would not be in contact with stopcock grease except for a short time when introduced into the mass spectrometer. Mercury cutoffs were appropriately installed to isolate the cell (volume of connecting tubing = 37 cc.) analytical system and gas burette. The acetone and methyl ethyl ketone mixtures were measured in a known volume which was connected with a mercury cutoff also serving as a manometer, and then collected in sample bulbs equipped with breakseals. Mass spectroscopic analyses of two synthetic samples (prepared under stopcock grease free conditions) containing 0.37 and 0.71% methyl ethyl ketone gave here 0.36 and 0.72% respectively. Obviously, with this procedure the mass spectroscopic results for methyl ethyl ketone may be used unambiguously.

RESULTS

The results of experiments done at three different acetone concentrations and at various temperatures are given in Table I. Included also, at 184°C. is the effect of variation of light intensity, seen from the rates of carbon monoxide production. Quantum yields of methyl ethyl ketone production are calculated on the assumption of a quantum yield of unity for carbon monoxide production.

TABLE I
PRODUCTS OF PHOTOLYSIS OF ACETONE

Temp., °C.	Time, sec.	$R_{C_2H_6}$	R_{CH_4}	$R_{CH_3COC_2H_5}$	R_{CO}	$\frac{2R_{C_2H_6} + R_{CH_4}}{R_{CO}}$	$\frac{2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5}}{R_{CO}}$	$\Phi_{CH_3COC_2H_5}$
		× 10^5 cc. N.T.P./sec.						
Mean acetone conc.—1.76 × 10^{-6} M./cc.								
105	3600	5.25	0.49	0	5.78	1.90	1.90	....
143*	7200	6.63	1.60	1.1	8.35	1.79	1.92	0.13
144	3600	6.06	1.70	1.2	7.72	1.79	1.95	0.16
159	3600	3.19	1.74	1.3	4.82	1.68	1.95	0.3
184	12600	0.63	1.29	0.6	1.70	1.50	1.86	0.4
183	3600	3.29	2.90	2.2	5.98	1.59	1.95	0.4
184	3600	5.25	4.36	2.3	9.22	1.61	1.86	0.3
184	2700	9.88	5.46	4.5	15.06	1.67	1.96	0.3
207	3600	2.26	4.34	2.2	5.94	1.49	1.86	0.25
240	3600	1.34	6.41	2.6	6.11	1.48	1.91	0.3
242	3090	2.41	10.28	4.0	10.52	1.43	1.82	0.3
242*	3600	0.77	4.59	1.3	4.11	1.49	1.81	0.3
284	3600	0.44	8.47	2.2	6.15	1.55	1.88	0.3
Mean acetone conc.—3.56 × 10^{-6} M./cc.								
144	3600	7.72	3.75	3.3	11.66	1.64	1.93	0.3
183	2700	5.33	8.86	5.9	12.77	1.53	2.00	0.5
240	1800	2.06	17.70	7.4	14.45	1.51	2.02	0.5
Mean acetone conc.—.88 × 10^{-6} M./cc.								
138	5160	2.66	0.47	0.5	3.29	1.76	1.91	0.15
184	7200	2.10	1.29	0.7	3.39	1.62	1.82	0.2
240	7200	0.90	2.94	1.2	3.18	1.49	1.86	0.3

**Stopcock-grease free system.*

It can be seen from the material balances obtained in the stopcock grease free system that the application of 15% correction to the rest of the results for methyl ethyl ketone is valid.

Mass spectrometric analyses occasionally showed traces of propane in the ethane fraction. However, after removing the ethane no significant fraction could be obtained at −150°C., i.e., propane. In the experiment at 284°C., about 20% of the ethane fraction consisted of ethylene. No other products could be found by the above method of analysis.

DISCUSSION

The constancy of the material balance

$$(2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5})/R_{CO},$$

over the temperature range studied indicates that reaction [6] is relatively insignificant at these conditions. Therefore, it is apparent that reactions [2], [3], and [4] account for 95 ± 3% of the methyl radicals produced, reaction [1] being the main source. The deviation falls within the possible error of 15% in methyl ethyl ketone analysis. Conversely, these results lend support to the postulated mechanism for acetone photolysis at these temperatures.

It is possible to obtain some information on the kinetics of reactions [2], [4], and [5]. If it is assumed that the acetonyl radicals produced in reaction [3] react only to produce methyl ethyl ketone and biacetonyl, then $R_{(CH_3COCH_2)_2}$ would be equal to $(R_{CH_4} - R_{CH_3COC_2H_5})/2$. Hence $(k_2^{\frac{1}{2}}k_5^{\frac{1}{2}})/k_4$ could be calculated as it is equal to $(R^{\frac{1}{2}}_{C_2H_6}\,R^{\frac{1}{2}}_{(CH_3COCH_2)_2})/R_{CH_3COC_2H_5}$. Such calculations were made and an average value of 0.7 ± 0.3 was found for $(k_2^{\frac{1}{2}}k_5^{\frac{1}{2}})/k_4$. These values, although considerably scattered, are fairly constant with temperature and are also in the range of ~0.5, the magnitude of $(Z_2^{\frac{1}{2}}Z_5^{\frac{1}{2}})/Z_4$, Z being the collision frequency. It seems unlikely that this is due to an accidental equivalence of $P_5^{\frac{1}{2}}$ and P_4 when both are small, and the results strongly support collision efficiencies for reactions [4] and [5] of the order of magnitude of that of [2], i.e., unity.

ACKNOWLEDGMENT

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THE ALKALOIDS OF PAPAVERACEOUS PLANTS

L. *DICRANOSTIGMA LACTUCOIDES* HOOK. F. ET THOMS. AND *BOCCONIA PEARCEI* HUTCHINSON[1]

By R. H. F. Manske

ABSTRACT

Dicranostigma franchetianum has been renamed *Stylophorum franchetianum* (Prain) comb. nov. because its alkaloids are the same as those of *S. diphyllum*. It is proposed to retain the name *D. lactucoides* because the contained alkaloids, namely protopine, isocorydine, sanguinarine, and chelerythrine present a combination hitherto encountered only in a *Glaucium*. *Bocconia pearcei* was shown to contain, in addition to chelerythrine (and presumably sanguinarine), small amounts of protopine and allocryptopine.

The genus *Dicranostigma* Hook. f. et Thoms. is presently considered to include three species. The uncertainty of the position of these species and of the genus is illustrated by the fact that at one time or another all were referred to *Chelidonium* Tourn. while one (*D. leptopodum*) was referred to *Glaucium* Tourn. and another (*D. lactucoides*) to *Stylophorum* Nutt.

It seemed probable that a chemical examination might aid in solving some of the moot points in the classification of these plants and the examination of one of them, *Dicranostigma franchetianum* (Prain) Fedde (2) has already been reported (4). This plant is the least named in the genus and was originally described as *Chelidonium franchetianum* Prain (5). Inasmuch as the alkaloids that it elaborates are the same as those elaborated by *Stylophorum diphyllum* (Michx.) Nutt. (4) the writer suggests that it should henceforth be known as *Stylophorum franchetianum* (Prain) comb. nov. This transfer out of *Dicranostigma* is specifically warranted because of the results of the chemical examination of *D. lactucoides* Hook. f. et Thoms. which is recorded in this communication. This much named plant was the type upon which the genus was founded but it has also been known as *Chelidonium dicranostigma* Prain (5), *C. lactucoides* (Hook. f. et Thoms.) Prain (6), and *Stylophorum lactucoides* Baill (1). The contained alkaloids, namely protopine, sanguinarine, chelerythrine, and isocorydine, indicate that the plant has affinities with *Sanguinaria* Dill. and *Bocconia* Plum. and with *Glaucium* but the absence of chelidonine definitely precludes any alliance with *Stylophorum* or *Chelidonium*. The taxonomic fate of the remaining species, *D. leptopodum* (Maxim.) Fedde must await its chemical investigation. Unfortunately it has not been available.

The alkaloids of *Bocconia pearcei* had already been examined (3) and a mixture of them from the same source confirmed the presence of chelerythrine and offered indirect proof of the presence of sanguinarine. Protopine and allocryptopine were also present but phenolic alkaloids, as in other species of this genus, were absent.

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Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ont.

EXPERIMENTAL*

D. lactucoides is a facultative biennial and the plant material, which was grown locally, was collected at practically all stages of growth. There was available a total of 3.94 kgm. of dried plant material including that from the roots. It was extracted with methanol in Soxhlet apparatus and the solvent was removed from the extract which was boiled with water and enough hydrochloric acid to render it acid to Congo red. The clear but reddish colored filtered extract was extracted with chloroform (extract C), then made alkaline with ammonia and again extracted with chloroform (extract AC).

Isocorydine

The extract C was freed of solvent, the residue extracted with dilute hydrochloric acid, filtered, and exhausted with ether. The aqueous solution was then rendered alkaline with an excess of sodium hydroxide (the small amount of precipitate here formed proved to consist largely of protopine), filtered, and again extracted with ether. The residue from the combined ether extract crystallized readily in contact with methanol and when recrystallized from the same solvent it was obtained in almost colorless stout prisms which, either alone or in admixture with authentic isocorydine, melted at 185°.

Sanguinarine and Chelerythrine

The chloroform extract (AC) was dissolved in hot dilute hydrochloric acid, filtered, and allowed to cool slowly. The deep red salt which then crystallized was decomposed with ammonia in the presence of chloroform. The residue from the chloroform extract was converted to its hydrobromide in acetone solution. The sparingly soluble orange salt thus obtained was decomposed with ammonia in the presence of a large volume of ether. When the washed ether solution was slowly evaporated a colorless base crystallized. This precipitate was washed with ether and then melted at 277° when placed in the melting point bath at 250°. This is the highest melting point ever recorded for sanguinarine but there can be no doubt about the identity of the compound. Analytical results are of no value in the identification because of the tenacity with which this alkaloid retains many solvents in molecular combination. A methoxyl determination gave a value corresponding to somewhat less than one group and this only after prolonged boiling. Since chelerythrine with two methoxyls yields methyl iodide corresponding to three methoxyls it is expected that sanguinarine under the same conditions will show one methoxyl. The ψ-cyanides of these bases are however characteristic and have sharp melting points. A solution of the base in chloroform was treated with a copious volume of methanol and then boiled with an aqueous solution of potassium cyanide, the mixed solvents being allowed to escape. While the somewhat concentrated solution was still hot, crystals of the desired product separated out. The substance was washed with water, with dilute acid, with methanol, and finally recrystallized from chloroform–methanol. Sanguinarine ψ-cyanide as thus obtained consisted of colorless stout prisms which melted at 227°. Found: N, 7.93, 7.97. Calc. for $C_{21}H_{14}O_4N_2$: N, 7.82.

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*All melting points are corrected.

The mother liquors from which the sanguinarine salts had been prepared were digested with an excess of potassium cyanide and the resulting precipitate separated and washed with water. It was then digested with cold dilute hydrochloric acid and the insoluble portion separated by filtration (the acid filtrate yielded protopine). When the dried product was recrystallized several times from acetone, then from chloroform–methanol, and again from acetone–methanol it melted at 258–259° and in admixture with authentic chelerythrine ψ-cyanide it melted at the same temperature.

Protopine

The acid extract obtained from the mixture which was precipitated by potassium cyanide was basified with ammonia and shaken with a large volume of ether. The residue from the ether extract crystallized readily when moistened with methanol and when the base was recrystallized from chloroform–methanol it melted sharply at 211° either alone or in admixture with protopine.

The total yield of alkaloids from this plant was approximately 0.2%. Of this, sanguinarine was the major constituent followed by isocorydine, protopine, and chelerythrine in that order. There were small amounts of alkaloid containing mother liquors, some of them phenolic in nature, which would undoubtedly yield other bases if more material were available.

Bocconia pearcei

The author is sincerely indebted to Mr. Isidoro Macció, Direccion Nacional de Quimica, Buenos Aires, Argentina, who supplied a specimen of total mixed alkaloids from *B. pearcei.* These alkaloids were dissolved in chloroform–methanol and digested with aqueous potassium cyanide. The amorphous resinous mixture that was obtained when the organic solvents had largely been expelled was digested with cold dilute hydrochloric acid. Systematic recrystallization of the insoluble portion from acetone, chloroform–methanol, and acetone–methanol served to yield pure chelerythrine ψ-cyanide melting at 259–260° and a series of fractions of lower melting points which undoubtedly consisted of a mixture of the ψ-cyanides of chelerythrine and sanguinarine.

The acid soluble portion from the above treatment with potassium cyanide was basified with ammonia and shaken with much ether. This residue from the washed ether extract readily yielded a crop of protopine (m.p. and mixed m.p. 210°). The methanolic filtrate from the protopine was neutralized with nitric acid and a further small amount of protopine separated as its sparingly soluble nitrate. The bases in the filtrate from this were again regenerated and in contact with methanol and seeding with allocryptopine this base rapidly separated. When recrystallized from methanol it consisted of colorless fine needles which melted, either alone or in admixture with allocryptopine, at 159°.

There were no fractions soluble in alkali and hence phenolic alkaloids were absent.

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THE EFFECT OF TEMPERATURE ON SUSPENSIONS OF GLASS BEADS IN TOLUENE CONTAINING VARIOUS PERCENTAGES OF WATER[1]

By A. E. J. Eggleton[2] and I. E. Puddington

ABSTRACT

The influence of temperature on the sedimentation volume and relative yield values of suspensions of spherical glass beads in toluene containing varying percentages of water has been measured. The increased sedimentation volume and yield value, due to the presence of water, found at room temperature virtually disappeared below approximately 0° C. This is in agreement with the theory which ascribes the effect of water to its interfacial tension against toluene. At temperatures above 0° C. there was a gradual fall in the sedimentation volume and yield value from the maximum found at 0° C. This is attributed to the increasing solubility of water in toluene. Suspensions containing no water or only a small quantity showed an unexpected steady increase in sedimentation volume and yield value as the temperature was lowered to −60° C. This effect was also observed with a suspension of glass beads in pentane. The results indicate a close connection between yield value and equilibrium sedimentation volume.

INTRODUCTION

The sedimentation volume of suspensions of inert materials in organic liquids has been a subject of interest for some time. Earlier work is typified by that of Ostwald and Haller (6) who investigated the sedimentation volumes of a number of inorganic oxides, carbonates, and silicates in various organic liquids, both polar and nonpolar. Differences in the sedimentation volumes were ascribed to the binding of differing numbers of layers of liquid to the particles, in other words to lyosorption.

The importance of small quantities of water has only been recognized comparatively recently. Kruyt and van Selms (3) found that the yield value of starch and quartz suspensions in organic liquids depended on the care taken in drying the materials and the amount of water subsequently added. Bloomquist and Shutt (1) related the sedimentation volumes of glass spheres in various organic liquids to their interfacial tension against water. Those with the largest values gave the largest sedimentation volumes. Organic liquids with which water was miscible gave low sedimentation volumes. Gallay and Puddington (2) showed how an attractive force between particles caused an increase in the sedimentation volume by preventing the close packing of the particles. McFarlane and Tabor (5) investigated the adhesion between two glass surfaces and found that it was directly related to the surface tension of a small drop of liquid placed at the point of contact, as predicted theoretically.

The present work is concerned with the effect of temperature on suspensions of glass beads in toluene. Clearly, if the effect of water is due to its interfacial tension against toluene we should expect changes in the properties of the suspensions when the temperature is lowered below 0° C. So that the system

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[2] *N.R.C. Postdoctorate Fellow, 1951–53, National Research Council, Ottawa.*

should be as simple as possible, spherical glass beads of definite size were chosen and suspended in toluene, which enabled the suspensions to be cooled to −60° C. without solidifying.

EXPERIMENTAL

Glass beads, −275 + 320 mesh, were supplied by the Flexolite Manufacturing Corporation. They were further fractionated by sedimentation against a constant upward current of water in a tube 3 cm. diameter and 100 cm. long. By successively increasing the rate of flow, fractions of increasing size were carried over the top of the tube and collected. Flocculation of the spheres, which would disturb the fractionation process, was prevented by dispersing them in a small quantity of sodium hexametaphosphate solution which, when diluted with the main body of liquid, gave a concentration of sodium hexametaphosphate approximately 0.1% by weight.

In order to conserve the solution a closed system was used, a small circulating pump returning the overflowed solution to a constant head device. Boiled out distilled water was used to prevent variations in the rate of flow caused by the formation of air bubbles in the connecting tubing.

A fraction of average diameter 43 μ was used for all experiments. Fig. 1 shows the distribution of sizes about the mean. The beads were cleaned with boiling nitric acid and aqua regia and finally extracted with hot distilled water in a Soxhlet apparatus for two weeks to remove traces of soluble material.

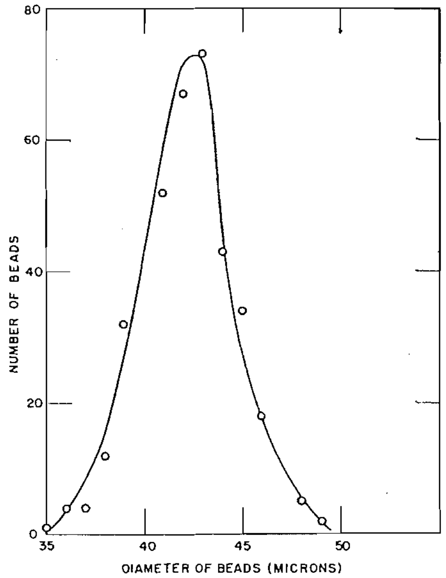

FIG. 1. Size distribution of beads.

Reagent grade toluene was freed from water and air by boiling off approximately a quarter of the original material, followed by refluxing under vacuum. For some of the experiments, where complete absence of water was desired, the toluene was let stand 24 hr. over calcium hydride and again refluxed under vacuum.

Pentane, 99.99% pure, was dried over calcium hydride and refluxed under vacuum.

Distilled water was boiled at atmospheric pressure to about half its original volume to remove as much air as possible and then distilled into a flask which had been baked at 350° C. under vacuum overnight. By repeatedly distilling the water back and forth on to a cold trap under vacuum, a sample was finally obtained which when distilled into a 1 mm. capillary tube formed a continuous thread showing the absence of dissolved air.

Fig. 2 shows the apparatus used for determining sedimentation volumes and relative yield values of suspensions which were contained in the tube *A*.

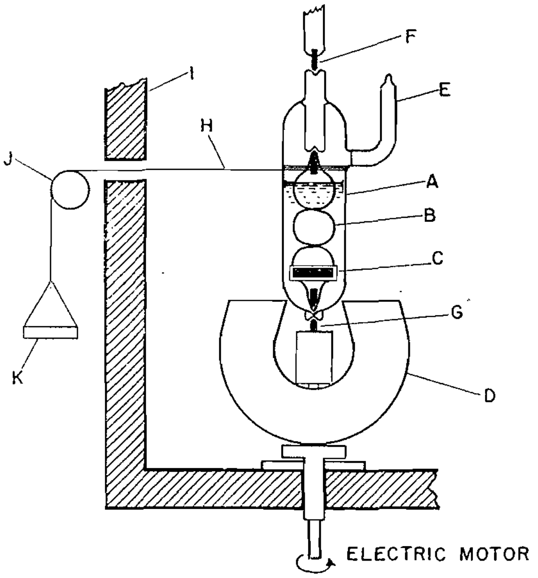

FIG. 2. Apparatus used for determining relative yield values and sedimentation volume of suspensions.

This tube (of pyrex, approximately 40 mm. by 12 mm. diameter) contained a spiral stirrer *B* pivoted at both ends on tungsten points bearing in conical depressions. Sealed in the stirrer, near the bottom, was a small iron slug *C*. This enabled the stirrer to be rotated at speeds up to approximately 3000 r.p.m. by a horseshoe magnet *D* which was attached to the shaft of a small electric motor.

Before filling, the tube was cleaned with chromic cleaning mixture, washed with distilled water, and dried. The required quantity of beads was weighed into the tube which was then sealed by the side-arm *E* to a vacuum apparatus. The glass beads were out-gassed at 350° C. overnight after which the pressure, read on a MacLeod gauge, was less than 10^{-5} mm. A calibrated bulb was filled with water vapor at measured temperature and pressure from the reservoir of de-gassed water, and then by immersing the tube *A* in dry ice the water contained in the bulb was condensed on the glass beads. The percentage of water by weight of beads could be calculated with sufficient accuracy from the volume, pressure, and temperature of water vapor in the calibrated bulb, using the ideal gas equation. By condensing more than one volume of water vapor on the beads, tubes containing up to 0.62% of water were prepared.

With the tube still immersed in dry ice the required quantity of toluene, which was not critical, was condensed in the tube, after which the side-arm was sealed off. The suspensions contained approximately 45% glass beads by weight.

The tube as shown in Fig. 2 was pivoted between two bearings *F* and *G*. The upper one, *F*, consisted of a tungsten point sealed in a short length of pyrex tube which was free to move vertically. It was kept in place by a small spring which enabled the tube to be inserted in place easily. The lower bearing *G* was attached to the shaft carrying the horseshoe magnet *D* and rotated with it. This bearing consisted of a chromium steel phonograph needle to avoid excessive wear on the glass tube.

A light nylon thread *H* was fastened at one end to side arm *E* of the tube and the other passed through the wall of the thermostat *I* and over the small aluminum pulley *J*, pivoted on steel points, to a small pan *K* on which weights could be placed. The apparatus, with the exception of the pan *K*, was contained in an air thermostat consisting of an insulated box which could be maintained between room temperature and −60° C. within ±0.3° C. by circulating air over dry ice contained in a separate compartment. The circulating fan was controlled by a bimetallic element.

In a typical run the tube was placed in the thermostat at room temperature and cooled slowly with the spiral stirrer in operation. Provided the temperature was very gradually lowered while passing through 0° C. the beads did not freeze to a solid mass. Once the temperature was below about −5° C. it was lowered rapidly to −60° C. to prevent the ice on the bead surface from recrystallizing and causing agglomeration. The tube was held at −60° C. for an hour or more with the stirrer rotating at 3000 r.p.m. to break up any agglomerates which may have been formed during the cooling process.

The stirring motor could be stopped suddenly, in about a second, by a brake. This was necessary when measuring sedimentation volumes since a gradual slowing down of the stirrer caused the beads to stick to the walls of the tube, particularly with those suspensions containing larger percentages of water. The tube was tapped lightly by hand until the layer of sedimented beads had reached a constant volume. The height of the sedimented volume was measured with a cathetometer using a scratch mark on the tube as a reference point. The tube had been previously calibrated with weighed quantities of water so that the sedimentation heights could be converted to volumes.

A large weight was placed on the scalepan *K* during these measurements to prevent the tube from rotating. When measuring relative yield values of suspensions, smaller weights were placed on the pan in order that, with the stirring motor in operation, the tube *A* rotated and the nylon thread wound round the tube until the scalepan was held at the top of its travel. The weights on the pan were then adjusted until they were just sufficient to pull the pan downwards and so rotate the tube when the stirring motor was suddenly stopped with the brake. This method gave more reproducible results than stopping the motor and then increasing the weights on the pan until the tube commenced rotating, since an indeterminate amount of settling occurred each time.

The method of plotting shearing stress against rate of shear and extrapolating to zero rate of shear was not used, since at high rates of shear the stirrer caused turbulence and cavitation in the suspension, while at low rates the beads settled and a two layer system was formed. Measurements of both sedimentation volume and yield value were made at various temperatures, increasing from −60° C. to room temperature.

RESULTS AND DISCUSSION

Fig. 3 shows the sedimentation volume per gram of beads for the various suspensions at different temperatures and Fig. 4 shows the corresponding relative yield values.

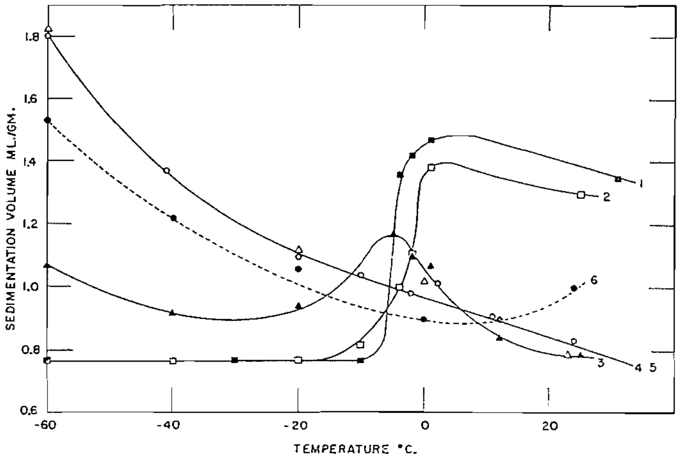

FIG. 3. Sedimentation volumes of suspensions. Curves 1–5 represent behavior of glass spheres in toluene with the following added percentages of water, 0.62, 0.47, 0.28, 0.10, and 0.0. Curve 6 shows behavior in dry pentane.

The suspensions containing 0.62% and 0.47% of water respectively show clearly that the effect due to the water disappears below 0° C. when the water surrounding the beads is frozen. This is in agreement with the hypothesis that the effect of water is due to its interfacial tension against toluene. When the water is frozen no 'necks' can be formed between adjacent particles and the increased viscosity no longer exists, the yield value being similar to that for dry beads at 20° C. The apparent small residual yield value in these two cases is possibly attributable to friction in the bearings. The small depression of the apparent freezing point of the water may be noted. This is not due to supercooling of the water as all measurements were made by cooling the suspension to −60° C. and then raising the temperature to successively

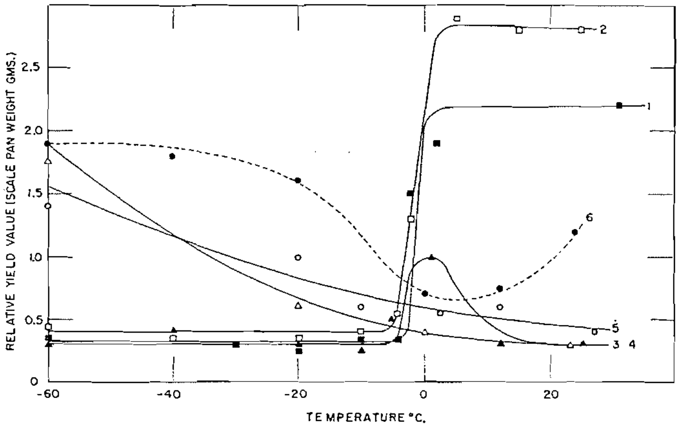

FIG. 4. Relative yield value of suspensions. Curves 1–5 represent behavior of glass spheres in toluene with the following added percentages of water, 0.62, 0.47, 0.28, 0.10, and 0.0. Curve 6 shows behavior in dry pentane.

higher values. The depression is probably due to slight solubility of alkalis present in the glass beads. Some earlier experiments were conducted with beads that had not been subjected to the prolonged extraction with hot distilled water. On cooling, these showed a continuous lowering of the sedimentation volume and yield value, with no sharp break at all. Values corresponding with those for water-free beads at room temperature were only obtained below −40° C.

The slight falling off of the yield value and sedimentation volume above 0° C. is probably the result of two factors. Increasing temperature will lower the interfacial tension between toluene and water and in addition some of the water will dissolve in the toluene, reducing the amount between the beads. This probably accounts for the behavior of the suspension containing 0.28% water which exhibits maximum yield value and sedimentation volume at −5° C., the values falling off rapidly above this temperature till at 25° C. a value similar to that for water-free beads is obtained. We may calculate the effect of solubility in the following manner. From the average diameter of the beads (43 μ) and their density 2.32 gm./ml. we obtain a value of 603 sq. cm./gm. for their geometrical surface area. Thompson *et al.* (8) measured the adsorption of carbon dioxide on similar glass beads. They found a B.E.T. surface area value close to the geometrical area for unetched beads but a value 21 times the geometrical area for beads which had been etched with water for three weeks. Using this figure and a value of 10.5 sq. A for the area of a water molecule (calculated from the liquid density) we calculate that 0.036% water by weight of the beads is required to form a monolayer. The water present in a suspension will be divided between the surface of the glass beads and solution in the toluene. If we assume that the toluene is saturated with water we can calculate from solubility tables (7) the amount remaining on the beads. The values for the suspension containing 0.28% water are 7.0 monolayers at 0° C. and 6.1 monolayers at 30° C.

McFarlane and Tabor (5) measured the adhesion of a small glass bead on a vertical glass plate, the adhesion being due to an adsorbed film of water. When approximately five monolayers had been adsorbed the adhesion increased rapidly from zero reaching the maximum value when about 20 monolayers had been adsorbed. Although the above calculation is only approximate it does show that the solution of water in the toluene changes the number of adsorbed monolayers significantly in the region where a rapid change in adhesion is occurring. Consequently we should expect the decrease in yield value and sedimentation volume which was experimentally observed.

In this connection we may note the paper by Kruyt and van Selms (4) in which the effect of varying percentages of water on the yield value of similar suspensions of glass beads is calculated. They arrived at a relation between the yield value and water content of a suspension by calculating the work required to separate a pair of glass beads with a known quantity of water in the 'neck' joining them. However, the yield value of a suspension would appear to have the dimensions of force rather than those of work. Once the shearing stress has reached the critical value the suspension will yield. Hence the adhesion between the beads is the important factor, as discussed in this work. The agreement between Kruyt and van Selms' calculation and their experimental results may be due to the fact that the calculation contained an adjustable parameter (the number of other beads which touch each bead). They have also taken no account of the fact that the real surface area of their beads may be considerably greater than the geometric area. Using values given in the paper by McFarlane and Tabor, a plot of adhesion against the number of monolayers gives a curve of similar shape to the yield value vs. percentage water graphs given by Kruyt and van Selms. An alternative explanation for their results, making reasonable assumptions about the real surface area of their glass spheres, is therefore possible.

The suspensions containing no water and 0.1% water showed, as expected, no break at 0° C. but exhibited an unexpected steady increase in the yield value and sedimentation volume as the temperature was lowered to −60° C. This indicates an increasing attractive force between the beads at low temperatures. It is suggested that this may be due to the adsorption of toluene molecules on the glass surface. These molecules will have fewer degrees of freedom than those in the liquid and their arrangement will tend towards that of the solid state. When two beads touch, local freezing at the point of contact may occur. The force required to separate the beads will increase at lower temperatures as the area of local freezing increases.

The presence of water already adsorbed on the glass surface will prevent the subsequent adsorption of toluene, so this process will not occur with the suspensions containing considerable amounts of water. However, it is difficult to understand why the suspension containing 0.1% of water has similar properties to the water-free suspension. On the basis of our previous calculation there will be nearly three monolayers of water on the surface of the glass beads and we should not expect toluene to be adsorbed on such a substrate. The anomalous increase of the sedimentation volume and yield value was also observed with a water-free suspension in pentane (dotted lines in Figs. 3 and 4). Thus the effect is not due to any special properties of the benzene ring and its cause remains uncertain.

ACKNOWLEDGMENT

Preliminary experiments related to this work were carried out by B. A. Dunell. To him and to P. G. Howe, with whom many helpful discussions were held, grateful acknowledgment is made.

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THE PRODUCTION OF Na^{22} BY A (H^3, n) REACTION IN A NUCLEAR REACTOR[1]

BY L. G. COOK AND K. D. SHAFER

ABSTRACT

The positron emitting Na^{22} of 2.6 year half-life has been prepared in a nuclear reactor by the double reaction $Li^6(n, \alpha)H^3$, $Ne^{20}(H^3, n)Na^{22}$. The over-all yield was 2.3×10^{-7} atoms of Na^{22} per atom of tritium formed. Eleven grams of lithium as aluminum alloy turnings in a neon atmosphere at 200 p.s.i. was irradiated for 175 days in a neutron flux of about 4×10^{12} n./cm.²/sec. About 380 μc. of Na^{22} was obtained in a sodium extract having a specific activity of 10 mc. Na^{22}/gm. of Na^{23}. A specific activity in the curie/gm. level would be expected from a longer irradiation in the highest flux (6×10^{13} n./cm.²/sec.) in the NRX reactor. The separation and purification of the sodium proved practicable by paper chromatography or ion exchange; the analyses for trace Li and Na^{23} were carried out by radioactivation.

INTRODUCTION

Neutron deficient positron emitting (or *K*-capture) nuclides are usually produced by charged particle reactions in accelerators followed by chemical separation of the product element. In nuclear reactors, however, the only general method of preparation is by the $(n, 2n)$ reaction. This reaction is not too satisfactory. The $(n, 2n)$ effective cross sections are low, thus preventing the attainment of high specific activity; also the product element is the same as the irradiated element, preventing the use of chemical separation to attain high specific activity.

For example, the reaction $Na^{23}(n, 2n)Na^{22}$ has a threshold of 12.2 Mev. (9) and a maximum total neutron cross section of 900 mbarns (2). Since the fraction of neutrons in a reactor with energies >12 Mev. is $\sim 10^{-4}$ (8), in a reactor position with thermal neutron flux of 4×10^{12} n./cm.²/sec., a 175 day irradiation would be expected to produce a specific activity of only $\sim 10^{-5}$ curies/gm.

However, by utilizing a double reaction, an improvement can sometimes be made. For example, if one mixes neon gas with lithium in a suitable way, and irradiates the mixture with thermal neutrons, the Li^6 captures neutrons with 930 barns (1) cross section, and provides a steady supply of 2.75 Mev. tritons (5) which in turn produce Na^{22} by a (H^3, n) reaction on Ne^{20}. (F^{18} and Cl^{34} have also been made by this general method (6).)

The preparation of the carrier free Na^{22} involves in principle a chemical separation of trace sodium from macro amounts of neon, lithium, and aluminum. In practice, the specific activity attainable depends on the neutron flux, the irradiation time, unavoidable traces of Na^{23} contamination, and, of course, the degree of dispersion of the lithium in the neon.

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Contribution from the Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 87.

EXPERIMENTAL

(1) *Irradiation Technique*

A 4% Li (by weight) in "super pure" aluminum alloy was prepared and fine wool-like turnings turned off on a lathe. Two hundred and seventy-six grams of these turnings were packed loosely in aluminum cartridges 1 in. diam. × 4 in. long, which were then slipped into an aluminum pressure tube. The pressure tube was installed in a position in the NRX reactor where the nominal neutron flux was 4×10^{12} n./cm.^{2}/sec., and filled with neon at 200 p.s.i.

After 175 reactor operating days the tube was taken out and the aluminum–lithium alloy wool removed to the laboratory for processing.

(2) *Extraction of Na^{22}*

The lithium–aluminum alloy wool was rinsed four times with distilled water, using 100 cc., 150 cc., 250 cc., and 900 cc. respectively. Twenty cubic centimeters of nitric acid were added to each washing, and the solutions boiled until the suspended material dissolved and the solutions became clear.

The hot acidified solution was then neutralized with aqueous ammonium carbonate to decided cloudiness, then cleared with ammonium oxalate solution. This neutralization and clearing was repeated four times at the boiling point, then finally the solution was made slightly basic with ammonium carbonate. The resultant aluminum oxalate – carbonate precipitate was compact, filtered easily, and in previous tests using Na^{24} tracer had been shown not to carry down trace sodium.

The filtrate contained the Na^{22}, lithium, and any trace accumulation of Na^{23}.

(3) *Purification of Na^{22} by Ion Exchange*

The Na^{22} was to be separated from the substantial amount of Li present, as well as from any other impurities. An ion exchange separation of Na, K, Rb, Cs, on Dowex 50 resin has been described (4). The same technique was found to give a clean separation of the lithium from the sodium. The lithium appeared as a peak between the 9th and 14th column volumes; the Na^{22} peak lay between the 16.5 and 23rd column volumes. To identify the Na^{22} positively, a γ–γ coincidence crystal counter was used to identify the positron annihilation radiation, and the positron energy was checked by determining the absorption curve in aluminum.

(4) *Purification of Na^{22} by Paper Chromatography (Alternative Process)*

A separation of sodium and lithium by paper chromatography has been described (3). The separation was demonstrated by detecting two chloride bands in the paper chromatograph, and not by direct analysis for sodium and lithium.

In the present work, direct analysis for sodium and lithium was used. The sodium was detected by the Na^{22} activity; the lithium was detected using the 0.88 sec. Li^8 activity, produced in a neutron reactor. The samples to be analyzed were placed in iron capsules, sent down a tube into the reactor, then blown through a pneumatic tube directly into a counting position, where the intensity and decay of the 0.88 sec. activity could be measured directly. In this way 10^{-7} gm. of Li can be detected.

Using absolute methyl alcohol as elutant, and placing the alkali salt on the paper as chloride, complete separation was obtained in three and one half hours. The lithium band extended from the 6th to the 10th inch, the solvent front being at 12 in. The sodium band extended from zero to the 5th inch, with its peak at 1.5 in. A 33 hr. creep period placed the sodium peak at 2.0 in., with no greater spreading than before. The lithium was not detectable until the 10th in. and was concentrated at the tip of the paper (12th inch).

(5) *Analysis of Product for Na^{22}/Na^{23} Ratio*

A sample of the unextracted rinse solution was evaporated and irradiated for 10 hr. in the NRX reactor to produce the reaction Na^{23} $(n, \gamma)Na^{24}$. The sample was then extracted and purified by the techniques described and the decay of the Na^{24} activity and the residual Na^{22} activity were observed. The Na^{22}/Na^{23} ratio in the sample was found to be 10 mc. Na^{22}/gm. Na^{23}.

(6) *Determination of Yield*

The over-all yield of Na^{22} was 14×10^6 disintegrations/sec. or $\sim$380 μc., and was obtained in the first three rinses of the alloy turnings. The last rinse had a negligible amount of Na^{22} in it. This confirmed the expectation that the Na^{22} formed in the gas phase would settle on nearby surfaces, and be easily washed off with water.

A straightforward calculation of the number of neutrons consumed in 11.0 gm. of Li in 175 days at a flux of 4×10^{12} n./cm.^{2}/sec. gives a neutron consumption of 4.1×10^{21} neutrons (making no allowance for "blackness" to neutrons; the turnings were spread out over a length of four feet). Thus the yield was 3.5×10^{-15} disintegrations/sec./atom of tritium formed, or 2.3×10^{-7} atoms of Na^{22}/atom of tritium formed.

A sample of sodium chloride which had been irradiated in the same nominal flux (4×10^{12} n./cm.^{2}/sec.) for five years was purified by the ion exchange procedure, and the Na^{22} content of the Na^{23} determined. A specific activity of 1.6×10^{-5} curies Na^{22}/gm. Na^{23} was found, confirming the predicted low yield of the $(n, 2n)$ reaction.

DISCUSSION

The yield of the $Na^{23}(n, 2n)Na^{22}$ reaction in a thermal neutron reactor has been determined. It has been found that the $Li^6(n, \alpha)H^3$, $Ne^{20}(H^3,n)Na^{22}$ reaction will produce Na^{22} with specific activity 10^4 times higher in a neutron flux of 4×10^{12} n./cm.^{2}/sec.

It would be expected that the use of 10 times higher fluxes (available in the interior of the NRX reactor), longer irradiation periods, and a program to reduce sodium pickup could be made to increase the specific activity to the curie/gm. level.

CONCLUSION

The double reaction $Li^6(n, \alpha)H^3$, $Ne^{20}(H^3, n)Na^{22}$ makes possible the preparation of Na^{22} in present thermal neutron reactors with specific activity of the order of one curie Na^{22}/gm. Na^{23}.

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PVT MEASUREMENTS IN THE CRITICAL REGION OF XENON[1]

By H. W. Habgood[2] and W. G. Schneider

ABSTRACT

Extensive PVT measurements of xenon extending from 1.8° above the critical temperature to the critical temperature, and in a few cases to 4° below the critical temperature, have been carried out at densities ranging from somewhat above the critical density to well below. In order to make the corrections for hydrostatic head small and easily calculable, a bomb having a height of only 1.0 cm. was used in the present measurements. The previously reported value for the critical temperature 16.590° is confirmed. The critical density is estimated to be 1.099 ± 0.002 gm./ml. compared with 1.105 gm./ml. found previously. The critical pressure is found to be 57.636 ± 0.005 atm.

The isotherms at temperatures above the temperatures of meniscus disappearance do not appear to have any flat portions. However, the critical isotherm is considerably flatter and broader over a range of densities than that corresponding to a van der Waals equation, and at the critical point the third and fourth derivatives of pressure with respect to volume appear to be zero.

INTRODUCTION

In order to obtain an improved understanding of critical phenomena a program has been under way in this laboratory to measure with the highest possible precision a number of properties in the critical region of a single substance. Xenon, being monatomic, and having a critical temperature conveniently close to room temperature, was chosen for this work. Previous publications have already described the liquid–vapor coexistence curve (15), density distributions in a vertical tube (16), and the velocity and absorption of ultra sound (2). We now wish to report measurements of the compressibility of xenon in the critical region. These measurements are used in the succeeding paper (5) to calculate thermodynamic properties in this region.

A major difficulty in making accurate measurements near the critical point results from the very high compressibility of the system which causes a partial compression of the medium under its own weight.* Accordingly the density inside the experimental bomb changes considerably with height, while it is only the average density which is directly measured. Also, the pressure is measured at a particular level in the system for which the density is not known; correction to any other level requires a knowledge of the density distribution in the fluid head. These effects were first discussed by Gouy in 1892 (3) but appear to have been ignored by subsequent workers. Their significance in actual measurements was first shown in the determinations by MacCormack and Schneider (6) of the isotherms of sulphur hexafluoride where, using a relatively tall bomb, the corrections for fluid head were several times larger than the uncertainties in the pressure measurements and significantly affected the shapes of the isotherms. The effect was further demonstrated in the

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[2] *National Research Laboratories Postdoctorate Fellow.*

* *This question has been discussed at greater length in a recent symposium (13).*

measurements of Weinberger and Schneider (15) on the liquid–vapor coexistence temperatures of xenon where observations in a tall bomb yielded a temperature–density coexistence curve with a flat top, while those in a similar bomb mounted horizontally and only 14 mm. high gave a round-topped coexistence curve and hence pointed to the existence of a unique critical density as postulated originally in classical theory. Recently Whiteway and Mason (18) have completely confirmed these observations.

Since the prediction of a flat-topped coexistence curve and of a region of horizontal isotherms above the temperature of meniscus disappearance was one of the main features of the theory of Mayer and Harrison (8), it is of considerable importance that experimental observations should be properly corrected for the effects of gravity. It was at first not clear whether the flat top observed with xenon in the tall bomb could be explained entirely by the gravitational effect. However, it was later shown (14), using the measured compressibilities given in the present paper, that the calculated density range of the flat top agreed closely with the observations.

In PVT measurements the necessary corrections for the effect of the fluid head may be calculated by successive approximations from the observed isotherms either to give the pressure at the level where the local density equals the average density of the filling, or to give the local density at the level where the pressure was measured. Our present measurements have been carried out using a horizontal glass bomb 10 mm. in diameter (i.e. height) in order to make these corrections very small and easily calculable. However, to illustrate the nature and extent of these gravitational effects we repeated measurements of the critical isotherm in a bomb 25 cm. tall. The details of this work have been reported elsewhere (4). The observations were in complete agreement with the expected pressure and density variations resulting from the gravitational field as calculated for different fillings on the basis of the isotherm obtained from the horizontal bomb. It was apparent, however, that calculation in the opposite direction, i.e. to derive the "true" isotherm from measurements in a tall bomb, would require several steps of approximation and the resulting uncertainty in the corrected isotherm would be much greater than the experimental scatter of the original measurements.

The geometry of the apparatus used by MacCormack and Schneider in the measurements on sulphur hexafluoride was such that calculation of the corrections for fluid head was particularly difficult and some rather rough approximations were used. The isotherms thus corrected did not show any horizontal portions in the immediate supercritical region. Later Wentorf and Boyd (17) using a somewhat shorter bomb* reported measurements also on sulphur hexafluoride which yielded horizontal portions in several isotherms in this region, the most impressive experimental evidence so far in favor of the Mayer–Harrison theory. They supported their results by applying "more realistic corrections" to the measurements of MacCormack and Schneider to

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* *Although most of the bomb volume was confined to a height of approximately 5.7 cm. the stirring mechanism fixed to the top of the bomb provided an additional volume and an additional hydrostatic head making the total effective height close to 19 cm. It is not clear from the report of Wentorf and Boyd whether their corrections for hydrostatic head took account of this.*

obtain similar horizontal isotherms. However, these new corrections merely involved correcting the observed pressure to the level at which the meniscus disappeared, and the xenon measurements referred to above (4) showed quite clearly that this procedure automatically gives a horizontal isotherm. Consequently the measurements of MacCormack and Schneider cannot be said to give definite confirmation to the "derby hat" region of horizontal isotherms reported by Wentorf and Boyd. For carbon dioxide, the measurements of Wentorf and Boyd (17) as well as the earlier measurements of Michels *et al.* (9) do not support any appreciable region of horizontal isotherms above the temperature of meniscus disappearance. In the case of xenon the measurements reported in the present paper likewise do not suggest any such "derby hat" region.

Previously published PVT measurements on xenon include isotherms from 16.65° C. (given as the critical temperature) to 300° C. over the density range 1–10 moles/liter reported by Beattie, Barriault, and Brierley (1), and vapor pressure measurements up to 0.56° below the critical temperature reported by Michels and Wassenaar (10). Palmer (11) using a schlieren technique has measured approximate density gradients in xenon near the critical point and from these has estimated $P-V$ isotherms.

METHOD

The method of measurement was closely similar to that used by MacCormack and Schneider (6). The bomb assembly is shown schematically in Fig. 1. The design of the bomb and stirrer has been previously described (15).

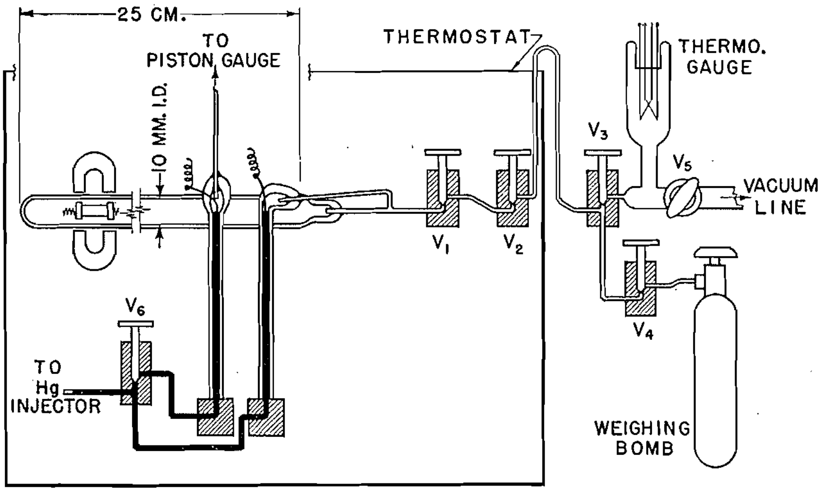

FIG. 1. Schematic diagram of the bomb assembly for PVT measurements in the critical region.

The glass capillary forming the xenon side of the mercury U-tube was bent at right angles just above the tungsten contact wire in order that the connecting tube to the bomb could be kept short and as nearly as possible at the same height as the bomb itself. The maximum possible head of xenon at any point in the system was 16 mm. The pressure was measured at a level 1 mm. above the center of the bomb, this being the position of the contact wire in the mercury U-tube.

The complete assembly inside the thermostat was mounted as a unit which could be rotated through 45° about a pivot point so that a dewar flask could be raised about the closed end of the bomb to condense in a charge of xenon from the brass weighing bomb. The thermostat bath itself, which has been previously described (15), was mounted on the platform of a hydraulic lift operated by compressed air. When the bomb was being charged, the bath with its stirrers, etc., was lowered and could be quickly raised as soon as the bomb had started to warm up.

The contents of the bomb were stirred before each pressure measurement but the stirrer was turned off during the actual measurement. Pressures measured with continuous stirring were 0.002–0.003 atm. higher than without, probably owing to a slight heating produced by the vigorous stirring. It was found that the slight temperature fluctuations in the heating–cooling cycle of the bath were rapidly transmitted to the bomb yielding noticeable pressure fluctuations lagging by about 30 sec. However, near the critical point it was necessary to wait one hour or longer to be sure that true thermal equilibrium had been attained.

The xenon used in the measurements was part of the same sample used by Weinberger and Schneider supplemented by additional material of equivalent purity obtained from the Linde Air Products. Analysis with the mass spectrometer failed to disclose any detectable impurities. The material was roughly fractionated from time to time between runs.

Errors

The mean temperature of the bath could be controlled to better than ±0.001° C. for short periods and within ±0.002° C. overnight. The temperature oscillations during the heating cycle ripple were about ±0.001°. The sensitivity of the temperature measurements using a resistance thermometer and a Mueller bridge was about 0.0005° C. and the absolute accuracy is estimated to be ±0.002° C.

The sensitivity of the piston gauge was ±0.0003 atm. at 50 atm. and the reproducibility of the pressure measurements at times approached this—indicating a somewhat better degree of temperature control than ±0.001° which would correspond to ±0.001 atm. The absolute accuracy of the pressure measurements, which depends mainly on the calibration of the piston gauge, is estimated to be around ±0.005 atm.

The absolute accuracy of the density measurements is estimated to be ±0.2%, although relative accuracies are much greater.

On some occasions, it was found on repeating a series of measurements that the pressure values were higher or lower by an almost uniform amount of up to 0.002 atm. This is now believed to be due to an uncertainty in the contacts in the U-tube, partly the result of contact not always being established at the extreme tip of the tungsten wire and partly due to a change in the curvature of the mercury surface. This contributes a somewhat further uncertainty to the pressure readings but has only a slight effect on the $(\partial P/\partial T)$ values which are used in the following paper.

MEASUREMENTS

The measurements were carried out in two series, (*a*) isotherms and (*b*) isochores. The first series was limited to temperatures in the immediate neighborhood of the critical temperature where it was desired to determine the exact shape of the isotherms as accurately as possible. Each isotherm included measurements of pressure at from 10 to 16 densities achieved by successive expansions from the bomb.

In series (*b*), isochores were determined at three densities above the critical density, at approximately the critical density, 8.4 moles/liter, and at 11 densities below, down to 2.5 moles/liter. Except for the three lowest densities, each covered the temperature interval from the two-phase region to 1.8° above the critical temperature and at the lowest densities measurements were carried to around 2° below the critical temperature, still in the gas region. A sufficient number of measurements were made in the two-phase region to establish the vapor pressure curve to 4° below the critical temperature. A major purpose of this series of measurements was to determine as accurately as possible the slopes of the isochores $(\partial P/\partial T)$ for use in calculating thermodynamic properties, and the experimental densities were chosen with this in view. The weight of the xenon was checked after each isochore to be sure that no leak had occurred which would tend to cause a steady decrease in pressure. Towards the end of the work a small leak did develop, amounting to around 50 mgm. out of a 15–20 gm. charge over the three or four days required for a run. This significantly affected the readings at the three lowest densities and corrections were applied, based on the slopes of the isotherms and assuming a steady rate of leakage.

The measurements are given in Tables I and II. The isochore measurements presented in Table II are given in the order in which they were obtained, determinations having been made with both increasing and decreasing temperatures, and successive measurements were made at the same temperature after the bomb had been allowed to stand overnight.

Fig. 2 is a small-scale plot showing most of the region covered by this work with the data of Table II plotted as isotherms. Individual points have not been shown since on this scale the scatter from the lines cannot be seen. The densities at which measurements were made are indicated by the arrows near the bottom of the figure.

In Fig. 3 the immediate critical region is shown on a larger scale using the data of Table I together with the isotherm at 16.690° from Fig. 2.

The results of Beattie, Barriault, and Brierley (1) at 16.65° are shown in Fig. 2. They reported that the xenon used in their investigation contained 0.14% krypton and this might account for their pressure being somewhat higher, agreeing almost with our 16.79° isotherm.

TABLE I

DENSITY–PRESSURE ISOTHERMS OF XENON NEAR THE CRITICAL POINT

Italicized values refer to two-phase region

16.550° C.		16.585° C.		15.590° C.	
Density, gm./ml.	Pressure, atm.	Density, gm./ml.	Pressure, atm.	Density, gm./ml.	Pressure, atm.
1.28383	57.6360	1.30426	57.7134	1.30705	57.7202
1.25847	57.6114	1.27870	57.6746	1.25890	57.6590
1.23352	57.5991	1.25268	57.6510	1.23305	57.6476
1.20875	57.5946	1.22686	57.6413		57.6505
1.18354	*57.5895*	1.20046	57.6332	1.20744	57.6398
1.15828	*57.5878*	1.17323	57.6318		57.6402
1.13320	*57.5870*	1.14733[a]	57.6319	1.18121	57.6370
1.10811	*57.5877*	*1.12343*	*57.6305*	1.15681	57.6358
1.08396	*57.5899*	*1.09576*	*57.6302*	1.13010	57.6360
1.05936	*57.5885*	1.06940[b]	57.6307		57.6367
1.03593	*57.5893*	1.04316	57.6298	1.10495	57.6358
1.01275	57.5871	1.01754	57.6273	1.07965	57.6361
0.98978	57.5806	0.99172	57.6212	1.05548	57.6353
0.96687	57.5742	0.96659	57.6120	1.03114	57.6347
0.94494	57.5611	0.94157	57.5973		57.6326
		0.91591	57.5744	1.00764	57.6308
		0.89197	57.5343	0.98294	57.6255
				0.96091	57.6131
				0.91503	57.5753

16.590° C.		16.600° C.		16.620° C.	
Density, gm./ml.	Pressure, atm.	Density, gm./ml.	Pressure, atm.	Density, gm./ml.	Pressure, atm.
1.30171	57.7118	1.29780	57.7195	1.27140	57.7077
1.27556	57.6731	1.27366	57.6849	1.24667	57.6899
1.24892	57.6522	1.24912	57.6668	1.22215	57.6788
	57.6554	1.22412	57.6587	1.19793	57.6735
1.22181	57.6436	1.20006	57.6534	1.17260	57.6721
1.19470	57.6380	1.17592	57.6484	1.14784	57.6680
1.16746	57.6361	1.15091	57.6483	1.12321	57.6658
1.13958	57.6356	1.12685	57.6475	1.09844	57.6655
	57.6365	1.10289	57.6473	1.07441	57.6633
1.11185	57.6358	1.07818	57.6466	1.05009	57.6643
1.08557	57.6354	1.05437	57.6469	1.02694	57.6624
1.05939	57.6349	1.03150	57.6446	1.00470	57.6582
1.03310	57.6331	1.00903	57.6423	0.98257	57.6496
1.00750	57.6311	0.98674	57.6384	0.95964	57.6397
	57.6318	0.96522	57.6260	0.93619	57.6234
0.98199	57.6248	0.92303	57.5886	0.91686	57.5984
0.95589	57.6138			0.87630	57.5248

[a] *Trace of gas.* [b] *Trace of liquid.*

TABLE II

TEMPERATURE–PRESSURE ISOCHORES OF XENON
Italicized values refer to two-phase region

1.27167 gm./ml. 9.6852 moles/l.		1.17819 gm./ml. 8.9733 moles/l.		1.14341 gm./ml. 8.7084 moles/l.	
Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.
16.378[a]	57.3853	*13.690*	*54.3397*	*16.190*	*57.1689*
16.490	57.5306	*14.290*	*55.0038*	*16.490*	*57.5211*
16.590	57.6646	*14.790*	*55.5674*	16.590	57.6374
16.690	57.7984	*15.290*	*56.1325*	16.690	57.7565 57.7573
16.790	57.9329	*15.790*	*56.7055*	16.790	57.8761
16.890	58.0673	*16.190*	*57.1684*	16.890	57.9967
16.990	58.2050	*16.390*	*57.4023*	16.990	58.1171
17.190	58.4717	16.490	*57.5195* *57.5201*	17.390	58.6013
17.390	58.7414	16.563[a]	. .	18.390	59.8195
17.590	59.0164	16.590	57.6364	17.390	58.6016
17.790	59.2889	16.690	57.7575	16.990	58.1159
17.990	59.5618	16.790	57.8814	16.590	57.6365
17.590	59.0153	16.990	58.1289	*16.190*	*57.1681*
17.190	58.4713	17.190	58.3774		
16.790	57.9342	17.590	58.8753		
16.390	57.4036	17.990	59.3777 59.3773		
		18.390	59.8816		
		16.990	58.1295		
		16.790	57.8822		
		16.590	57.6376		
		16.390	*57.4036*		

1.09947 gm./ml. 8.3738 moles/l.		1.08216 gm./ml. 8.2451 moles/l.		1.07904 gm./ml. 8.2205 moles/l.	
Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.
16.190	*57.1697*	*12.721*	*53.2805*	*15.990*	*56.9362*
16.390	*57.4032*	*14.390*	*55.1181*	*16.190*	*57.1675*
16.590[a]	57.6364	*15.385*	*56.2430*	*16.390*	*57.4026*
16.690	57.7540	*15.890*	*56.8256*	*16.490*	*57.5203* *57.5210*
16.790	57.8722	*16.390*	*57.4042*	16.590	57.6369
16.990	58.1045	16.590	57.6382 57.6390	16.690	57.7542
17.190	58.3411	16.690	57.7542	16.790	57.8701
17.590	58.8109	16.790	57.8704	16.990	58.1030 58.1067
17.990	59.2815	16.990	58.1034	17.190	58.3366
18.390	59.7523	17.190	58.3357 58.3363	17.390	58.5651
17.590	58.8127	17.590	58.7989	17.790	59.0340
16.990	58.1057	17.990	59.2640	17.990	59.2634
16.790	57.8713	18.490	59.8437	18.190	59.4945
16.590[a]	57.6359	*16.190*	*57.1704*		
16.490	*57.5206*	*16.390*	*57.4034*		
16.390	*57.4048*	16.590	57.6365 57.6370		
		16.690	57.7547		
		16.790	57.8720		

[a] *Maximum temperature of liquid-vapor coexistence.*

TABLE II–(*Continued*)

1.06706 gm./ml. 8.1269 moles/l.		1.05461 gm./ml. 8.0321 moles/l.		1.00835 gm./ml. 7.6798 moles/l.	
Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.
16.290	*57.2845*	*14.890*	*55.6799*	*15.990*	*56.9366*
16.490	*57.5170*	*15.990*	*56.9407*	*16.190*	*57.1688*
	57.5188	*16.390*	*57.4021*	*16.390*	*57.4035*
16.590	57.6349	16.590	57.6368	16.506[a]	57.5370
16.690	57.7523	16.690	57.7525	16.690	57.7435
16.790	57.8674	16.790	57.8677	16.790	57.8519
16.990	58.0956	16.990	58.0961	16.990	58.0754
17.190	58.3280		58.0983		58.0745
17.590	58.7870	17.190	58.3279	17.390	58.5138
17.990	59.2474	17.590	58.7792	17.590	58.7326
18.390	59.7031	18.190	59.4606	17.790	58.9519
16.990	58.0975	18.390	59.6868	17.990	59.1677
16.790	57.8675	17.990	59.2333		59.1681
16.690	57.7517	16.990	58.0975	18.390	59.6056
16.590	57.6347	16.790	57.8700	17.990	59.1676
16.390	*57.4028*	16.690	57.7551	18.390	59.6047
		16.590	57.6408	17.190	58.2964
				17.390	58.5145
				16.790	57.8538
				16.690	57.7442
				16.590	57.6325
				16.513[a]	57.5449

0.96356 gm./ml. 7.3386 moles/l.		0.96048 gm./ml. 7.3151 moles/l.		0.86446 gm./ml. 6.5839 moles/l.	
Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.
15.390	*56.2438*	*15.390*	*56.2480*	*15.190*	*56.0114*
15.790	*56.7018*	16.390[a]	57.4001	*15.390*	*56.2416*
15.990	*56.9351*	16.590	57.6178	*15.590*	*56.4704*
16.190	*57.1660*	16.790	57.8297	*15.690*	*56.5838*
16.372	*57.3788*	16.990	58.0395	15.740[a]	. .
16.506	57.5271	17.190	58.2499	15.990	56.9003
16.590	57.6172	17.690	58.7739	16.290	57.1836
16.690	57.7235	18.390	59.4990	16.490	57.3715
16.790	57.8359	16.890	57.9358	16.590	57.4682
16.990	58.0458	16.690	57.7224	16.690	57.5594
17.190	58.2579	16.590	57.6176	16.790	57.6565
17.590	58.6760	16.490	57.5119	16.990	57.8405
17.990	59.0929	16.390[a]	57.3997	17.390	58.2150
18.390	59.5085	*16.290*	*57.2861*	17.890	58.6777
18.790	59.9269			18.390	59.1406
19.190	60.3410			16.790	57.6524
16.790	57.8318			16.090	56.9920
16.690	57.7256			15.890	56.8008
16.590	57.6192				56.7993
16.490	57.5122			15.790	56.6943
16.590	57.6193			*15.690*	*56.5858*

[a] *Maximum temperature of liquid-vapor coexistence.*

TABLE II—(*Concluded*)

0.74938 gm./ml. 5.7074 moles/l.		0.61835 gm./ml. 4.7094 moles/l.		0.33003 gm./ml. 2.5145 moles/l.	
Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.	Temp., ° C.	Pressure, atm.
14.790	55.3803	12.755	52.4665	14.046	40.7519
15.290	55.7823	14.690	53.6729	14.990	41.0089
15.790	56.1804		53.6738		41.0078
16.190	56.4945	15.373	54.0964	15.990	41.2805
16.490	56.7310	15.890	54.4101	16.990	41.5530
16.690	56.8864	16.790	54.9645		41.5550
16.990	57.1219	17.290	55.2661	17.990	41.8273
17.390	57.4343		55.2639	14.990	41.0074
17.790	57.7447	17.890	55.6289		
18.390	58.2099	18.390	55.9317		
16.190	56.5003	16.790	54.9564		
15.990	56.3434	16.390	54.7136		

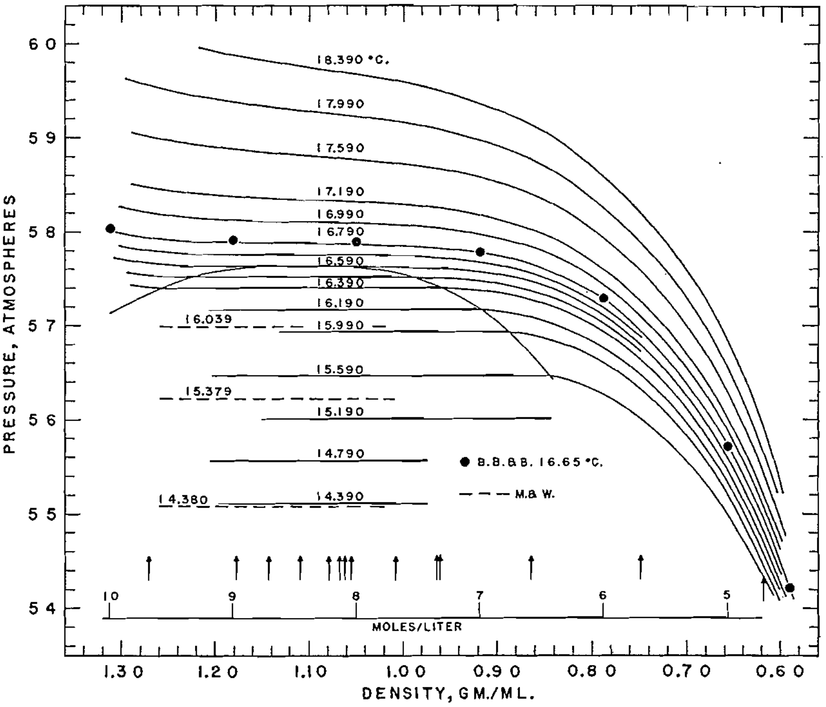

FIG. 2. Pressure–density isotherms of xenon plotted from isochore measurements. Densities at which measurements were made are indicated by arrows at the bottom of the figure.

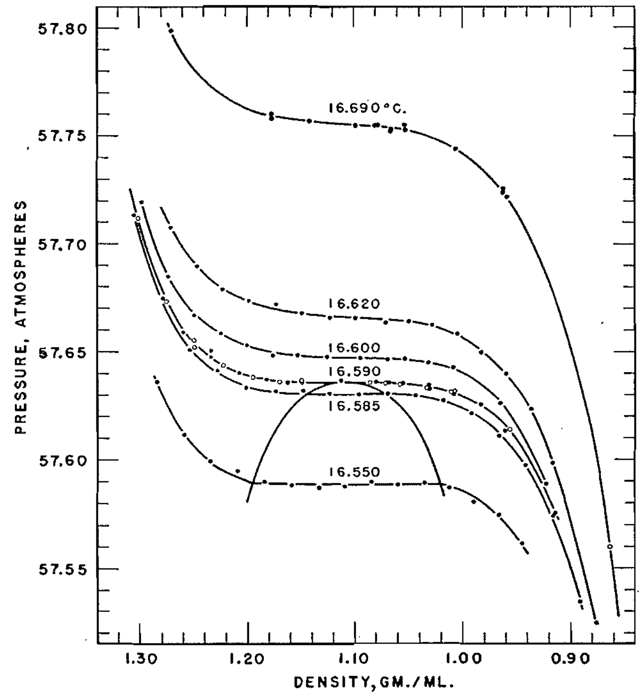

FIG. 3. Pressure–density isotherms of xenon in the immediate neighborhood of the critical point.

Vapor Pressure

Our pressure measurements in the two-phase region may be compared with the vapor pressure measurements of Michels and Wassenaar (10). Four of their values between 12.86° C. and 16.04° may be compared with a smoothed curve through our values and this is shown in Table III. The difference appears to increase more or less regularly with decreasing temperature but since we have only one measurement near the lowest value, it is difficult to tell whether this represents a significant trend.

TABLE III
VAPOR PRESSURE MEASUREMENTS
COMPARISON WITH MICHELS AND WASSENAAR (9)

Temp., ° C.	Pressure, M. and W., atm.	Pressure, N.R.C. (smoothed), atm.	Δ M. and W. − N.R.C.
16.039	56.9917	56.9915	+0.0002
15.379	56.2289	56.2324	−0.0035
14.380	55.0868	55.1036	−0.0168
12.863	53.3871	53.4346	−0.0475

Coexistence Curve

The liquid–vapor coexistence curve shown in Figs. 2 and 3 is that determined by Weinberger and Schneider (15). Our measurements were made less precisely than theirs which bracketed the coexistence temperatures within one or two thousandths of a degree by repeated heating and cooling. Within about 0.04° of the critical temperature we agree approximately with their curve but beyond that on the low density side our observations correspond to a shift of the coexistence curve by about 1% towards higher density. Not enough measurements were made on the high density side to decide whether this corresponded to a shifting of the whole curve to higher densities or just a slight narrowing of the two-phase region.

Corrections for Nonuniform Density

The isotherms at 16.590°, 16.600°, and 16.620° in Fig. 3 have been corrected for the effect of the density gradient set up across the bomb due to gravitational effects. This results in a difference between the average filling density and the density at the level of pressure measurement. Using the method described previously (15), a curve of density *vs.* height was calculated from the uncorrected isotherm (drawn from the data in Table I). The bomb was then imagined to be divided into horizontal layers each 1 mm. thick. Assuming a given density at the level where the pressure was measured, 1 mm. above the center, the corresponding densities in the various layers were obtained from the curve and the approximate average density of the bomb contents calculated. The differences between these average densities and the densities 1 mm. above the center represented the corrections to be applied to the observed average densities. These corrections amounted to a maximum of 0.03 gm./ml. and resulted in a shifting of the experimental points away from the flattest part of the isotherms making the isotherms somewhat flatter still. In terms of pressure the maximum corrections, using the horizontal bomb, are only 0.0002 atm. and so may be neglected for most of the measurements. They would probably be significant for the isotherm at 16.585° but the calculations were a little more uncertain here and were not carried out.

DISCUSSION

Critical Temperature

We have taken the critical temperature to be 16.590° as found by Weinberger and Schneider. From our observations we believe that this represents within ±(0.002–0.003°) the temperature of meniscus disappearance. When a critical filling of xenon at this temperature is allowed to settle after it has been thoroughly stirred, it separates after about one hour into two layers of rather light opalescence separated by a band of dark brown opalescence. After 12–24 hr. this band has become very dark and narrowed to about 1 mm. in thickness. It is not possible, however, to see a sharp surface. Lowering the temperature 0.002° to 0.003° produces a definite dividing line in the middle of the opalescent band. During the measurements at 16.585° an unmistakable surface was present and the observed density range of the two-phase region was in good agreement with the coexistence curve of Weinberger and Schneider. At 16.600° and even at 16.620° there was slow stratification on standing, with a middle layer of heavier opalescence which, however, did not become so concentrated as at 16.590°.

The critical temperature may also be estimated as the highest temperature at which $(\partial P/\partial \rho)_T = 0$ by plotting the minimum slopes of the P–ρ isotherms against temperature. The slopes were determined from large-scale plots and the minimum values are shown in Fig. 4. The three isotherms nearest the critical temperature can be drawn more accurately than the others which were taken from the isochore measurements and hence only included three densities above the critical density. However, the graph gives no reason for believing that the maximum temperature of zero slope differs from the temperature of meniscus disappearance.

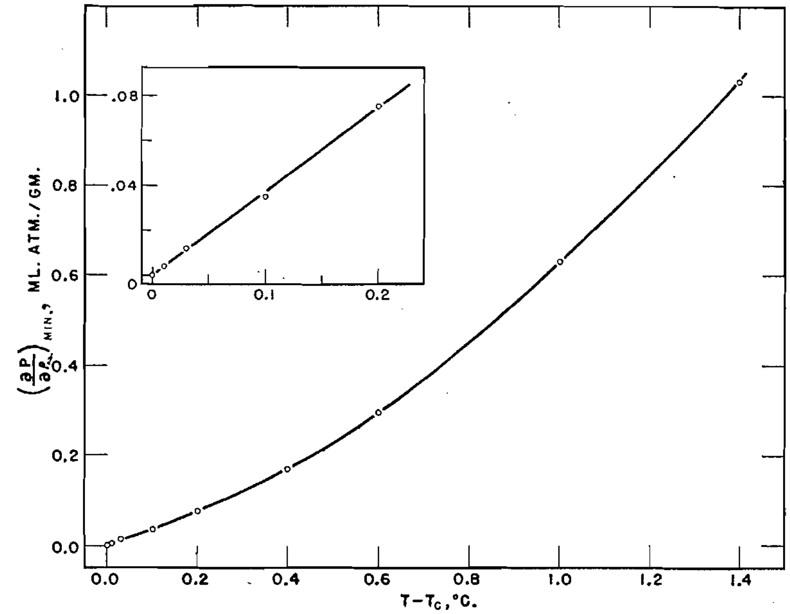

FIG. 4. Plot of the minimum slopes of the isotherms at and above the critical temperature. The immediate critical region is shown in the insert.

For carbon dioxide Michels *et al.* (9) found that $(\partial P/\partial \rho)_{\min}$ was linear in temperature up to 0.5° above the critical temperature. MacCormack and Schneider (6) for sulphur hexafluoride over a range of 1.5° found a curve somewhat similar in shape to ours.

Critical Density

The critical density may be estimated, in a manner similar to that used for the critical temperature, by plotting the densities of minimum slope of the isotherms against temperature. This has been done in Fig. 5. A straight line through the points indicates a critical density of 1.099 gm./ml. but it is doubtful from the scatter of the points whether the assumption of such a linear relationship is justified. The rectilinear diameter for the liquid–vapor coexistence curve found by Weinberger and Schneider is also shown in Fig. 5 and this gives a critical density of 1.105 gm./ml. As stated earlier, our coexistence observations would indicate, if anything, a still higher critical

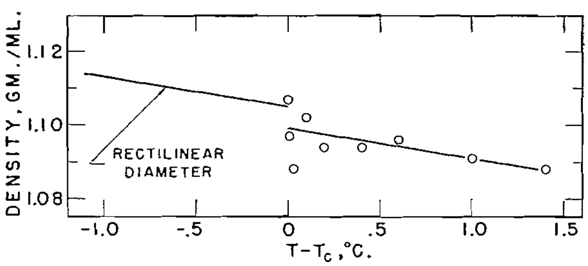

FIG. 5. Densities of minimum slopes of the isotherms at and above the critical temperature. The rectilinear diameter of the liquid–vapor coexistence curve is also shown.

density. Thus, it appears unlikely that a linear continuation of the rectilinear diameter above the critical temperature would include the densities of minimum slope of the isotherms. The coexistence curve reported by Whiteway and Mason gave a critical density of 1.110 ± 0.002 gm./ml.

An alternative method of estimating the critical density from the PVT measurements is to plot $(\partial^2P/\partial T^2)$ at the critical temperature against density, the critical density then being the density where this quantity becomes zero. Such a plot is shown in the following paper and it also gives a value for the critical density of 1.099 gm./ml.

Critical Pressure

The critical pressure is obtained directly from the critical isotherm as 57.636 ± 0.005 atm.

Relationship to Theories of the Critical State

Mayer has recently discussed (7) the status of three of the current theories which predict the nature of the critical isotherms. The simple "derby hat" picture of Mayer and Harrison (8) predicts flat, horizontal isotherms at temperatures above the temperature of meniscus disappearance; the modified "derby hat" theory of Rice (12) predicts a flat, horizontal critical isotherm with linear but sloping isotherms immediately above the critical temperature; and the singular point theory of Zimm (19) describes the critical point as a singularity in the critical isotherm where all derivatives of P with respect to ρ are zero.

Our critical isotherm is significantly flatter and broader than that corresponding to the van der Waals equation and, indeed, over a short density range and within the experimental uncertainty could be fitted as well to a horizontal line as to a curve. It was shown in a previous publication (16) that the observed density distributions resulting from the gravitational field in a vertical tube at the critical point are not in good agreement with a van der Waals isotherm but can be quantitatively accounted for by the present isotherm.

Our measurements offer no support for the Mayer–Harrison theory since there is no obvious region of flat, horizontal isotherms above the critical temperature. The isotherms could be easily reconciled with either the second or third theory although Rice's theory would predict a flattopped coexistence curve whereas the observed coexistence curve (15) appeared to be definitely rounded at the apex.

In connection with the third picture we have calculated $(\partial^2 P/\partial \rho^2)$ by numerical differentiation from our smoothed critical isotherm. These values are plotted in Fig. 6 together with the corresponding values calculated for a van der Waals critical isotherm using the experimentally determined critical constants. The degree to which the experimental isotherm is flatter than the van der Waals isotherm is clearly seen. The curve from the experimental isotherm, while having a considerable degree of uncertainty, suggests that at the critical point the third derivative of P with respect to ρ is very close to zero and the fourth derivative is identically so, since this is a point of inflection.

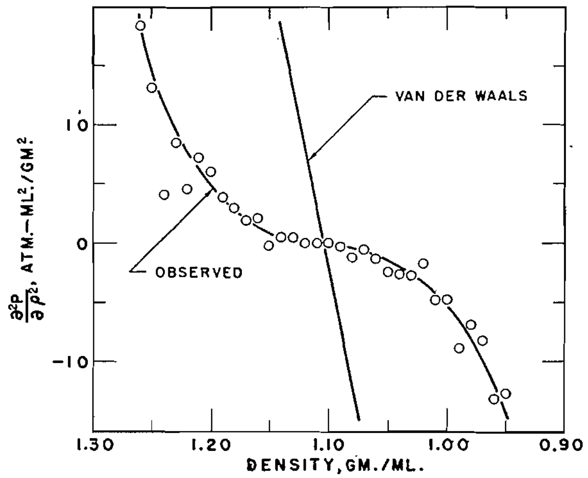

FIG. 6. $\partial^2 P/\partial \rho^2$ for the critical isotherm and for a van der Waals isotherm.

ACKNOWLEDGMENT

The authors wish to express their thanks to Mr. A. Stevenson for help in the design and construction of the apparatus, to Mr. G. Ensell for making the glass bombs and the glass capillaries in the U-tube, and to Dr. F. P. Lossing and his associates for the mass spectrometer analysis.

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THE PHOTOLYSIS OF MERCURY DIMETHYL WITH DEUTERIUM[1]

BY RICHARD E. REBBERT[2] AND E. W. R. STEACIE

ABSTRACT

Mercury dimethyl was photolyzed in the presence of deuterium in the temperature range from 27°C. to 253°C. The activation energy for the reaction

$$CH_3 + D_2 \rightarrow CH_3D + D$$

was found to be 12.7 ± 0.5 kcal./mole. This is in satisfactory agreement with the work done with acetone and deuterium.

INTRODUCTION

Recently a very extensive investigation was carried out in this laboratory of the reaction of methyl and deuterated methyl radicals with hydrogen, deuterium, and deuterium hydride (2, 7). However, in all this work the methyl radicals were obtained from the photolysis of acetone and the temperature was kept above 135°C. It was thought profitable to reinvestigate some of these reactions using mercury dimethyl as the source of methyl radicals.

Earlier work using the photolysis of mercury dimethyl to investigate the reaction

$$CH_3 + H_2 \rightarrow CH_4 + H$$

gave a very definite curvature in the Arrhenius plot below 100°C. (4). This has been interpreted by some as evidence of "hot" radicals. However, above 100°C. the activation energy obtained agrees very well with the results from the photolysis of acetone with hydrogen. Unfortunately the amount of methane obtained at very low temperatures is too small to measure accurately. Phibbs and Darwent decomposed about 30 per cent of their mercury dimethyl at low temperatures in order to get enough methane to measure accurately. However, if deuterium is used in place of hydrogen, one needs only to measure the ratio CH_3D/CH_4 which can be done fairly accurately on a mass spectrometer even at low temperatures and low percentage conversions. This was our reason for choosing deuterium. In the present work the CH_3D/CH_4 ratio was in the range 1.00 to 3.00. In this range the ratio can be determined with an accuracy of from 2 to 4%.

EXPERIMENTAL

Apparatus

The apparatus was the same as that used in the previous work on the photolysis of mercury dimethyl (6) with the exception that a palladium thimble was used to get rid of the excess deuterium after photolysis and also to purify the deuterium before the reaction.

The quartz reaction cell had a volume of 179.5 cc. and since the light beam almost completely filled the cell, the volume of the cell was considered to be the

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[2] *National Research Council of Canada Postdoctorate Fellow 1951-53.*

reaction volume. Neutral density filters were used at low temperatures to reduce the intensity in the hope of increasing the amount of methane formed relative to the ethane formation.

Material

The mercury dimethyl was obtained from the Delta Chemical Works and fractionated. It was better than 99 per cent pure. Commercial cylinder deuterium was used and this was purified by passing it through a palladium thimble at approximately 350°C. This was analyzed on the mass spectrometer and contained 3% HD and a very small amount of H_2. A small correction was applied for the presence of deuterium hydride.

Method of Calculation

When mercury dimethyl is photolyzed alone methane and ethane are produced by the reactions

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + CH_3HgCH_2 \qquad [1']$$

and

$$2CH_3 \rightarrow C_2H_6. \qquad [2]$$

In the presence of deuterium we also have the reaction

$$CH_3 + D_2 \rightarrow CH_3D + D. \qquad [1]$$

Also, owing to the 3% HD, we will have the following reactions occurring to a small extent—

$$CH_3 + HD \rightarrow CH_4 + D \qquad [3]$$

$$CH_3 + DH \rightarrow CH_3D + H. \qquad [4]$$

Thus the total rate of formation of deuterated methanes will be

$$R^{T}_{CH_3D} = R^{1}{}_{H_3D} + R^{4}{}_{H_3D} = k_1[CH_3][D_2] + k_4[CH_3][HD]$$

and the total rate of formation of methane will be

$$R^{T}_{CH_4} = R^{1'}_{CH_4} + R^{3}_{CH_4} = k_1'[CH_3][Hg(CH_3)_2] + k_3[CH_3][HD].$$

Therefore, we have

$$\frac{R^{T}_{CH_3D}}{R^{T}_{CH4}} = \frac{\dfrac{k_1}{k_{1'}}\dfrac{[D_2]}{[Hg(CH_3)_2]} + \dfrac{k_4}{k_{1'}}\dfrac{[HD]}{[Hg(CH_3)_2]}}{1 + \dfrac{k_3}{k_{1'}}\dfrac{[HD]}{[Hg(CH_3)_2]}}$$

or

$$\frac{k_1}{k_2^{\frac{1}{2}}} = \frac{k_1'}{k_2^{\frac{1}{2}}}\left\{\frac{R^{T}_{CH_3D}\,[Hg(CH_3)_2]}{R^{T}_{CH_4}\quad [D_2]} + \frac{R^{T}_{CH_3D}}{R^{T}_{CH_4}}\,\frac{k_3}{k_{1'}}\,\frac{[HD]}{[D_2]} - \frac{k_4}{k_{1'}}\,\frac{[HD]}{[D_2]}\right\}.$$

We can measure the ratio $R^{T}_{CH_3D}/R^{T}_{CH_4}$ on the mass spectrometer. We know the concentration of mercury dimethyl, deuterium, and deuterium hydride. $k_1'/k_2^{\frac{1}{2}}$ was previously measured (5), and $k_3/k_2^{\frac{1}{2}}$ and $k_4/k_2^{\frac{1}{2}}$ have been determined by Whittle and Steacie (7). The second and third terms in the above equation are the correction terms needed because of the presence of deuterium hydride in the deuterium sample. Together they amount to about 10 per cent of the uncorrected term.

There is no doubt that the above mechanism is incomplete and that there are some complications (1, 3). However, a recent investigation (5) has shown that *under the conditions used here* the simple mechanism is adequate.

The intensities employed in the present investigation were varied at different temperatures in order to obtain sufficient methane to permit accurate analysis. In all cases, however, the intensities were in the range in which we have previously shown (5) that the ratio $k_1/k_2^{\frac{1}{2}}$ is independent of intensity. The experiments in the temperature range 378–526°C. were at the same intensities as the highest intensity runs in the previous work. The run at 347°C. was at an intensity one-half as great, and those at the lowest temperatures were at intensities 1/15th as great.

Results

The results are given in Table I and they are plotted in Fig. 1. Also in Fig. 1 the results from the photolysis of acetone with deuterium (2) are plotted. The agreement between the two sources of methyl radicals is seen to be very good. The best line through the points has been found by the method of least squares to be

$$13 + \log k_1/k_2^{\frac{1}{2}} = 6.70 - (2778/T).$$

The slope of this line gives a value of 12.7 kcal. per mole for $E_1 - \frac{1}{2}E_2$. The results from acetone give 11.7 kcal. per mole for this activation energy. Usually

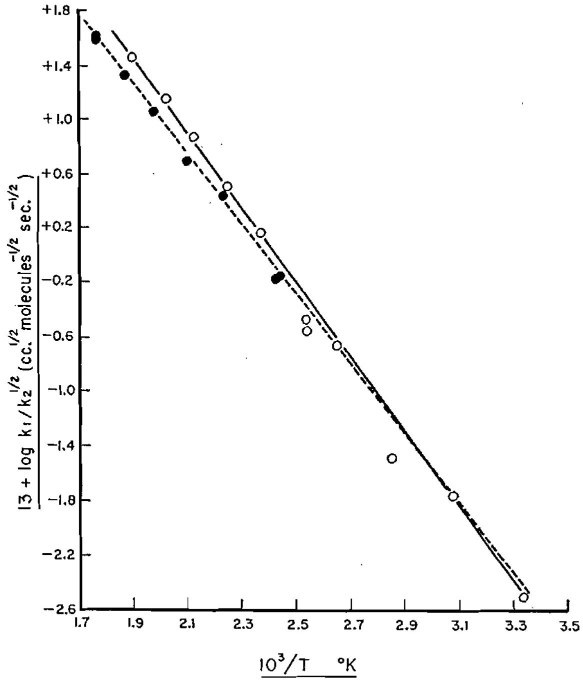

FIG. 1. Reaction of methyl radicals with deuterium. Open circles—mercury dimethyl photolysis. Filled circles—acetone photolysis.

TABLE I

THE PHOTOLYSIS OF MERCURY DIMETHYL WITH DEUTERIUM

Temp., °K.	Pressure of $Hg(CH_3)_2$, mm.	Pressure of D_2, mm.	CH_3D/CH_4	$k_1/k_2^{\frac{1}{2}} \times 10^{13}$
300	29.8	116.0	1.00	0.0033
324	31.6	129.0	1.46	0.0182
347	34.7	153.7	1.00	0.0339
378	37.9	136.7	1.55	0.229
395	39.4	159.7	1.42	0.339
395	41.0	134.9	0.98	0.282
422	43.0	153.7	2.32	1.52
446	46.7	159.4	2.40	3.24
472	47.1	174.6	3.03	7.41
496	49.6	148.1	2.55	13.5
526	51.6	113.8	2.08	27.5

about 5 per cent of the mercury dimethyl was decomposed and in no case was more than 10 per cent of the mercury dimethyl photolyzed.

DISCUSSION

The present work gives added proof in support of the lower value for the activation energy, namely about 12 kcal. per mole, for the reaction of a methyl radical with deuterium. Thus we have the following situation for this reaction—

	E_1 in kcal. per mole
Majury and Steacie (source: acetone)	11.7
Whittle and Steacie (source: acetone)	11.8
Davison and Burton (source: acetone)	12.2—12.7*
Rebbert and Steacie (source: mercury dimethyl)	12.7

**Corrected by Wijnen and Steacie, Faraday Soc. Discussions, 14: 118. 1953.*

In view of this agreement we consider the low value for this reaction to be established.

The agreement between results with acetone and mercury dimethyl indicates that the results are not affected by "hot" radical effects, under the conditions employed. Even at room temperature, under our conditions, there are no indications of any deviation from the Arrhenius plot on this account. This does not, of course, preclude the occurrence of hot radical effects with mercury dimethyl under certain special conditions (3).

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We are indebted to Miss Frances Gauthier of these laboratories for the mass spectrometric analyses used in this work.

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HYDROGEN PEROXIDE: THE LOW TEMPERATURE HEAT CAPACITY OF THE SOLID AND THE THIRD LAW ENTROPY[1]

By Paul A. Giguère[2], I. D. Liu[2,3], J. S. Dugdale[4],
and J. A. Morrison[5]

ABSTRACT

The heat capacity of crystalline hydrogen peroxide between 12° K. and the melting point has been determined with a low temperature adiabatic calorimeter. The heat of fusion was also measured and found to be 2987 ± 3 cal./mole. The two samples of hydrogen peroxide used were 99.97 mole % pure as deduced from behavior on melting and from premelting heat capacities; the triple point was estimated to be 272.74° K.

The only anomaly observed in the heat capacity measurements was the absorption of 1.3 cal./mole at 216.8 ± 0.15° K., the lower eutectic temperature of H_2O–H_2O_2 solutions. Such an effect is to be expected if the only significant impurity is water. The entropy of hydrogen peroxide as an ideal gas at 1 atm. pressure and 25° C. computed from the thermal measurements is 55.76 ± 0.12 cal./mole deg. Comparison of this datum with the recalculated statistical entropy leads to a value of 3.5 kcal./mole for the height of a hypothetical single barrier hindering internal rotation in the molecule. From these results it is concluded that hydrogen peroxide does not consist of two tautomeric modifications.

INTRODUCTION

Knowledge of the thermal properties of solid hydrogen peroxide has hitherto been fragmentary and uncertain (15, 5). The accurate determination of the heat capacity of the compound in the solid state down to low temperatures was considered to be of special interest, primarily because it would make possible a calculation of the third law entropy. An X-ray investigation of the crystal structure of hydrogen peroxide (1) has shown that it should not retain any appreciable residual entropy at the absolute zero. On the other hand, evaluation of the statistical entropy of the ideal gas from structural and spectroscopic data (7) is hampered by the lack of sufficient information on the internal rotation of the two OH groups in the molecule. The potential barrier restricting that motion is expected to have two unequal maxima (22) which makes difficult a rigorous calculation of the contribution of that internal degree of freedom to the various thermodynamic functions. Another important point is the question of whether transitions (18) and tautomeric forms (6) of hydrogen peroxide exist in the solid state (cf. Discussions of the Faraday Society, 14: 140–142. 1953).

Because of the tendency of hydrogen peroxide to decompose spontaneously in contact with most materials, the project held certain experimental difficulties. For convenience, the work was divided between two laboratories, one

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[3] *Holder of a Fellowship from the Bureau of Scientific Research of the Province of Quebec.*

[4] *National Research Laboratories Postdoctorate Fellow.*

[5] *National Research Laboratories.*

at Laval University where facilities existed for preparing the samples of pure hydrogen peroxide and for sealing them in suitable containers, and the other at the National Research Council where the calorimetric measurements could be made.

EXPERIMENTAL

The Preparation of the Samples

The starting material for preparing the pure hydrogen peroxide was the very stable 90% solution supplied by the Buffalo Electro-Chemical Company. Some six liters of this solution was concentrated to about 99.6% hydrogen peroxide by distillation at reduced pressure through a 1 meter fractionating column filled with small glass helices and heated electrically to prevent flooding. Extensive precautions were taken to avoid contamination of the solution. All glassware was treated with fuming sulphuric acid following the procedure recommended by Huckaba and Keyes (11). The still was assembled through ground glass-joints on which only a trace of silicone grease was used. A fritted glass disc was placed on the vacuum line to filter off all dust particles from the air let in after a distillation.

Further concentration of the peroxide was achieved by fractional crystallization as described elsewhere (4). The apparatus was made simpler by using a straight filtering tube with the two flasks connected at each end. For separating the solid from the mother liquor the whole assembly was merely turned upside down and then suction was applied at the outlet tube. The entire operation was rendered still more effective by growing a single large crystal instead of a mass of tiny ones. To this end the flask filled with some 700 gm. of concentrated peroxide solution was wrapped in a thick glass-wool lagging before it was placed in an ice machine at −10° C. Crystallization was initiated by seeding and it proceeded very slowly (two days for solidification of about 90% of the sample). The progress of purification was followed by measuring the freezing point (4) which did not change further after three or four operations.

The Calorimeter Vessels

Having once prepared the pure hydrogen peroxide it was important that it should not come in contact with anything except very inert materials such as specially treated glass or pure aluminum. For this reason and because glass-to-aluminum seals are not available, the calorimeter vessels were made entirely of pure (1S) aluminum. As will be seen from Fig. 1, the construction was such that no soldering or brazing was used. The tapered re-entrant well in the base of the calorimeter receives the thermometer–heater assembly. With this design the thermometer may be attached after the filling of the calorimeter is completed. The resistance thermometer and calorimeter heater were cast with Wood's metal into a tapered brass tube which fitted closely the tapered re-entrant well. The brass tube was held firmly in place with a threaded collar which screwed into the bottom of each vessel. Thermal contact between the brass tube and the well was enhanced by a light film of silicone grease.

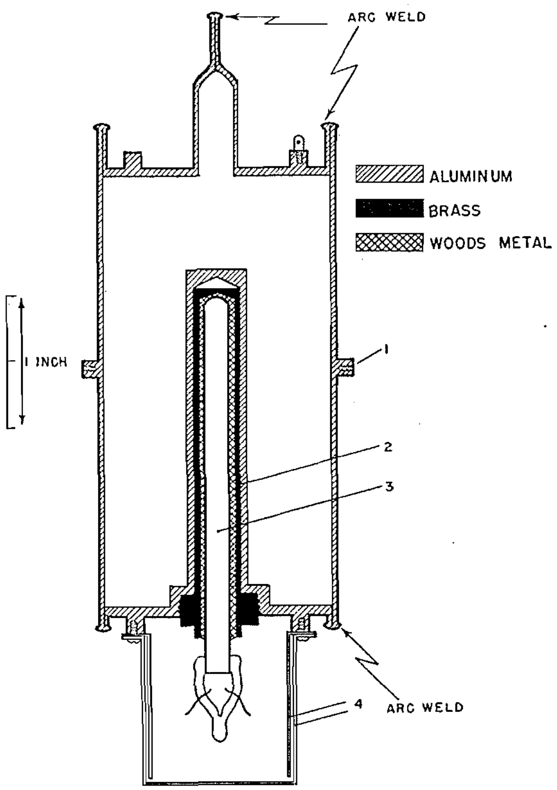

FIG. 1. Aluminum calorimeter vessel. 1. Point of attachment of difference thermocouple. 2. Tapered brass tube. 3. Platinum resistance thermometer. 4. Anchoring ring for lead wires and radiation shield.

The Filling of the Calorimeter Vessels

Although special precautions were taken in assembling the calorimeter vessels, their inside surfaces needed extensive passivation treatment before use. This long and tedious operation involved the following steps. The metal was first degreased by rinsing with acetone and then treated for a few minutes with a 3% solution of sodium hydroxide followed by numerous rinsings with distilled water. Thereafter each vessel was filled with 25% nitric acid, allowed to stand for several hours, and washed again thoroughly with distilled water. Finally, repeated fillings with solutions of hydrogen peroxide of increasing concentration from 30% to 99% over a period of a few weeks brought the surfaces to a satisfactory level of inertness in the case of three out of the six vessels originally made. The rate of decomposition of 99% hydrogen peroxide in these was of the order of 0.001% in 24 hr. at room temperature and less than one tenth of this at 0°, which was deemed entirely safe.

After prolonged evacuation for drying, the vessels were filled with helium gas at atmospheric pressure for better thermal conductivity, and the pure liquid peroxide was poured in directly. A temporary closure was effected at once by pinching off the thin filling tubes, and after the vessels were accurately weighed, the tubes were welded in an argon arc with the containers immersed in ice water to prevent decomposition of the peroxide. They were then cooled gradually to the temperature of dry ice and were kept at this temperature during transport to the National Research Laboratories in Ottawa. It was assumed that the rate of decomposition of the frozen peroxide would be negligible, and this was confirmed by the subsequent experiments. At no time during the experiments was there any sign of thermal effects due to decomposition of the hydrogen peroxide.

The Cryostat

The cryostat used for this work was similar to one already described in a previous publication (20). Adiabatic operation was possible over the entire temperature range from 11° K. The design of the cryostat proved to be particularly convenient for mounting the calorimeter vessel without melting the sample of hydrogen peroxide. By careful arrangement of the procedure it was possible to assemble the cryostat in about an hour, during which time the temperature of the calorimeter vessel rose from that of dry ice to about −5° C.

The Measurements

The resistance of the platinum thermometer and the energy supplied to the calorimeter were measured after the methods which have become standard for this type of work (26). All of the measurements were made with a White double potentiometer. The standard resistors and standard cells have been checked periodically against standards maintained by the Division of Physics of the National Research Laboratories. Time of input of energy to the calorimeter was determined with a synchronous clock operated from a constant frequency power supply through a switch coupled directly to that controlling the heater current. The indications of the clock have been checked many times by comparison with the time signals from the Dominion Observatory. The error in the clock has never exceeded 0.02 seconds. Platinum resistance thermometer T-3 was used for this work. The calibration of this thermometer has been described elsewhere (14).

RESULTS

The Heat Capacity

Of the three different samples of hydrogen peroxide prepared in separate calorimeter vessels only two were used for the measurements (containing 3.3706 and 2.9175 moles respectively). Since it was not known beforehand whether or not the peroxide would decompose appreciably on melting (8), it seemed preferable to measure the heat capacity with one sample and the heat of fusion with the other.

The results are given in Table I as smoothed values of the heat capacity at rounded values of the temperature. (In all the calculations the calorie was taken equal to 4.184 absolute joules). The difference plot in Fig. 2 shows the deviations of the experimental results from a smooth curve. It will be noted that over most of the temperature range the mean precision was better than 0.1%; below 30° K. the uncertainty was greater (of the order of 0.3%).

TABLE I
THE HEAT CAPACITY OF SOLID HYDROGEN PEROXIDE

T, ° K.	C_p, cal./mole deg.	T, ° K.	C_p, cal./mole deg.
12	0.062	70	4.188
13	0.079	75	4.545
14	0.099	80	4.895
15	0.124	85	5.243
16	0.151	90	5.568
17	0.181	95	5.865
18	0.215	100	6.144
19	0.253	110	6.676
20	0.295	120	7.164
22	0.387	130	7.614
24	0.494	140	8.039
26	0.611	150	8.438
28	0.735	160	8.822
30	0.872	170	9.191
32	1.015	180	9.556
34	1.165	190	9.917
36	1.325	200	10.283
38	1.484	210	10.657
40	1.648	220	11.044
42	1.815	230	11.437
44	1.985	240	11.857
46	2.157	250	12.30*
48	2.328	255	12.57*
50	2.505	260	12.98*
55	2.941	265	13.83*
60	3.372	268	15.70*
65	3.794		

* *Marked premelting.*

Premelting of the solid became evident around 250° K. as illustrated in Fig. 3. A few measurements of the heat capacity of the second sample made in the region above 250° K. yielded results indistinguishable from those obtained with the first sample. The dotted line in Fig. 3 represents the heat capacity of pure solid hydrogen peroxide estimated as described below. Calculations showed that the correction to be applied for evaporation into the dead space of the calorimeter was negligible.

During the heat capacity measurements on the first sample a small absorption of energy was detected around 217° K. The amount of heat involved seemed to depend upon the extent to which the calorimeter had been cooled previously. After cooling to temperatures below 77° K., the energy amounted to 3.4 cal. while with cooling to around 200° K. it was only 1.9 cal. An attempt was made to determine the temperature region over which this energy was absorbed by following the temperature of the calorimeter while it received energy at a constant rate from its surroundings. From this experiment it appeared that the heat was absorbed between 216.78° and 216.94° K. That this effect was due to the melting of an eutectic mixture of hydrogen peroxide and the addition compound $H_2O_2 . 2H_2O$ is suggested by two facts. First, the temperature region is very close to the eutectic temperature reported by Foley and Giguère (216.7° K. (4)). Second, assuming the eutectic mixture to be an ideal one and the impurity present (0.032 mole %—see below) to be

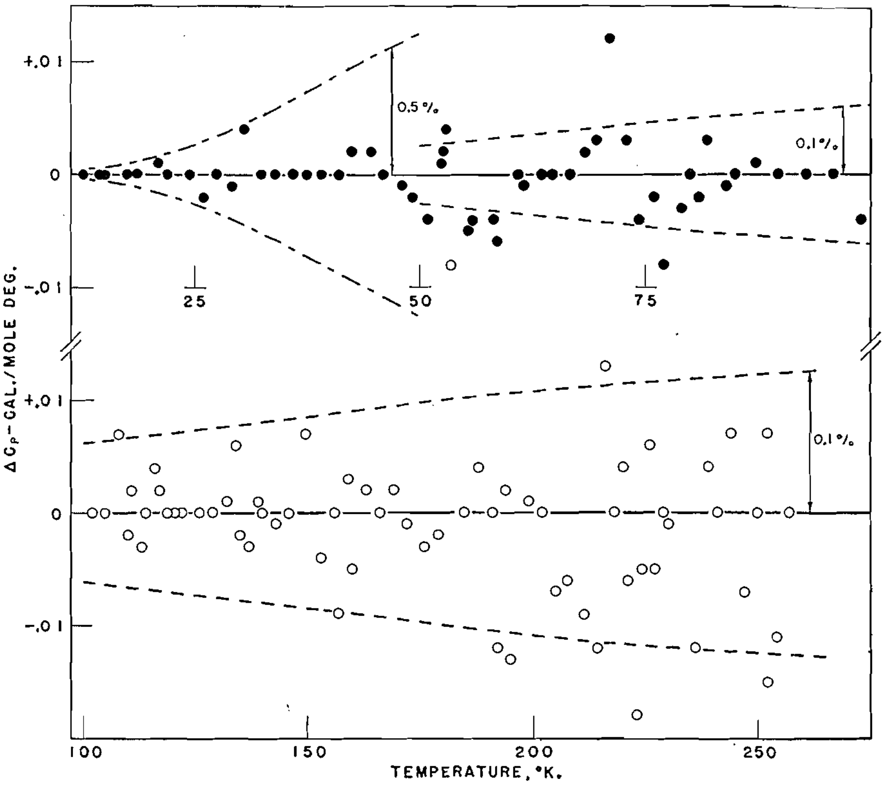

FIG. 2. Deviations of experimental heat capacities from a smooth curve.

entirely water, the calculated energy to be expected at the eutectic temperature is 3.9 cal., which agrees very well with the maximum amount found experimentally.

Apart from this absorption of energy, no other anomalies were observed. It is estimated that at the higher temperatures any transition involving an energy greater than 0.1 cal./mole concentrated in a temperature interval of 4° or less would be detected in these measurements; at the lower temperatures even smaller quantities are detectable.

The Heat of Fusion

The heat of fusion of hydrogen peroxide was determined by measuring the energy required to heat the calorimeter and the second sample over a temperature interval which included the triple point. From this quantity was subtracted the energy required to heat (*a*) the pure solid up to the triple point, (*b*) the liquid from the triple point to the final temperature, and (*c*) the calorimeter vessel from the initial to the final temperature. The premelting energy is then included in the heat of fusion. The value so obtained was 2987 ± 3 cal./mole which may be compared with 2920 cal./mole determined by Foley and Giguère (5) using an ice calorimeter. The latter value is based upon a rather uncertain estimate of the heat capacity of the solid just below the melting point. However, using the corrected heat capacity of the solid does not remove the discrepancy.

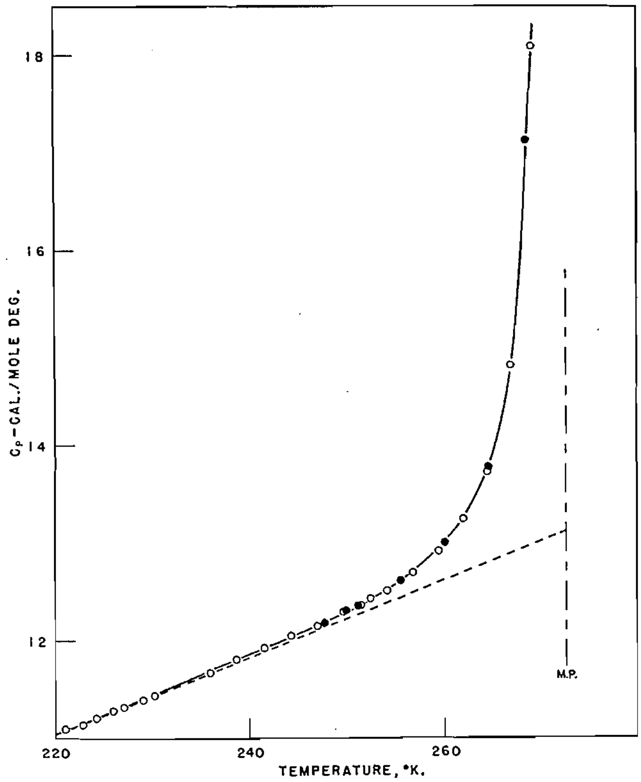

FIG. 3. The heat capacity of solid hydrogen peroxide in the premelting region.
○ — Sample 1. ● — Sample 2. ----- Pure solid (equation [1]).

The Purity of the Samples

The melting temperatures as a function of the fraction melted are given in Table II. From these results the calculated triple point of hydrogen peroxide is 272.74° K. and the estimated impurity content 0.032 mole %.

TABLE II
THE MELTING POINT OF H_2O_2
(0° C. = 273.16° K.)

% Melted	T, ° K.
49.9	272.708
65.2	272.714
98.8	272.725
100	272.725

Impurity: 0.032 mole %.
Triple point: 272.74° K.

The degree of purity of the hydrogen peroxide used could also be estimated from the heat capacity in the premelting region. The excess heat capacity was calculated using (*a*) the phase diagram for the system H_2O–H_2O_2 (4) and (*b*) a constant value for the heat of fusion (2987 cal./mole). The amount of impurity was then so chosen that the derived heat capacity of the pure solid was a linear function of the temperature. A calculated impurity of 0.038 mole % together with the expression for the heat capacity of the pure solid (plotted in Fig. 3)

$$C_p = 2.31 + 0.03967\ T \text{ cal./mole deg.} \qquad [1]$$

suffice to represent the experimental results very closely between 220° and 271° K. The good agreement between the estimates of impurity from the melting temperatures and from the premelting heat capacities, as well as the shape of the heat capacity curve in the premelting region (2) provide definite evidence that the impurity (water) does not form solid solutions with hydrogen peroxide. This confirms the results of two independent investigations of phase equilibria in this binary system (4, 18).

DISCUSSION

The first important conclusion to be drawn from the above results is that there are no transitions either of the first or the second order in solid hydrogen peroxide, notwithstanding assertions to the contrary (18). This provides further evidence that ordinary hydrogen peroxide contains no measurable proportion of a tautomeric form, H_2O–O, as has been suggested (29). Numerous structural studies as well as recent measurements of the magnetic susceptibility of the solid (21) and of the ionization potential of the molecule (25) may be cited in support of this conclusion. On the other hand the possibility is not ruled out that an unstable isomer, such as proposed by Geib and Harteck (6), could be formed under special conditions (low temperature reaction between oxygen and atomic hydrogen, etc.). But this hypothetical isomer should not be reversibly convertible into normal hydrogen peroxide.

The present results for the heat of fusion and the triple point of hydrogen peroxide lie outside the limits of error assigned by Foley and Giguère for their determinations (4, 5). Because the experimental method used this time was much more accurate there is no question that the new values are to be preferred. The limitations of the freezing point method for measuring melting points are well known (3). That thermodynamic equilibrium was not perfectly realized in the determinations by the above authors was indicated by the uncertainty of their calculated melting point at zero impurity. More recent measurements made with an improved type of apparatus (9) have yielded a melting temperature of −0.43° C. for the pure compound (28) in agreement with the present value after correction for the pressure effect (5) ($dt/dp = 0.007°$ atm.$^{-1}$).

It is perhaps worth emphasizing that the present calorimetric determination of impurities in hydrogen peroxide is the most precise reported so far. The usual procedures based upon chemical analysis are not capable of an accuracy much greater than 0.1%. Because of this, previous workers have often assumed erroneously that they had succeeded in preparing 100% pure hydrogen peroxide.

The Entropy of Hydrogen Peroxide

The computation of the entropy of hydrogen peroxide from the thermal data is outlined in Table III. The contribution of the solid between 12° K. and the triple point was deduced by integrating values of C_p/T using Simpson's rule. Up to 250° K. the values of C_p were taken from Table I and thereafter from equation [1].

TABLE III
THE ENTROPY OF H_2O_2

	Cal./mole deg.	
ΔS (0° to 12° K.) Debye extrapolation	0.02	
ΔS (12° to 272.74 ° K.) Solid	13.30 ± 0.01	
$\Delta S_{272.74°}$ (2987/272.74) Fusion	10.95 ± 0.01	
Entropy of the liquid at 272.74° K.		24.27 ± 0.02
*ΔS (272.74° to 298.16° K.) Liquid	1.90 ± 0.01	
*$\Delta S_{298.16}$ (12330/298.16) Vaporization	41.34 ± 0.07	
**$\Delta S_{\text{compression}}$ R ln (1.95/760)	−11.85 ± 0.02	
Correction for ideal gas	0.10	
Entropy of the ideal gas at 298.16° K. and 1 atm. pressure		55.76 ± 0.12

* *Reference (19).* ** *Reference (27).*

An alternative calculation of the entropy of the liquid at the triple point was also made using only experimentally measured quantities. Up to 250° K. the procedure was as above. From 250° K. to the point where melting was complete, the total entropy was computed by means of the expression

$$\Delta S = \sum_n \frac{\Delta Q_n}{T_n} \qquad [2]$$

where ΔQ_n is the energy supplied in the nth heat capacity measurement and T_n is its mean temperature. From this was subtracted the increase in entropy of the calorimeter vessel. The result of this calculation was within 0.01 cal./mole deg. of that given in Table III. Thus, to this degree of precision the entropy of the liquid is independent of any assumption concerning the behavior of the heat capacity of the pure solid in the premelting region.

The specific heat of the liquid was taken as 21.35 cal./mole deg. and the latent heat of vaporization as 12.33 kcal./mole at 25° C. from the results of recent redeterminations to be published soon (19). For the entropy of compression to one atmosphere the equilibrium vapor pressure of hydrogen peroxide at 25° C. (1.95 mm. Hg) was obtained by extrapolation of the equation of Scatchard and co-workers (27). Finally, the Berthelot equation of state with the approximate critical constants $T_c = 459°$ C. (16), $P_c =$ 240 atm. (13), was used to evaluate the small correction for gas imperfection.

The value thus obtained for the third law entropy at 25° C. is significantly higher than the entropy calculated previously by the statistical method (54.18 cal./mole deg. (7)). Since the various structural and vibrational data of the molecule are known with fair accuracy, except those pertaining to the internal rotational mode, it was obvious that the discrepancy was to be traced to the latter. On reviewing the statistical calculations, it was discovered that an error had been made in selecting a value for n in the expression for the rotational partition function (10)

$$Q_f = (8\pi^3 I\gamma kT)^{\frac{1}{2}}/hn. \qquad [3]$$

Although the potential energy restricting free rotation about the O–O bond exhibits two maxima, these are unequal and therefore distinguishable. Consequently, n in equation [3] must be taken as 1 and not 2 as was chosen previously. After correcting this term, the statistical entropy is only 0.45 units smaller than the third law entropy, and the two can be made equal by using a barrier height of about 3.5 kcal./mole (instead of 5 kcal./mole as in the earlier calculations (7)). Hitherto, values ranging from a few hundred calories (17) up to 12 kcal./mole (12) have been proposed for the potential barriers in hydrogen peroxide. The various thermodynamic functions for gaseous hydrogen peroxide have been recalculated up to 1500° K. (Table IV), the contribution of internal rotation being estimated after the method of Pitzer and Gwinn (24) with a barrier height $V_0 = 3.5$ kcal./mole and the simple sinusoidal potential function

TABLE IV
REVISED VALUES OF THE THERMODYNAMIC FUNCTIONS FOR HYDROGEN PEROXIDE GAS AT 1 ATM. PRESSURE

T, °K.	$-\frac{F^0 - H_0^0}{T}$, cal./mole deg.	$\frac{H^0 - H_0^0}{T}$, cal./mole deg.	S^0, cal./mole deg.	C^0, cal./mole deg.	$H^0 - H_0^0$, cal./mole deg.
298.16	46.33	9.42	55.76	11.00	2810
300	46.39	9.43	55.82	11.02	2830
350	47.87	9.69	57.54	11.47	3391
400	49.17	9.94	59.11	11.93	3976
500	51.44	10.42	61.84	12.68	5210
600	53.38	10.85	64.23	13.28	6511
700	55.09	11.21	66.31	13.76	7848
800	56.61	11.58	68.17	14.15	9263
900	57.99	11.89	69.86	14.51	10702
1000	59.26	12.15	71.40	14.84	12153
1100	60.43	12.41	72.83	15.15	13656
1200	61.56	12.65	74.17	15.45	15186
1300	62.52	12.87	75.41	15.72	16737
1400	63.50	13.09	76.58	15.97	18322
1500	64.41	13.29	77.69	16.20	19935

$$V = \tfrac{1}{2}V_0(1 - \cos n\theta). \qquad [4]$$

Because of this approximation there still remains some uncertainty in the revised thermodynamic quantities, especially at the higher temperatures.

The internal rotational mode may be treated differently, namely as a double minimum oscillator such as the ammonia molecule. Then a satisfactory approximation consists of taking the energy levels for an equivalent single minimum oscillator with each level being doubly degenerate (23). This is tantamount to adding an $R \ln 2$ term to the entropy and free energy functions. However, here again the calculated functions will be less accurate at higher temperatures because then the molecules change gradually from pure oscillation towards free internal rotation. It turns out that the values of the entropy calculated by the two methods agree fairly well even at 1500° K.* but the enthalpy and heat capacity functions are appreciably different. More exact calculations of these various quantities must await further spectroscopic data and an adequate theoretical treatment of the molecule.

ACKNOWLEDGMENT

The success of these experiments depended to a large extent upon careful fabrication of the calorimeter vessels. For this work the authors are indebted to Messrs. A. Dubois, A. Lavergne, and F. C. Mason of the National Research Laboratories. They also wish to thank Dr. A. Cholette of Laval University for valuable assistance with the sealing of the vessels.

RÉSUMÉ

La capacité calorifique du peroxyde d'hydrogène à l'état solide a été mesurée entre 12° K. et le point de fusion au moyen d'un calorimètre adiabatique. La chaleur latente de fusion a également été déterminée et trouvée égale à 2987 ± 3 cal./mole. Les deux échantillons de peroxyde d'hydrogène qui ont servi pour ces mesures étaient d'un haut degré de pureté, soit 99.97 mole %, ainsi qu'il ressort des variations de la capacité calorifique qui ont précédé fusion. De ces mêmes données on a déduit que le point triple du peroxyde d'hydrogène se trouve à 272.74° K.

La seule anomalie que l'on ait remarquée au cours des mesures fut l'absorption d'une faible quantité de chaleur, 1.3 cal./mole, à 216.8° K., le point eutectique des solutions concentrées du peroxyde d'hydrogène. Cette observation conduit au même résultat que celui déjà mentionné pour la pureté des échantillons employés.

A partir de ces données on peut calculer l'entropie calorimétrique du peroxyde d'hydrogène considéré comme gaz parfait à 25° C. et à 1 atm. En comparant cette valeur, (55.76 ± 0.12 cal./mole deg.) avec celle que donne la méthode statistique il appert que la rotation interne des deux groupes OH dans la molécule est gênée par une énergie potentielle équivalente à un seuil unique d'environ 3.5 kcal./mole.

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* *A hypothetical frequency of 400 cm.$^{-1}$ (based on the calorimetric entropy) was assumed for the oscillator.*

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THE MECHANISM OF THE HYDRATION OF TRICALCIUM SILICATE AND β-DICALCIUM SILICATE[1]

By W. A. G. Graham, J. W. T. Spinks, and T. Thorvaldson

ABSTRACT

Labelled tricalcium silicate, prepared by heating together inactive dicalcium silicate and lime labelled with Ca^{45}, has been hydrated in saturated solutions of calcium hydroxide at 21°C. Parallel studies of the rate of liberation of lime due to hydrolysis and the coincident appearance of Ca^{45} in the solution indicate that the $CaO:SiO_2$ ratio in the precipitated hydrated silicate is 3:2. A similar result is obtained when inactive tricalcium silicate is hydrated in an active lime solution. Comparable studies on the hydrolysis of labelled β-dicalcium silicate indicate the formation of a product with the same $CaO:SiO_2$ ratio. The method appears to have rather general application.

INTRODUCTION

In the well known "crystallization theory" of the hydration of Portland cement, it is assumed that the anhydrous compounds pass into solution, with or without hydrolysis, forming hydrated products of lower solubility which separate from the supersaturated solution. The condition of supersaturation is maintained as long as any of the more soluble anhydrous substances remain in contact with the solution. Thus, during complete hydration, the hydraulic compounds "pass through" the liquid phase although the amount dissolved at any given moment may be very small.

Many studies have been made on the hydration of the calcium silicates, considered to be present in Portland cement, and on the composition of the products obtained. Using silica sol and solutions of calcium hydroxide Le Chatelier (3, pp. 59–62) obtained hydration products with $CaO:SiO_2$ ratios varying between 1 and 1.7, depending on the concentration of lime in the solution at the end of the precipitation. He found that the only product to which the properties of a definite chemical compound could be attributed had the composition, $CaO.SiO_2.2\frac{1}{2}H_2O$, and considered that the lime present in excess of this ratio was "fixed by a phenomenon of superficial attraction well known for finely divided chemical precipitates."

Le Chatelier (3, p. 84) assigned this formula to the chemical compound obtained on hydration of the silicates present in Portland cement. Many later investigators have arrived at similar conclusions while others have considered that, under the conditions existing in mortars and concrete, compounds with $CaO:SiO_2$ ratios of 3:2 or 2:1 are formed. A summary of the literature on the hydration of Portland cement and of the pure cement compounds at ordinary temperatures has been compiled by Steinour (6). It is interesting to note that in the latest studies on hydrated calcium silicates at ordinary temperatures, Taylor (4, 5) has concluded that the product formed at concentrations of calcium hydroxide somewhat below saturation has a $CaO:SiO_2$ ratio varying from 1 to 1.5 and states that his X-ray data are consistent with the view that the lime in excess of a ratio of 1:1 is held

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either in the adsorbed state or in solid solution in a zeolite type of crystal. He found, however, that on hydration of tricalcium silicate at 17°C. in a solution approaching saturation with lime (>1.13 gm. calcium oxide per liter), a product with a $CaO:SiO_2$ ratio of 2:1 was formed, giving an X-ray pattern differing slightly from that of the product obtained at the lower concentrations of lime.

It is evident that a quantitative chemical study of the hydration products of Portland cement during the course of the hydration presents great difficulties on account of the intimate mixture of several compounds and of the lack of effective methods for separating the hydration products from each other and from the unhydrated material. Even when the pure silicates are used, the latter difficulty applies. Furthermore, complete hydration and uniform hydration products are not easily obtained.

The availability of radioactive calcium-45 as a tracer has opened up new methods for the study of the mechanism of the hydration, both of cements and of the pure cement compounds. For instance, in the study of the hydration of the silicates one may incorporate Ca^{45} in the anhydrous silicate and hydrate the product in water or in a solution of calcium hydroxide. As an alternative, the inactive* silicate may be hydrated in a solution of calcium hydroxide labelled with the isotope, Ca^{45}. By following the rate of liberation of lime due to hydrolysis and the coincident appearance of Ca^{45} in the solution, or in the second case by determining the simultaneous rate of removal of Ca^{45} from the solution by the precipitation of the hydration product, one obtains experimental data which appear to distinguish decisively between postulated $CaO:SiO_2$ ratios for the composition of the precipitated hydrated silicate under the experimental conditions used.

The data reported in the present paper deal with the hydration of tricalcium silicate and β-dicalcium silicate at 21°C. in slightly supersatured solutions of lime, thus approximating the condition of lime saturation present for the most part during the hydration of the silicates in rich mortars and concrete.

MATERIALS

The chemicals used in the preparation of the silicates and the solutions of calcium hydroxide were of very high purity. 'Reagent' calcium carbonate, reprecipitated from dilute solution, contained negligible amounts of impurities. The silica gel (16% H_2O) had initially a nonvolatile residue with hydrofluoric and sulphuric acids of 0.16% and passed a 325-mesh sieve (<44 microns). After extracting with hydrochloric acid and washing free from chlorides, the nonvolatile residue was $<0.06\%$. Determination by flame photometer gave 0.004% sodium oxide and $<0.001\%$ potassium oxide.

Preparation of the Silicates

Carefully proportioned mixtures of calcium carbonate and silica gel in the $CaO:SiO_2$ ratio of 2:1 were given a preliminary ignition in platinum crucibles in a muffle furnace, the temperature being raised gradually to about

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**Unless otherwise indicated the terms "active" and "inactive" will refer only to the radioactivity of the materials under discussion and not to chemical activity.*

950°C. to avoid mechanical loss. Two ignitions in the temperature range, 1400 to 1700°C. in an induction furnace followed. The product "dusted" and passed a 200-mesh sieve (<74 microns) without grinding. A sample of γ-dicalcium silicate labelled with Ca^{45} was thus prepared and converted to β-dicalcium silicate by heating at 950 to 1000°C. and cooling rapidly. After several prolonged heatings microscopic examination indicated that less than 1% remained in the γ form. Tests for free lime were negative.

A second sample of γ-dicalcium silicate which was not labelled with Ca^{45} was prepared for use as the starting material for the preparation of tricalcium silicate. The product was mixed in stoichiometric proportions with Ca^{45} labelled calcium carbonate and, after a preliminary ignition to 950°C., was heated repeatedly in the induction furnace in the 1400 to 1700°C. range with rapid cooling and intermediate grinding to pass a 325-mesh sieve (in dry air, using a dust-tight safety chamber) until tests for free lime were negative, or only a small quantity was found by the alcohol–glycerol method. Four labelled samples of tricalcium silicate (and a fifth unlabelled) were prepared in the course of the present work.

Calcium Hydroxide

The solutions of calcium hydroxide were prepared from freshly ignited calcium oxide which was shaken in stoppered bottles of glass or polyethylene in a room thermostated at 21.0 ± 0.1°C. Supersaturated solutions were quickly formed and the shaking was continued until saturation was approached. The concentration of the solutions was determined by titration with 0.06 molar hydrochloric acid which was standardized against a very pure sample of calcium carbonate as well as against calcium hydroxide solution, the concentration of which had been determined by precipitation of the calcium as oxalate. Special precautions were taken against access of carbon dioxide to the lime and to the solutions of calcium hydroxide, and the water used was carbon-dioxide-free. The hydroxide solutions used at various times contained from 1.135 to 1.244 gm. calcium oxide per liter at 21°C.

THE HYDROLYSIS OF THE SILICATES

All the work, except the counting of the radioactive samples, was done in a room at 21.0 ± 0.1°C. The silicates, ground to pass a 325-mesh sieve, were shaken in a rotary shaker with the 'saturated' solution of calcium hydroxide in steel tubes completely lined with pure silver or gold foil. A thin film of silicone stopcock grease was used at the ground cap joint. A blank using a silver-lined tube and saturated solution, shaken for 116 days, showed a loss in titer of less than 3 parts in 1000 which may be considered to be close to the experimental variation for duplicate determinations. The saturated solution of calcium hydroxide was used in the hydrolysis experiments to prevent the formation of a hydrosilicate low in lime, in the initial stages of the hydration, and in the case of tricalcium silicate to attempt to produce the hydrosilicate of $CaO:SiO_2$ ratio of 2:1 for the existence of which Taylor (4) found evidence.

A supersaturated solution of lime was formed on the hydrolysis of the silicate but no precipitation of lime could be detected until the solution reached a high degree of supersaturation. Thus, when 0.1 gm. portions of tricalcium silicate were shaken with 100 ml. of the saturated lime solution on a rapidly revolving rotary shaker, the supersaturation usually reached about 20% before there was any evidence of precipitation of calcium hydroxide. This corresponds to the liberation of 1 mole calcium oxide per mole of the silicate. For greater extent of hydrolysis, 0.05 gm. portions of the silicate were used with 100 ml. of the saturated lime solution. When β-dicalcium silicate was used, precipitation of lime occurred at a lower degree of supersaturation thus limiting the degree to which hydrolysis of this compound could be carried under the conditions of our experiments. All the experimental work described in this paper was carried on in the metastable range of supersaturation.

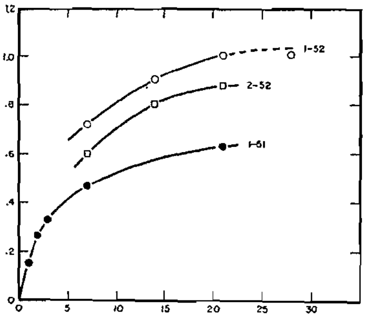
The amount of lime liberated in a given time interval was determined as the difference between the titer of 25 ml. portions of the original saturated lime solution and the hydrolyzate after centrifuging. The small solubility of the silicate caused no appreciable error. The activity of the calcium in the hydrolyzate was determined on 0.500 ml. portions by a Geiger counter after precipitation of the calcium as oxalate (window thickness 1.6 mgm. per sq. cm; scale of 64 scaler). Care was taken to keep the geometry constant. Before and after the counting of the unknown a standard sample of radioactive calcium and a preparation of the silicate being hydrolyzed was counted. The latter was prepared by decomposing (with hydrochloric acid) the same weight of the silicate as that used in 100 ml. in the hydrolysis experiment, removing the silica by dehydration, and making the solution up to 100 ml. A 0.500 ml. portion was then counted in exactly the same manner as the hydrolyzate. It was found that the additional calcium in the hydrolyzate did not affect the count appreciably. The ratio of the activity of the hydrolyzate to the activity of the solution from the silicate (after correction for background) was thus independent of the decay of the calcium-45, and the counting of the 'standard sample' of radioactive calcium served as an additional check.

Effect of Variation in the Method of Preparation of Tricalcium Silicate

Five samples of tricalcium silicate were prepared in a similar manner except for the time of ignition in the 1400 to 1700°C. range. The number of ignitions, the total time, and the free lime content were as follows:

Sample No.	Total time at 1400–1700°C., min.	Number of ignitions	Free lime, % CaO
1–52	25	1	5.4
2–52	85	2	0.13
1–53	200	3	0.30
1–51	250	3	0.57
2–53	360	5	0.00

The rates of liberation of lime of three of the samples at 21°C. on hydrolysis of 0.1 gm. portions in 100 ml. of saturated calcium hydroxide are plotted in Fig. 1. It shows that the rate is in the inverse order to the time of ignition, suggesting that progressive recrystallization of the silicate had occurred during the heating. No data are, however, available on the relative particle size, except that all the samples were ground to pass a 325-mesh sieve. Lime liberated by the hydrolysis of the dicalcium silicate present in the samples (which was small except in the case of sample 1–52) was considered to be negligible in the time involved. This is supported by the experimental data of Fig. 4. A correction was made for the free lime contained in sample 1–52 on the assumption that all the free lime passes quickly into solution. This represents an over-correction so that the actual rate of hydrolysis of sample 1–52 was greater than that shown in Fig. 1. Precipitation of calcium hydroxide had begun in the case of sample 1–52 at the 28 day point. The corresponding curves (not shown) for the other two samples of tricalcium silicate were in agreement. The rate of hydrolysis of sample 1–53 was slightly higher and that for sample 2–53 slightly lower than for sample 1–51.



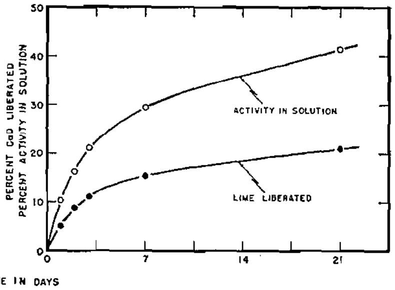


FIG. 1. The effect of the time of heating at 1400-1700°C. on the rate of hydrolysis of tricalcium silicate. (No. 1–52, 25 min., No. 2–52, 85 min., No. 1–51, 250 min.)

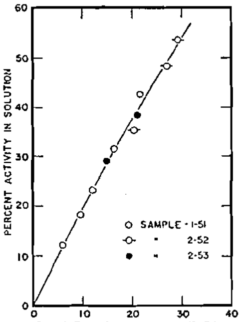
FIG. 2. Relative rates of increase with time of activity and alkalinity of the liquid phase during the hydration of labelled tricalcium silicate.

The Hydrolysis of Labelled Tricalcium Silicate and β-Dicalcium Silicate in a Saturated Solution of Calcium Hydroxide: The Relative Rates of the Appearance of Activity and of Alkalinity in the Liquid Phase

Fig. 2 gives the percentage of the total lime in the silicate liberated on hydrolysis as determined by titration, and the corresponding percentage of the total calcium activity found in the solution plotted against time for tricalcium silicate sample 1–51. It is evident that at any given time the percentage of the total activity in the solution is much greater than the percentage of the total lime of the silicate found in the solution. A similar relationship was found in the case of samples 1–52, 2–52, and 2–53.

In the preparation of tricalcium silicate the Ca^{45} was, in all cases, introduced in the third molecule of lime which was added to the already prepared inactive γ-dicalcium silicate. Considering the relationship between the activity and lime in the hydrolyzate, it might be thought that this indicates that the last molecule introduced into the crystal lattice was the first to be liberated on hydrolysis, thus supporting the view that the three molecules of calcium oxide in tricalcium silicate are not chemically equivalent — a conclusion which would be of great interest on account of the uncertainty as to the structure of this substance (1, 2).

There are, however, some obvious objections to this explanation of the experimental data. Fig. 1 shows the great variation in the relative rates of liberation of lime on hydrolysis of different samples of tricalcium silicate, but when time is eliminated as a parameter as in Fig. 3, which is a plot of the percentages of the total activity found in the solution against the lime liberated by hydrolysis as determined by titration, the experimental results for all the labelled samples, 1–51, 2–52, and 2–53, fall on the same curve. (The values for sample 1–52 are not included on account of the difficulty in correcting for the large amount of free lime in the sample.) If one assumes the existence of two types of lattice positions for Ca^{++} in the crystals of the silicate, one would expect some interchange between them to occur during the heating at 1400 to 1700°C. Such exchange should cause the samples of tricalcium silicate heated for the longer periods of time to give curves (Fig. 3) approaching a slope of 45°, corresponding to the uniform distribution of the Ca^{45} throughout the crystals. As the results for all the samples fall on the same curve, it appears probable that the Ca^{45} was uniformly distributed throughout the lattice of sample 2–52 as well as those heated for longer time, and that these hydrolysis experiments, therefore, cannot give any evidence for or against the equivalence of the three lime molecules in tricalcium silicate. Fig. 3, however, indicates that the mechanism of the hydrolysis of tricalcium silicate is independent of the rate.



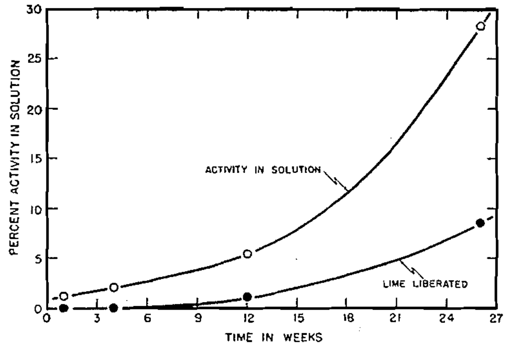


FIG. 3. The hydration of tricalcium silicate labelled with Ca^{45} in a saturated solution of calcium hydroxide. The relative increase in calcium hydroxide content and in the activity of the solution.

FIG. 4. The hydration of radioactive β-dicalcium silicate labelled with Ca^{45} in a saturated solution of calcium hydroxide. The relative increase with time of the activity and alkalinity of the liquid phase.

Data for the hydrolysis of a sample of labelled β-dicalcium silicate in a saturated solution of calcium hydroxide plotted in Fig. 4 are also of interest.

Here, too, the percentage of total activity found in the hydrolyzate is far in excess of the percentage of total lime liberated as calculated from the increase in the titer.

THEORETICAL CALCULATIONS

The theoretical curve for the activity of the calcium in the hydrolyzate plotted against the lime liberated, as determined by titration, can be calculated for any postulated lime: silica ratio of the hydrosilicate on the basis of the assumption that the anhydrous silicate (labelled with Ca^{45}) passes into solution in the form of ions and that the 'life' of the Ca ions is long enough to allow uniform distribution throughout the hydrolyzate, under the conditions of agitation used, before precipitation of the calcium in the form of calcium hydrosilicate occurs. The presence of calcium in undissociated molecules in the solution would not change the conclusion reached, provided the interval of time before precipitation is long enough for attainment of exchange equilibrium. The activity present in the solution at any moment will be a function of the amount of anhydrous silicate which has entered the solution, the specific activity of the anhydrous silicate, the amount of calcium hydroxide in the original solution, and the ratio of lime to silica in the precipitated calcium hydrosilicate. The problem is simplified somewhat for a given series of experimental determinations where the specific activity of the sample of anhydrous silicate (corrected for the rate of decay) is a constant and the volume and concentration of the original solution of calcium hydroxide is fixed.

The Hydration of Labelled Tricalcium Silicate in Inactive Calcium Hydroxide Solution

A mathematical expression for the percentage activity in the solution during the hydrolysis and hydration of tricalcium silicate according to the over-all equation

$$2(3CaO.SiO_2) + (n + 3)\ H_2O \rightarrow 3CaO.2SiO_2.nH_2O + 3Ca(OH)_2,$$

may be developed as follows:

Let a represent the number of moles of lime in the original solution and b the specific activity of the labelled silicate defined in terms of the activity per mole of lime present in the silicate. Let x be the amount of anhydrous silicate which has passed into the solution expressed in terms of moles CaO and $f(x)$ be the specific activity of CaO in solution in units of activity per mole of CaO. Consider the hydrolysis of $\frac{1}{3}\ dx$ moles of tricalcium silicate, which in the first step of this mechanism liberates dx moles of calcium oxide to the solution. We take dx sufficiently small that it does not appreciably change the specific activity of calcium oxide in the solution, $f(x)$. In the second step of this mechanism calcium oxide to the extent of one-half of the amount of calcium oxide liberated, or $\frac{1}{2}\ dx$, of specific activity $f(x)$, is removed to form the hydration product. It is clear that the calcium radioactivity liberated to the solution is bdx while that removed is $\frac{1}{2} f(x)dx$, so that the net increase in the total calcium radioactivity in solution is $bdx - \frac{1}{2} f(x)dx$. When x moles have been liberated, the increase is

$$[1] \qquad \int_0^x (b - \tfrac{1}{2} f(x))\, dx.$$

To find $f(x)$,we consider the liberation of Δx moles of calcium oxide by tricalcium silicate which has already liberated x moles. There has been an increase of only $\frac{1}{2}x$ moles of calcium oxide in the solution, in which the specific activity of calcium oxide is $f(x)$. After x moles have been liberated, the total calcium radioactivity in solution is

$$(a + \tfrac{1}{2}x)f(x).$$

If we permit Δx moles to be liberated with no precipitation, the resulting total calcium radioactivity in solution will be

$$(a + \tfrac{1}{2}x)f(x) + b\Delta x,$$

and the new specific activity will be

$$f(x + \Delta x) = \frac{(a + \frac{1}{2}x)f(x) + b\Delta x}{a + \frac{1}{2}x + \Delta x}.$$

We now form

$$\frac{f(x + \Delta x) - f(x)}{\Delta x} = \left[\frac{(a + \frac{1}{2}x)f(x) + b\Delta x}{a + \frac{1}{2}x + \Delta x} - f(x)\right] \Big/ \Delta x$$
$$= \frac{b - f(x)}{a + \frac{1}{2}x + \Delta x}.$$

In the limit as $x \rightarrow 0$, this expression becomes

$$\frac{df(x)}{dx} = \frac{b - f(x)}{a + \frac{1}{2}x}.$$

If we solve this differential equation under the conditions that $f(x) = 0$, when $x = 0$, we get

$$[2] \qquad f(x) = b - [4a^2b/(2a + x)^2].$$

Now substitute [2] in [1] and obtain for the total calcium radioactivity in solution

$$\int_0^x \left(\tfrac{1}{2}b + \frac{2a^2b}{(2a + x)^2}\right) dx = \tfrac{1}{2}bx + 2a^2b \int_0^x \frac{dx}{(2a + x)^2}$$
$$= b\left[\tfrac{1}{2}(2a + x) - \frac{2a^2}{(2a + x)}\right]$$

on integration.

For convenience, we convert this into percentage activity in solution by dividing by the total calcium activity in the tricalcium silicate used, namely b times moles of calcium oxide in the solid, and multiplying by 100; whence,

$$[3] \qquad \%\text{ activity in solution} = \frac{\frac{1}{2}(2a + x) - [2a^2/(2a + x)]}{(\text{moles CaO originally in solid})} \times 100.$$

On the basis of the over-all process postulated above, for each mole of tricalcium silicate which "passes through" the liquid phase three moles of lime pass into solution and 1.5 moles pass out of the solution in the hydrated silicate. The value of x in equation [3] is therefore twice the number of moles of lime liberated as determined by titration.

An expression for the percentage activity in the solution if the over-all reaction for the hydrolysis and hydration is represented by the equation

$$3CaO.SiO_2 + (n+1)\ H_2O \rightarrow 2CaO.SiO_2.nH_2O + Ca(OH)_2,$$

may be developed in analogous fashion.

In this process of hydration defining a, b, x, and $f(x)$ as before, when $\frac{1}{3}dx$ moles of tricalcium silicate pass through the liquid phase dx moles of labelled calcium oxide pass into solution carrying bdx units of radioactivity and $\frac{2}{3}dx$ moles are removed from solution carrying $\frac{2}{3}f(x)dx$ units of radioactivity as defined above. As in equation [1] above, we express the increase in total calcium radioactivity in solution as

$$[4] \qquad \int_0^x (b - \tfrac{2}{3}f(x))\,dx.$$

If, after x moles of calcium oxide from the silicate have passed into the solution with the concurrent precipitation of hydrated silicate, we consider the liberation of Δx moles of calcium oxide to the solution we may obtain by the same process as before the expression

$$\frac{df(x)}{dx} = \frac{b - f(x)}{a + \frac{1}{3}x},$$

which on integration and simplification yields

$$[5] \qquad f(x) = b - [27a^3b/(3a+x)^3],$$

where as before $f(x) = 0$ when $x = 0$.

Substitution of [5] in [4] yields, on integration,

$$b[\tfrac{1}{3}(x+3a) - \{9a^3/(3a+x)^2\}]$$

for the total radioactivity in the solution, whence,

$$[6] \quad \%\ \text{activity in solution} = \frac{\frac{1}{3}(x+3a) - [9a^3/(3a+x)^2]}{(\text{moles CaO originally in solid})} \times 100.$$

The value of x in equation [6] is three times the number of moles of lime which have been liberated as determined by titration.

A general expression for the activity in the solution for any postulated lime:silica ratio in the hydration product may be developed for the hydrolysis of tricalcium silicate in the same manner. If a and x are defined as before and r is the CaO:SiO$_2$ ratio in the hydrate, the final expression for the percentage of the total activity in the solution becomes,

$$[7] \quad \frac{x - \frac{1}{3}rx - \frac{r-3}{3}\left\{\frac{3a}{3-r}\right\} + \frac{r-3}{3}\left\{\frac{3a}{3-r}\right\}^{3/(3-r)}\left\{\frac{3a}{3-r} + x\right\}^{r/(r-3)}}{(\text{moles CaO in original silicate})} \times 100$$

where $x = 3/(3 - r)$ times the number of moles of lime which have been liberated as determined by the increase in the titer of the solution.

The Hydration of Labelled Dicalcium Silicate in Inactive Calcium Hydroxide Solution

An expression for the hydrolysis of dicalcium silicate labelled with Ca^{45} with the formation of the 3:2 calcium hydrosilicate may be derived in a similar manner.

In this case, with the same definitions for a, b, x, and $f(x)$ as before, when $\frac{1}{2}dx$ moles of the silicate pass through the solution, dx moles of labelled calcium oxide pass into solution carrying bdx units of activity, but $\frac{3}{4}\,dx$ moles are removed from the solution carrying $\frac{3}{4}\,f(x)dx$ units of activity. After x moles of lime (from the silicate) have entered the solution with the concurrent precipitation of the hydrosilicate, the activity of the solution is given by

$$[8] \qquad \int_0^x \left(b - \tfrac{3}{4}f(x)\right) dx.$$

Evaluating $f(x)$ as before, we obtain

$$[9] \qquad f(x) = b - \frac{256a^4b}{(4a+x)^4},$$

taking $f(x) = 0$ when $x = 0$. Substituting [9] in [8], integrating and simplifying, we obtain, upon dividing by the total initial calcium activity in the solid and multiplying by 100,

$$[10] \quad \%\text{ activity in solution} = \frac{\frac{1}{4}(4a+x) - [64a^4/(4a+x)^3]}{(\text{moles CaO originally in solid})} \times 100.$$

The value of x in equation [10] is four times the number of moles of lime which have been liberated as determined from the increase in the titer of the solution.

Fig. 5 shows the theoretical curves for the hydrolysis of tricalcium silicate with the formation of a 3:2 calcium hydrosilicate (Curve A), the formation of a 2:1 calcium hydrosilicate (Curve B), and also the hydrolysis of dicalcium silicate with the formation of a 3:2 calcium hydrosilicate (Curve C), for 0.1 gm. portions of the silicate in 100 ml. of a calcium hydroxide solution containing initially 1.2 gm. calcium oxide per liter. There is a wide divergence between the theoretical curves for the two hydrosilicates.

The Hydrolysis of Inactive Tricalcium Silicate in a Saturated Calcium Hydroxide Solution Labelled with Ca^{45}

An expression for the change in the activity of a solution of labelled calcium hydroxide during the hydrolysis of a sample of inactive tricalcium silicate can also be developed. On the assumption that a hydrated 3:2 calcium hydrosilicate is formed, the fraction of the initial activity which remains in the solution after x moles of the calcium oxide of the silicate have passed into the solution with the consequent precipitation of hydrosilicate is given by the expression:

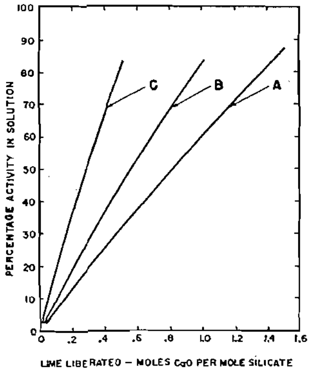
$$[11] \qquad 2a/(2a + x)$$

where a = moles of calcium oxide originally present in the solution, and x, the number of moles of lime which have passed from the solid into the liquid phase, is equal to twice the increase in the concentration of calcium oxide in the solution.

The corresponding expression for the activity in the solution for the formation of a hydrated silicate with a $CaO:SiO_2$ ratio of 2:1 is:

$$[12] \qquad \text{Per cent activity remaining in solution} = [9a^2/(3a + x)^2] \times 100.$$

In this case x has a value three times the number of moles of lime liberated as determined by titration.



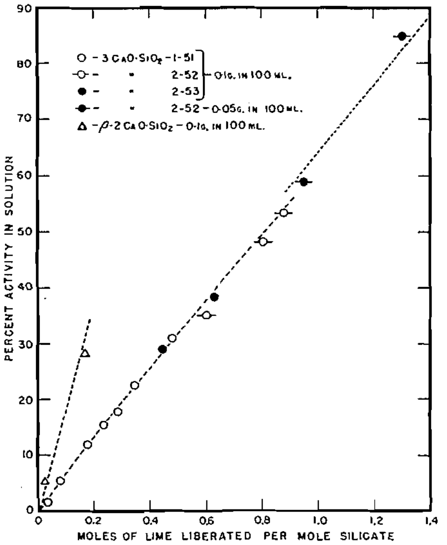


FIG. 5. Theoretical curves for the hydration of tricalcium silicate and dicalcium silicate labelled with Ca^{45} in a solution of calcium hydroxide (0.1 gm. portions of the silicate in 100 ml. of solution containing 1.2 gm. calcium oxide per liter).

A. Tricalcium silicate to give a 3:2 calcium hydrosilicate.
B. Tricalcium silicate to give a 2:1 calcium hydrosilicate.
C. Dicalcium silicate to give 3:2 calcium hydrosilicate.

FIG. 6. Experimentally determined points for the hydration of labelled tricalcium silicate and β-dicalcium silicate at 21°C., in saturated solutions of calcium hydroxide, showing the theoretical curves for the formation of a product with a $CaO:SiO_2$ ratio of 3:2.

EXPERIMENTAL RESULTS

Table I gives the experimental and calculated data for the hydrolysis and hydration of three samples of labelled tricalcium silicate and one sample of labelled β-dicalcium silicate at 21°C. Fig. 6 shows plots of the data together with the theoretical curves for the formation of a hydrate of the composition $3CaO.2SiO_2.nH_2O$. No corrections were applied to the experimental data for the small amount of free lime present in some of the samples, as the validity of such corrections is doubtful and would be only of the order of magnitude of the experimental error in counting (probable error about

TABLE I

THE HYDRATION OF TRICALCIUM SILICATE AND β-DICALCIUM SILICATE (LABELLED WITH Ca^{45}) IN SOLUTIONS OF CALCIUM HYDROXIDE AT 21°C.

Silicate Sample No.	Initial conc. of lime sol'n., millimoles/ 100 ml.	Time of shaking	Lime liberated as determined by titration, mole CaO/mole silicate	Percent of activity in the hydrolyzate	
				Exp.	Calc.
$3CaO.SiO_2$					Basis $3CaO.2SiO_2.nH_2O$
1–51	2.194	6 hr.	0.030	1.7	2.0
1–51	2.125	12 hr.	0.079	5.5	5.3
1–51	2.125	24 hr.	0.178	11.9	11.6
1–51	2.125	36 hr.	0.238	15.3	15.5
1–51	2.125	48 hr.	0.287	17.9	18.6
1–51	2.189	72 hr.	0.348	22.6	22.4
1–51	2.189	1 wk.	0.479	31.0	30.6
2–52	2.195	1 wk.	0.602	35.1	38.0
2–52	2.195	2 wk.	0.806	48.2	49.9
2–52	2.201	3 wk.	0.879	53.4	54.2
2–52*	2.184	4 wk.	0.950	59.1	60.4
2–52*	2.184	11 wk.	1.31	84.9	82.3
2–53	2.184	1 wk.	0.446	29.1	28.5
2–53	2.184	2 wk.	0.627	38.4	39.5
β-$2CaO.SiO_2$	2.200	12 wk.	0.023	5.4	4.5
β-$2CaO.SiO_2$	2.200	26 wk.	0.170	28.3	31.8

**0.05 gm. $3CaO.SiO_2$ in 100 ml. solution.*
Weight of silicate in 100 ml. solution 0.1 gm.

one per cent). The experimental results are in agreement with the assumption that the product formed during the hydrolysis and hydration of both silicates at 21°C. is the 3:2 calcium hydrosilicate.

It should be noted that the dotted curve in the upper right hand corner of Fig. 6 is the calculated curve for the hydrolysis of 0.05 gm. portions of active tricalcium silicate in 100 ml. of the lime solution used in the experiments, while the other curves are calculated for the hydrolysis of 0.1 gm. portions of the silicates in 100 ml. of lime solution, the formation of a hydrosilicate of $CaO:SiO_2$ ratio of 3:2 being postulated in all cases.

When the experimental results with active tricalcium silicate are plotted as in Fig. 6, precipitation of calcium hydroxide from the super-saturated solution gives abnormally high values for the percentage of total activity found in the hydrolyzate. This is due to the fact that such precipitation reduces the value for lime liberated per mole of silicate, as determined from the increase in titer, proportionally more than the activity count. Such divergence from consistent values for the activity is probably a more sensitive means than microscopic examination for detecting the beginning of precipitation of hydrated lime.

Fig. 7* is a plot of the calculated theoretical curves for the hydration of inactive tricalcium silicate in a solution of calcium hydroxide (0.1135 gm. calcium oxide per 100 ml.) labelled with Ca^{45} for the formation of the 3:2 calcium hydrosilicate (Curve A) and of the 2:1 calcium hydrosilicate (Curve

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**The authors are indebted to Mr. F. W. Birss for making some of the determinations recorded in Fig. 7.*

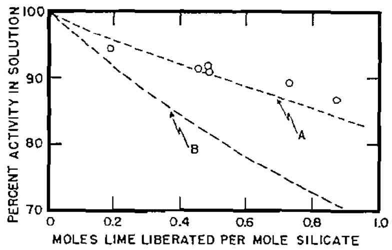

FIG. 7. Theoretical curves for the hydration of inactive tricalcium silicate in labelled calcium hydroxide solution together with experimental points at 21°C. (0.1 gm. portions of silicate in 100 ml. calcium hydroxide solution containing 1.13 gm. calcium oxide per liter).

B), respectively. The points are the experimental values obtained when tricalcium silicate 1–53 was shaken with calcium hydroxide solution of the above concentration. The experimental results are in general agreement with the assumption that a hydration product of the composition $3CaO.2SiO_2.nH_2O$ is formed. It may be noted that in this series the total amount of tricalcium silicate used in an experiment does not enter into the calculation of the expected percentage activity in the solution, only the amount of the silicate passing through the solution being significant. Also, since the solution is at the maximum of activity at the beginning of the runs when the rate of hydrolysis is very high (see Fig. 1), the results are particularly sensitive to any interruptions in shaking. Such interruptions and any lack of attainment of complete homogeneity of the hydrolyzate at all stages would tend to give low values for the removal of activity from the solution or high values for the activity as plotted in Fig. 7.

The question of the effect of exchange of calcium between the solution and the hydrated silicate has to be considered. In the experiments with labelled tricalcium silicate such exchange, if it occurs, would tend to lower the values for the activity found in the hydrolyzate while in the case of the hydrolysis of inactive tricalcium silicate in active calcium hydroxide solution the values would tend to increase. Considering the hydration of labelled tricalcium silicate to form the 3:2 hydrosilicate and assuming that complete exchange equilibrium between the calcium of the hydrolyzate and the hydrated portion of the silicate occurs, the expression for the per cent activity in the hydrolyzate becomes

$$x(2a + x) \times 100/[2(a + x)(\text{moles CaO in original silicate})].$$

For similar conditions with the formation of the 2:1 calcium hydrosilicate the expression would be

$$x(3a + x) \times 100/[3(a + x)(\text{moles CaO in original silicate})],$$

x and a being defined as above.

If these expressions are plotted as in Fig. 5, the curves have a slightly lower slope than the corresponding curves 'A' and 'B'. Under the conditions of our experiments, the change in the activity of the hydrolyzate which would be caused by complete exchange equilibrium of the calcium between the solution and the hydrated solid is, however, only a small fraction of the difference in percentage activity for corresponding points on curves 'A' and 'B' of Fig. 5.

Similar considerations apply to the experiments with inactive tricalcium silicate in the labelled solution of calcium hydroxide. Here the per cent activity in the solution for complete exchange equilibrium is given by $(2a + x)\ 100/[2(a + x)]$ for the formation of the 3:2 hydrosilicate and by $(3a + x)\ 100/[3(a + x)]$ for the formation of the 2:1 product. The calculated curves differ slightly from curves 'A' and 'B' of Fig. 7. Again the change in the activity of the solution caused by complete exchange equilibrium under the conditions of our experiments is only a small fraction of the calculated difference in percentage activity for the formation of the two hydrosilicates.

Such exchange of calcium between the hydrolyzate and the hydration product could, therefore, not affect the conclusions arrived at above as to the composition of the hydrated silicate. The extent to which exchange occurs is being further studied.

While our experiments give no indication of the formation of a hydrated dicalcium silicate when tricalcium silicate is hydrated in a saturated solution of calcium hydroxide at 21°C., our results do not necessarily contradict those of Taylor (4) since his work was done at 17°C.

The results of our experiments are in fact in accord with the conclusions of Jeffery (2) that tricalcium silicate is composed of discrete ions of calcium, oxygen, and (SiO_4) and of Bernal, Jeffery, and Taylor (1) that in the initial stage of hydration the anhydrous silicates act only as a source of calcium and silicate ions from which the hydration products can be formed. From our experiments it would seem that in a saturated solution of calcium hydroxide at 21°C. the $(SiO_4)^{4-}$ ions undergo chemical change before, or incidental to, the formation of the hydrated silicate.

The work described in this paper illustrates a new approach to the study of the mechanism of the hydrolysis and hydration of slightly soluble solids by the use of radioactive tracers. It appears that the method could be extended to the study of the mechanism of many other chemical reactions especially when the progress of the reaction can be followed independently by both chemical and radiochemical methods.

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PREPARATION OF ION-EXCHANGE RESINS[1]

BY I. H. SPINNER,[2] J. CIRIC, AND W. F. GRAYDON

ABSTRACT

Ion-exchange resins as membranes and in granular form have been prepared by the copolymerization of divinylbenzene with various esters of *p*-styrenesulphonic acid and subsequent hydrolysis. The synthesis of the sulphonated styrene monomers is described. Equilibrium data for the sodium–hydrogen ion exchange on a resin prepared in this manner are discussed in terms of postulated variations of sulphonate group environment.

INTRODUCTION

Polystyrenesulphonic acid ion-exchange resins have been prepared previously by the sulphonation of cross-linked polystyrene (5, 7, 10). It is evident that this process yields an ion-exchange resin in which the environment of some sulphonate groups may differ markedly from that of other sulphonate groups. Sulphonate groups may exist in regions which on a micro scale are more or less highly cross-linked, or more or less highly sulphonated than the average for the resin bead. There is, in addition, the possibility of producing benzene nuclei bearing two sulphonate groups. A capacity of 1.2 sulphonate groups per benzene nucleus has been reported (7). Even resins with an over-all capacity of less than one sulphonate group per benzene nucleus may contain disubstituted nuclei near the surface of the bead. Also it is probable that sulphonation of divinylbenzene nuclei occurs.

Observed variations in the mass law "relative affinity coefficients" or equilibrium quotients of ion-exchange resins prepared by the sulphonation of polystyrene have been considered on the implicit assumption that all of the sulphonate groups are identical (2, 4, 6). Thus the exchange groups on a resin have been considered as a fraction of a mole of exchange groups and have been assigned in effect a standard free energy.

Alternatively, if the assumption is made that the variations in the sulphonate group environments are not negligible, the sulphonate groups may be considered as a mixture of exchange groups with various standard free energies. The exchange process is then considered as a number of simultaneous equilibrium reactions. It is apparent that such a process if treated as a single equilibrium reaction would not yield a constant value for the equilibrium quotient, even if resin activity coefficients were unity and swelling pressure variations were negligible. Walton in 1943 (11) recognized that ion-exchangers bearing more than one type of exchange group, such as phenolic, carboxylic, or sulphonic, would give rise to an equilibrium quotient which would be a function of the mole fraction of exchanging ions on the resin. Boyd (3) has mentioned the

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[2] *Part of the work described herein was included in a thesis submitted by I. H. Spinner to the Department of Chemical Engineering, University of Toronto, in partial fulfillment of the requirements for the degree of Master of Applied Science in January, 1953.*

possible significance of chemical or structural nonuniformities in monofunctional ion exchange resins. Thus it seems that the possibility of a significant departure from sulphonate group identity ought to be eliminated before variations in the mass law equilibrium quotients are attributed to other causes.

In order to test this hypothesis, it would be of interest to prepare a polystyrenesulphonic acid resin by the copolymerization of monomers which differ in reactivity ratios from the styrene–divinylbenzene system. In addition it would be desirable to use ionogenic monomers which could be converted after polymerization to sulphonic exchange groups without polymer sulphonation. Thus the possibility of disubstitution or divinylbenzene substitution could be eliminated. The esters of *p*-styrenesulphonic acid have been chosen as a group of compounds fulfilling these desiderata.

EXPERIMENTAL

Preparation of Monomers

p-(β-Bromoethyl)-benzenesulphonylchloride

β-Phenylethylbromide (180 gm.) was reacted with 500 ml. of chlorosulphonic acid essentially in accordance with the procedure of Inskeep and Deanin (8), except that the temperature was maintained at 3–5°C. The product was extracted with ether, crystallized at dry ice temperature, and recrystallized rapidly from dry methanol. The yield was 160 gm. (56%), m.p. 54–55°C.

Anal. calc. for $C_8H_8BrSO_2Cl$: C, 33.91%; H, 2.85%; S, 11.31%.
Found:* C, 34.16%; H, 2.89, 2.90%; S, 11.46, 11.50%.

Inskeep and Deanin did not separate the para isomer but they established the presence of the para compound by the preparation and oxidation of *p*-vinylbenzene-N,N′-dimethylsulphonamide. The derivative *p*-(β-bromoethyl)-benzene-N,N′-dimethylsulphonamide was prepared, m.p. 98.5–99°C. Inskeep and Deanin (8) reported m.p. 99–100°C. The derivative *p*-vinylbenzene-N,N′-dimethylsulphonamide was prepared, m.p. 62–63°C. Reported m.p. 63–63.5°C. The derivative *p*-(β-bromoethyl)-benzenesulphonamide was prepared m.p. 184.5–185.5°C. Reported m.p. was 185.5–186°C. The derivative *p*-vinylbenzenesulphonamide was prepared, m.p. 139–140°C.

n-Propyl-p-(β-bromoethyl)-benzenesulphonate

One hundred grams of *p*-(β-bromoethyl)-benzenesulphonylchloride were suspended in 200 gm. of *n*-propanol and allowed to stand until the solid had dissolved. The solution was neutralized slowly at 10°C. with 6 *N* aqueous sodium hydroxide solution. The propyl ester separated as an oil. The suspension was diluted to 500 cc. with cold water. The aqueous layer was saturated with sodium chloride and the oil was extracted with ether. The ether solution was washed with cold water, dried, concentrated in vacuum in the cold, and the ester distilled at 1μ in a Hickman still. The yield was 85.5 gm. (80%), m.p. 6–8°C., n_D^{25} 1.5442, d_{25}^{25} 1.385.

Anal. calc. for $C_{11}H_{15}O_3BrS$: C, 43.00%; H, 4.92%; S, 10.44%; Br, 26.01%.
Found:* C, 43.63%, 43.48%; H, 5.17%, 5.01%; S, 10.30%, 10.57; Br, 25.97%, 25.80%.

All analyses done by Micro-Tech Laboratories, Skokie, Illinois.

n-Propyl-p-vinylbenzenesulphonate

Fifty-five grams of *n*-propyl-*p*-(β-bromoethyl)-benzenesulphonate were dissolved in 120 cc. of ethanol and heated to 50°C., 11.5 gm. of potassium hydroxide dissolved in 140 cc. of ethanol at 50°C. were added. The reaction mixture was diluted to 500 cc. with cold water and the ester was extracted with ether. A trace of tertiary butyl catechol was added to the solution, which was then dried. The ether was removed in vacuum in the cold and the ester distilled at 1μ in a Hickman still. A yield of 23.7 gm. (55%) of the colorless liquid product was obtained, n_{D}^{25} 1.5374, d_{25}^{25} 1.165. Attempts to cause crystallization were unsuccessful.

Anal. calc. for $C_{11}H_{14}O_3S$: C, 58.37%; H, 6.23%; S, 14.17%.
Found:* C, 58.10%, 58.04%; H, 6.26%, 6.40%; S, 14.15%, 14.27%.

A number of similar esters, which are listed below, were prepared by the method given above. Purification was found to be difficult because of decomposition and polymerization. In general the crude product was used for the preparation of the resins.

Methyl-p-(β-bromoethyl)-benzenesulphonate

Using 85 gm. of *p*-(β-bromoethyl)-benzenesulphonyl chloride, 45.0 gm. (75%) of white solid was obtained. After recrystallization from petroleum ether (b.p. 80–100°C.) the solid melted at 66–66.5°C.

Anal. calc. for $C_9H_{11}O_3BrS$: C, 38.72%; H, 3.97%; S, 11.48%; Br, 28.62%.
Found:* C, 38.74%, 38.83%; H, 4.04%, 4.20%; S, 11.65%, 11.75%; Br, 28.64%, 28.38%.

The ethyl and butyl esters of *p*-vinylbenzenesulphonic acid were also prepared. These products were both oils which were difficult to purify. In both cases traces of bromine were found in the final product and in both cases this impure product was used for polymerization. The major impurity was expected to be the bromide which would not interfere with the polymerization.

Polymerization and Hydrolysis

p-Vinylbenzenesulphonamide could not be copolymerized successfully with styrene and divinylbenzene by suspension techniques owing to its water solubility. Solution polymerization in methanol gave a polymer which was hydrolyzed for 72 hr. with 25% hydrochloric acid.

Suspension copolymers of styrene, divinylbenzene, and the other monomers were prepared according to the following recipe based on monomer mixtures totalling 100 gm. The monomers containing 1 gm. of benzoyl peroxide were added to 1000 ml. of the stabilizing solution, in a three-necked standard taper flask fitted with a reflux condenser and stirrer. The stabilizing solution contained 0.1% hydroxyethyl cellulose (Cellosize WPL_H). The speed of the stirrer was adjusted to give beads of the desired size (1 mm. or larger) and the temperature was maintained at 90°C. When the beads had hardened, agitation was stopped and heating continued for an additional 40 hr. The copolymer of *p*-vinylbenzene-N,N′-dimethylsulphonamide was hydrolyzed for 120 hr. with 25% hydrochloric acid under reflux. The ester copolymers were hydrolyzed with 5% sodium

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**All analyses done by Micro-Tech Laboratories, Skokie, Illinois.*

hydroxide. The copolymers were then conditioned with 2 *N* sodium chloride and 2 *N* hydrochloric acid, thoroughly rinsed, and the capacities determined by the addition of 2 *N* sodium chloride to a known weight of exchanger and titration with 0.1 *N* sodium hydroxide.

Polymerization charge	Yield, gm.	Maximum capacity, mgm. equiv./gm. dry H resin
20.0 gm. *p*-vinylbenzenesulphonamide 60 gm. divinylbenzene solution (21%)	16.0	1.80
20.2 gm. *p*-vinylbenzene-N,N′-dimethylsulphonamide 20.7 gm. divinylbenzene solution (21%)	30.8	0.94
8.3 gm. *n*-butyl-*p*-vinylbenzenesulphonate 8.3 gm. divinylbenzene solution (21%)	15.3	2.91
8.0 gm. *n*-propyl-*p*-vinylbenzenesulphonate 2.0 gm. divinylbenzene solution (55.4%)	8.0	1.94
21.4 gm. ethyl-*p*-vinylbenzenesulphonate 8.5 gm. divinylbenzene solution (55.4%)	23.6	3.12

One of the difficulties encountered in the preparation of the polymers was the loss resulting from the hydrolysis of the esters in the suspension polymerization. This hydrolysis during polymerization is indicated by the intercept at zero time in the polymer hydrolysis curves of Fig. 1. Thus the nominal cross-linking is somewhat higher than the composition of the polymerization charge would indicate. The polymer prepared from the butyl ester was obtained with greatest yield and was used for the equilibrium determinations. This hydrolyzed resin prepared from the butyl ester is called for conveneince, ester resin.

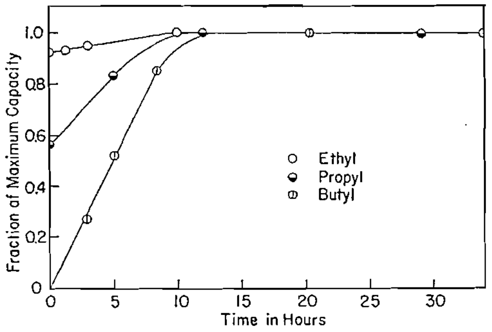

FIG. 1. Hydrolysis of ester copolymers.

Equilibrium Quotient Determinations

A sample of about 2 mgm. equiv. of the hydrogen form of the resin was placed in a flask and the capacity determined by the addition of 2 *N* sodium chloride solution and titration with 0.1 *N* sodium hydroxide solution using bromcresol green as the indicator. The same sample after complete conversion to either the hydrogen or sodium form was equilibrated with solutions containing 0.1 N sodium chloride and 0.1 N hydrochloric acid solutions in various proportions. After equilibrium had been attained, the solution was analyzed for sodium chloride by evaporation and for hydrochloric acid by titration. The resin sample was drained by suction, thoroughly rinsed, and the hydrogen ion on the resin determined as in the capacity determinations. The sodium ion on the resin was calculated from the difference between the hydrogen ion on the resin and the capacity. In all cases equilibrium quotient values were obtained using resin initially in the hydrogen form and also using resin initially in the sodium form. Equilibrium quotients were also determined in a similar way on a sample of this butyl ester resin which had been sulphonated by treatment with sulphuric acid to a capacity of 4.87 mgm. equiv. per gm.

Ion-exchange Membranes

One of the major difficulties encountered in the preparation of unsupported "homogeneous" ion-exchange membranes by the sulphonation of polystyrene films is the low tensile strengths which the products possess. The copolymerization of ester monomers with divinylbenzene permits the preparation of resins which because of low capacity have much less tendency to swell. For example, such films prepared by the copolymerization of *n*-propyl-*p*-vinylbenzenesulphonate with divinylbenzene had the following characteristics:

TABLE I
ION-EXCHANGE MEMBRANES

Capacity, mgm. equiv./gm. dry hydrogen form	Yield strength, lb. per sq. in.
1.22	2010
1.92	1670
2.72	1270

The detailed properties of films of this sort will be discussed in a subsequent contribution.

DISCUSSION

One of the features of the equilibrium data obtained for the ester resin, as given in Fig. 2, Plot 1, is that the equilibrium quotients are more nearly constant than those reported in the literature for sulphonated polystyrene resins of comparable cross-linking.

The postulate has been made that the constancy of the ion-exchange equilibrium quotient may be a function of the detailed structure of the resin. Hence it is of interest to consider the variations which would be obtained for the equilibrium quotient of a hypothetical ion-exchange resin in which the sulphonate groups are of two types. The environment of type 1 sulphonate groups is assumed to be significantly different from the environment of type 2 sulphonate

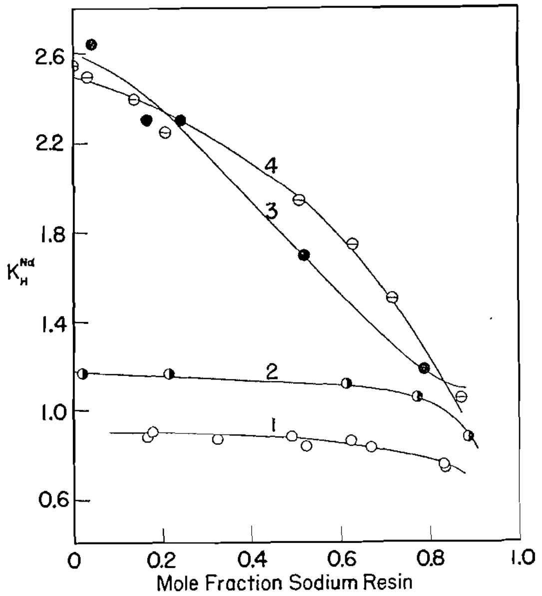

FIG. 2. Equilibrium data:
○ Butyl ester copolymer:—2.91 mgm. equiv./gm. 14–15 mole % divinylbenzene.
◑ Above resin sulphonated:— 4.87 mgm. equiv./gm. 14–15 mole % divinylbenzene.
● Data of Reichenberg (10):— 5.00 mgm. equiv./gm. 15 mole % divinylbenzene.
⊖ Data of Bonner (2):— 5.10 mgm. equiv./gm. 14 mole % divinylbenzene.
Solid lines are results for hypothetical exchanger with parameters as shown in Table II.

groups. All sulphonate groups within a type are assumed to be identical. Activity coefficients are assumed to be unity and swelling pressure variations are assumed to be negligible. For this hypothetical resin the following equations can be written for the uni-univalent exchange of the ionic species A and B:

$$\left(\frac{A}{B}\right)_{R_1} = K_1\left(\frac{A}{B}\right)_s \qquad \left(\frac{A}{B}\right)_{R_2} = K_2\left(\frac{A}{B}\right)_s$$

where: $\left(\frac{A}{B}\right)_{R_1}$ represents the mole ratio of A to B on the type 1 sulphonate groups,

subscript $_{R_2}$ represents type 2 sulphonate groups,

subscript $_s$ represents solution.

These two equations may be combined to give the following expression for the over-all exchange on the resin:

$$\left(\frac{A}{B}\right)_R = \frac{\left[C_1K_1 + (1 - C_1)K_2\right]\left(\frac{A}{B}\right)_s + K_1K_2\left(\frac{A}{B}\right)_s^2}{1 + \left[(1 - C_1)K_1 + C_1K_2\right]\left(\frac{A}{B}\right)_s}$$

where: subscript $_R$ represents the resin as a whole,

C_1 represents the fraction of the whole resin capacity which is type 1 capacity.

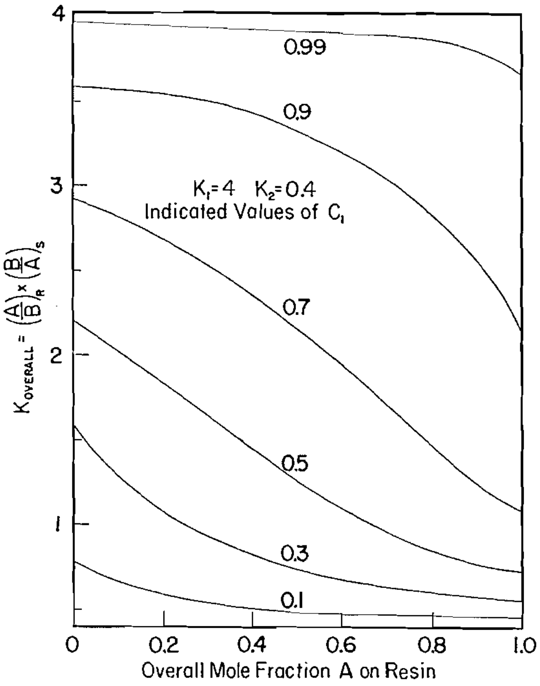

FIG. 3. Equilibrium plots for hypothetical exchanger. Effect of variation in C_1 parameter.

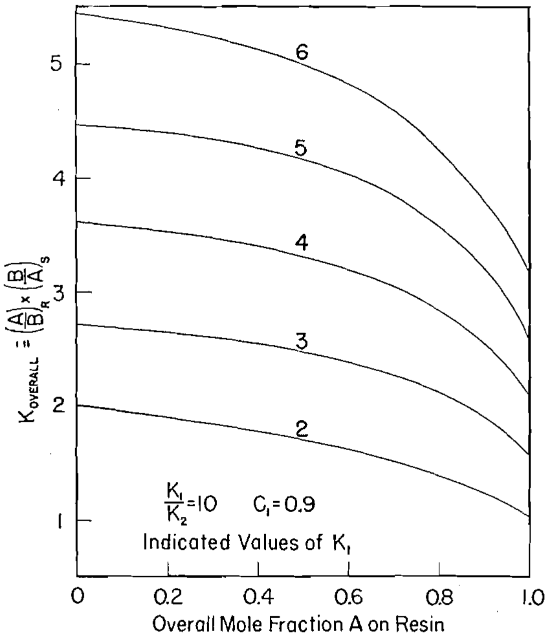

FIG. 4. Equilibrium plots for hypothetical exchanger. Effect of variation in K_1, K_2, parameters.

This equation has been evaluated for various values of the parameter C_1 and the equilibrium quotient versus mole fraction on the resin plots are given in Fig. 3. The effect of variations in the parameters K_1 and K_2 with constant C_1 are illustrated by Fig. 4. These figures illustrate that for the hypothetical resin, variations of C_1 determine the general shape of the equilibrium coefficient plot. Variations in the K_1 and K_2 parameters change the position of the curve on the equilibrium coefficient scale but have only a secondary effect on the form of the curve. This sensitivity to the C_1 parameter is, of course, diminished as the values of K_1 and K_2 approach each other. Thus for the hypothetical resin, the equilibrium plot could be regarded as an indication of the relative amounts of type 1 and type 2 exchange groups. Numerically, C_1 values which approach zero or unity are indicative of uniformity of sulphonate group environment in the resin.

The model described above is considered only as a first approximation to the polystyrenesulphonic ion-exchange resins. However, even this simple assumption permits the correlation of the experimental data. Equilibrium quotients reported (2, 10), can be fitted closely by the equation for the hypothetical resin with the following parameters:

TABLE II
PARAMETER VALUES FOR FIG. 2 PLOTS

Resin type	Curve	C_1	K_1	K_2
Ester resin	1	0.966	0.946	0.00485
Sulphonated ester resin	2	0.966	1.210	0.0275
Sulphonated polystyrene (10)	3	0.873	2.837	0.183
Sulphonated polystyrene (2)	4	0.620	3.950	0.410

Considering only the experimental values of the equilibrium quotients in Fig. 2, curves 1 and 2, and without regard to the hypothetical model, certain conclusions may be drawn. The process of increasing the capacity of the ester resin by sulphonation did not produce any marked increase in the variation of the equilibrium quotient. Hence, the disubstitution of benzene nuclei, and the substitution of divinylbenzene nuclei, if they occur at all, have only a small effect on the constancy of the equilibrium quotient of the ester resin.

The sulphonation of the ester resin also indicated that the value of the equilibrium quotient for an ion-exchange is a function of the capacity of the resin. It is of some interest to note that the equilibrium quotients for the ester resin given in Fig. 2, Curve 1, lie significantly below unity while the values obtained for the same resin after sulphonation are all above 1. These data if correlated on the basis of variations in swelling pressure (6) would require a reversal of sign in the pressure–volume term.

The ester resin prior to sulphonation differed nominally from the sulphonated polystyrene resins only in capacity. All were nominally 14–15 mole % divinylbenzene copolymers. After sulphonation the ester resin was nominally similar to the two sulphonated polystyrene resins with respect to capacity and cross-linking. However, the equilibrium quotient data for the sulphonated ester resin was very different from those reported for sulphonated polystyrene resins. This leads to the conclusion that nominal cross-linking and capacity are not sufficient to characterize a polystyrenesulphonic ion-exchange resin.

If the hypothetical model is accepted as a representation of the polystyrenesulphonic ion-exchange resins, the equilibrium quotient data as given in Fig. 2 may be considered in terms of the relative amounts of sulphonate groups in two different environments. The parameter C_1 in Table II is the fraction of the total groups which are in type 1 environment. This fraction is not changed by the sulphonation of the ester resin. Hence the detailed structure of the polymer is assumed to be the major factor determining the C_1 parameter.

The fraction (C_1) for the ester resin is very different from the C_1 parameter for the sulphonated polystyrene resins. Thus the detailed structure of the ester copolymer is assumed to be very different from that of the styrene–divinylbenzene copolymer.

The detailed structure of a resin is dependent on the reactivity ratios of the monomers used in the polymerization. The data at present available do not permit a prediction of the detailed structure of divinylbenzene copolymers. However, following the methods discussed by Alfrey, Bohrer, and Mark (1) and using the reported data for butyl vinyl sulphonate (9), it has been estimated that monomer reactivity ratios similar to those for *p*-cyanostyrene could be expected for the ester monomer. This indicates that the polymer detail structure for the ester resin could be considerably different from the detail structure of a styrene–divinylbenzene copolymer.

CONCLUSIONS

1. A method of preparation of cross-linked polystyrene–sulphonic ion-exchange resins is described. The resin products have properties which differ considerably from the properties of resins which are prepared by the sulphonation of cross-linked polymers. The method permits the preparation of low capacity ion-exchange resins in which the sulphonate groups are distributed throughout the resin. Unsupported ion-exchange films of high tensile strength may be prepared by this method.
2. The equilibrium quotients for the sodium–hydrogen exchange on resins prepared from the ester monomer are lower and more constant than values reported for similar resins prepared by the sulphonation of cross-linked polystyrene.
3. The nominal cross-linking and capacity are not sufficient to characterize a resin of the polystyrenesulphonic type.
4. Variations in the detailed structure of the resins are postulated as a possible explanation.
5. An equation is developed with parameters which may be interpreted in terms of variations of detailed structure.

ACKNOWLEDGMENT

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THE RATE OF DISSOLUTION OF COPPER[1]

BY BENJAMIN C.-Y. LU[2] AND W. F. GRAYDON

ABSTRACT

The rate of dissolution of polycrystalline metallic copper in sulphuric acid solutions has been determined as a function of temperature, oxygen pressure, rotation speed, hydrogen ion concentration, sample area, and corroding solution volume. A typical set of conditions would involve a volume of 500 ml. of air-saturated sulphuric acid solution at room temperature and a cylindrical sample of copper of 11 sq. cm. area rotated at 1000 r.p.m. An empirical rate equation has been given which represents the data with an average deviation of ±5%. The rate equation is discussed in terms of a mechanism in which it is postulated that the rate controlling step in the dissolution of copper is the oxidation of cuprous ion at the solution–copper interface.

INTRODUCTION

Although a number of publications have appeared concerning the corrosion of copper, only a few have presented data which are subject to direct interpretation in terms of a mechanism. Many of the rates of corrosion of copper data are based on the metal weight loss divided by the time of the corrosion run. Often no attempt is made to determine the effect of time as a variable. Thus the rate "constants" so obtained may be time dependent. Such rate constants are very difficult to correlate and the prediction of copper corrosion rates is therefore uncertain. In addition, other variables which may be important are often neglected, as, for example, the volume of the corroding medium.

In this work we have attempted to choose and control conditions so that the data obtained may be subject to interpretation on the basis of a mechanism for the dissolution of copper. We have tried to avoid the more complex and more practical situations. It is anticipated that the data so obtained may serve as a basis for further work by providing some indication of the dissolution mechanism under relatively simple conditions.

EXPERIMENTAL

Materials

The copper samples used in this investigation were machined from refinery copper rod and bar stock.* A typical analysis for this material is given below.

Copper	99.95+%	Selenium	0.001%
Nickel	0.0002%	Tellurium	0.0004%
Iron	0.0004%	Bismuth	<0.0001%
Arsenic	0.0004%	Gold	0.003 oz. per ton
Antimony	0.0001%	Silver	0.30 oz. per ton
Lead	0.0002%		

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ontario.

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[2] *Cominco Research Fellow, 1952-53.*

**We are indebted to Anaconda American Brass Limited of Toronto who supplied the copper stock and the analysis.*

Metallographic examinations of the samples used were obtained.* The photomicrographs are shown in Fig. 1.

All reagents used were "Analar" reagent grade and all solutions were prepared using redistilled water.

Apparatus

The rates of dissolution were determined for a cylinder of copper which was rotated on a lucite rod. The dissolving medium was contained in a pyrex beaker fitted with a lucite baffle plate and cover. The ends of the copper cylinder were protected from the dissolving medium by lucite washers. The beaker was surrounded by a thermostat. An inlet tube for gas bubbling was provided. The baffle plate was adjusted to prevent gas from impinging on the sample.

Procedure

The cylindrical copper sample about three quarters of an inch in length and diameter was polished with 3/0 emery paper, washed with water, and dried with absolute alcohol. The corroding solution was saturated with the oxygen–nitrogen mixture. The sample was rotated on the lucite rod in the corroding medium with the gas bubbling continuously at a rate of about one liter per minute.

Three milliliter samples of the corroding solution were withdrawn from time to time and analyzed for copper using the polarograph (5). Because of the possibility of hydrogen peroxide formation (1) the samples were evaporated to dryness at 110°C. prior to the diffusion current measurements.

RESULTS AND DISCUSSION

The stoichiometry for the dissolution of copper is as follows:

$$Cu + 2H^+ + \tfrac{1}{2}O_2 \rightarrow Cu^{++} + H_2O.$$

All of the data reported here have been obtained under such conditions that hydrogen ion and oxygen were in great excess. The copper flux was of the order of 5×10^{-5} moles per liter per hour. The oxygen concentration in the bulk of the solution was of the order of 2×10^{-4} moles per liter and it was continuously replenished by bubbling. The hydrogen ion concentration in the bulk of the solution was at least 10^{-3} moles per liter and it remained unchanged during each rate determination.

All of the rate data obtained under these conditions are of the typical form shown in Fig. 2. The data have been plotted in subsequent diagrams as the square root of the cupric ion concentration versus the time, since this plot was found to be linear in all cases.

It will be noted that all of the plots in Figs. 3 to 8 show an ordinate intercept implying a copper concentration of about 2×10^{-5} molar at zero time. The data plotted in Fig. 7 show that this intercept may be reduced to a value corresponding to about 2×10^{-6} molar cupric solution at zero time by leaching the dissolution apparatus with hydrochloric acid for considerable periods of time. Thus the intercept is considered to result from the adsorption of copper ions

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**Metallographic examinations were done by Dr. W. C. Winegard, Department of Metallurgy, University of Toronto.*

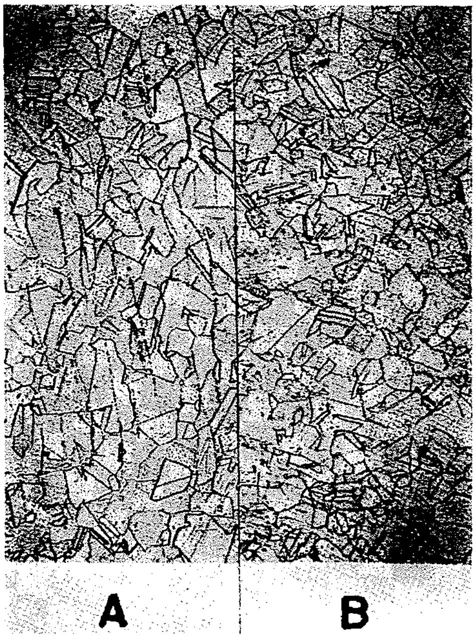


FIG. 1, A. Photomicrograph ×100 typical of samples 1, 2, and 3 cut from bar stock.
FIG. 1, B. Photomicrograph ×100 of sample cut from rod stock.

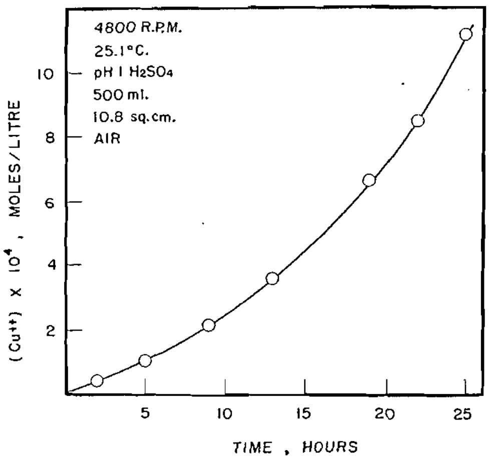


FIG. 2. Rate of dissolution of copper. The figures in the upper left hand corner refer to the sample rotation speed, temperature, acidity, and the acid species in the corroding medium, the volume of the corroding medium, the area of the copper sample, and the composition of the gas in equilibrium with the corroding medium.

on the glass and lucite rod. All of the data given were determined in apparatus which was cleaned and rinsed in the normal way only. Thus each plot shows an intercept which is somewhat variable and which may be regarded as dependent on the history of the dissolution apparatus. In addition it is possible that a portion of the intercept may result from the dissolution of an oxide layer on the metal sample. From the data of Miley and Evans (6) we estimate that this possibility might account for an intercept corresponding to about 2×10^{-6} moles per liter of copper.

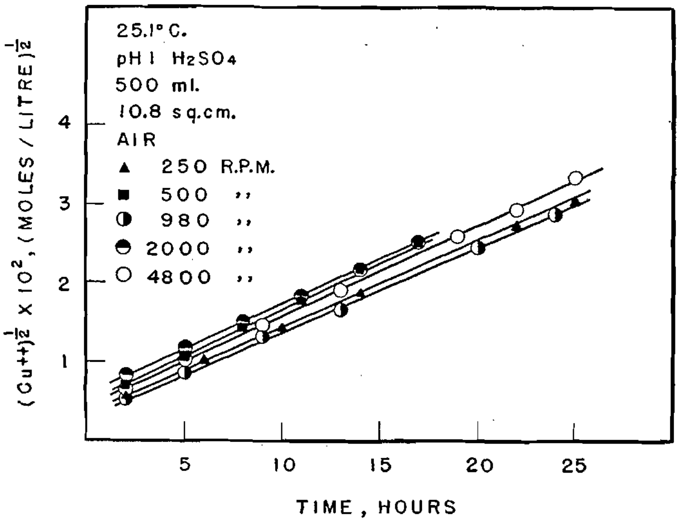


FIG. 3. The effect of rotation speed.

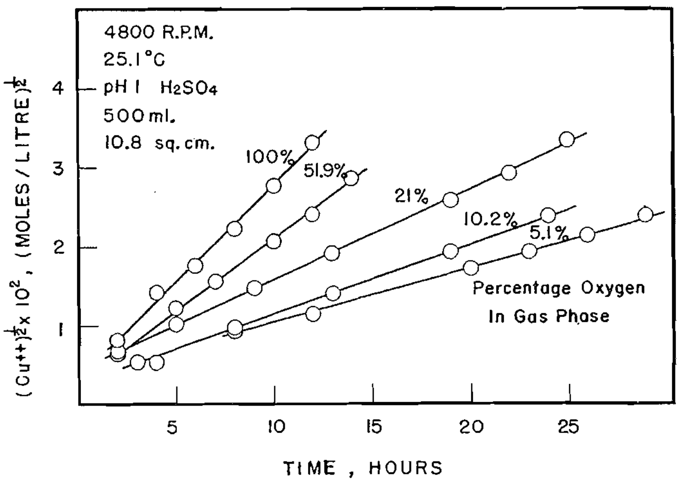


FIG. 4. The effect of oxygen concentration.

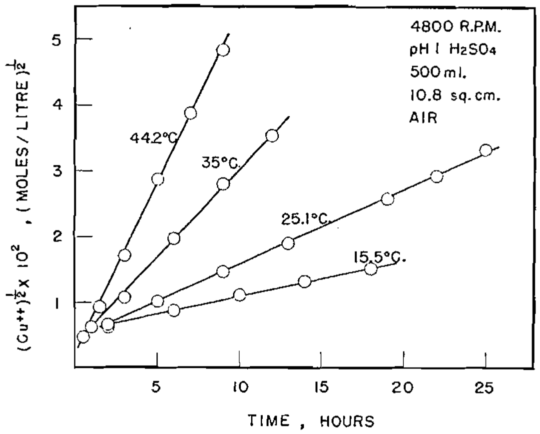


FIG. 5. The effect of temperature.

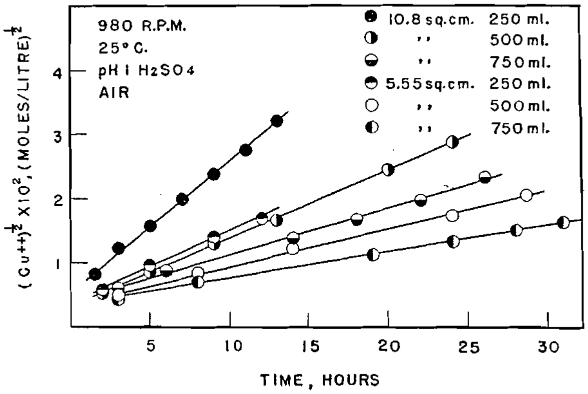


FIG. 6. The effect of sample area and solution volume.

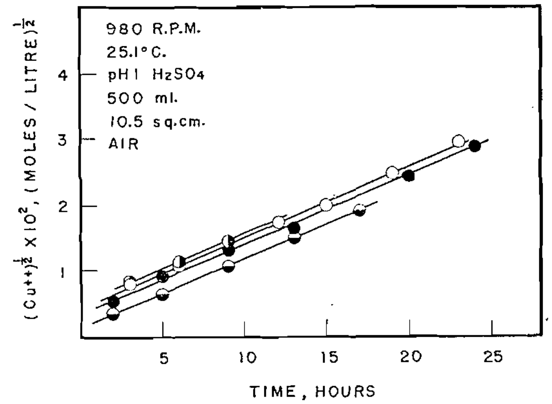


FIG. 7. Variation in the intercept at zero time.

◑ and ○ Apparatus was washed and allowed to stand overnight in redistilled water after each run.

● Apparatus was washed and allowed to stand overnight in 6 N hydrochloric acid then rinsed with redistilled water.

⊖ Apparatus was washed with five portions of 6 N hydrochloric acid. The total time of contact being 48 hr. Rinsed and allowed to stand in pH 1 sulphuric acid overnight.

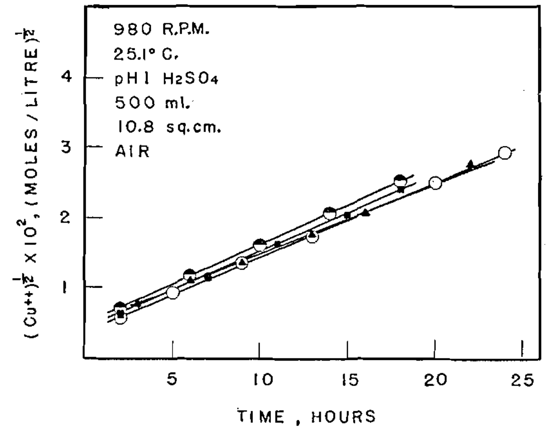


FIG. 8. Rates for various copper samples.

◓ Sample from bar 1. ■ Sample from bar 2. ▲ Sample from bar 3. ○ Sample from rod 4. Three samples from rod 4 were used in obtaining data in Figs. 2–7.

Rate Dependence on Cupric Ion Concentration

The data shown in Figs. 3 to 8 illustrate clearly the linearity of the plot of the square root of the cupric ion concentration against time.

Thus for the conditions used in this work we may write,

$$d[\mathrm{Cu}^{++}]/dt = k[\mathrm{Cu}^{++}]^{\frac{1}{2}}.$$

This rate dependence has been considered on the basis of the following assumptions.

(1) The cupric-ion concentration in the bulk of the solution is assumed to be essentially the same as the cupric-ion concentration at the copper–solution interface.

(2) The cuprous-ion, cupric-ion equilibrium, $\mathrm{Cu} + \mathrm{Cu}^{++} \rightleftharpoons 2\mathrm{Cu}^{+}$, is assumed to be established at the interface.

(3) The rate of dissolution of copper is assumed to be controlled by the removal of cuprous ions from the interface by a reaction which is first order with respect to cuprous ion.

$$-d[\mathrm{Cu}_i^{+}]/dt = K[\mathrm{Cu}_i^{+}],$$

where subscript i refers to copper–solution interface, or

$$d[\mathrm{Cu}^{++}]/dt = K[\mathrm{Cu}_i^{+}].$$

By assumption (2) $\quad d[\mathrm{Cu}^{++}]/dt = KK'[\mathrm{Cu}_i^{++}]^{\frac{1}{2}},$

where $\quad K' = [\mathrm{Cu}^{+}]/[\mathrm{Cu}^{++}]^{\frac{1}{2}}.$

By assumption (1) $\quad d[\mathrm{Cu}^{++}]/dt = KK'[\mathrm{Cu}^{++}]^{\frac{1}{2}}.$

Rate Dependence on Revolutions Per Minute

The possibility that this first order removal of cuprous ion might be by diffusion seems to be eliminated by the very small effect of rotation speed on the rate of dissolution of copper. As may be seen from Table I the variation in rate is less than 8% between 250 and 4800 r.p.m.

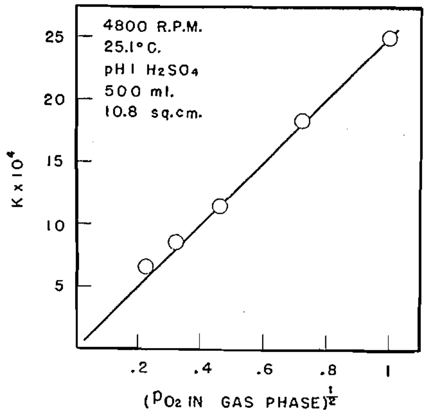
TABLE I
SLOPES FROM FIGURE 3

R.p.m.	$(d[\mathrm{Cu}^{++}]^{\frac{1}{2}}/dt) \times 10^3$
250	1.08
500	1.15
980	1.11
2000	1.09
4800	1.15

These observations confirm and extend the data of Glauner (2) who found little variation between 150 and 350 r.p.m. The possibility that this small effect of r.p.m. might result from diffusion in the pores of an oxide layer seems unlikely because of the low pH of the corroding media. Although some elevation of pH at the interface is to be expected, a hydrogen ion flux of about 10^{-4} gram-ions per liter per hour from a bulk concentration of 10^{-1} gram-ions per liter could have only a negligibly small effect. On the basis of the small effect of sample r.p.m. on the dissolution rate, it is assumed that cuprous ion is removed from the interface by a chemical reaction.

Rate Dependence on Oxygen Pressure

The data plotted in Fig. 9 show that the rate of dissolution of copper is proportional to the square root of the oxygen pressure in the gas phase with which the dissolving solution is equilibrated. Russell and White (7) reported that the corrosion of copper was directly proportional to the concentration of dissolved oxygen. However, in their work the corrosion of copper was measured in terms of weight loss over a 24 hr. period.



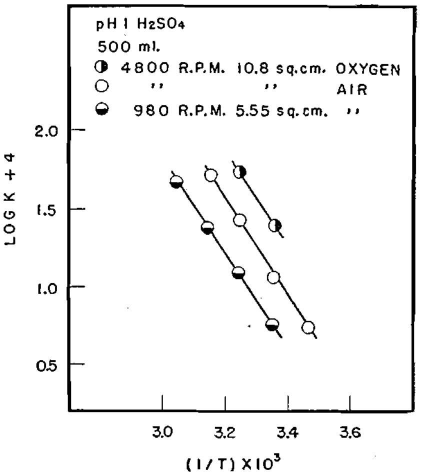


FIG. 9. Rate of dissolution as a function of oxygen concentration. K is slope of plot from Fig. 4.

FIG. 10. Rate of dissolution as a function of temperature. K is slope of plot from Fig. 5.

This method of calculating "rate constants" gives values which are dependent on the time. If the data of Russell and White are recalculated on the basis of the square root of cupric ion concentration versus time, the rate constant obtained is a function of the square root of the oxygen concentration.

To interpret the above we assume that the rate determining reaction in the dissolution of copper under the conditions of these experiments is of the following nature:

$$Cu_i^+ + O_i \rightarrow Cu_i^{++} + O_i^-.$$

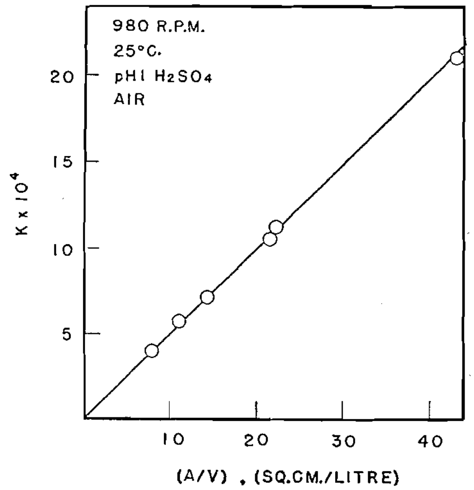
This oxygen dependence implies either a surface adsorption isotherm which is linear over the range of oxygen concentrations used or alternatively that the oxygen dissociation occurs in the liquid phase.

Rate Dependence on Temperature

High temperature coefficients for the rate of dissolution of copper have been reported (4). It has been implied that chemical reaction control rather than diffusion control is thereby indicated. As shown in Fig. 10 we find a temperature coefficient corresponding to an activation energy for the dissolution of copper of 14 kilocalories per mole. In order to compute the activation energy for the controlling reaction on the basis of the mechanism postulated above, the activation energy for dissolution must be corrected for the temperature variations of the assumed equilibria.

$$\begin{aligned} Cu_i^{++} + Cu &\rightleftharpoons 2\,Cu_i^+ \\ O_2 \text{ gas} &\rightleftharpoons O_2 \text{ solution} \\ O_2 \text{ solution} &\rightleftharpoons 2\,O_i. \end{aligned}$$

Thermodynamic data are available for the first two of these equilibria but not for the third. The value of 14 kilocalories does not in itself confirm the chemical



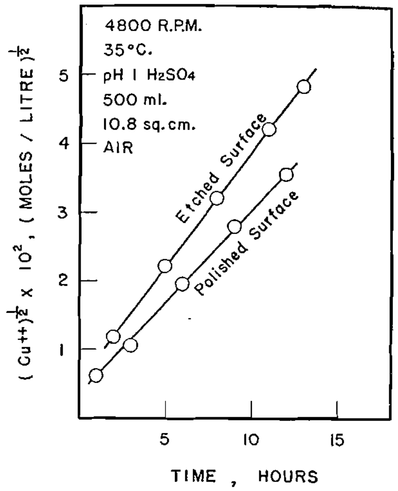


FIG. 11. Rate of dissolution as a function of sample area and solution volume. K is slope of plot from Fig. 6.
FIG. 12. Effect of surface roughness.

reaction control of dissolution. The chemical reaction mechanism which is assumed above is thus based, at present, on the r.p.m. and oxygen concentration dependence data.

From Fig. 10 it may be seen that the activation energy of dissolution is not affected by the variations in the conditions used. These data thus indicate that there is no change in the controlling mechanism.

Rate Dependence on Sample Area and Corroding Solution Volume

The rate of dissolution of copper has been found to be directly proportional to the area of the sample used and inversely proportional to the volume of the corroding medium as shown in Fig. 11. Some dependence on the volume of the solution is required whether the mole rate of dissolution or the concentration rate is considered.

$$d[\mathrm{Cu}^{++}]/dt = K[\mathrm{Cu}^{++}]^{\frac{1}{2}}/v$$

or

$$-d|\mathrm{Cu}|/dt = K[\mathrm{Cu}^{++}]^{\frac{1}{2}}$$

where | | represents number of moles.

The area of the sample used in the above correlation was the gross apparent surface area obtained by micrometer measurement. The precision of the data indicates either that the method of polishing produces a true surface area which is proportional to the gross surface area or that the rate of dissolution of copper is not sensitive to minor variations in surface roughness. Large variations in surface roughness, produced by etching in sulphuric acid solution for about 70 hr., did change the rate of dissolution as shown in Fig. 12. This effect of surface roughness was also observed as an increase of rate constant for polished samples which were allowed to dissolve for periods up to 48 hr.

The Effect of Hydrogen Ion Concentration

The data discussed above were obtained in solutions at pH 1. As shown in Fig. 13 there is only a small variation in the rate of dissolution for solutions of lower pH than this value. However, the rate decreases sharply for solutions more dilute with respect to hydrogen ion. The reduction in the rate may result from film formation on the metal at higher pH values. Alternatively the rate dependence may result from the adsorption of hydrogen ion at the interface. This latter possibility could be interpreted in terms of a rate controlling reaction of the following nature.

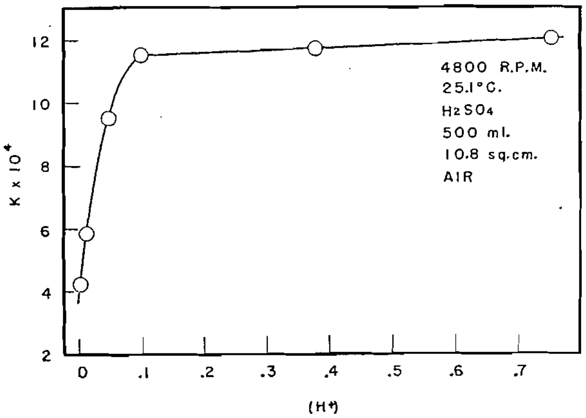


FIG. 13. Rate of dissolution as a function of hydrogen ion concentration.
K represents $d[\mathrm{Cu}^{++}]^{\frac{1}{2}}/dt$ and $[\mathrm{H}^+]$ represents hydrogen ion concentration in gram-ions per liter.

$$\mathrm{Cu}_i^{+} + \mathrm{H}_i^{+} + \mathrm{O}_i \rightarrow \mathrm{Cu}_i^{++} + \mathrm{OH}_i$$

Although the data at present do not permit a conclusive choice of reactions for the rate of dissolution of copper, the following set of reactions is presented as a suggestion.

$$\begin{array}{llll}
\mathrm{Cu}_i^{++} + \mathrm{Cu} & \rightleftharpoons 2\,\mathrm{Cu}_i^{+} & & \text{Equilibrium} \\
\mathrm{Cu}_i^{+} + \mathrm{H}_i^{+} + \mathrm{O}_i & \rightarrow & \mathrm{Cu}_i^{++} + \mathrm{OH}_i & \text{Slow} \\
\mathrm{Cu}_i^{+} + \mathrm{OH}_i & \rightarrow & \mathrm{Cu}_i^{++} + \mathrm{OH}_i^{-} & \\
\hline
\mathrm{Cu} + 2\mathrm{H}^{+} + \tfrac{1}{2}\mathrm{O}_2 & \rightarrow \mathrm{Cu}^{++} + \mathrm{H_2O} & &
\end{array}$$

This mechanism satisfies the rate dependence on cupric ion and oxygen concentrations and also the stoichiometry.

Empirical Equation and Range of Application

The data discussed above may be summarized in the form of the following equation

$$-\,d|\overline{\mathrm{Cu}}|/dt = K\,e^{-(14.1/RT)}\,[\mathrm{Cu}^{++}]^{\frac{1}{2}}\,(p_{\mathrm{O}_2})^{\frac{1}{2}},$$

where $|\overline{\mathrm{Cu}}|$ represents moles of copper per unit area

or
$$d[\mathrm{Cu}^{++}]/dt = 4.92 \times 10^{6}\, e^{-(14.1/RT)}\, [\mathrm{Cu}^{++}]^{\frac{1}{2}}\, (p_{\mathrm{O}_2})^{\frac{1}{2}}\, \frac{A}{V}$$

where

$[\mathrm{Cu}^{++}] = 0\text{–}2.5 \times 10^{-3}$ moles/liter
$T = 288\text{–}328$°K.
$A = 5.47\text{–}11.10$ sq. cm.
$V = 0.25\text{–}0.75$ liter
$t = 3\text{–}30$ hr.
$(p_{o_2}) = 0.051\text{–}1.00$ atm.
$[H^+] = 0.1\text{–}0.75$ gm. ions per liter.

The value 4.92×10^6 is an average of 40 plots. The average deviation from this value was $\pm 0.24 \times 10^6$ absolute or about 5%.

The major portion of this work was done with three samples cut from a single copper rod. In order to eliminate the possibility that the data obtained might be applicable to that rod only, the data given in Fig. 8 were obtained. As shown in Table II below the data obtained for four samples, each refined at a different time were found to be within the average deviation stated above.

TABLE II
RATE CONSTANTS FROM FIGURE 8

Sample	$K \times 10^{-6}$	Deviation from average	Deviation from 4.92×10^6
1	4.94	.22	.02
2	4.78	.06	.14
3	4.39	.33	.53
4	4.78	.06	.14
Average	4.72	±.17	±.21

Very little data have been published for the dissolution of copper with time as a variable. Data of this sort have been presented by Katz (3) for nearly neutral or slightly acidified corroding media.

From our own data on hydrogen ion concentration dependence it is apparent that no correlation of rate constant values is to be expected. However, the data of Katz when replotted as the square root of the weight loss against time gave linear plots for time up to 30 days at 16.3°C. This would indicate that the equilibrium reaction assumed in our mechanism is a valid assumption for the conditions used by Katz.

Glauner (2) has also published data for the dissolution of copper as a function of time. Three of his experiments were conducted in sulphuric acid media. Although the experimental conditions were different from those described in this paper, Glauner's data when replotted on the square root basis gave linear plots up to 50 hr. as illustrated in Fig. 14. In addition the rate constants calculated from Glauner's replotted data were in good agreement with the constant determined above as shown in Table III.

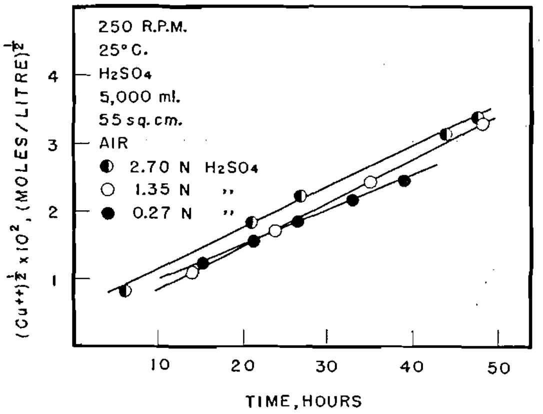


FIG. 14. Replotted data of Glauner (2) for polycrystalline copper of random orientation in sulphuric acid.

TABLE III

RATE CONSTANTS FROM DATA OF GLAUNER (2)

Sulphuric acid normality	Rate constant for Glauner's data	Rate constant predicted	Deviation
0.27	4.36×10^6	4.92×10^6	0.56
1.35	5.31×10^6	4.92×10^6	0.39
2.70	5.13×10^6	4.92×10^6	0.21
Average	4.93×10^6	4.92×10^6	±0.39

CONCLUSIONS

An empirical equation has been established for the rate of dissolution of metallic copper in oxygenated sulphuric acid solutions.

It is suggested that the rate of dissolution of copper is controlled by the rate of oxidation of cuprous ion at the copper–solution interface.

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THERMODYNAMIC PROPERTIES OF XENON IN THE CRITICAL REGION[1]

BY H. W. HABGOOD[2] AND W. G. SCHNEIDER

ABSTRACT

Using the detailed compressibility data in the critical region of xenon given in the preceding paper, supplemented by measurements of Beattie, Barriault, and Brierley over a wider range of temperatures and densities, thermodynamic properties have been calculated for the critical region—extending from the critical temperature to 50° above it and from low densities to somewhat above the critical density. The values of C_v at the critical density are in good agreement with those calculated from acoustical data at temperatures higher than $T_c + 1°$; closer to the critical temperature however, the C_v values derived from the equation of state data become much greater than those derived from the acoustic data. This difference can be accounted for by dispersion effects in the high frequency acoustic data near the critical point.

INTRODUCTION

The compressibility data for xenon in the region of the critical point presented in the preceding paper (4) have been used to derive the thermodynamic properties in this region. By supplementing our data with those of Beattie, Barriault, and Brierley (1), we have been able to extend these calculations down to low densities and to a temperature 50° above the critical in order to show the variations in the various properties near the critical point. Of the various thermodynamic properties, the specific heat is of particular interest. C_v has a finite maximum at the critical point and C_p becomes infinite.

Somewhat similar calculations have previously been carried out for carbon dioxide by Michels, Bijl, and Michels (5). They found an increase in C_v at the critical point of about 10 cal./mole deg. over the low density value, but their measurements (6) in this region were not very detailed. A recent calorimetric study, also on carbon dioxide, by Michels and Strijland (7) indicated values in excess of 20 cal./mole deg. for the increase in C_v. These authors give references to earlier workers who have attempted to determine C_p or C_v at the critical point calorimetrically.

From our measurements $(\partial P/\partial T)_V$ can be evaluated more accurately than $(\partial V/\partial T)_P$ or $(\partial P/\partial V)_T$. We have therefore used the following relationships in calculating thermodynamic properties:

$$[1] \qquad C_{V_{T,\rho}} - C_{V_{T,0}} = \lim_{\rho_1\to 0}\left[-T\int_{\rho_1}^{\rho}\frac{1}{\rho^2}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho d\rho\right],$$

$$[2] \qquad (C_p - C_v)_{T,\rho} = \frac{T}{\rho^2}\,\frac{(\partial P/\partial T)_\rho^2}{(\partial P/\partial \rho)_T},$$

$$[3] \qquad (S^* - S)_{T,\rho} = \lim_{\rho_1\to 0}\int_{\rho_1}^{\rho}\left[\frac{1}{\rho^2}\left(\frac{\partial P}{\partial T}\right)_\rho - \frac{R}{\rho}\right]d\rho,$$

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

$$(A^{*} - A)_{T,\rho} = \lim_{\rho_1 \to 0} \int_{\rho_1}^{\rho} \left(\frac{RT}{\rho} - \frac{P}{\rho^2} \right) d\rho, \qquad [4]$$

where the starred quantities refer to an ideal gas. From these quantities the differences from the ideal gas values for E, H, and F may be readily calculated as:

$$(E^{*} - E)_{T,\rho} = (A^{*} - A) + T(S^{*} - S), \qquad [5]$$

$$(F^{*} - F)_{T,\rho} = (A^{*} - A) + (RT - [P/\rho]), \qquad [6]$$

$$(H^{*} - H)_{T,\rho} = (E^{*} - E) + (RT - [P/\rho]). \qquad [7]$$

CALCULATIONS AND DISCUSSION

Evaluation of $(\partial P/\partial T)$ *and* $(\partial^2 P/\partial T^2)$

It was necessary to determine $(\partial P/\partial T)$ and $(\partial^2 P/\partial T^2)$ over the temperature range of interest and at all densities down to zero density. From our measurements we first determined $(\partial P/\partial T)$ and $(\partial^2 P/\partial T^2)$ as functions of temperature for each isochore. Some attempts were made to fit analytical functions to the data but none of these were very promising and graphical methods were used.

Large-scale plots of P against T were made for each density. For convenience, the difference between the measured pressure and that corresponding to an arbitrary isochore of constant slope was plotted. The various isochores formed a family of gently curved lines, each branching from the vapor pressure curve at the maximum temperature of liquid–vapor coexistence. For most of the isochores sufficient measurements had been taken to establish independently the vapor pressure curve for each. These curves were in good agreement except for two which seemed obviously displaced to slightly lower pressures, presumably by small constant errors, and which were so drawn in order to minimize the effect on the slopes.

The temperature of branching for each isochore taken as the temperature of apparent intersection of the two arms of the curve was in good agreement with the observed maximum coexistence temperature. Within 0.01° of the critical temperature, the maximum coexistence temperature was not always determined but was sometimes taken from the coexistence curve of Weinberger and Schneider (9) which appeared to agree with our observations in this region.

The average deviation of the measured pressures from the curves was less than 0.001 atm. and a few deviations were as high as 0.004 atm. The greatest scatter occurred in the neighborhood of the branching point where the high specific heat and slow approach to equilibrium made determinations more difficult. This was partly compensated by the greater number of measurements taken in this region.

From these curves pressures were read off at intervals of 0.01° to 0.05° and from the differences were constructed curves of $(\partial P/\partial T)$ vs. $T - T_c$ where T_c is the critical temperature, 16.590°C. These curves are shown in

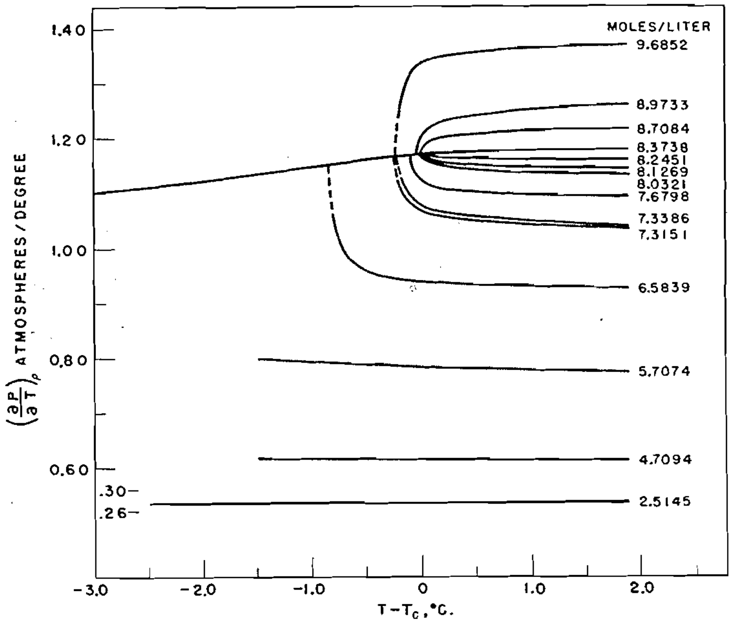

FIG. 1. $(\partial P/\partial T)_\rho$ from smoothed isochores.

Fig. 1. From them, curves of $(\partial^2 P/\partial T^2)$ vs. $T - T_c$ were obtained by a similar process.

Qualitatively, the general shape of the curves in Fig. 1 appears to be clearly established, particularly at densities away from the critical where the slope, i.e. $(\partial^2 P/\partial T^2)$, increases regularly in absolute value with decreasing temperature towards the condensation point, presumably becoming infinite when a second phase appears. Near the critical density we have assumed that the curves have the same general nature although the value of the slope very close to the branch point can be little more than a rough estimate. To some extent, the uncertainty can be reduced by smoothing $(\partial P/\partial T)$ against ρ for various temperatures.

The degree of uncertainty in the curves of $(\partial P/\partial T)$ may be illustrated by plotting directly the values of $\Delta P/\Delta T$ obtained from the differences between successive measurements. This is done in Fig. 2 for the isochore at 7.68 moles/liter where the measured pressures exhibit an average degree of scatter from a smooth curve. On this plot of the observed $(\Delta P/\Delta T)$'s we have superimposed $(\partial P/\partial T)$ obtained from the smoothed P–T curve as described above. It can be seen that while $(\partial P/\partial T)$ is fairly well established over most of the range, a relatively small shifting near the steep portion of the curve could cause a considerable change in the value of $(\partial^2 P/\partial T^2)$ at a particular temperature.

At low densities $(\partial^2 P/\partial T^2)$ is very small and the data of Beattie *et al.* (1) covering a wide temperature range were more satisfactory than measurements restricted to just a few degrees. Their data were also used to cover the complete density range at higher temperatures so that C_v could be calculated at

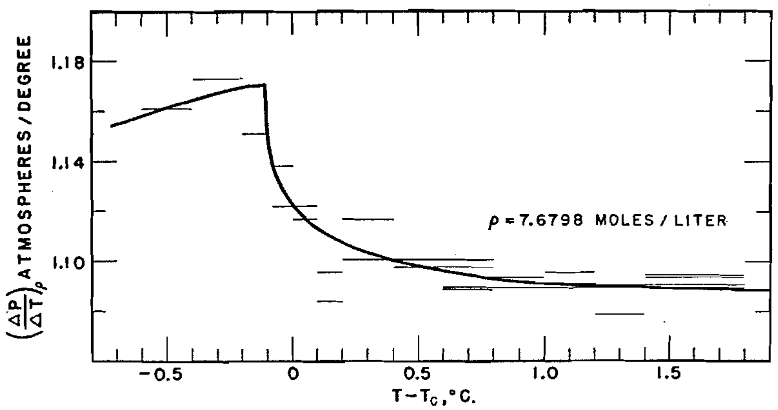

FIG. 2. Experimental values of $(\Delta P/\Delta T)$ at 7.68 moles/liter. Solid curve taken from Fig. 1 obtained from smoothed isochore.

temperatures up to 50° above the critical. Unfortunately, their measurements did not extend below 16.65° so there is added uncertainty in the derivatives at the lowest temperatures.

While the required derivatives could be calculated from the Beattie–Bridgeman equation of state [1] or the virial equation [2] to which their data were fitted, these values, particularly $(\partial^2 P/\partial T^2)$, would require correction by a graphical analysis of the relatively large and systematic deviations. It was therefore more convenient and almost equally accurate to apply graphical methods directly to their data. This was done by drawing smooth curves through plots of $\Delta P/\Delta T$ vs. T obtained from readings at successive temperatures for each density. The first interval was 8.35° and succeeding intervals were 25°. Away from the critical point the curves could be drawn with but slight uncertainty and near the critical point, values of $(\partial P/\partial T)$ from our measurements could be fitted smoothly to these plots. Values of $(\partial^2 P/\partial T^2)$ were then obtained as the slopes of these curves.

Heat Capacities at Constant Volume and Constant Pressure, C_v and C_p

To determine C_v according to Equation 1 values of $-(1/\rho^2)\ \partial^2 P/\partial T^2$ were plotted against density for various temperatures. The limiting value at zero density is $(\partial^2 B/\partial T^2)$ where B is the second virial coefficient in the virial equation

$$[8] \qquad PV = RT + \frac{B(T)}{V} + \ldots.$$

This was estimated from the virial coefficients given by Beattie *et al.* (2). These curves are shown in Fig. 3, the points for some temperatures being omitted for clarity. C_v was then determined by graphical integration of the area under the appropriate curve from 0 to the desired density.

The values for C_v are given in Table I, the zero density value for an inert gas being 2.98 cal./mole deg. These values are plotted as functions of density in Fig. 4. For the three temperatures nearest the critical the values appear to

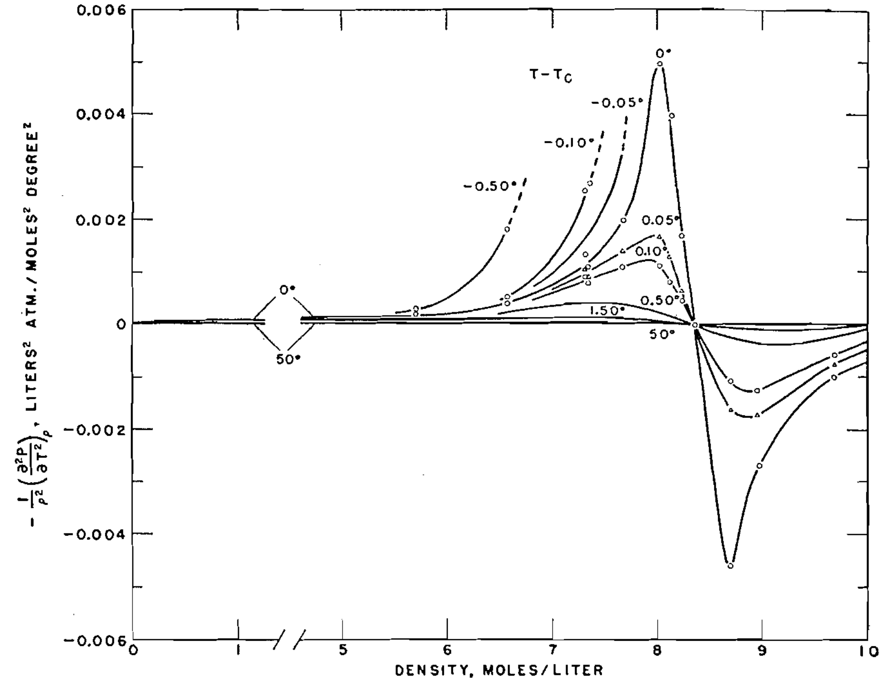

FIG. 3. Curves of $-(1/\rho^2)\ (\partial^2P/\partial T^2)$ vs. ρ for evaluation of C_v.

TABLE I
HEAT CAPACITY AT CONSTANT VOLUME, C_v (CAL./MOLE DEG.)

$T-T_c$, °C. \ Density, moles/l.	0	3	6	7	8	8.37	9	10
0.00	2.98	4.56	7.12	9.92	23.1	30.1	16.4	(6.5)
0.05	2.98		7.07	9.66	18.1	20.4	14.6	(7.4)
0.10	2.98		7.03	9.33	16.0	17.5	13.5	(8.1)
0.20	2.98		6.94	8.92	13.8	14.6	11.9	8.3
0.50	2.98		6.66	8.22	10.80	11.11	10.08	8.01
1.50	2.98	4.48	6.47	7.39	8.04	8.01	7.65	6.79
5.00	2.98	4.23	5.78	6.29	6.50	6.47	6.30	5.81
10.00	2.98	4.02	5.25	5.58	5.71	5.68	5.56	5.23
50.00	2.98	3.58	4.06	4.14	4.16	4.15	4.12	4.01

be obviously in error at the highest densities. This is believed to be mainly the result of fewer measurements having been made at densities greater than the critical. For the vapor region below the critical temperature it was possible from the curves of Fig. 3 to estimate C_v at densities approaching the condensation point but these values are considerably more uncertain.

The density of maximum C_v is 8.37 moles/liter which is somewhat lower than the critical density found by Weinberger and Schneider, 8.42 moles/liter. As mentioned in the preceding paper, our observations of coexistence temperatures and densities would support the critical density found by Weinberger

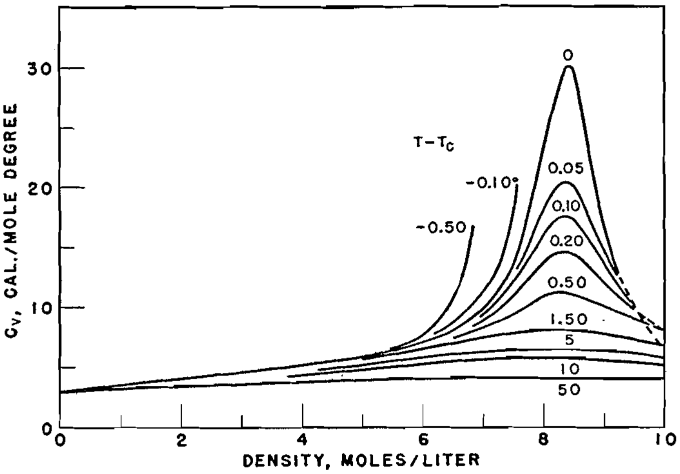

FIG. 4. Heat capacity at constant volume, C_v.

and Schneider or even a slightly higher value. It would thus appear that the density of maximum C_v is slightly lower than the critical density as determined from the coexistence curve, but the evidence is rather incomplete. It is difficult to give a reliable estimate of the probable accuracy of these C_v values. The principal source of uncertainty is in the determination of $(\partial^2P/\partial T^2)$ and the nature of this uncertainty is such as to favor somewhat lower values of C_v.

The values of C_v determined in this manner may be compared with C_v calculated from the measured velocity of sound, c, using the relationship

$$[9] \qquad c^2 = \frac{Tv^2}{C_v}\left(\frac{\partial P}{\partial T}\right)^2 - v^2\left(\frac{\partial P}{\partial v}\right).$$

Chynoweth and Schneider (3) measured ultrasonic velocities at the critical density at frequencies of 250 kc. and 1250 kc. Using these velocities and the values of $(\partial P/\partial T)$ and $(\partial P/\partial v)$ found in the present work we have calculated C_v from Equation 9 from 0.4° below the critical temperature to 2.0° above. These values together with the values for the critical density from Table I are presented in Fig. 5. There is seen to be an apparent frequency dependence in C_v near the critical point, the value from PVT data, which may be considered to represent a low frequency limit, being much greater than the high frequency values. Such behavior has been noted previously by Schneider and Chynoweth (8) and explained in terms of structural relaxation processes near the critical point. It was also pointed out that the variation with frequency should more properly be considered to be not in C_v but in the quantities $(\partial P/\partial T)$ and $(\partial P/\partial v)$, i.e., the critical system is very highly compressible to a slowly applied force but only slightly compressible to very rapidly varying pressure changes. The region of this dispersion is confined to within less than 1° of the critical temperature. This is also the region of maximum ultrasonic absorption and of visible opalescence. Above T_c + 1° the C_v's obtained from the two

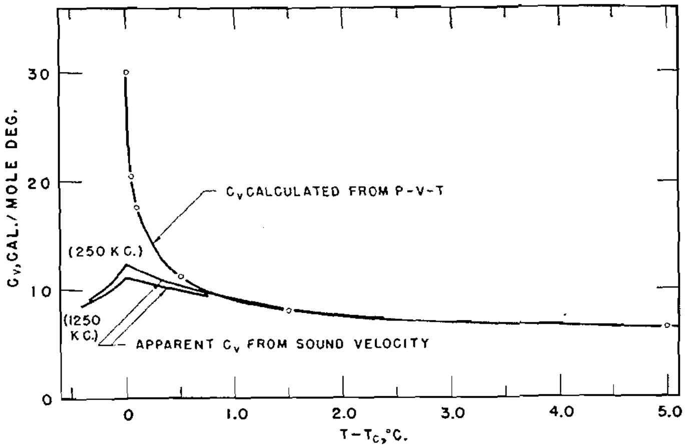

FIG. 5. C_v at the critical density compared with C_v calculated from acoustical measurements.

sources agree within 3% which may be regarded as a very satisfactory check. It is perhaps worth pointing out that to determine C_v using Equation 9 and the velocity of sound, one need know only the first derivatives at the point in question rather than second derivatives at all densities down to zero.

To calculate $C_p - C_v$ according to Equation 2, $(\partial P/\partial \rho)_T$ was required. For our data this was estimated from large-scale plots of the $P - \rho$ isotherms and for the data of Beattie *et al.* it was determined from the Beattie–Bridgeman equation supplemented by a graphical analysis of the deviations. $(\partial P/\partial T)$ had already been obtained in determining $(\partial^2 P/\partial T^2)$ for the evaluation of C_v. The resulting values of $C_p - C_v$ are given in Table II and plotted in Fig. 6.

TABLE II
$C_p - C_v$ (CAL./MOLE DEG.)

$T - T_c$, °C. \ Density, moles/l.	0	3	6	7	7.5	8	8.37	9	10
0	1.99	11.08	160	818	2700	23,400		13,600	200
0.10	1.99				2200	12,300	30,600	9,500	
0.20	1.99				1800	7,300	13,800	4,200	
0.50	1.99				1300	2,700	4,600	1,600	
1.50	1.99	10.76			610	900	955	640	
5.00	1.99	10.20	75	146	198	206	196	177	94.3
10.00	1.99	9.50	51.4	79.9	91.2	98.2	99.7	88.7	66.2
50.00	1.99	6.34	14.7	17.0	17.7	18.0	18.0	17.7	16.8

The very large values are determined almost entirely by the $(\partial P/\partial \rho)$ term in the denominator which becomes very small near the critical point. The uncertainty in this region is consequently much greater than elsewhere. Fig. 6 shows the rather wide range of densities over which C_p is very large.

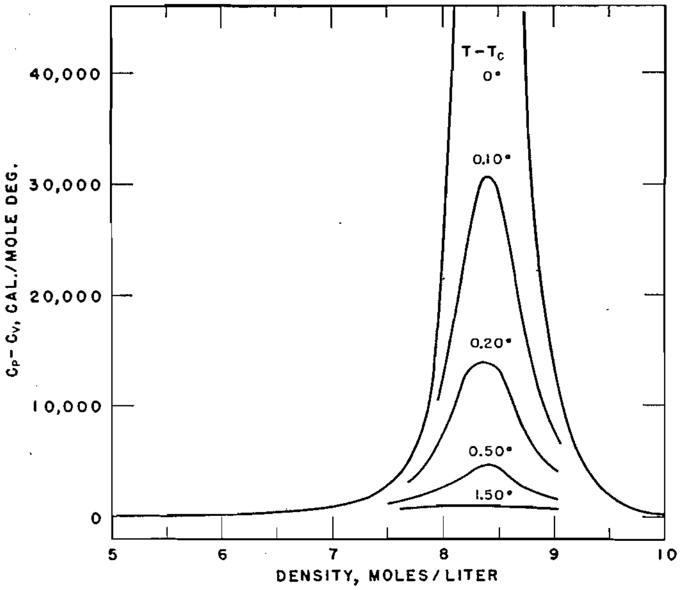

FIG. 6. Difference in heat capacities at constant volume and at constant pressure, $C_p - C_v$.

This explains, in part, the difficulty in achieving a true temperature equilibrium in a system near the critical point.

Entropy

Evaluation of the entropy in excess of the ideal gas value was straightforward once $(\partial P/\partial T)$ had been determined. The quantity $[(1/\rho^2)(\partial P/\partial T) - R/\rho]$ was found to be approximately constant over the whole density range. It was plotted against density and the area under the curve determined graphically. The limiting value at zero density is (dB/dT), B being the second virial coefficient in Equation 8. The probable errors are estimated to be 1% or less.

TABLE III
ENTROPY, $S^* - S$ (CAL./MOLE DEG.)

$T - T_c$, °C. \ Density, moles/l.	3	6	7	8	8.37	9	10
0	0.771	1.498	1.722	1.928	1.999	2.089	2.228
0.05		1.497	1.720	1.924	1.995	2.087	2.228
0.10		1.496	1.719	1.922	1.992	2.085	2.227
0.20		1.495	1.716	1.917	1.987	2.081	2.224
0.50	0.768	1.490	1.710	1.908	1.977	2.073	2.219
1.50	0.761	1.477	1.693	1.886	1.955	2.052	2.202
5.00	0.747	1.443	1.651	1.841	1.911	2.010	2.170
10.00	0.726	1.401	1.603	1.789	1.860	1.962	2.128
50.00	0.627	1.205	1.388	1.569	1.641	1.751	1.938

Table III lists the values of $(S^* - S)$ where S^* is the value for an ideal gas. The entropy considered as a function of density and temperature shows only a slight abnormality near the critical point.

Other Properties

To calculate the differences from the ideal gas values of A, the Helmholtz free energy, the quantity $[RT/\rho - P/\rho^2]$ was found to give an almost linear plot against density and differences from linearity could be plotted on a large scale and evaluated graphically. A small constant correction was applied to make the measurements of Beattie *et al.* consistent with ours since their pressures were slightly higher. $A^* - A$ is tabulated in Table IV.

TABLE IV
HELMHOLTZ FREE ENERGY, $A^* - A$ (CAL./MOLE)

$T - T_c$, °C. \ Density, moles/l.	3	6	7	8	8.37	9	10
0.00	221.03	410.57	466.22	518.15	536.96	566.56	611.66
1.50	219.91	408.36	463.69	515.33	534.03	563.49	608.37
5.00	217.32	403.04	457.58	508.54	528.03	556.07	600.38
10.00	213.66	395.94	449.45	499.47	518.59	546.15	589.64
50.00	186.84	344.44	390.42	433.15	449.31	472.67	508.98

The differences from the ideal gas values of E, the internal energy, F, the Gibbs free energy, and H, the enthalpy, were calculated directly according to Equations 5 to 7 and are given in Tables V, VI, and VII.

TABLE V
INTERNAL ENERGY, $E^* - E$ (CAL./MOLE)

$T - T_c$, °C. \ Density, moles/l.	3	6	7	8	8.37	9	10
0	444.46	844.73	965.14	1076.67	1116.20	1171.88	1257.37
1.50	441.61	838.48	956.75	1064.57	1103.57	1161.14	1249.67
5.00	437.56	828.28	944.30	1051.20	1091.24	1148.64	1240.05
10.00	431.34	815.83	929.83	1035.84	1076.07	1134.17	1227.60
50.00	399.86	753.77	861.96	966.15	1006.91	1067.47	1167.28

TABLE VI
GIBBS FREE ENERGY, $F^* - F$ (CAL./MOLE)

$T - T_c$, °C. \ Density, moles/l.	7	8	8.37	9	10
0.00	842.73	919.54	946.66	987.33	
1.50	838.32	914.57	941.63	982.20	
5.00	827.26	902.79	930.59	969.61	1028.65
10.00	812.23	886.60	913.93	952.33	1009.68
50.00	698.16	757.78	777.39	805.27	843.69

TABLE VII
ENTHALPY, $H^* - H$ (CAL./MOLE)

Density, moles/l. / $T - T_c$, °C.	7	8	8.37	9	10
0.00	1341.65	1478.06	1525.90	1592.65	
1.50	1331.38	1463.81	1511.17	1579.85	
5.00	1313.98	1445.45	1493.80	1562.18	1668.32
10.00	1292.61	1422.97	1471.41	1540.35	1647.64
50.00	1169.70	1290.78	1334.99	1400.07	1501.99

These properties likewise, considered as functions of density and temperature, do not show any pronounced effect at the critical point. If they are considered as functions of pressure and temperature as is often done, the behavior at the critical point becomes more extreme reflecting the P–ρ relationship here.

ACKNOWLEDGMENT

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THE HYDROLYSIS OF THE CONDENSED PHOSPHATES[1]

II (A). THE ROLE OF THE HYDROGEN ION IN THE HYDROLYSIS OF SODIUM PYROPHOSPHATE

II (B). THE DISSOCIATION CONSTANTS OF PYROPHOSPHORIC ACID

By J. D. McGilvery and Joan Pedley Crowther

ABSTRACT

The general rate equations for the hydrolysis of pyrophosphate anion proposed by Muus have been proved to be inapplicable over the pH range 2.0 to 11.0. A general rate equation is proposed which is based on the assumption that each anionic species of pyrophosphoric acid hydrolyzes at a rate which depends on its concentration, and that the only role of the hydrogen ion concentration is to determine the proportion of each species present in the solution. A mechanism for the hydrolysis of pyrophosphate anion is suggested.

The dissociation constants of pyrophosphoric acid have been determined at 65.5°C. for the concentration range 0.08 to 0.18 molar.

II (A). THE ROLE OF THE HYDROGEN ION IN THE HYDROLYSIS OF SODIUM PYROPHOSPHATE

Introduction

In the first paper (9) on this subject, it was established that the rate of hydrolysis of sodium pyrophosphate in solution depended on the hydrogen ion concentration but that this hydrolysis was a first order reaction when a constant hydrogen ion concentration was maintained. Fig. 1 is the curve obtained by plotting the first order rate constants against the pH of the pyrophosphate solutions.

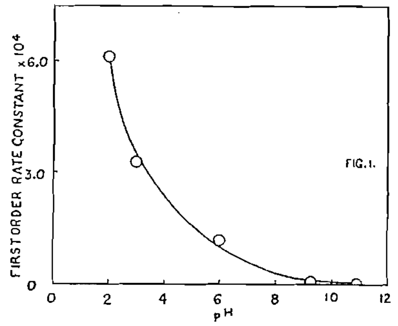

Fig. 1. Effect of pH on rate of hydrolysis of sodium pyrophosphate in solution.

Although there was no evidence of a base-catalyzed hydrolysis over the entire pH range investigated, Fig. 1 shows that hydrogen ion is an effective catalyst. It is also evident that the relationship between the rate of hydrolysis and the hydrogen ion concentration is not a simple one. If, for example, we assume a rate equation of the form:

$$[1] \qquad dC/dt = -k[H^+]^n C$$

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where C is the concentration of pyrophosphate at time t (this includes all the various forms of pyrophosphate which may be present in the solution, as e.g. $H_4P_2O_7$, $H_3P_2O_7^-$, etc.), it is found that the data are best satisfied by a value of about 1/4 for n.

It is difficult to conceive of a mechanism which would satisfactorily explain the fractional power of the hydrogen ion concentration. Furthermore, this rate equation implies that all the pyrophosphate forms in the solution are equivalent in so far as hydrolysis is concerned. Although this might be true, it seems likely that the reactivity of a pyrophosphate anion is influenced by its degree of ionization. Since pyrophosphoric acid is polybasic, pyrophosphate solutions contain a variety of partially dissociated anionic species, the relative amounts of which are determined by the pH of the solution and the dissociation constants. Thus, in a pyrophosphate solution, the following ions would be present: $H_3P_2O_7^{1-}$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, and $P_2O_7^{4-}$. In addition some undissociated acid $H_4P_2O_7$ would occur. For convenience in what follows, references to the anionic species present in pyrophosphate solutions will include the undissociated $H_4P_2O_7$.

Rate Equations for Hydrolysis of Sodium Pyrophosphate Solution

If the ease of hydrolysis of sodium pyrophosphate solutions depends on the anionic species, i.e. $H_3P_2O_7^{1-}$, $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$, and $H_4P_2O_7$, it is doubtful whether any simple rate equation which takes the form of equation [1] will fit the observational data over a wide range of hydrogen ion concentrations.

A general rate equation for the acid-catalyzed hydrolysis of pyrophosphate solutions is:

$$[2] \qquad -dC/dt = f_0[H^+][H_0]+f_1[H^+][H_1]+f_2[H^+][H_2]+f_3[H^+][H_3]+f_4[H^+][H_4],$$

where C is the concentration of pyrophosphate at time t;
t is the reaction time;
$[H^+]$ is the hydrogen ion concentration;
$[H_0]$, $[H_1]$, $[H_2]$, $[H_3]$, and $[H_4]$ are the concentrations of $P_2O_7^{4-}$, $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$, $H_3P_2O_7^{1-}$, and $H_4P_2O_7$, respectively;
$f_0[H^+]$, $f_1[H^+]$, $f_2[H^+]$, $f_3[H^+]$, and $f_4[H^+]$ are the hydrogen ion concentration functions associated with the rate of hydrolysis of H_0, H_1, H_2, H_3, and H_4, respectively;
and $[H_0]$, $[H_1]$, $[H_2]$, $[H_3]$, and $[H_4]$ are interrelated in accordance with the dissociation constants of pyrophosphoric acid.

In order to find a rate equation for the hydrolysis of pyrophosphate solutions which fitted the experimental data, simple forms of equation [2] were investigated.

Muus (7) considered that the different anionic species of pyrophosphoric acid reverted at different rates, and the rate equation which he proposed assumed that:

$$f_i[H^+] = k_i[H^+]$$

where the k_i's are the hydrolysis rate constants associated with the various anionic species and $i = 0, 1, 2, 3, 4$. Thus Muus' (7) rate equation took the form:

$$[3] \qquad -dC/dt = [H^+]\{k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4]\},$$

where the symbols represent the same factors as above. Muus (7), however, only investigated the hydrolysis of pyrophosphate solutions over the pH range 0.91 to 1.4, and hence could not verify equation [3] outside this range. Within this pH range, Muus (7) believed that the anion $H_3P_2O_7^-$ (H_3) was the only species of pyrophosphate that played a significant rate determining role, and hence equation [3] reduced to the form:

$$-dC/dt = k_3[\mathrm{H}^+][H_3]. \tag{3a}$$

Another simple assumption from a kinetic point of view is that each anionic species hydrolyzes at its own specific rate which is quite independent of the hydrogen ion concentration. In such a picture, the only role of the hydrogen ion is to determine the proportion of each species present in the pyrophosphate solution, and thus

$$f_i[\mathrm{H}^+] = k_i, \text{ where } i = 0, 1, 2, 3, 4.$$

The rate equation would then be:

$$-dC/dt = k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4], \tag{4}$$

where the symbols represent the same factors as above.

The above rate equations cannot be tested for applicability without a knowledge of the relationship between the proportions of each anionic species and the pH of the solution. To obtain such information the dissociation constants of a pyrophosphoric acid solution of suitable concentration were determined at 65.5°C. (II(B)) and the following values obtained:

$$K_1 = [\mathrm{H}^+][H_3]/[H_4] = 0.107 \; (\sigma = 0.009 \text{ where } n = 4), \tag{5}$$

$$K_2 = [\mathrm{H}^+][H_2]/[H_3] = 7.58 \times 10^{-3} \; (\sigma = 0.20 \times 10^{-3} \text{ where } n = 6), \tag{6}$$

$$K_3 = [\mathrm{H}^+][H_1]/[H_2] = 1.45 \times 10^{-6} \; (\sigma = 0.04 \times 10^{-6} \text{ where } n = 7), \tag{7}$$

$$K_4 = [\mathrm{H}^+][H_0]/[H_1] = 9.81 \times 10^{-9} \; (\sigma = 0.13 \times 10^{-9} \text{ where } n = 12), \tag{8}$$

where σ is the standard deviation (3) and equations 5, 6, 7, and 8 are simultaneous. The following equations relate the concentration of the various pyrophosphate anionic species to the dissociation constants, the hydrogen ion concentration, and the total pyrophosphate concentration:

$$[H_0] = K_1K_2K_3K_4\,C\,R, \tag{9}$$

$$[H_1] = K_1K_2K_3[\mathrm{H}^+]\,C\,R, \tag{10}$$

$$[H_2] = K_1K_2[\mathrm{H}^+]^2\,C\,R, \tag{11}$$

$$[H_3] = K_1[\mathrm{H}^+]^3\,C\,R, \tag{12}$$

$$[H_4] = [\mathrm{H}^+]^4\,C\,R, \tag{13}$$

where $R = 1/(K_1K_2K_3K_4 + K_1K_2K_3[\mathrm{H}^+] + K_1K_2[\mathrm{H}^+]^2 + K_1[\mathrm{H}^+]^3 + [\mathrm{H}^+]^4)$. Fig. 2, which shows the effect of the pH of the solution on the proportions of the various anionic species of pyrophosphate present, was constructed with the aid of equations [9] to [13], and the dissociation constants.

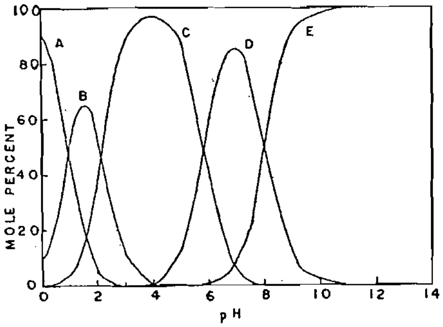


FIG. 2. Effect of pH on distribution of anionic species of pyrophosphate. A, $H_4P_2O_7$; B, $H_3P_2O_7^{1-}$; C, $H_2P_2O_7^{2-}$; D, $HP_2O_7^{3-}$; E, $P_2O_7^{4-}$.

The necessary data to solve equations [3] and [4] for the rate constants $k_0, k_1 \ldots k_4$ have now been obtained, and are summarized in Table I. It will be noted that Abbott's (1) rate data have been included in Table I. Since our studies only covered the pH range 2.0–11.0, no rate data were obtained in the pH region where the concentration of $H_4P_2O_7$ was comparatively large. Therefore Abbott's (1) data, at pH 0.91 where 53% $H_4P_2O_7$ was present, were used to obtain a rough approximation of the rate constant, k_4. It should be noted that values of k_4, based on this data, are a very rough estimate since Abbott's (1) data were obtained for a 0.05 *M* pyrophosphate solution at 75°C. and our data were obtained for a 0.12 *M* solution at 65.5°C. Furthermore, Abbott (1) did not measure the rate at a constant hydrogen ion concentration.

Evaluation of k_i's Assuming Muus' (7) Rate Equation

$$[3] \qquad -dC/dt = [H^+]\{k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4]\}.$$

Since the hydrolysis of sodium pyrophosphate is a first order reaction at constant hydrogen ion concentration:

$$[14] \qquad kC = [H^+]\{k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4]\},$$

where k is the over-all first order rate constant.

Using the data in Table I, equation [14] was solved and the following values obtained for the various rate constants:

$$\begin{aligned} k_0 &= 3.9 \times 10^5 \text{ min.}^{-1}, \\ k_1 &= -7.2 \times 10^6 \text{ min.}^{-1}, \\ k_2 &= 0.40 \text{ min.}^{-1}, \\ k_3 &= -0.21 \text{ min.}^{-1}, \\ k_4 &= 9.4 \times 10^{-2} \text{ min.}^{-1} \end{aligned}$$

Since k_1 and k_3 are negative values implying that orthophosphate anion was forming pyrophosphate anion (against which there is experimental evidence (4, 5)), equation [14] and hence equation [3] is inapplicable. If equation [3*a*] were applicable, the values for k_0, k_1, k_2, and k_4 would have been insignificant or zero, and k_3 would have been positive. Since neither condition was satisfied on solving, equation [3*a*] is not applicable. Thus Muus' (7) rate equations are not applicable over the pH range 2.0–11.0.

TABLE I

CONCENTRATION OF INDIVIDUAL PYROPHOSPHATE ANIONS IN MOLES PYROPHOSPHATE PER LITER AT VARIOUS HYDROGEN ION CONCENTRATIONS

pH	Hydrogen ion concentration	First order rate constant (k in min.$^{-1}$)	$P_2O_7^{4-}$ $[H_0]$	$HP_2O_7^{3-}$ $[H_1]$	$H_2P_2O_7^{2-}$ $[H_2]$	$H_3P_2O_7^{1-}$ $[H_3]$	$H_4P_2O_7$ $[H_4]$
10.9	1.26×10^{-11}	4.8×10^{-6}	1.22×10^{-1}	1.57×10^{-4}	—	—	—
9.3	5.01×10^{-10}	1.0×10^{-5}	1.17×10^{-1}	5.95×10^{-3}	2.06×10^{-6}	—	—
7.34	4.57×10^{-8}	5.0×10^{-5}*	2.11×10^{-2}	9.83×10^{-2}	3.10×10^{-3}	—	—
6.0	1.0×10^{-6}	1.25×10^{-4}	7.07×10^{-4}	7.21×10^{-2}	4.97×10^{-2}	—	—
3.0	1.0×10^{-3}	3.31×10^{-4}	—	1.56×10^{-4}	1.08×10^{-1}	1.42×10^{-2}	1.33×10^{-4}
2.5	3.16×10^{-3}	4.35×10^{-4}*	—	—	8.57×10^{-2}	3.57×10^{-2}	1.06×10^{-3}
2.0	1.0×10^{-2}	5.42×10^{-4}	—	—	5.01×10^{-2}	6.62×10^{-2}	6.18×10^{-3}
0.91	1.23×10^{-1}	2.22×10^{-3}**	—	—	3.41×10^{-3}	5.54×10^{-2}	6.37×10^{-2}

*Rate constant source: *Fig. 1.*
**Rate constant source: *Abbott (1).*

Evaluation of k_i's Assuming Alternate Rate Equation

$$[4] \qquad -dC/dt = k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4],$$

where the symbols represent the same factors as above.

Using data from Table I, equation [4] was solved, and the following approximate values for the rate constants were obtained:

$$k_0 = 4.7 \times 10^{-6} \text{ min.}^{-1},$$
$$k_1 = 5.25 \times 10^{-5} \text{ min.}^{-1},$$
$$k_2 = 2.8 \times 10^{-4} \text{ min.}^{-1},$$
$$k_3 = 7.3 \times 10^{-4} \text{ min.}^{-1},$$
$$k_4 = 3.9 \times 10^{-3} \text{ min.}^{-1}.$$

These rate constants satisfy two necessary conditions for the applicability of equation [4] in that they are positive numbers and approximately satisfy all the data in Table I. However, the equation is not necessarily acceptable. This equation (developed by following the reasoning outlined earlier) contains sufficient constants that even if the reaction mechanism were not as pictured, a good fit might conceivably be obtained. However, since equation [4] permits a reasonable explanation of the role of the hydrogen ion and since our data approximately fit this equation, it is proposed as the general rate equation for the hydrolysis of pyrophosphate anion pending evidence to the contrary.

Order of Reaction

At constant hydrogen ion concentration equation [4] reduces to an equation for a first order reaction as demanded by the experimental data. Rewriting equation [4]:

$$[4a] \quad -\frac{dC}{dt} = C \text{ times the expression}$$
$$\left\{\frac{K_1K_2K_3K_4k_0 + K_1K_2K_3[\mathrm{H}^+]\,k_1 + K_1K_2[\mathrm{H}^+]^2\,k_2 + K_1[\mathrm{H}^+]^3\,k_3 + [\mathrm{H}^+]^4\,k_4}{K_1K_2K_3K_4 + K_1K_2K_3[\mathrm{H}^+] + K_1K_2[\mathrm{H}^+]^2 + K_1[\mathrm{H}^+]^3 + [\mathrm{H}^+]^4}\right\}$$

where C is the pyrophosphate concentration at time t.

The bracketed expression is a constant when the hydrogen ion concentration is constant, and equation [4a] becomes:

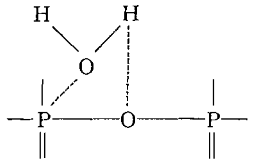
$$[15] \qquad -dC/dt = kC,$$

where k is the over-all first order rate constant.

Mechanism of Reaction

The magnitude of the rate constants evaluated for equation [4] indicate that the order of stability of the pyrophosphate anionic species is: $P_2O_7^{4-} > HP_2O_7^{3-} > H_2P_2O_7^{2-} > H_3P_2O_7^{1-} > H_4P_2O_7$. In addition the rate equation formulated implies that the hydrolysis is a simple reaction between water molecules and these various pyrophosphate anions. The question now arises as to why there should be such profound differences in the ease of hydrolysis of the various species.

A possible explanation might be based on the assumption that the primary steps in the hydrolysis are the formation of loose bonds between a phosphorus atom and the oxygen atom of a water molecule, and between the oxygen atom of the P–O–P linkage and the hydrogen atom of the water molecule:



It follows that the orientation of a water molecule approaching a pyrophosphate anion will be of considerable importance. As is well known, water is a polar molecule—the fractional negative charge being located on the oxygen atom, and the fractional positive charge being located on the hydrogen atoms. It seems reasonable to suppose that, as the phosphorus atom becomes less negative, the possibility of a water molecule approaching in the required orientation for hydrolysis increases. Since the negativity of the phosphorus atoms in the various pyrophosphate anionic species decreases in the order: $P_2O_7^{4-}$, $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$, $H_3P_2O_7^{1-}$, $H_4P_2O_7$, it follows that the rate of hydrolysis of these various species will increase in the same order.

II (B). THE DISSOCIATION CONSTANTS OF PYROPHOSPHORIC ACID

INTRODUCTION

The dissociation constants of pyrophosphoric acid have been determined by Abbott and Bray (2) at 18°C. Muus (7) has also determined the second and third dissociation constants at 40°C., but he based his calculations on the assumption that the first dissociation constant was greater than two. As Abbott and Bray (2) found the value 0.14 for the first dissociation constant, Muus' (7) values seem unlikely. Since insufficient thermodynamic data were available to accurately extrapolate Abbott and Bray's (2) values, these dissociation constants were determined at 65.5°C.

EXPERIMENTAL

Procedure and Results

An electrometric titration method was employed for the determination of the dissociation constants. A mechanically stirred solution of sodium pyrophosphate, maintained at 65.5 ± 0.1°C., was titrated with 3 *N* hydrochloric acid. The changes in the pH of the solution were plotted against the volume of acid added. The inflection points occurred at pH 10.0, 6.8, and 4.0. In the light of considerations which will be discussed shortly, regions between these inflection points were selected for further investigation.

Having thus delineated the critical pH regions, accurate measurements of the acid increments and the resulting pH values were made. Fifty milliliter portions of a 0.179 molar sodium pyrophosphate solution were titrated with 1 *N* hydrochloric acid. The experimental conditions were as described above, but particular care was taken to minimize the time required in obtaining the measurements. None of the samples were subjected to acid conditions for more than five minutes. This procedure was followed on three separate portions of the sodium pyrophosphate solution, and the averages of the results are recorded in Table II. For the same volume of acid added, the pH readings checked within ±0.02 units. In the present experiments, the accuracy of the pH measurements is the limiting factor in calculating the dissociation constants.

TABLE II

Volume N HCl added (ml.)	Average pH*	Average hydrogen ion concentration (gew/l.)
0	9.52	3.020×10^{-10}
2.00	8.48	3.311×10^{-9}
3.00	8.26	5.495×10^{-9}
4.00	8.05	8.913×10^{-9}
6.00	7.66	2.188×10^{-8}
12.00	6.06	8.710×10^{-7}
12.50	5.95	1.122×10^{-6}
13.00	5.87	1.349×10^{-6}
14.00	5.65	2.239×10^{-6}
19.00	2.88	1.318×10^{-3}
19.50	2.72	1.905×10^{-3}
20.00	2.57	2.692×10^{-3}
24.00	1.90	1.259×10^{-2}
25.00	1.78	1.660×10^{-2}

**These figures are the averages of three separate determinations.*

Theory of the Method

It is possible to estimate the dissociation constants of a polybasic acid such as pyrophosphoric by a method of successive approximations utilizing the data obtained from an electrometric titration of the material. Although theoretically all of the anionic species will be present at a given pH, the concentrations of one or more of the species will always be small enough at that pH to be neglected in making approximate calculations of the dissociation constants (6). These values of the dissociation constants may then be used to estimate the concentrations of the components which were neglected in the first approximation. The appropriate corrections may then be made, and the dissociation constants estimated for a second time. This process may, of course, be continued indefinitely, but it was found that the second approximation was satisfactory in every case.

As stated earlier the inflection points in the electrometric titration curve of sodium pyrophosphate at 65.5°C. occur at the pH values: 10.0, 6.8, and 4.0, and at these points the concentration of $P_2O_7^{4-}$, $HP_2O_7^{3-}$, and $H_2P_2O_7^{2-}$ respectively, predominate. At intermediate points two of the species predominate, and it is in these regions that the most accurate estimations of the dissociation constants may be obtained. The method of calculation also permits the inclusion of one minor component in obtaining the first approximation of K_1, K_2, and K_3. The pH regions chosen and the anionic species assumed to be present in calculating the first approximations to the various dissociation constants are shown in Table III. The predominating species in each pH range are underlined.

TABLE III

Dissociation constant	Anionic species assumed present	pH Range
K_1	$\underline{H_4P_2O_7}$, $\underline{H_3P_2O_7^{1-}}$, $\underline{H_2P_2O_7^{2-}}$	< 2
K_2*	$\underline{H_3P_2O_7^{1-}}$, $\underline{H_2P_2O_7^{2-}}$, $HP_2O_7^{3-}$	2.5-3.0
K_3	$\underline{H_2P_2O_7^{2-}}$, $\underline{HP_2O_7^{3-}}$, $P_2O_7^{4-}$	5.6-6.2
K_4	$\underline{HP_2O_7^{3-}}$, $\underline{P_2O_7^{4-}}$	8.0-9.5

**In the pH region below pH 4, $H_4P_2O_7$, $H_3P_2O_7^{1-}$, and $H_2P_2O_7^{2-}$ predominate, but little $H_4P_2O_7$ would be present in the region 2.5 – 3.0. At 18°C., Abbott and Bray's (2) dissociation constants indicate that approximately three per cent $H_4P_2O_7$ is present at pH 3. Furthermore, Thomsen's (8) heat of ionization data for the reaction:*

$$H_4P_2O_7 \rightleftharpoons H^+ + H_3P_2O_7^-,$$

show that increasing the temperature will shift the equilibrium to the right. Thus the first approximation to the second dissociation constant was calculated assuming that no $H_4P_2O_7$ was present in the pH range 2.5–3.0.

Calculation of the Fourth Dissociation Constant (K_4)

The initial solution of sodium pyrophosphate is in the pH range where $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ are the only anionic species present in significant amounts. Therefore to a first approximation:

[1] $$H_0 + H_1 = P_T,$$

where H_0 and H_1 are the amounts of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ respectively, and P_T is the total amount of pyrophosphate present.

A quantity of acid is now added which lowers the pH of the solution but does not take it out of the range where $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ are the only major components. However, the acid does convert an equivalent amount of $P_2O_7^{4-}$ to $HP_2O_7^{3-}$ as indicated by the equation:

[2] $$P_2O_7^{4-} + H^+ \rightleftharpoons HP_2O_7^{3-}.$$

The amounts of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ present become $(H_0 - H_a^+)$ and $(H_1 + H_a^+)$ respectively, when H_a^+ is the equivalent amount of acid added.

The dissociation constant K_4 is defined by the expression:

[3] $$K_4 = [H^+]\,[P_2O_7^{4-}]/[HP_2O_7^{3-}].$$

Since a ratio of anionic species is involved, it is immaterial which units are employed to express the amounts of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ so long as they are identical for both species. Therefore, before adding acid:

[4] $$K_4 = [H^+]_i H_0/H_1.$$

After adding acid:

[5] $$K_4 = [H^+]_f (H_0 - H_a^+)/(H_1 + H_a^+),$$

where $[H^+]_i$ and $[H^+]_f$ are the initial and final hydrogen ion concentrations. Equating [4] and [5] and substituting $(P_T - H_1)$ for H_0, a quadratic in H_1 is obtained which may be solved. Although two positive solutions are obtained, only one solution gives reasonable results in the calculation of K_4. The latter calculation is made by simply substituting values for H_1, H_0 (which is $P_T - H_1$), and $[H^+]_i$ in equation [4].

Calculation of the Third Dissociation Constant (K_3)

Having now obtained a value for K_4 it is possible to determine K_3 using much the same procedure as in estimating K_4.

A quantity of acid is added to the initial solution of sodium pyrophosphate such that the resulting pH of the solution lies in the range 5.6–6.2 where $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ are the major components and $P_2O_7^{4-}$ is the largest minor component. The acid added is consumed in two reactions:

[2] $$P_2O_7^{4-} + H^+ \rightleftharpoons HP_2O_7^{3-}$$

and

[6] $$HP_2O_7^{3-} + H^+ \rightleftharpoons H_2P_2O_7^{2-}.$$

If the total amount of acid added is H_b^+ and an amount B is consumed in reaction [2], then $(H_b^+ - B)$ is consumed in reaction [6]. Consequently the amounts of the various species after the addition of the acid are as follows:

$$\begin{array}{lll} P_2O_7^{4-} & = H_0 - B & = P_T - H_1 - B, \\ HP_2O_7^{3-} & = H_1 + B - (H_b^+ - B) & = H_1 - H_b^+ + 2B, \\ H_2P_2O_7^{2-} & = & \quad H_b^+ - B. \end{array}$$

If the hydrogen ion concentration at this point is designated by $[H^+]_f$ then by substituting in equation [3], the following equation is obtained:

[7] $$K_4 = [H^+]_f\,(P_T - H_1 - B)/(H_1 + H_b^+ + 2B).$$

Since B is the only unknown it may be evaluated.

The third dissociation constant K_3 is defined by the expression:

[8] $$K_3 = [H^+]\,[HP_2O_7^{3-}]/[H_2P_2O_7^{2-}].$$

Therefore:

[9] $$K_3 = [H^+]_f\,(H_1 - H_b^+ + 2B)/(H_b^+ - B).$$

Since all the factors on the right-hand side of equation [9] are known, K_3 may be evaluated.

Calculation of the Second (K_2) *and First* (K_1) *Dissociation Constants*

The second and first dissociation constants are determined in a similar manner making the appropriate assumptions with regard to the anionic species present.

Table IV illustrates the distribution of the various anionic species in each pH range used in the calculation of dissociation constants.

H_c^+ and H_d^+ are the amounts of acid added to the pyrophosphate solution to change from the initial pH to pH values in the ranges 2.5–3.0 and <2.0 respectively.

C is the amount of acid consumed in the reaction:

[6] $$HP_2O_7^{3-} + H^+ \rightleftharpoons H_2P_2O_7^{2-},$$

when H_c^+ is the amount of acid added.

TABLE IV
DISTRIBUTION OF ANIONIC SPECIES ASSUMED IN CALCULATION OF DISSOCIATION CONSTANTS

Amounts ionic species assumed present	Dissociation constant			
	K_1	K_2	K_3	K_4
	pH range			
	8.0–9.5	5.6–6.2	2.5–3.0	< 2.0
H_0	$P_T - H_1 - \mathrm{H}_a^+$	$P_T - B$	—	—
H_1	$H_1 + \mathrm{H}_a^+$	$\mathrm{H}_1^+ + 2B - \mathrm{H}_b^+$	$P_T - C$	—
H_2	—	$\mathrm{H}_b^+ - B$	$P_T + 2C - \mathrm{H}_c^+ - H_1$	$P_T - D$
H_3	—	—	$\mathrm{H}_c^+ - C - P_T + H_1$	$2P_T + 2D - \mathrm{H}_d^+ - H_1$
H_4	—	—	—	$\mathrm{H}_d^+ - D - 2P_T + H_1$

Similarly D is the amount of acid consumed in the reaction:

[10] $$\mathrm{H_2P_2O_7^{2-} + H^+ \rightleftharpoons H_3P_2O_7^{1-}},$$

when H_d^+ is the amount of acid added.

On substituting the data in Table II into the approximate equations developed in this manner, the following average values for the dissociation constants of pyrophosphoric acid were obtained:

$K_1 = 0.122$ ($\sigma = 0.014$ where $n = 4$),
$K_2 = 7.29 \times 10^{-3}$ ($\sigma = 0.37 \times 10^{-3}$ where $n = 6$),
$K_3 = 1.45 \times 10^{-6}$ ($\sigma = 0.04 \times 10^{-6}$ where $n = 7$),
$K_4 = 9.72 \times 10^{-9}$ ($\sigma = 0.12 \times 10^{-9}$ where $n = 12$),

where σ is the standard deviation (3).

Using the above dissociation constants and the method of calculation outlined, the following set of values were obtained as a second approximation to the dissociation constants. Further approximations did not alter the values appreciably.

$K_1 = 0.107$ ($\sigma = 0.009$ where $n = 4$),
$K_2 = 7.58 \times 10^{-3}$ ($\sigma = 0.20 \times 10^{-3}$ where $n = 6$),
$K_3 = 1.45 \times 10^{-6}$ ($\sigma = 0.04 \times 10^{-6}$ where $n = 7$),
$K_4 = 9.81 \times 10^{-9}$ ($\sigma = 0.13 \times 10^{-9}$ where $n = 12$),

where σ is the standard deviation (3).

The standard deviations indicate the precision of the experiment but not the accuracy.

Since no attempt was made to distinguish between the concentration and the activity of these anionic species, the concentration range in which the dissociation constants are applicable must be specified. Abbott and Bray (2) found that the values of the dissociation constants changed very little with the molarity of the pyrophosphate solution if that concentration were higher than 0.08 molar. Thus the dissociation constants, determined above, are considered to be applicable at least over the concentration range 0.08 to 0.18 molar.

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CONSTITUTION OF A POLYURONIDE HEMICELLULOSE FROM WHEAT LEAF[1]

By G. A. Adams[2]

ABSTRACT

Crude hemicellulose of mature wheat leaves has been prepared by alkaline extraction of leaf holocellulose. Purification by repeated complexing with Fehling's solution yielded a polyuronide hemicellulose ($[\alpha]_D^{25}$ − 93°) composed of D-xylose (88.5%), L-arabinose (6.90%), and uronic acid anhydride (5.27%). Methylation studies indicated a molecular structure comprising a main xylan chain of 30 anhydro-D-xylose residues to which three L-arabinose residues and one D-glucuronic acid unit were attached as side chains by glycosidic linkages. Periodate oxidation data supported the proposed structure and the yield of formic acid indicated a molecule containing approximately 32 sugar residues. Estimations of the degree of polymerization of the molecule by measurements of viscosity and reducing power agreed with the foregoing values. The structure of the hemicellulose closely resembled that of one isolated previously from wheat straw.

Although fructosans (3, 13) and galactans (6) have been found in leaves of annual plants, little information is available on the occurrence and nature of hemicelluloses of the "xylan" type in similar materials. In the wheat plant, "xylans" have been reported in the straw and bran although these hemicelluloses may not have consisted exclusively of anhydro-D-xylose units. The presence of L-arabinose and D-glucuronic acid in the crude hemicelluloses indicated a more complex molecule, and a hemicellulose fraction of wheat straw has been shown to consist of D-xylose, L-arabinose, and D-glucuronic acid (1). From wheat flour an araboxylan or xyloaraban molecule has recently been isolated by Perlin (11). Since preliminary experiments indicated the presence of hemicelluloses of the "xylan" type in mature wheat leaves, a further investigation was made to determine whether these hemicelluloses were of the same type as found in the straw and bran.

Hemicelluloses, extracted from wheat leaf chlorite holocellulose by dilute potassium hydroxide in 27% yield, contained pentosan (90.9%), uronic acid anhydride (6.08%), and lignin (2.1%). On hydrolysis, xylose and arabinose were released in a ratio of 4.3 : 1 along with traces of glucose and galactose. The crude pentosan was subjected to further purification by repeated precipitation as a copper complex with Fehling's solution as described by Chanda *et al.* (7). Although this treatment reduced the arabinose content markedly, there remained a xyloaraban containing a xylose to arabinose ratio of 12.8 : 1 beyond which no further reduction was possible. The constant composition of the hemicellulose indicated strongly that the pentoses were combined in the same molecule. Ready removal of the hexoses showed that they were not an integral part of the pentosan molecule.

Graded hydrolysis of the hemicellulose with 0.02 N oxalic acid readily released the arabinose without appreciably affecting the xylose. This observation indicated that the arabinose units were on the periphery of the molecule

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and were readily attacked. In addition, the acid lability suggested that the arabinose was in the furanoside configuration while the xylose was in the more stable pyranoside form. Recovery of at least a portion of the xylose units in polymer form after removal of the arabinose units suggested a molecular structure consisting of a chain of xylose units to which the arabinose units were attached as side groups. The uronic acid groups were probably attached to the xylan chain as the recovered portion retained almost its original uronic acid content.

The purified hemicellulose was methylated initially with dimethyl sulphate and strong alkali and finally to constant methoxyl content with Purdie's reagent. Fractionation with chloroform – petroleum ether solution yielded a fully methylated fraction having $[\alpha]_D^{25} - 88°$ (*c*, 1.0% in chloroform) and OCH_3 content 38.6%, (calculated for $C_7H_{12}O_4 : OCH_3$, 38.8%). Hydrolysis of the methylated product yielded the following products which were identified as described in the experimental section: (I) 2-methyl-D-xylose; (II) 2,3-dimethyl-D-xylose; (III) 2,3,4-trimethyl-D-xylose; (IV) 2,3,5-trimethyl-L-arabinose; (V) 2-methyl-3[2,3,4-trimethyl-D-glucuronosido]D-xylose.

Identification of almost all of the arabinose in the original hemicellulose as 2,3,5-trimethyl-L-arabinose provided proof that the arabinose residues existed as side chains attached by glycosidic linkages to a main structure. The absence of monomethyl and dimethyl arabinose units precluded the existence of a separate araban structure and provided additional evidence that the arabinose units were an integral part of the hemicellulose molecule.

The 2,3,4-trimethyl-D-xylose which appeared in the methanolysis mixture originated from the nonreducing end of the xylan chain and the amount (3.0% molar) corresponded to 33 residues per nonreducing end group.

The presence of 2,3-dimethyl-D-xylose as the main component of the free methylated sugar mixture indicated that the xylose units were linked 1,4; the pyranose form required for this linkage was reasonably established by stability to acid. The change in specific rotation of the methylated polysaccharide from $-88°$ to $+58°$ on hydrolysis indicated that the xylose units were joined in the β-configuration.

Branch points in the main xylan chain were indicated by the presence of 2-methyl-D-xylose (11.6% molar). Since 2-methyl xylose was the only monomethyl xylose found, it was apparent that $C_{(3)}$ must be the site of side group attachment in the 1,4-linked xylan chain. The presence of one monomethyl residue was obscured in the hydrolysis mixture by its attachment to a glucuronic acid residue as an aldobiuronic acid unit. The number of branch points as indicated by 2-methyl xylose (11.6%) exceeded the number of side groups as represented by 2,3,5-trimethyl arabinose (9.1%). The excess monomethyl xylose may be explained by incomplete methylation of the original hemicellulose and/or by demethylation of 2,3-dimethyl xylose (8). The possibility that other types of branching exist in the molecule cannot be rejected although no direct evidence for them was found.

The methylated aldobiuronic acid ester was reduced with sodium borohydride and the product hydrolyzed with dilute acid. The trimethyl glucose derived from the uronic acid could only be 2,3,4-trimethyl glucose because reduction of a methylated uronic acid could not yield a 2,3,6-trimethyl derivative. The monomethyl xylose corresponded chromatographically to 2-methyl xylose; the possibility that it was another monomethyl derivative was unlikely unless this xylose residue was substituted differently from those in the rest of the molecule. Therefore the methylated aldobiuronic acid was 2-methyl-3[2,3,4-trimethyl glucuronosido]D-xylose; the high positive rotation (+78°) indicated an α linkage. The uronic acid unit occupied the position of a nonreducing end group and was linked glycosidically to a xylose unit. From analysis of the original hemicellulose, the amount of uronic acid was calculated to be one mole. The structure of the aldobiuronic acid residue in the wheat leaf appears to be identical with that found in wheat straw hemicellulose (1, 5) and in pear cell wall xylan (8).

Methylated sugars I, II, III, and IV occurred in a molar ratio of 4 : 25 : 1 : 3. In addition, one mole of glucuronic acid was present in the hemicellulose molecule. From the foregoing data a possible structure for the molecule is proposed as follows: a straight chain of approximately 29 D-xylopyranose units joined by 1,4-β-glycosidic linkages and terminated by one reducing and one nonreducing end group. Three L-arabinose units and one D-glucuronic acid unit are attached as side groups to the main chain by 1,3-glycosidic bonds. With one xylose residue bound into the aldobiuronic unit, a total of 30 xylose units are present in the main chain which along with the arabinose and glucuronic acid units make up a total of 34 units in the molecule.

Periodate oxidation of the hemicellulose provided additional evidence for the proposed structure which theoretically should consume 0.97 moles of periodate per mole ($C_5H_8O_4$). Actual consumption was 0.94 moles of periodate after 168 hr. when the oxidation appeared complete. The calculated yield of formic acid from the proposed molecule was 0.118 moles per sugar unit. Although the formation of formic acid continued slowly after 168 hr. oxidation, it was considered complete at that time, when 0.128 moles had been formed. For the molecular structure proposed, this value corresponds to a molecule containing approximately 32 sugar units since two moles of formic acid originate from the reducing end and one mole each from the nonreducing end and glucuronic acid respectively. The xylose residues which were branch points in the molecule were not oxidized by periodate and on hydrolysis yielded small amounts of free sugar.

Estimates of the number of sugar units from the reducing power measured by three different methods were in reasonable agreement and indicated one reducing group per approximately 30–35 sugar residues.

Viscosity measurements on the acetylated and methylated hemicellulose gave degree of polymerization values of 46 and 37 respectively. While these results are somewhat higher than those given by chemical methods, they are, nevertheless, of the same general order of magnitude.

One of the main features of the wheat leaf polyuronide hemicellulose is its close similarity to the hemicellulose of wheat straw (1). The general structure of the molecule is almost identical except that the proportion of L-arabinose and D-glucuronic acid is less. The glucuronic acid of wheat straw appeared to consist entirely of the monomethoxyl derivative but less than 50% of the wheat leaf glucuronic acid was in this form. The molecular dimensions of the two molecules are of the same general order and both appear to be small short chain structures with side groups of L-arabinose and D-glucuronic acid. Concepts of "xylan" in plant tissues have undergone modification in recent years and now permit inclusion of arabinose (11, 4) and D-glucuronic acid (8, 9) in the molecule. Wheat straw (1) and wheat leaf hemicelluloses appear to have all three components joined in a single molecule.

EXPERIMENTAL

Preparation of Wheat Leaf Holocellulose

The blades of wheat leaves were harvested by hand from wheat plants which had been cut two to three weeks previously and stored out-of-doors. The leaf material was then ground in a Wiley mill and screened to give a fraction which passed 40 mesh and was retained on 60 mesh. Extraction with ethanol–benzene (1 : 2) for 16 hr. and subsequently with ethanol for five hours removed pigments, lipoids, and waxy substances. Water soluble material was removed by two four-hour extractions at 85°C. The residue was then thoroughly washed with cold water and dried in air. Holocellulose was prepared from this residue in 76% yield by the acid chlorite method (2).

Isolation of Leaf Hemicellulose from Holocellulose

Air-dry holocellulose (350 gm.) was extracted by stirring for 20 hr. at room temperature with 12 liters of 4% potassium hydroxide in an atmosphere of nitrogen. The residue was recovered by filtration on cloth and subjected to two further extractions. The combined extracts were clarified in a Sharples supercentrifuge and brought to pH 7.0 with acetic acid. The white precipitate which formed was recovered and washed thoroughly with water (Hemicellulose I). Further reduction of the pH to 5.0 and addition of four volumes of ethanol brought a further precipitate (Hemicellulose 2). The total yield of hemicellulosic material was 27%. Acid hydrolysis of both fractions yielded xylose and arabinose and a small amount of glucose and galactose. Since these analyses, as well as the optical rotations of the two fractions, were very similar, the fractions were combined.

Purification of the Leaf Hemicellulose

Crude hemicellulose (40 gm.) was purified by repeated complexing with Fehlings' solution (7). Table I shows that the xylose : arabinose ratio of the

TABLE I
EFFECT OF COPPER COMPLEXING TREATMENTS ON XYLOSE : ARABINOSE RATIO IN WHEAT LEAF HEMICELLULOSE

Number of treatments	Xylose : arabinose
None	4.3 : 1
3	11.6 : 1
6	12.8 : 1
9	12.8 : 1

hemicellulose remained constant after six treatments. No glucose or galactose was detected in the purified product.

The composition of the purified hemicellulose was as follows: ash, 0.34%; nitrogen, nil; methoxyl, 0.5%; uronic acid anhydride, 5.27%; D-xylose, 88.5%; L-arabinose, 6.9%; and $[\alpha]_D^{25}$ − 93° (*c*, 1% in sodium hydroxide (2%)).

Graded Hydrolysis

In a preliminary experiment, hemicellulose (50 mgm.) was heated under reflux in a boiling water bath with oxalic acid (5 ml., 0.02 *N*). Chromatographic examination of the hydrolyzate at regular time intervals showed that at the end of three hours only a trace of xylose had appeared although arabinose was present in large amounts. Repetition of this experiment on a quantitative basis permitted measurement of the maximum yield of arabinose with minimal removal of xylose. The results given in Table II show that at the end of a one-hour heating period, 100% of the arabinose and only 0.8% of the xylose had been released. Addition of five volumes of ethanol to the hydrolyzate yielded a precipitate which on hydrolysis gave only xylose. Uronic acid anhydride estimation on this precipitate gave a value of 5.06%.

TABLE II
GRADED HYDROLYSIS OF WHEAT LEAF HEMICELLULOSE WITH 0.02 *N* OXALIC ACID

Hydrolysis time, hr.	Percentage individual sugar released	
	Arabinose	Xylose
1	100	0.8
2	100	1.2
3	100	2.4
4	100	4.4

Methylation

Hemicellulose (15.0 gm.) was methylated with dimethyl sulphate and sodium hydroxide (40%) by a procedure previously described (1). The partially methylated product was recovered after each two methylation treatments by dialysis and evaporation. After 10 treatments the product was recovered as a friable yellowish solid (OCH_3, 36.4%) soluble in methanol, acetone, and methyl iodide. The partially methylated product (15.7 gm.) was dissolved in methyl iodide (200 ml.) and refluxed at 45°C. during the addition of silver oxide (50 gm.) over a period of four hours. The methylated hemicellulose was recovered by chloroform extraction and subjected to two similar treatments. The final product was a porous yellow solid; yield 16.0 gm.; OCH_3, 38.3% (theoretical value for dimethyl xylan 38.8%); $[\alpha]_D^{25}$ − 84.5 (*c*, 0.49% in chloroform). Two further methylations by the Purdie method failed to increase the methoxyl content.

Fractionation of Methylated Hemicellulose

The methylated hemicellulose (16.0 gm.) was extracted under gentle reflux with solvent mixtures of chloroform – petroleum ether (b.p. 30–60°C.). After filtration through a glass filter ("C" porosity) the solvent was removed under reduced pressure and the product dried *in vacuo* at 50°C. The results of the fractionation are given in Table III. Fraction 5 comprised 75% of the product and was fully methylated; this material was used in subsequent studies.

TABLE III
FRACTIONATION OF METHYLATED WHEAT LEAF HEMICELLULOSE

Fraction No.	Chloroform – petroleum ether solvent mixture	Yield, %	OCH_3, %	$[\alpha]_D^{25}$
1	0 : 100	0.2	—	—
2	10 : 90	0.9	—	—
3	20 : 80	2.3	33.8	−69
4	30 : 70	19.8	38.3	−84
5	40 : 60	75.7	38.6	−88

Hydrolysis Products of Methylated Hemicellulose

Fraction 5 (100 mgm.) was heated with methanolic hydrogen chloride (10 ml.; 8%) in a sealed tube at 100°C. for 18 hr. After removal of the solvent, the sirupy methyl glycosides were hydrolyzed with hydrochloric acid (10 ml.; 0.5 *N*) for eight hours at 100°C. The hydrolyzate was worked up in the usual way and the free methylated sugars separated chromatographically on filter paper using the solvent system *N*-butanol–ethanol–water–ammonia (40 : 10 : 49 : 1). Sugar spots were developed with aniline phthalate spray and authentic samples of methylated sugars were used as reference compounds. The following sugars were detected: (1) 2,3,5-trimethyl arabinose (R_f 0.81–83); (2) 2,3-dimethyl xylose (R_f 0.66–0.69); (3) 2-methyl xylose (R_f 0.43–0.47); (4) a pink spot (R_f 0.15–0.17) indicative of uronic acids. Repetition of the foregoing experiment using a methyl ethyl ketone – water (2 : 1) solvent system showed the presence of the same sugars. The free methylated sugars were extracted from a quantitative chromatogram and analyzed by the alkaline hypoiodite method (7). The results are given in Table IV.

TABLE IV
COMPOSITION OF HYDROLYZATE FROM METHYLATED HEMICELLULOSE

Component sugar	Molar composition, %
Monomethyl pentose	11.6
Dimethyl pentose	76.4
Trimethyl pentose	12.1

Separation of Methylated Pentoses

For separation and confirmation of the identity of the free methylated sugars, larger quantities were prepared in the following way. Methylated hemicellulose (Fraction 5; 7.7 gm.) was heated under reflux with methanolic hydrogen chloride (300 ml.: 8%) until the rotation became constant ($[\alpha]_D^{25}$ +59°).

After removal of the chloride ions with silver carbonate, and excess silver ions as silver sulphide, the solution was concentrated to a brown sirup (8.05 gm.). The methyl glycosides were hydrolyzed to free sugars with hydrochloric acid (300 ml.; 0.5 *N*) until the rotation became constant (+22.5°). Yield of free methylated sugars was 7.80 gm.

The mixture of methylated sugars was separated on a column of powdered cellulose (8) and the following fractions were obtained: (I) trimethyl pentose (0.87 gm.); (II) dimethyl xylose (4.76 gm.); (III) monomethyl pentose (0.71 gm.); (IV) uronic acid fraction (0.35 gm.).

Examination of the Fractions

Fraction I.—This sirup did not crystallize on standing. The specific rotation value of −11° suggested the product was a mixture of 2,3,5-trimethyl arabinose ($[\alpha]_D^{25}$ −39.5°) and 2,3,4-trimethyl xylose ($[\alpha]_D^{25}$ +24.2°). Demethylation of the sirup (25 mgm.) with hydrobromic acid (48%) at 100°C. for 12 min. showed on chromatographing that arabinose and xylose were both present. Use of authentic samples of 2,3,5-trimethyl arabinose and 2,3,4-trimethyl xylose indicated that complete separation could be achieved readily on paper chromatograms using the solvent system ethanol–benzene–water (47 : 170 : 15). Therefore, the trimethyl pentose fraction (460 mgm.) was separated chromatographically into fraction I*a* (120 mgm.) and fraction I*b* (315 mgm.). The composition of the trimethyl pentose fraction (12.1% of the methylated sugars) was therefore trimethyl xylose (I*a*) (3.0% molar) and trimethyl arabinose (I*b*) (9.1% molar).

Fraction Ia.—This material was clarified by filtration through charcoal and then dissolved in ethyl ether to which a few drops of petroleum ether (b.p. 35–60°C.) had been added. On seeding with 2,3,4-trimethyl-D-xylose crystallization occurred. Recrystallization from the same solvent yielded 2,3,4-trimethyl-D-xylopyranose, m.p. 89–90° (undepressed on admixture with an authentic sample) and $[\alpha]_D^{25}$ +19.8 (*c*, 1.0% in water).

Analysis: calculated for $C_8H_{16}O_5$: OCH_3 48.4%; found; OCH_3, 48.1%.

Fraction Ib.—Clarification with charcoal yielded a sirup having η_D^{20} 1.4525; $[\alpha]_D^{25}$ −35.2°; OCH_3, 47.9% (calculated for $C_8H_{16}O_5$, 48.4%). Oxidation of this sugar with bromine yielded a lactone which was converted to the corresponding amide by methanolic ammonia. Recrystallization of the amide yielded pure 2,3,5-trimethyl-L-arabonamide, m.p. 138°C. and $[\alpha]_D^{25}$ − 17.9° (*c*, 1.10 in water).

Analysis: calculated for $C_8H_{17}O_5N$: OCH_3, 44.9; found: OCH_3, 44.8.

Fraction II.—Chromatographic examination of the clarified sirup indicated that only 2,3-dimethyl-D-xylose was present, and the physical constants $[\alpha]_D^{25}$ +24° (*c*, 1% in water) and η_D^{25} 1.4733 provided further evidence of its identity.

Analysis: calculated for $C_7H_{14}O_5$: OCH_3, 34.8%; found: OCH_3, 34.8%.

A crystalline anilide was prepared having m.p. 123–124°C.; (reported value 124°C.). An X-ray powder photograph of this anilide showed it to be identical with 2,3-dimethyl-D-xylose anilide.

Fraction III.—This fraction partially crystallized on standing. After clarification of the alcoholic solution with charcoal, it was readily recrystallized from methanol, m.p. 133°C. and $[\alpha]_D^{25}$ $+37°$ (*c*, 1% in water).

Analysis: calculated for $C_6H_{12}O_5$: OCH_3, 18.9%; found: OCH_3, 18.7%. A crystalline anilide had a m.p. 123° alone or admixed with an authentic sample of 2-methyl-D-xylose anilide.

Fraction IV.—Chromatographic examination of this fraction (320 mgm.) on filter paper showed two spots characteristic of uronic acids, a spot due to methylated xylose and two spots presumably due to unhydrolyzed hemicellulose. Further chromatographing on a small cellulose column failed to separate the uronic acids satisfactorily. The components of the fraction were converted to their glycoside form by heating with methanolic hydrogen chloride (25 ml.; 5%) for six hours. The methanolysis mixture after the usual neutralization treatment with silver carbonate was heated with saturated barium hydroxide solution (25 ml.) for three hours at 60°C. to convert the uronic acid ester into the barium salt. After removal of the excess barium ions with carbon dioxide, the aqueous solution was extracted for 24 hr. with ethyl ether. This solvent dissolved the methyl pentosides but only a small amount of the barium salt of the uronic acid; the latter was then recovered by evaporation. The barium salt (480 mgm.) was taken up in hydrochloric acid (20 ml., 0.5 *N*) and heated at 100°C. for three hours. After neutralization with silver carbonate, the solution was concentrated to a sirup (336 mgm.) which was taken up in methanol. The sirup was heavily spotted on filter paper and chromatographed in methyl ethyl ketone – water (2 : 1) solvent system. The portion of the paper containing the methylated uronic acid was cut out and extracted thoroughly with hot ethanol. Evaporation of the extract yielded the free methylated aldobiuronic acid which was reconverted to its glycoside methyl ester form (290 mgm.) with $[\alpha]_D^{20}$ $+78°$.

Reduction with Sodium Borohydride

Alcoholic solution of the uronic acid sirup was treated with sodium borohydride (150 mgm.) dissolved in ethanol (5 ml.). After the solution had been allowed to stand overnight, acetic acid was added and the pH reduced to 7.0. The solution was evaporated to dryness, extracted with hot ethyl ether, and a sirup (39 mgm.) recovered. Hydrolysis of the sirup (15 mgm.) yielded the free sugars which were separated on a filter paper chromatogram with the methyl ethyl ketone – water solvent. Four spots on the paper were identified as 2-methyl xylose, 2,3,4-trimethyl-D-glucose, 2,3-dimethyl xylose, and unreduced uronic acid, the latter two substances being present in only small amounts. Appropriate reference compounds were run on the same chromatogram. The identity of the methylated uronic acid was established as 2,3,4-trimethyl-D-glucuronic acid by the presence of 2,3,4-trimethyl-D-glucose.

Periodate Oxidation

In a typical oxidation experiment, leaf hemicellulose (100 mgm.) was suspended in periodic acid solution (4.6 gm. periodic acid in 100 ml. of water) and neutralized with sodium hydroxide to methyl red end point. All oxidations were carried out in the dark on a shaking apparatus at 16°C. Analyses were performed at various time intervals for periodate consumption and formic acid production (7). The results were as follows:

	Time, hr.				
	48	72	120	168	216
Periodate consumed,*moles per $C_5H_8O_4$	0.61	0.76	0.82	0.94	0.96
Formic acid produced, moles per $C_5H_8O_4$	0.110	0.119	0.126	0.128	0.129

**Corrected for periodate consumed in formic acid production.*

Reducing Power of Hemicellulose

Three methods of determining reducing power were used. The hypoiodite oxidation method of Chanda *et al.* (7), modified by substitution of a sodium hydroxide – disodium hydrogen phosphate buffer (pH 11.40), indicated one reducing group per 30–35 pentose residues. Somogyi's copper reduction method (12) gave a result of one reducing group per 34–36 sugar units. Approximately 32 sugar units per reducing group were indicated by Meyer's dinitrosalicylic acid method as modified by Chanda *et al.* (7).

Viscosity Measurements on Hemicellulose Derivatives

Viscosity measurements were made using an Oswald-Cannon-Fenske viscometer in a water bath at 25°C. ± 0.02°. The derivatives used were the fully acetylated hemicellulose dissolved in *m*-cresol and fully methylated hemicellulose in chloroform solution. The plots of η_{sp}/c versus c were straight lines and, when extrapolated to zero concentration, gave intrinsic viscosity $[\eta]$. Using a K_m factor of 11×10^{-4} (10) for the acetyl derivative and 12×10^{-4} (7) for the methyl derivative, substitution in Staudinger's equation $[\eta] = K_mP$ gave degree of polymerization (P) values of 46 for the former and 37 for the latter derivative respectively.

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LYCOCTONINE: PERIODATE OXIDATION STUDIES[1]

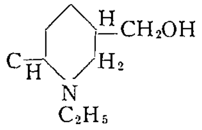
BY O. E. EDWARDS AND LÉO MARION

ABSTRACT

The periodate oxidation of lycoctonam and des(oxymethylene)-lycoctonam gives rise to diketones, showing that lycoctonine contains a ditertiary vicinal glycol. Evidence is presented relating two of the methoxyl groups to this glycol system. The properties and reactions of isomeric compounds formed by the action of weak base or activated alumina on the diketones are discussed and possible explanations of the isomerization considered. The unusual spectra of the various compounds are discussed.

INTRODUCTION

Evidence has been presented for the presence in lycoctonine ($C_{19}H_{21}(OH)_3(OCH_3)_4(NC_2H_5)$) of the partial structure:



and for the presence of a vicinal glycol system (11), thus accounting for the three hydroxyls in the base. A study of the periodic acid cleavage of lycoctonam (the lactam obtained on oxidation of the methylene next to the nitrogen in lycoctonine) and of des(oxymethylene)-lycoctonam (lycoctonam in which the hydroxymethyl group has been replaced by hydrogen) has confirmed the presence of the vicinal glycol and given information about two of the methoxyls in the compounds. The well-characterized compounds which have now been obtained are indicated in the flowsheet below.

Since the carbonyls formed by the oxidation of the glycol system in these lactams are resistant to oxidation by moist silver oxide, potassium permanganate in acetone, and chromic anhydride in glacial acetic acid, they must be ketonic (a hindered aldehyde like strophanthidin is oxidized readily by potassium permanganate in acetone (20)). Hence the vicinal hydroxyls in lycoctonine are both tertiary.

The infrared absorption maxima (Table I) indicate that one carbonyl (carbonyl 1) (1765 cm.$^{-1}$) is in a five membered ring and that the other (carbonyl 2) (1708 cm.$^{-1}$) is in a six membered or larger ring, or in a chain. Carbonyl 1 is readily reduced catalytically or by sodium borohydride, although in the des(oxymethylene) series it appears to be more hindered than in the lycoctonam series. Carbonyl 2 is resistant to both sodium borohydride and to catalytic reduction in acid.

The diketones rapidly reduce Tollens' reagent at room temperature and Fehling's solution at 100°, and since the ketols (in which carbonyl 1 is reduced)

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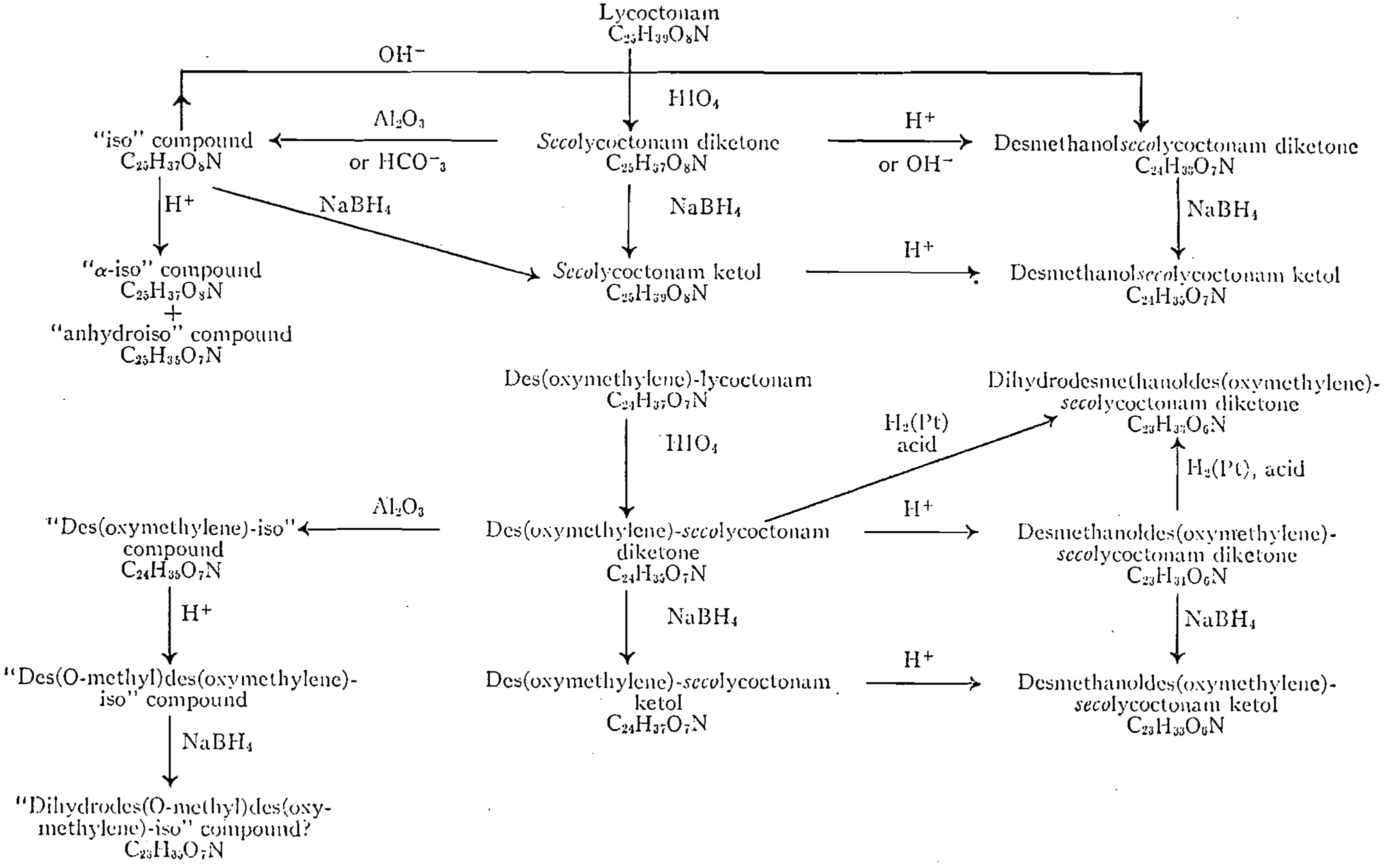
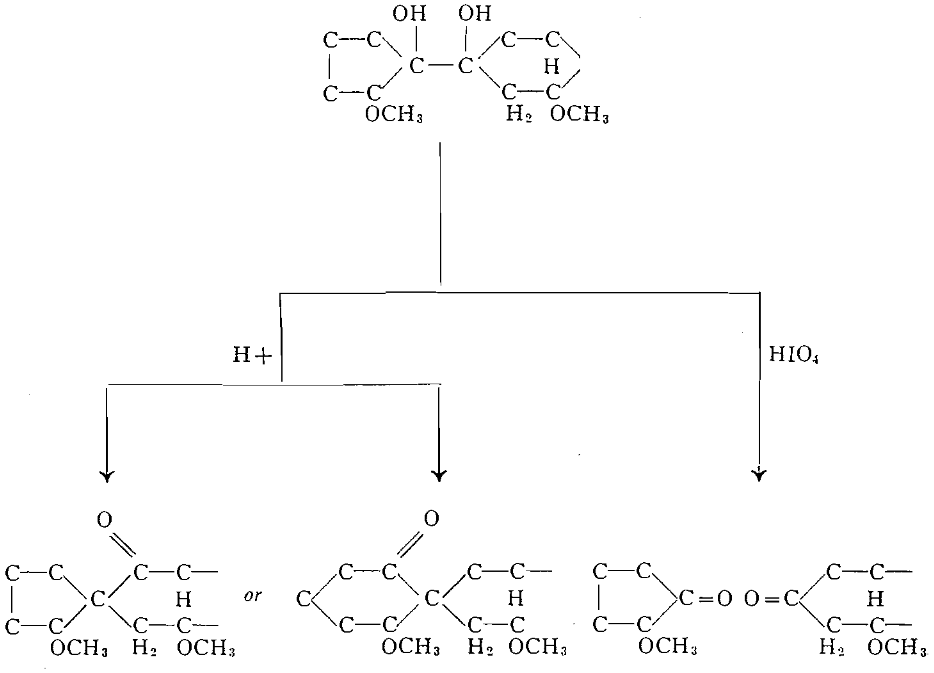
FLOWSHEET


Lycoctonam
$C_{25}H_{39}O_8N$
OH⁻
HIO₄
"iso" compound
$C_{25}H_{37}O_8N$
Al₂O₃
or HCO⁻₃
*Seco*lycoctonam diketone
$C_{25}H_{37}O_8N$
H⁺
or OH⁻
Desmethanol*seco*lycoctonam diketone
$C_{24}H_{33}O_7N$
H⁺
NaBH₄
NaBH₄
NaBH₄
"α-iso" compound
$C_{25}H_{37}O_8N$
+
"anhydroiso" compound
$C_{25}H_{35}O_7N$
*Seco*lycoctonam ketol
$C_{25}H_{39}O_8N$
H⁺
Desmethanol*seco*lycoctonam ketol
$C_{24}H_{35}O_7N$
Des(oxymethylene)-lycoctonam
$C_{24}H_{37}O_7N$
HIO₄
H₂(Pt)
acid
Dihydrodesmethanoldes(oxymethylene)-
*seco*lycoctonam diketone
$C_{23}H_{33}O_6N$
H₂(Pt), acid
Al₂O₃
"Des(oxymethylene)-iso"
compound
$C_{24}H_{35}O_7N$
Des(oxymethylene)-*seco*lycoctonam
diketone
$C_{24}H_{35}O_7N$
H⁺
Desmethanoldes(oxymethylene)-
*seco*lycoctonam diketone
$C_{23}H_{31}O_6N$
H⁺
NaBH₄
NaBH₄
"Des(O-methyl)des(oxymethylene)-
iso" compound
Des(oxymethylene)-*seco*lycoctonam
ketol
$C_{24}H_{37}O_7N$
H⁺
Desmethanoldes(oxymethylene)-
*seco*lycoctonam ketol
$C_{23}H_{33}O_6N$
NaBH₄
"Dihydrodes(O-methyl)des(oxy-
methylene)-iso" compound?
$C_{23}H_{35}O_7N$

are inert to these reagents it must be carbonyl 1 which is involved in the positive tests. Since α-methoxy ketones show this ease of oxidation (14) it is reasonable to postulate the presence of a methoxyl α to carbonyl 1. Since α-methoxy ketones are also readily hydrolyzed by mineral acids (5,25) attempts were made to hydrolyze a methoxyl in various derivatives containing carbonyl 1. In all of these derivatives except one, however, no hydrolysis took place with hot 6 *N* acid. Thus the α-methoxyl (if present) is generally inert. In the case of the "des(oxymethylene)-iso" compound (see flowsheet) hot 6 *N* sulphuric acid did hydrolyze one methoxyl. The resulting product did not react with diazomethane (27) but it did react with periodic acid to give products which have not been characterized. Thus the presence of an α-methoxyl, although indicated, will require further proof.

Both diketones are sensitive to acid and alkali, losing the elements of methyl alcohol to give α-β unsaturated ketones. The fact that the elimination takes place with the ketols, and that it is the infrared absorption peak due to carbonyl 2 that shifts when the conjugated system is formed (Table I), indicates that it is this carbonyl that is involved in the reaction. Since β methoxy and β hydroxy ketones show a parallel ease of elimination, catalyzed by acid or base (8,32), it can be concluded that there is a methoxyl β to carbonyl 2. The ultraviolet spectra (λ_{max} 223 mμ) indicate a low degree of substitution of the double bond (13,34). Thus a tentative formulation of the glycol group and its transformation products (11) is:



Anhydro Compound

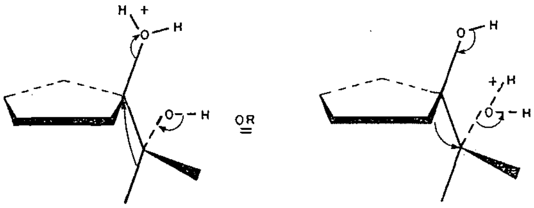
Carbonyl 1 Carbonyl 2
Diketones

TABLE I
INFRARED SPECTRA IN CHLOROFORM

Compound	Frequency in cm.$^{-1}$		
	Carbonyl 1	Carbonyl 2	Lactam
*Seco*lycoctonam diketone	1766	1707	1631
*Seco*lycoctonam diketone monoacetate	1764	1708	1649
Des(oxymethylene)-*seco*lycoctonam diketone	1765	1707	1644
Desmethanol*seco*lycoctonam diketone	1766	1679	1628
Desmethanoldes(oxymethylene)-*seco*lycoctonam diketone	1765	1679	1642
Dihydrodesmethanoldes(oxymethylene)-*seco*-lycoctonam diketone	1761	1705	1646
"Iso" compound	1743		1632
"Iso" compound monoacetate	1740		1650
"Des(oxymethylene)-iso" compound	1742		1645 (Broad)
"Anhydroiso" compound	1736		1652
"Des(O-methyl)des(oxymethylene)-iso" compound	1755	1712 (Weak)	1644

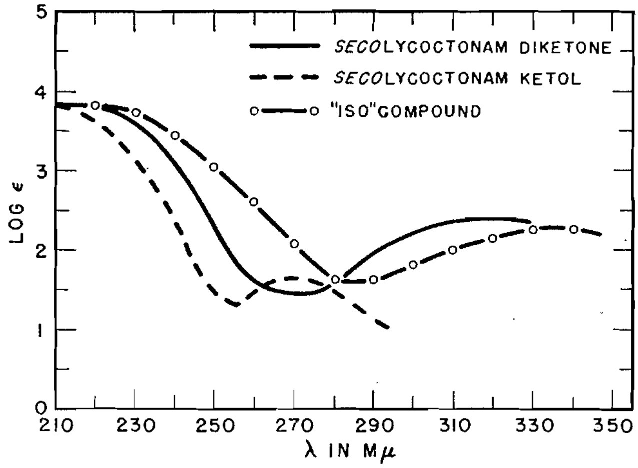
The choice of the migrating group in the pinacolic rearrangement is determined by the fact that the anhydro compounds (11) do not behave like α-methoxy ketones, or like β-methoxy ketones with hydrogen on the α-carbon.

Since the glycol system is ditertiary and hindered, the rate of periodate cleavage does not permit a decision in regard to the orientation of the two hydroxyls relative to each other (33). However, the ready pinacolic dehydration in what is probably a rigid molecule must mean that the hydroxyls have a "gauche" orientation as shown in order that the coplanarity of centers necessary for easy elimination and migration (3,4) exist.



The formation of the "iso" compounds is of great significance. The reaction involves the base-catalyzed conversion of carbonyl 2 to a hydroxyl group (the "iso" compound and "des(oxymethylene)-iso" compound contain a new hydroxyl which is difficult to acetylate). The spectra of these two compounds are characterized by the appearance of a maximum at 219 mμ in the ultraviolet and a shift of the infrared peak due to carbonyl 1 to near 1740 cm.$^{-1}$ (Table I). The reaction is reversible, as shown by the formation of the ketols on catalytic reduction or reduction by sodium borohydride and by the formation of the desmethanol diketone on treatment with strong alkali. However, the reaction is not brought about or reversed in refluxing acetone or methanol or in hot 6 *N* acid.

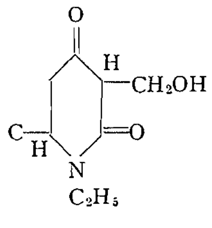
Hot 6 *N* acid converts the "iso" compound to a mixture consisting mainly of two products. One, the "α-iso" compound is isomeric with the "iso" com-



pound. It is no longer a ketone, and is not readily acetylated (i.e., the primary hydroxyl is no longer free to react) although it has two active hydrogens. The other product, "anhydroiso" compound corresponds to "iso" compound less a molecule of water. It has no hydroxyls, but still contains carbonyl 1. Both products have uneventful ultraviolet spectra compared to the "iso" compound.

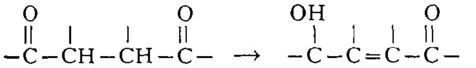
The formation of the "iso" compounds can be interpreted as involving either (*a*) the conversion of carbonyl 2 to a stable enol, (*b*) a reversible shift from a ketone to an unsaturated alcohol form, or (*c*) a readily reversible internal aldol condensation. A consideration of these possibilities follows:

(*a*) The iso compound does not react with diazomethane. However, it is reported (29) that stable enols are quite inert to the reagent. Although the shift of the band due to carbonyl 1 from 1765 cm.$^{-1}$ to 1740 cm.$^{-1}$ on conversion from the diketone to the iso compound could be due to strong hydrogen bonding as occurs in chelated enols (15,19,23) this is unlikely since the new hydroxyl is not involved in such bonding (the OH stretching peak is at 3530 cm.$^{-1}$ in chloroform which indicates only weak bonding). A stable enol could arise from a β-diketone or β-keto lactam system. The first possibility is unlikely since such systems have ultraviolet maxima near 255 mμ (6). If the "iso" compound was the enol of a β-keto lactam such as is illustrated, it would be expected to have an ultraviolet absorption maximum near 240 mμ (24) in contrast to the actual maximum at 219 mμ. Such a structure should also dehydrate to an α-β unsaturated ketone or eliminate formaldehyde on treat-



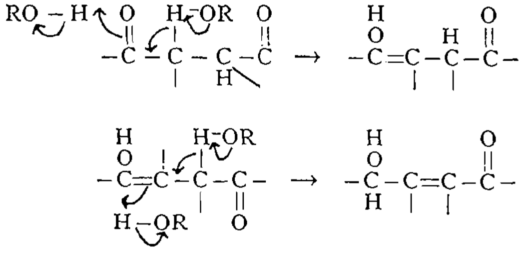
ment with hot mineral acid, neither of which takes place. Thus it seems unlikely that the iso compounds are enols of β-dicarbonyl systems.

(*b*) The ultraviolet maxima at 219 mμ suggests the presence of unsaturation. In addition the "des(oxymethylene)-iso" compound has a band at 3010 cm.$^{-1}$ (mull) which can be attributed to hydrogen attached to doubly bound carbon. A double bond could arise from the following kind of transformation, involving either the two ketone carbonyls or the lactam carbonyl and carbonyl 2



$$-\overset{O}{\overset{\|}{C}}-\overset{|}{C}H-\overset{|}{C}H-\overset{O}{\overset{\|}{C}}- \longrightarrow -\overset{OH}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-\overset{O}{\overset{\|}{C}}-$$

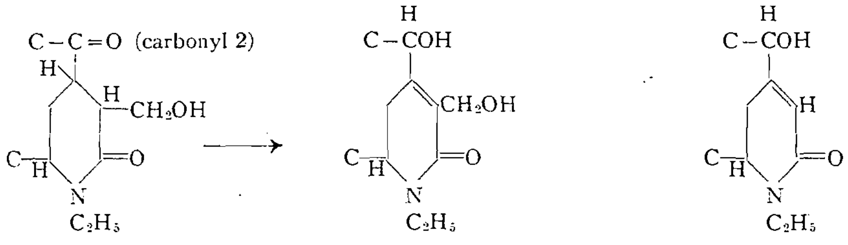
The reverse of this reaction is well known (12,17,28) but the only analogy for the forward reaction known to the authors is the conversion of levulinic acid to β-angelica lactone. It is conceivable, however, (assuming the ketone carbonyls to be close in space), that steric hindrance of carbonyl 2 and some hydrogen bonding stabilization of the hydroxyl form might promote the conversion. A possible mechanism for the base catalyzed reaction is shown:



The reversal of the reaction on reduction of carbonyl 1 could be due to lessening of the hindrance due to the rigid carbonyl (carbonyl 1), the greater intrinsic stability of the diketone system, and the stabilizing influence of hydrogen bonding between carbonyl 2 and the hydroxyl derived from carbonyl 1.

It seems unlikely that the two ketone carbonyls are involved in such a change. The ultraviolet maximum is very weak (log ϵ 3.8) and at very short wave length for an α-β unsaturated ketone. In addition, this postulate would require that the two tertiary hydroxyls in lycoctonine be on a cyclobutane ring. This is unlikely since then the anhydro compounds should be cyclobutanones (I.R. evidence indicates a carbonyl on a five or six membered ring) or cyclopropyl ketones (a very unlikely type of product).

The alternative is that carbonyl 2 is γ to the lactam carbonyl as shown.

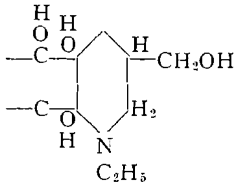


"iso" compound

"Des(oxymethylene)-iso" compound

The absence of the 3010 cm.$^{-1}$ band in the "iso" compound is in agreement with this formulation.

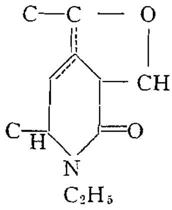
Carbonyl 2 cannot be in the nitrogen ring, since hydroxylycoctonine (11) would then contain the partial structure



This should react with two moles of periodic acid. Actually hydroxylycoctonine consumes only one mole of the reagent in 68 hr.

The maximum at 219 mμ seems reasonable for an α-β unsaturated lactam, since α-β unsaturated lactones (16) and α-β unsaturated acids (31) have maxima in this region. However, seven membered α-β unsaturated lactams with an NH have maxima in the 240 mμ region (18,26). No spectra of simpleN-alkyl α-β unsaturated lactams have been reported. Thus the above possibility cannot be ruled out on spectral grounds.

The "anhydroiso" compound can be explained on this basis as the product of dehydration to the five-membered ether with the double bond moving out of conjugation (weak ultraviolet absorption). The "α-iso" compound could arise from hemiacetal formation between carbonyl 1 and the primary hydroxyl,



again with the double bond moving out of conjugation. Attempts to demonstrate the presence of an allyl alcohol system in the "iso" compounds by manganese dioxide oxidation (1,30) has been fruitless. The "des(oxymethylene)-iso" compound was inert and the "iso" compound gave a mixture of products, none of which had their main absorption maximum above 220 mμ.

(*c*) An aldol condensation of carbonyl 2 with one of the positions α to carbonyl 1, with the resulting aldol being unable to dehydrate, is a possible explanation of the formation of the iso compounds. However, with such an explanation the spectra cannot be accounted for on classical grounds. (See the discussion of spectra.)

Hypothesis (*b*) is attractive as regards establishing a relation between the glycol system and the nitrogen ring. However, no clear decision can be reached between it and hypothesis (*c*) with the evidence in hand.

When the "iso" compound was hydrogenated over Adams' catalyst in ethanol, desmethanol*seco*lycoctonam ketol was obtained. This means that either before or after reduction of carbonyl 1 the "iso" reaction was reversed and under unusually mild conditions the methoxyl β to carbonyl 2 was eliminated to give the α-β unsaturated ketone. Less surprising is the elimination of the same methoxyl in the reduction of des(oxymethylene)-*seco*lycoctonam diketone in ethanol containing hydrochloric acid. Here, however, the resulting double bond is rapidly reduced giving the dihydrodesmethanol diketone.

Spectra

The position of the C=O stretching frequency of carbonyl 1 in the diketones (Table I) is very unusual for a cyclopentanone. Interaction across space between carbonyls has been shown to shift their maxima as much as 10 wave numbers toward higher frequencies (23), and this effect probably accounts for the anomalies in the diketone spectra. The shift of the peak for carbonyl 1 on formation of the "iso" compounds (Table I) could be due to conjugation or strong hydrogen bonding, or to the disappearance of the above-mentioned interaction. The first two are unlikely, as discussed earlier, hence the last explanation is favored. However, if the "iso" compounds are α-β unsaturated lactams, a shift of the C=O stretching bond for the lactam to smaller frequencies is to be expected. The examination of the spectra of suitbale models may clarify the absence of such a shift in this case.

The presence of the primary hydroxyl produces a decided lowering of the lactam carbonyl frequency (Table I and Table I, reference 1) even in dilute chloroform solution, thus indicating intramolecular hydrogen bonding between the two functions.

Bands in a region generally associated with CH_2CO groups (21,22) appear in the spectra (1410–1430 cm.$^{-1}$) of most of the compounds. However, some of these may be due to hydroxyl groups, since the band at 1418 cm.$^{-1}$ in the "iso" compound disappears when the monoacetate is made. From an examination of the compounds without hydroxyls, it appears that there is no methylene flanking carbonyl 1, but that one or two are next to carbonyl 2. The integrated absorption intensities (10,000 units) of the bands ($CHCl_3$ solution) are much larger than those cited in the literature (2), hence no conclusion can be drawn from this information as to the number of such methylenes.

The ultraviolet spectra of the diketones are most unusual, the high intensity end absorption and the position of the carbonyl maxima being similar to those of conjugated ketones. However, carbonyl 2 when alone (ketols) has a very normal spectrum, and several compounds containing no keto group but carbonyl 1 ("anhydroiso" compound and "des(O-methyl)des(oxymethylene)-iso" compound) have quite normal spectra for compounds with isolated carbonyls. In the spectra of the "iso" compounds the carbonyl maxima are at extremely long wave lengths (337 mμ), a fact which cannot readily be reconciled with the partial structures considered above. There is some possibility that there is no conjugation in the "iso" compounds and that their ultraviolet spectra are exaggerations of the abnormal diketone spectra. An interaction across space between the two ketone carbonyls or between carbonyl 1 and the lactam carbonyl might be the cause of the abnormal absorption.[2] There is some evidence for similar interaction effects in the literature (7,10). However, 21-acetoxy-pregnene-3-ol-20-one and etiocholan-3-α-ol-11,17-dione which show interaction effects in the infrared (23) have normal ultraviolet spectra, and cyclodecane-1,6-dione has both normal ultraviolet and infrared spectra[3]. Such an effect, if it exists, would be expected to be very dependent on the angle and extent of overlap of the carbonyls, and the diketones from lycoctonine might be quite unique in that regard. If such an effect is present, then the aldol condensation explanation (*c*) of the "iso" compounds is plausible.

Another abnormality in the ultraviolet spectra is the absence of the short wave length maxima in the desmethanol ketols, although they are definitely α-β unsaturated ketones.

Further work to confirm or disprove the postulates put forward in this paper is underway.

EXPERIMENTAL

All melting points are corrected to within ±1°. The rotations were taken in absolute ethanol at 25 ± 2° C. The alumina used in chromatography was acid washed, and the cited activity is according to Brockmann (9). Ultraviolet spectra were determined on a Beckmann DU spectrophotometer. The log ϵ value for the maximum or minimum is placed in parentheses after the wave length.

The infrared spectra were determined on a Perkin-Elmer single beam model 12B spectrophotometer or on a Perkin-Elmer double beam instrument, model 21. The peaks are indicated by a wave number and the percentage absorption (in parentheses). Shoulders are indicated by an S after the wave number. The compounds were dispersed as mulls in nujol unless otherwise stated.

Secolycoctonam Diketone

Lycoctonam hydrate (11) in solution in four to five molar equivalents of 0.05 molar periodic acid, adjusted to pH 5 using sodium acetate in the dark at room temperature, consumed 0.5 mole of reagent in 24 hr. and one mole in 70 hr. After 115 hr. the molar consumption was 1.2. The product could be extracted nearly quantitatively with methylene dichloride, from which it was obtained as a froth which has not crystallized. A sample of the product (0.94 gm.) was chromatographed on 15 gm. of alumina of activity 3. Six 35 cc. eluate fractions of 50% benzene–chloroform, and five of chloroform contained 679 mgm. This yielded 581 mgm. of crystalline *seco*lycoctonam diketone monoacetate (see below). Methanol in chloroform eluted 272 mgm., of which 175 mgm. (m.p. 217°) crystallized from acetone solution (see "iso" compound).

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[2] *This possibility was originally put forward in discussion by Dr. R. A. McIvor.*

[3] *The authors wish to thank Dr. R. N. Jones for providing samples of the two steroids, and Dr. A. G. Anderson Jr. for a generous gift of cyclodecane-1,6-dione.*

The amorphous *seco*lycoctonam diketone rapidly gave a silver mirror with Tollen's reagent and reduced hot Fehling's solution.

Ultraviolet spectrum: λ_{min} 272 mμ (2.14); λ_{max} 318 mμ (2.45); log ϵ 3.82 at 2.10 mμ; and 3.77 at 220 mμ.

Infrared spectrum (30 mgm. per ml. in $CHCl_3$; 0.1 mm. cell): 3465 (5), 3010 (28), 2950 (29), 2900 (20), 2835 (16), 1766 (37), 1713 (32), 1635 (50), 1467 (28), 1420 (19), 1385 (18), 1358 (16), 1328 (13), 1306 (14), 1055S (18), 1028S (36), 1100 (60), 1070S (25), 1045 (20), 1025 (19), 978 (17).

Secolycoctonam Diketone Monoacetate

A solution of 293 mgm. of *seco*lycoctonam diketone in 5 cc. of pyridine and 5 cc. of acetic anhydride was left at room temperature for 24 hr. The reagents were removed under reduced pressure, the product taken up in chloroform, and washed with acid and base. The product recovered from the chloroform crystallized from ether solution. The 269 mgm. of crystals after recrystallization from acetone–ether melted at 178–181°. Chromatography on alumina did not raise the melting point. The compound did not react with potassium permanganate in acetone containing a little acetic acid in three hours at room temperature. $[\alpha]_D$ 62 ± 1° (c = 2.56). Found: C, 61.98; H, 7.71; N, 2.45. Calc. for $C_{27}H_{39}O_9N$: C, 62.17; H, 7.54; N, 2.69.

Ultraviolet spectrum (Fig. 1): λ_{min} 270 mμ (1.44); λ_{max} 320 (2.41).

Infrared spectrum (29 mgm. per ml. in $CHCl_3$, 0.1 mm. cell): 3010 (26), 2960 (26), 2910 (18), 2835 (16), 1763 (40), 1746 (46), 1712 (37), 1650 (51), 1468 (27), 1430 (16), 1386 (23), 1370 (21), 1325 (10), 1303 (11), 1375S (14), 1130S (29), 1100 (60), 1042 (30), 975 (14).

Saponification of Secolycoctonam Diketone Monoacetate

(*a*) To a solution of 200 mgm. of the monoacetate in 2 cc. of methanol was added 200 mgm. of sodium bicarbonate and 2 cc. of water. The mixture was heated to boiling on the steam bath to effect complete solution. After the solution had stood at room temperature for 20 min. a further 1 cc. of water was added, the solution heated for a few minutes, then left at room temperature for 100 min. The faintly yellow solution was extracted with chloroform, giving 195 mgm. of froth. This was dissolved in a minimum volume of acetone, then ether added. Twenty-eight milligrams of "iso" compound, m.p. 214° (see below) deposited. No desmethanol*seco*lycoctonam diketone was obtained, and the residual material when freed from solvent had absorption in the ultraviolet nearly identical to that of the original acetate.

(*b*) A solution of 34 mgm. of the monoacetate in 1 cc. of methanol and 1 cc. of 5% sodium hydroxide solution was left at room temperature for 10 min., diluted with 3 cc. of water, and left for a further 35 min. Extraction with chloroform gave 39 mgm. of froth which crystallized from ether giving 20 mgm., m.p. 204°. When 59 mgm. of similar material was recrystallized three times from acetone–ether, 29 mgm. were obtained, m.p. 203–205.5° (imm. at 185°), identical with desmethanol*seco*lycoctonam diketone (see below).

Desmethanolsecolycoctonam Diketone

(*a*) Potassium hydroxide (0.164 gm.) was added to 26 mgm. of *seco*lycoctonam diketone in 3 cc. of water, and the solution left at room temperature for one hour. It was then neutralized and extracted with chloroform. The 25 mgm. of product crystallized readily from ether giving 20 mgm., m.p. 196°. One recrystallization raised the melting point to 201°. This material gave no mixed melting point depression with the product from hydrolysis of the monoacetate with sodium hydroxide in aqueous methanol.

(*b*) A solution of 116 mgm. of *seco*lycoctonam diketone in 6 cc. of 6 *N* sulphuric acid was heated on the steam bath for 40 min. The solution was cooled, neutralized, and extracted with methylene dichloride. The 105 mgm. of product crystallized from acetone–ether, giving 92 mgm., m.p. 203°. The melting point was raised to 203–205.5° by recrystallization from a very concentrated acetone solution. $[\alpha]_D$ 88 ± 1° (c = 2.40). Found: C, 64.30, 64.71, 64.57; H, 7.72, 7.93, 7.65; OCH_3, 20.55, 20.23. Calc. for $C_{24}H_{33}O_7N$: C, 64.41; H, 7.43; 3 OCH_3, 20.80.
Ultraviolet spectrum: λ_{max} 221 mμ (4.04); λ_{min} 275 (1.82); λ_{max} 322 (2.49).
Infrared spectrum: 3394 (46), 1753 (56), 1670S (64), 1655 (75), 1412 (53), 1327 (39), 1304 (32), 1296 (31), 1279 (24), 1267 (24), 1245 (33), 1234 (35), 1220 (48), 1203 (50), 1178 (28), 1163 (33), 1155 (38), 1132 (46), 1116 (67), 1094 (66), 1082S (61), 1056 (42), 1033 (30), 1020 (33), 1009 (37), 981 (31), 968 (43), 956S (31), 903 (26), 870 (20), 853 (23), 822 (17), 793 (12), 756 (29), 728 (31), 686 (27).

When 51 mgm. of the compound was refluxed for 1.5 hr. with 2 cc. of 6 *N* sulphuric acid, the 51 mgm. extracted by chloroform gave 39 mgm. of unchanged material. The remainder did not crystallize.

Secolycoctonam Ketol

Sodium borohydride (25 mgm.) was added to a solution of 56 mgm. of *seco*lycoctonam diketone in 2 cc. of water. After 0.5 hr. the solution was acidified and extracted with chloroform. The 52 mgm. of froth crystallized from acetone–ether, giving 41 mgm., m.p. 206–214°. After two recrystallizations this melted at 210–215° (dec.) then resolidified and melted over a range up to 280°. $[\alpha]_D$ −50 ± 1° (c = 2.20). Found: C, 62.29, 61.79, 62.19; H, 8.53, 8.30, 8.04; OCH_3, 25.91. Calc. for $C_{25}H_{39}O_8N$: C, 62.36; H, 8.16; 4 OCH_3, 25.78.
Ultraviolet spectrum (Fig. 1): λ_{min} 255 mμ (1.31); λ_{max} 270 mμ (1.60).
Infrared spectrum: 3485 (57), 3390 (68), 1710 (73), 1616 (92), 1510 (19), 1494 (24), 1413 (29), 1357 (27), 1344 (26), 1333 (29), 1324 (27), 1296 (31), 1276 (52), 1252 (31), 1236 (59), 1209 (69), 1184 (42), 1166 (48), 1140 (42), 1117S (71), 1105S (86), 1098 (87), 1081 (73), 1065 (59), 1053 (55), 1045S (47), 1025 (32), 997 (38), 974 (29), 957 (37), 894 (18), 867 (15), 805 (22), 782 (19), 754 (18), 705 (17).

Desmethanolsecolycoctonam Ketol

(*a*) Eleven milligrams of *seco*lycoctonam ketol in an evacuated tube was heated to around 240° until decomposition stopped and the product solidified. The product was extracted and recrystallized from acetone, giving 5 mgm., m.p. 291° and 2 mgm. m.p. 289°. Neither crop depressed the melting point of the products from (*b*) and (*c*).

(*b*) To a solution of 63 mgm. of desmethanol*seco*lycoctonam diketone in a mixture of 1 cc. of methanol and 3 cc. of water was added 30 mgm. of sodium borohydride. After 0.5 hr. the solution was acidified and extracted with chloroform. The 60 mgm. of crystals obtained on evaporation of the chloroform melted at 279°. After two recrystallizations from methanol 29 mgm. m.p. 291° was obtained.

(*c*) A solution of 52 mgm. of *seco*lycoctonam ketol in 2 cc. of 6 *N* sulphuric acid was heated on the steam bath for 0.5 hr. Chloroform extracted 50 mgm. of product. When recrystallized twice from methanol–acetone this melted at 294–299°. $[\alpha]_D$ −76 ± 10° (c = 0.85) (sparingly soluble in ethanol). Found: C, 64.06; H, 7.65; OCH_3, 20.59. Calc. for $C_{24}H_{35}O_7N$: C, 64.12; H, 7.85; 3 OCH_3, 20.7.
Ultraviolet spectrum: λ_{min} 285 mμ (1.97); λ_{max} 305 mμ (2.03).
Infrared spectrum: 3345 (53), 3215 (53), 1683 (29), 1662 (76), 1640 (88), 1430 (38), 1400 (19), 1356 (28), 1336 (25), 1320 (19), 1287 (18), 1270 (14), 1242S (28), 1221 (57), 1205 (44), 1196 (45), 1170 (33), 1140 (44), 1115 (74), 1096 (80), 1062 (54), 1046 (38), 1025S (15), 1010S (17), 995 (29), 975 (22), 959 (22), 905 (12), 864 (16), 845 (11), 831 (26), 800 (6), 767 (13), 753 (11), 710 (12), 695 (16).

"*Iso*" *Compound*

*Seco*lycoctonam diketone (152 mgm.) was adsorbed from benzene on 5 gm. of alumina, activity 3–4, and left on the column for 15½ hr. Thirty cubic centimeters of benzene, 100 cc. of 50% C_6H_6–$CHCl_3$, and 50 cc. of chloroform eluted 71 mgm., from which some desmethanol*seco*lycoctonam diketone was obtained. Chloroform containing 0.25% of methanol eluted 77 mgm. which crystallized from acetone giving 53 mgm. m.p. 216°. After two recrystallizations from acetone the compound melted at 218° after softening at 213° (immersed at 195°). This proved identical with the product from the original chromatogram of the periodate cleavage products. $[\alpha]_D$ 58 ± 2° (c = 0.72). Found: C, 62.25; H, 7.82; N, 3.07; OCH_3, 24.4, 26.89. Calc. for $C_{25}H_{37}O_8N$: C, 62.61; H, 7.78; N, 2.92; 4 OCH_3, 25.88.
Ultraviolet spectrum (Fig. 1): λ_{max} 218 mμ (3.82), λ_{min} 285 mμ (1.62), λ_{max} 335 mμ (2.26).
Infrared spectrum: 3430 (54), 3325 (43), 1734 (74), 1632 (92), 1418 (70), 1398 (44), 1345 (49), 1325 (39), 1295 (54), 1269 (59), 1226 (62), 1217 (58), 1197 (53), 1161 (56), 1148S (67), 1138 (79), 1133 (79), 1107 (87), 1099 (86), 1091 (82), 1077 (60), 1063 (70), 1055 (71), 1030 (68), 1016 (49), 1002 (57), 981 (61), 944 (40), 934S (29), 923S (24), 902 (16), 875 (12), 831 (13), 803 (13), 760 (21), 725 (21), 700 (14), 685 (20), 663 (13), 648 (21).

When 25 mgm. of "iso" compound was treated for one hour with diazomethane in methanol–ether, 21 mgm. of unchanged compound was recovered.

A solution of 20 mgm. of "iso" compound and 90 mgm. of potassium hydroxide in 1.5 cc. of methanol was diluted with 1.5 cc. of water and left at room temperature for one hour. The solution was concentrated to half volume under reduced pressure and extracted with chloroform. The 12 mgm. of neutral product crystallized from acetone–ether when seeded with desmethanol*seco*lycoctonam diketone. The 8 mgm. of crystals after one recrystallization melted at 205° (hot stage) and showed no depression with desmethanol*seco*lycoctonam diketone. A comparison of infrared spectra confirmed the identity.

A solution of 76 mgm. of "iso" compound and 40 mgm. of sodium borohydride in 4 cc. of 50% aqueous methanol was left at room temperature. After acidification the solution was extracted with chloroform. The 76 mgm. of product crystallized from concentrated acetone solution giving 8 mgm., m.p. 275°, and 52 mgm., m.p. 204–211°. The former proved to be desmethanol*seco*lycoctonam ketol, while the latter, after one recrystallization, was shown by mixed melting point and comparison of infrared spectra to be *seco*lycoctonam ketol.

The "iso" compound was inert to hydrogen over Adams' catalyst in ethanol containing hydrochloric acid (3 cc. alcohol, two drops concentrated acid).

"Iso" compound (19.7 mgm.) in 3 cc. of ethanol in the presence of platinum from 10 mgm. Adams' catalyst absorbed 1.03 cc. (N.T.P.) of hydrogen (1.1 moles) in 40 min., after which the reaction was stopped. (Another experiment showed that the hydrogenation proceeded at a reduced rate until over two moles were absorbed.) The product crystallized completely. One recrystallization from methanol–acetone gave 10 mgm. m.p. 283–288° (hot stage). Mixed m.p. with a sample of desmethanol*seco*lycoctonam ketol was 283–293° (hot stage).

A mixture of 82 mgm. of "iso" compound and 1.2 gm. of active (1) manganese dioxide in 6 cc. of dry benzene was shaken for two hours. The manganese dioxide was removed by filtration and washed with benzene. The benzene solution contained 56 mgm. of product. A solution of this material in ether containing a little acetone deposited a few milligrams of crystals, after addition of petroleum ether. After recrystallization from acetone–ether this melted at 152° and had λ_{max} 219 mμ (3.7), λ_{min} 285 mμ (1.7), and λ_{max} 340 mμ (2.2) (assumed mol. wt. 480). Methanol extraction of the manganese dioxide gave 27 mgm. of ether-insoluble product. This was combined with the noncrystalline material and chromatographed on 2.5 gm. of alumina (activity 3–4). Fifty per cent chloroform–benzene eluted 18 mgm. which did not crystallize. The main fraction had no short-wave-length maximum, log ϵ 3.76 (215 mμ), λ_{min} 312 mμ (2.1), λ_{max} 330 mμ (2.15) (assumed mol. wt. 480). Chloroform eluted 7 mgm. of amorphous material. Methanol (0.5%) in chloroform eluted 25 mgm. which deposited 6 mgm. of crystals from acetone–ether. After recrystallization these melted at 182° and had λ_{max} 219 mμ (3.66), λ_{min} 285 mμ (1.61), and λ_{max} 335 mμ (2.10) (assumed mol. wt. 480).

"Iso" Compound Monoacetate

Thirty milligrams of "iso" compound was warmed gently with a mixture of 1 cc. of pyridine and 1 cc. of acetic anhydride until it dissolved. The solution was left at room temperature for 22 hr., the reagents distilled under reduced pressure, and a chloroform solution of the residue washed with dilute acid and base. The product crystallized from ether–petroleum ether, giving 24 mgm. m.p. 176°. One recrystallization raised the m.p. to 177° (immersed at 150°) (21 mgm.). Found: C, 62.87, 62.75; H, 7.24, 7.63; OCH_3, 24.66. Calc. for $C_{27}H_{39}O_9N$: C, 62.17; H, 7.54; 4 OCH_3, 23.79.

Ultraviolet spectrum: λ_{max} 218 mμ (3.82); λ_{min} 285 mμ (1.62); λ_{max} 337 mμ (2.25).

Infrared spectrum: 3500 (30), 1738 (82), 1651 (80), 1335 (43), 1325 (38), 1300 (45), 1291 (49), 1275 (47), 1266 (47), 1248 (75), 1232 (80), 1211 (61), 1195 (41), 1180 (35), 1167 (49), 1145 (52), 1125 (78), 1115 (75), 1094 (79), 1072 (52), 1045 (70), 1026 (50), 990 (50).

"Anhydroiso" and "α-iso" Compounds

A suspension of 77 mgm. of "iso" compound in 3 cc. of 6 *N* sulphuric acid was heated for 45 min. on the steam bath. Solution was complete in 20 min. The 77 mgm. of neutral product extracted by chloroform was adsorbed from benzene on 2.5 gm. of alumina, activity 2.

Eluant (30 cc. portions)	Weight eluted, mgm.
1. Benzene	2
2. 50% Benzene–chloroform	35
3. 50% Benzene–chloroform	9
4. 50% Benzene–chloroform	2
5. ½% Methanol in chloroform	30
6. ½% Methanol in chloroform	4

Fraction 2 crystallized readily from ether, giving 13 mgm., m.p. 204°. This could be readily sublimed at 175°, 5×10^{-4} mm. pressure, without changing the melting point. $[\alpha]_D$ 81 ± 2° ($c = 0.56$). Found: C, 64.89; H, 7.70; OCH_3, 26.78, 26.66. Calc. for $C_{25}H_{37}O_7N$: C, 65.06; H, 7.64; 4 OCH_3, 26.78.

Ultraviolet spectrum: λ_{min} 270 (0.89); λ_{max} 300 (1.9).

Infrared spectrum: 1732 (79), 1646 (88), 1550 (14), 1485 (58), 1450 (62), 1437S (43), 1382 (51), 1365 (52), 1345 (36), 1326 (35), 1306 (30), 1288 (32), 1273 (45), 1257 (53), 1216 (59), 1205S (43), 1185 (45), 1168 (51), 1135 (77), 1100 (90), 1086 (86), 1070 (50), 1048 (47), 1025 (36), 1004 (72), 991 (45), 975 (35), 950 (32), 940 (29), 920 (21), 910 (20), 895 (34), 885 (51), 850 (48), 810 (15), 775 (32), 725 (9), 649 (4).

Fraction 5 crystallized from ether after prolonged scratching, giving 21 mgm., m.p. 167–176°. After two recrystallizations from acetone-ether this melted at 171–175°. $[\alpha]_D$ 66 ± 1° ($c = 2.18$). Found: C, 63.04; H, 7.64; N, 3.19; OCH_3, 25.59; active hydrogen, 0.41, 0.39. Calc. for $C_{25}H_{37}O_8N$: C, 62.61; H, 7.78; N, 2.92; 4 OCH_3, 25.88; 2 active hydrogens 0.42.

Ultraviolet spectrum: log ϵ 3.22 (225 mμ) and 1.11 (250 mμ) – no features.

Infrared spectrum: 3505 (52), 3450 (32), 1643 (89), 1560 (13), 1486 (61), 1400 (44), 1362 (40), 1327 (42), 1311 (60), 1295 (40), 1267S (38), 1260 (49), 1225 (67), 1205 (50), 1200S (47), 1174 (36), 1158 (40), 1141S (54), 1129 (72), 1110 (80), 1082 (78), 1050 (62), 1030 (59), 1016 (54), 993 (45), 975 (48), 951 (49), 925 (26), 912S (20), 895 (23), 855 (25), 835 (26), 805 (10), 782S (13), 775 (30), 750 (11), 735 (12), 718 (9), 700 (6), 665 (15), 646 (12).

When 20 mgm. of "α-iso" compound was treated at room temperature for five hours with acetic anhydride and pyridine, 19 mgm. of crystalline material m.p. 175° was recovered. This proved identical with starting material (mixed m.p. and infrared spectrum).

Des(oxymethylene)-secolycoctonam Diketone

A solution of 0.5 gm. of des(oxymethylene)-lycoctonam, 0.5 gm. of paraperiodic acid, and 0.8 gm. of hydrated sodium acetate was left for six days at room temperature in the dark (molar uptake of periodate 0.61 in 72 hr., 1.0 in six days). The solution was made nearly neutral with sodium bicarbonate and extracted with chloroform. The 488 mgm. extracted crystallized readily from ether, giving 320 mgm., m.p. 159° and 40 mgm., m.p. 156°. One recrystallization raised the melting point to 160°. An eight funnel countercurrent distribution between benzene and water gave material from funnels three to six melting at 160 to 162°. $[\alpha]_D$ 85 ± 1° (c = 2.39). This reduced Tollen's reagent at room temperature and Fehling's solution on the steam bath, but was unchanged by permanganate in acetone in 1.5 hr. An aqueous solution of the compound was unaffected by two hours contact with fresh silver oxide. Found: C, 64.29, 64.59, 63.80; H, 7.47, 7.56, 7.91; N, 3.40; OCH_3, 27.39. Calc. for $C_{24}H_{35}O_7N$: C, 64.12; H, 7.85; N, 3.12; 4 OCH_3, 27.61.

Ultraviolet spectrum: log ϵ 3.79 (215 mμ); λ_{min} 265 mμ (1.67); λ_{max} 322 mμ (2.42).

Infrared spectrum (30 mgm. per ml. of chloroform, 0.1 mm. cell): 3010 (42), 2960 (39), 2900 (27), 2840 (26), 1765 (48), 1711 (48), 1646 (68), 1468 (36), 1432 (28), 1385 (22), 1360 (20), 1327 (17), 1294 (18), 1110 (60), 1095 (68), 1028 (16), 1002 (19), 966 (15), 942 (10), 904 (8).

(5 mgm. per ml. in carbon disulphide, 1 mm. cell): 2940 (58), 2880 (45), 2820 (44), 1758 (71), 1713 (68), 1663 (93), 1378 (42), 1358 (39), 1347 (29), 1295 (32), 1268 (33), 1250 (34), 1235 (49), 1210 (61), 1100 (87), 1038 (27), 1004 (32), 967 (28).

Desmethanoldes(oxymethylene)-secolycoctonam Diketone

Ninety milligrams of des(oxymethylene)-*seco*lycoctonam diketone in 4 cc. of 6 *N* sulphuric acid was heated on the steam bath for 30 min. The cooled solution was neutralized and extracted with chloroform. The 86 mgm. of product crystallized from acetone–ether giving 71 mgm. m.p. 229° and 11 mgm. m.p. 225°. After three recrystallizations from acetone the compound melted at 228–230° (immersed at 205°) $[\alpha]_D$ 86 ± 1° (c = 1.88). Found: C, 66.15, 66.44; H, 8.03, 7.71; N, 3.62; OCH_3, 21.4. Calc. for $C_{23}H_{31}O_6N$: C, 66.16; H, 7.49; N, 3.36; 3 OCH_3, 22.30.

Ultraviolet spectrum: λ_{max} 223 mμ (4.04); λ_{min} 275 mμ (1.82); λ_{max} 321 mμ (2.50).

Infrared spectrum (29.8 mgm. per ml. of chloroform, 0.1 mm. cell): 3000 (32), 2940 (33), 2890S (20), 2825 (16), 1762 (44), 1678 (49), 1465 (33), 1433 (23), 1386 (21), 1359 (20), 1332 (14), 1296 (13), 1270 (18), 1155 (18), 1115 (58), 1095 (58), 1052 (18), 1000 (19), 961 (15), 861 (12), 845 (14).

The compound was recovered unchanged after two hours refluxing with 6 *N* sulphuric acid. It reduced Tollen's reagent rapidly at room temperature.

Des(oxymethylene)-secolycoctonam Ketol

A solution of 73 mgm. of des(oxymethylene)-*seco*lycoctonam diketone and 30 mgm. of sodium borohydride in 2 cc. of 50% aqueous methanol was left at room temperature for 30 min. The solution was acidified and the product extracted quantitatively with chloroform. This crystallized, on addition of ether to a very concentrated acetone solution, yielding 56 mgm., m.p. 180–183°. After two recrystallizations from the same solvents, the compound melted at 182–185°. $[\alpha]_D$ $-69 \pm 1°$. Found: C, 63.88; H, 8.07. Calc. for $C_{24}H_{37}O_7N$:C, 63.83; H, 8.26.

Ultraviolet spectrum: log ϵ 3.83 at 212 mμ; shoulder at 265–280 mμ, log ϵ 1.9. Infrared spectrum: 3365 (86), 1713 (86), 1626 (97), 1355 (74), 1293 (70), 1281 (70), 1253S (49), 1230 (86), 1211 (85), 1180S (62), 1140 (88), 1105 (94), 1089 (79), 1060 (70), 1006 (67), 966 (58), 929 (34), 916 (34), 905 (35), 886 (29), 851 (39), 805 (37), 773 (25), 720 (41), 684 (34), 642 (48).

Desmethanoldes(oxymethylene)-secolycoctonam Ketol

Twenty-eight milligrams of des(oxymethylene)-*seco*lycoctonam ketol in 2 cc. of 6 *N* sulphuric acid was heated for 0.5 hr. The solution was neutralized and extracted with chloroform. An acetone–ether solution of the product deposited 26 mgm. of crystals, m.p. 217°. After recrystallization the compound melted at 214–217° (immersed at 190°). $[\alpha]_D$ $-97 \pm 1°$. Found: C, 66.33, 66.03; H, 8.12, 8.02; N, 3.44; OCH_3, 22.85. Calc. for $C_{23}H_{33}O_6N$: C, 65.84; H, 7.93; N, 3.34; 3 OCH_3, 22.19.

Ultraviolet spectrum: log ϵ 4.04 (212 mμ); log ϵ 4.00 (220 mμ); log ϵ 3.96 (225 mμ); λ_{min} 280 mμ (1.89); λ_{max} 305 mμ (1.99).

Infrared spectrum: 3320 (63), 1670 (77), 1624 (89), 1335 (36), 1290 (27), 1250 (32), 1230 (53), 1210 (50), 1197 (48), 1140 (57), 1114 (77), 1092 (77), 1075 (45), 1055 (46), 1000 (46), 970 (26), 951 (28), 895 (15), 856 (21), 834 (23), 755 (21), 720 (12), 695 (11).

"Des(oxymethylene)-iso" Compound

Des(oxymethylene)-*seco*lycoctonam diketone (162 mgm.) was adsorbed from benzene onto 5 gm. of alumina (activity 2) and left on the column for 15 hr. Benzene eluted a mixture of desmethanoldes(oxymethylene) diketone and starting material; 25% chloroform in benzene gave starting material; then 50% chloroform–benzene, chloroform, and 0.5% methanol in chloroform eluted 105 mgm. An ether solution of this deposited 76 mgm. of crystals. This was best purified by chromatography on alumina (activity 2). The product then was obtained melting at 220–230°. After three recrystallizations from acetone it melted at 222–232°. $[\alpha]_D$ $31 \pm 1°$ ($c = 1.99$). Found: C, 63.69, 64.39; H, 7.43, 8.15; N, 3.28; OCH_3, 27.43. Calc. for $C_{24}H_{35}O_7N$: C, 64.12; H, 7.85; N, 3.12; 4 OCH_3, 27.61.

Ultraviolet spectrum: λ_{max} 219 mμ (3.82); λ_{min} 285 mμ (1.71); λ_{max} 340 mμ (2.27).

Infrared spectrum: 3520 (33), 3010 (27), 1742 (74), 1652 (92), 1480 (46), 1429 (50), 1394 (37), 1360 (55), 1335S (31), 1329 (34), 1322S (30), 1308 (34), 1298 (49), 1293 (50), 1282 (41), 1269S (30), 1255 (39), 1224 (58), 1209 (53), 1185 (40), 1174 (44), 1155 (60), 1127 (89), 1117 (85), 1096 (78), 1080S (58), 1065S (53), 1056 (64), 1045 (49), 1011 (42), 1000 (54), 990 (50), 972 (32), 964 (32), 935 (37), 894 (14), 871 (14), 845 (21), 800S (23), 795 (26), 788S (14), 742 (14), 691 (20), 648 (29), 608 (25).

The compound was inert to hydrogen in the presence of Adams' catalyst in acetic acid or in ethanol containing a little concentrated hydrochloric acid. The compound was recovered unchanged after it was shaken in benzene solution with active manganese dioxide (1) for two hours.

"Des(O-methyl)des(oxymethylene)-iso" Compound

Thirty-six milligrams of "des(oxymethylene)-iso" compound in 2 cc. of 6 *N* sulphuric acid was heated on the steam bath for 45 min. Methylene dichloride extracted 36 mgm. which crystallized from acetone–ether giving 30 mgm. m.p. 162° and 3 mgm. of less pure crystals. Recrystallization from the same solvents raised the melting point to 162–164° (preliminary loss of solvent of crystallization). $[\alpha]_D$ $-97 \pm 2°$ ($c = 1.25$). Found: C, 63.77; H, 7.60; OCH_3, 20.85; active hydrogen 0.41. Calc. for $C_{23}H_{33}O_7N$: C, 63.43; H, 7.64; 3 OCH_3, 21.38; two active hydrogens, 0.46.

Ultraviolet spectrum: log ϵ 3.6 (215 mμ); log ϵ 3.3 (220 mμ); log ϵ 3.1 (250 mμ); λ_{min} 270 mμ (1.29); λ_{max} 312 mμ (1.73).

Infrared spectrum: 3530 (47), 3465 (45), 3380 (42), 1755 (81), 1710 (33), 1657 (92), 1427 (61), 1360 (60), 1321 (46), 1278 (49), 1210 (80), 1187 (63), 1151S (41), 1098 (94), 1075 (68), 1035 (51), 1002 (57), 990 (50), 965 (34), 950 (33), 903 (25), 854 (19), 841 (18), 805 (22), 780 (16), 750S (18), 741 (23), 710 (19), 700 (21), 666 (12), 643 (13).

The compound proved inert to hydrogen over Adams' catalyst in ethanol containing hydrochloric acid.

When 14 mgm. of the compound and 38 mgm. of paraperiodic acid in 2 cc. of water were left at room temperature for 24 hr., only traces of product could be extracted from neutral, acidic, or basic medium.

"Dihydrodes(O-methyl)des(oxymethylene)-iso" Compound

A solution of 55 mgm. of "des(O-methyl)des(oxymethylene)-iso" compound and 43 mgm. of sodium borohydride in 2 cc. of methanol and 0.5 cc. of water stood for one hour at room temperature. Dilute sulphuric acid was added slowly until gas evolution ceased (pH still near 8), water was added, and the solution extracted with chloroform. The 62 mgm. of product was insoluble in ether. It crystallized in part from wet acetone giving 25 mgm., m.p. above 330°. The acetone soluble part crystallized from concentrated aqueous solution, giving 8 mgm. m.p. 82–86°. The high melting solid appeared to be the salt of a borate complex. It was dissolved in 1 cc. of methanol, and 1 cc. of 6 *N* sulphuric acid and 0.5 cc. of water added. After two hours at room temperature

the solution was extracted with chloroform. The product crystallized from chloroform–ether, giving 17 mgm. m.p. 161° and 4 mgm. m.p. 157°. The crystals melting at 86° proved to be a higher hydrate of this compound (infrared and mixed m.p. comparisons of dried samples). One recrystallization raised the melting point to 162°. The compound was dried *in vacuo* at 100° over phosphoric anhydride for 3.5 hr. Found: C, 60.07; H, 7.77; OCH_3, 18.84. Calc. for $C_{23}H_{35}O_7N.H_2O$: C, 60.64; H, 8.19; 3 OCH_3 20.44.
Ultraviolet spectrum: Only end absorption.
Infrared spectrum: (30 mgm. per ml. in chloroform, 0.1 mm. cell): 3425 broad, 3000 (38), 2945 (39), 2900S (29), 2825 (22), 1631 (61), 1465 (29), 1450S (28), 1385 (26), 1359 (25), 1328 (21), 1315 (22), 1298 (20), 1137S (29), 1120 (53), 1095 (63), 1037 (25), 1000 (24), 958 (13).

Dihydrodesmethanoldes(oxymethylene)-secolycoctonam Diketone

(*a*) A solution of 31.5 mgm. of des(oxymethylene)-*seco*lycoctonam diketone in 4 cc. of absolute ethanol containing three drops of concentrated hydrochloric acid was hydrogenated under one atmosphere pressure using Adams' catalyst (prereduced from 25 mgm. of oxide). In three hours 1.0 mole of hydrogen was taken up. The solution was filtered, concentrated to small volume under reduced pressure, and the residue taken up in sodium carbonate solution. Methylene dichloride extracted 31 mgm. which crystallized spontaneously on standing overnight. After three recrystallizations from ether the product melted at 177°. $[\alpha]_D$ 38 ± 1° (c = 1.85). Found: C, 65.19, 66.18; H, 8.02, 7.99; OCH_3, 22.27. Calc. for $C_{23}H_{33}O_6N$: C, 65.84; H, 7.93; 3 OCH_3, 22.19.
Ultraviolet spectrum: log ϵ 3.81 (212 mμ); log ϵ 3.80 (220 mμ); λ_{min} 267 (1.96); λ_{max} 320 (2.40).
Infrared spectrum: 1756 (74), 1701 (73), 1663 (90), 1423 (58), 1358 (42), 1345S (33), 1324 (34), 1292 (27), 1271 (37), 1215S (31), 1241 (48), 1210 (70), 1180S (34), 1173 (35), 1151 (35), 1139 (43), 1120S (72), 1107 (81), 1095 (74), 1088S (72), 1050 (26), 1040 (32), 1013 (38), 998 (41), 963 (33), 925 (20), 903 (18), 858 (16), 843 (16), 800 (13), 725 (25), 675 (5).

(*b*) A suspension of platinum from 12.8 mgm. of platinum oxide (Adams') in a solution of 51 mgm. of desmethanoldes(oxymethylene)-*seco*lycoctonam diketone in 3 cc. of ethanol and three drops of concentrated hydrochloric acid took up 1.07 moles of hydrogen in 40 min. The product crystallized readily from ether, giving 42 mgm., m.p. 169°. After purification by chromatography on alumina the product melted at 171°, and proved identical with the product from (*a*) (mixed m.p. and comparison of infrared spectra).

Periodate Oxidation of Hydroxylcoctonine

Hydroxylcoctonine (41 mgm.) in 5.0 cc. of 0.05 molar periodic acid solution buffered to pH 5 using sodium acetate consumed 0.74×10^{-4} mole (mole ratio 0.87) of the reagent in five hours at room temperature. After addition of sodium carbonate, thorough extraction with chloroform removed only 6 mgm. from the aqueous layer. This crystallized from ether, m.p. 140°, mixed m.p. with hydroxylcoctonine 143–148°. Under similar conditions in 21 hr. 1.07 moles of periodic acid was consumed per mole of base (only 1 mgm. of base could be extracted (36 mgm. used)), and in 68 hr. the molar uptake of reagent was 1.13.

21-Acetoxypregnene-3-ol-20-one

Recrystallized from ether m.p. 180–183°.

Ultraviolet spectrum: log ϵ 2.62 (215 mμ); λ_{min} 240 mμ (1.81); λ_{max} 280 mμ (2.11).

Etiocholan-3 α-ol-11,17-dione

Ultraviolet spectrum: log ϵ 2.23 (215 mμ); λ_{min} 240 mμ (near 0); λ_{max} 295 mμ (1.83).

Cyclodecane-1,6-dione

Recrystallized from ether m.p. 99–100°.

Ultraviolet spectrum: log ϵ 0.45 (230 mμ); λ_{max} 285 mμ (1.59).

Infrared spectrum (15 mgm. per ml. in chloroform, 0.1 mm. cell): 2940 (26), 2890 (15), 1707 (66), 1443 (28), 1420 (29), 1372 (22), 1345 (19), 1146 (35), 1112 (25), 1042 (12), 980 (11).

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CALCULATION OF ELECTRON TRAP DEPTHS FROM THERMOLUMINESCENCE MAXIMA*

By A. H. Booth

The thermoluminescence curve, obtained by plotting the intensity of light emission against temperature for a constant rate of heating, is valuable for finding the distribution of electron traps in a phosphor. Each maximum in the light intensity corresponds to the emptying of a trap whose energy level is a function of the temperature at the maximum. This temperature is an easily measured experimental quantity but it has hitherto not been possible to evaluate the trap depth from this alone. Accessory data were required, such as the decay rate or the light sum stored at the peak (4), which might be difficult to obtain or imprecise. It will be shown here how the trap depth can be calculated using only the positions of the maxima at two different rates of heating.

Randall and Wilkins (3) derived the equation for the thermoluminescence or "glow" curve for a single trap depth, assuming first order kinetics and no re-trapping, in the form

$$[1] \qquad I = C n_0 s \exp\left[-\int^{T}(s/B)\exp(-E/kT)\,dT\right]\exp(-E/kT),$$

where I is the brightness, C and n_0 are arbitrary constants, E is the trap depth, s is an atomic frequency factor, and B is the rate of heating. From this they did not solve for the conditions for the maximum (the glow peak) directly, but wrote

$$E = T^* [1 + f(s, B)]\ k \log_e s$$

where T^* is the temperature at the maximum; and showed by plotting a numerical example of equation [1], using Bünger and Flechsig's (1) values for s and E in KCl(Tl) phosphor, that $f(s, B)$ is small compared with unity when B is in the range 0.5 to 2.5 degrees/sec. This linear relationship becomes, with the same value of $s(2.9 \times 10^9 \text{ sec.}^{-1})$

$$E = 25\ k\ T^* \text{ (for } B \text{ in the range given).}$$

This last result has been widely quoted as a general rule of thumb; but the numerical constant depends on s, and this will be different for each trap, even in the same substance. In very simple cases where s can be obtained from the intercept on the plot of $1/T$ against the logarithm of the phosphorescence decay constant, E will be known from the slope, so that the glow curve data are then redundant.

It may have escaped attention that, even though the integral in the first exponential bracket cannot be expressed in closed form, an *exact* solution for the maximum in equation [1] can be had by setting the derivative equal to

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zero in the usual way. For we can write

$$u\ .\ dv/dT + v\ .\ du/dz\ .\ dz/dT = 0,$$

where u and v are the two exponentials (in the order written) and $u = e^z = du/dz$. Whence, directly,

$$\frac{E}{k(T^*)^2} = \frac{s}{B}\exp\left(-E/kT^*\right). \tag{2}$$

This equation gives a curve which differs very little from a straight line, $E = a\,k\,T^*$. It is 6% below it at 100°K., 6% above it at 900°K. Thus, Randall and Wilkin's linear approximation will be excellent in most cases. The effect of heating rate on the maximum can now be given in explicit form:

$$\log_e B_0/B_1 = (2\log_e T_0^* + E/kT_1^*) - (2\log_e T_1^* + E/kT_0^*)$$

$$\sim a_1 - a_0 \text{ (using the linear approximation).}$$

Similarly,

$$\log_e s_0/s_1 \sim a_0 - a_1.$$

A more useful application of equation [2] follows. If the maxima are determined for two different rates of heating we have simultaneous equations in the unknowns E and s. Hence,

$$E = \frac{k\,T_1^*\,T_0^*}{T_0^* - T_1^*}\ .\ (\log_e B_0/B_1 + 2\log_e T_1^*/T_0^*).$$

If needed, s can be found by substituting E back into [2].

Experimentally, such an approach appears attractive. Easily measured shifts in the maxima can be had with heating rates well within the practical range. Different workers (2, 3) have used rates of 0.03 to 3.0 degrees/sec. With the 0.67 ev. trap in KCl(Tl), for example, such a difference should cause a shift of nearly 50 degrees in the position of the maximum. This is, in fact, borne out experimentally in the references given, the peaks being at about 300° and 350°K. respectively.

In principle one should be able to obtain all trap depths from quite complex curves, although the relative contributions of peak and subpeaks may often be difficult to analyze. The assumption of first order kinetics seems to be generally valid for each individual trap, but a number of traps lying close together in depth may have decay rates which, in sum, obey an inverse power law (3). The identification of individual traps is then not feasible in any event.

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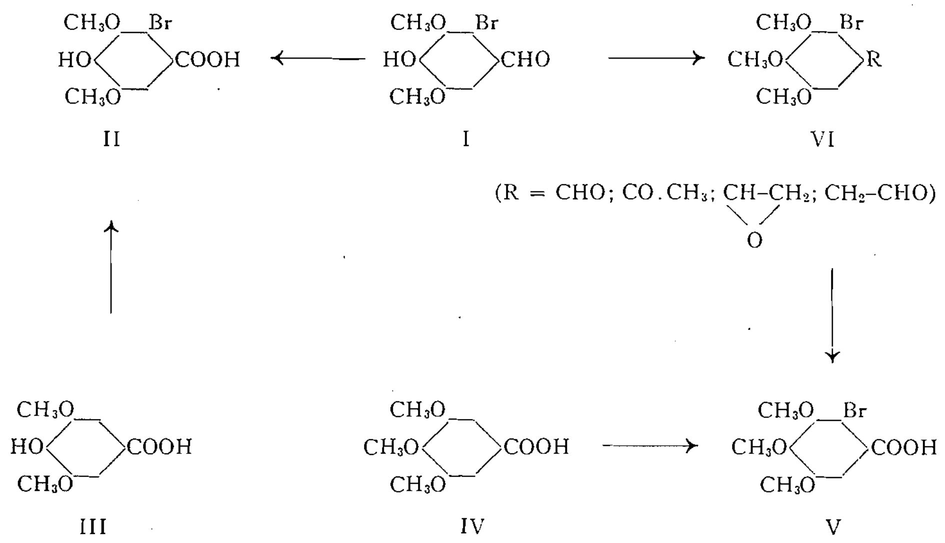
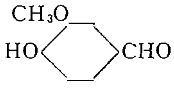
REACTIONS OF SYRINGALDEHYDE INVOLVING HALOGENATION

By K. R. Kavanagh and J. M. Pepper

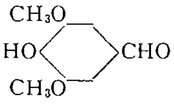
In a manner similar to that whereby vanillin may be prepared by the oxidation of softwood lignins, a mixture of vanillin and syringaldehyde would be so obtained by the oxidation of hardwood lignins. The value of this preparation of these aromatic aldehydes as pure chemicals would be increased if their separation could be achieved readily. Pearl and Dickey (8) have summarized the various laboratory methods that have been used. A paper chromatographic separation has subsequently been described by Stone and Blundell (12). The aim of the present work, in part, was to determine whether syringaldehyde (VIII) could be separated from vanillin (VII) by bromination or iodination of the VII under conditions wherein no reactions occurred with the VIII. The halogenation of vanillin in the reactive 5-position is well established, but there have been no reports on any similar introduction of halogen into the syringaldehyde molecule. Any such reaction would be expected to be minimized owing to the absence of any such activated position ortho to the phenolic hydroxyl group. The decreased ortho-directing tendency of methoxyl groups, due likely to steric effects, has been pointed out by Rosenwald (11). Syringaldehyde was treated with iodine under similar conditions to those used for the preparation of 5-iodovanillin (9), that is, iodine dissolved in a potassium iodide solution was added slowly to an alkaline solution of the aldehyde. A dense, black, iodine-containing product resulted which gave no definite melting point. A similar iodination of a 1:1 molar mixture of vanillin and syringaldehyde was then attempted using an amount of iodine equimolar to the vanillin with which it was thought reaction would be more rapid. The same black product resulted and was not studied further. In the attempts to brominate syringaldehyde according to the procedure for the preparation of 5-bromovanillin (6), the previously unreported 2-bromosyringaldehyde (I), m.p. 186–187°C., was obtained. On repeating this reaction with equimolar amounts of vanillin, syringaldehyde, and bromine, a precipitate resulted which consisted of a mixture of 5-bromovanillin (m.p. 164°C.) and I. Neither of the halogenation methods appeared to be a practical means of separation of mixtures of VII and VIII. The 2-bromosyringaldehyde (I) was identified by analyses and conversion to the known derivatives.

Repeated attempts to convert syringic acid (III) to the reference compound 2-bromosyringic acid (II) according to the direct bromination procedure of Levine (5) were unsuccessful. It is interesting to note that Bogert and Plaut (1) reported a similar failure. 2-Bromo-3,4,5-trimethoxybenzoic acid (V) was made from 3,4,5-trimethoxybenzoic acid (IV) according to the method of Feist and Dschu (3) only if the powdered iron catalyst that they recommend was omitted; otherwise, unchanged IV was recovered. The oxidation of I with silver oxide according to the method used by Pearl (7) for the oxidation of vanillin gave a product having the required properties





VII



VIII

of II. Other structure proof of I was obtained by its methylation with diazomethane to VI, which was subsequently oxidized with potassium permanganate to a product V, identical with that obtained from IV. Since the reaction of aromatic aldehydes with diazomethane may give rise to the mixture of products shown as VI (2), no purification was attempted at this stage in the belief that all such products would be oxidized to V.

Two derivatives, the oxime and the acetate of 2-bromosyringaldehyde, were prepared as pure compounds and their analyses reported.

EXPERIMENTAL

A. Iodination Studies

Syringaldehyde (5 gm.) (9) was reacted with iodine under the same relative conditions as those used for the preparation of 5-iodovanillin (9). A black residue (5.5 gm.) resulted, which gave a positive Beilstein test, had no definite melting point but charred slowly to leave a residue. A similar treatment of equimolar amounts of syringaldehyde (5 gm.), vanillin (4.2 gm.), and iodine (7 gm.) again resulted in a similar black precipitate (9.3 gm.).

B. Bromination Studies

Syringaldehyde (6 gm.) was reacted with bromine under the same relative conditions as those used for the preparation of 5-bromovanillin (6). The resulting light yellow product (4.7 gm.) was recrystallized three times from glacial acetic acid; colorless needles, m.p. 186–187°C. A similar treatment of equimolar (0.017 mole) amounts of syringaldehyde (3 gm.) and vanillin (2.5 gm.) with bromine (1.4 gm.) (0.0087 mole) gave rise to a white product (1.5 gm.) which, after two recrystallizations from ethanol, yielded a product (m.p. 152–155°C.) (0.9 gm.) whose mixed melting point (159–161°C.) with an authentic sample (m.p. 164°C.) indicated that it was mainly 5-bromovanillin. A further experiment using an equimolar (0.017 mole) amount of bromine yielded a product which, after recrystallization from ethanol, weighed 2.0 gm., m.p. 135–143°C.

C. Preparation and Identification of 2-Bromosyringaldehyde

Preparation

Several runs were made to study the optimum conditions of preparation of this new compound. Neither decreasing the rate of addition of bromine nor refluxing the reaction mixture for from 15 min. to six hours after complete addition materially affected the yield. The following procedure illustrated the sythesis. Syringaldehyde (6 gm.) was dissolved, with warming, in glacial acetic acid (15 ml.). To this hot solution was added, dropwise, over a period of 20 min., a solution of bromine (5.3 gm.) in acetic acid (10 ml.). The crude reaction product which separated was removed by filtration; weight, 6.2 gm. After recrystallization from glacial acetic acid, then ethanol, colorless needles resulted. Yield, 3.8 gm., m.p. 186–187°C. Calc. for $C_9H_9O_4Br$: mol. wt. 261; C, 41.4; H, 3.48; Br, 30.6; OCH_3, 23.8%. Found: mol. wt. (Rast) 262, 265; C, 41.55, 41.60; H, 3.65, 3.60; Br, 30.7, 30.86; OCH_3, 23.2, 23.6%.

2-Bromosyringaldehyde oxime.—The oxime was prepared in the usual way; m.p. 132–133° C.* Calc.for $C_9H_{10}O_4BrN$: C, 39.2; H, 3.65; OCH_3, 22.5%. Found: C, 39.9, 39.2; H, 4.1, 4.0; OCH_3, 22.2%.

2-Bromosyringaldehyde acetate.—This monoacetate was prepared according to the method used for the preparation of the analogous derivative of vanillin (10). Recrystallization from ethanol gave white needles, m.p. 113.5–114.5°C. Calc. for $C_{11}H_{11}O_5Br$: C, 43.62; H, 3.66; OCH_3, 20.4%. Found: C, 43.70; H, 3.82; OCH_3, 20.4, 19.9%.

Identification

Synthesis of 2-bromo-3,4,5-trimethoxybenzoic acid (IV).—Starting with 3,4,5-trimethoxybenzoic acid the method of Feist and Dschu (3) was followed but the required product, m.p. 148.5–150°C. (reported (3), 148°C.) was obtained only if the powdered iron catalyst, mentioned in their procedure, was omitted.

Oxidation of 2-bromosyringaldehyde to 2-bromosyringic acid.—To the washed silver oxide prepared from silver nitrate (2.4 gm.) (7) was added water (24 ml.), sodium hydroxide (2.8 gm.), and 2-bromosyringaldehyde (2 gm.). After gentle heating with stirring for 20 min., the solution was filtered and the

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*It was observed that this oxime, after recrystallization from either ethanol–water or water alone, melted at 100–102°C. after air-drying. Further drying in an Abderhalden drier or in a vacuum desiccator raised the melting point to 132–133°C. This suggested that the oxime forms a stable hydrate of unknown exact composition. Calc. for $C_9H_{10}O_4BrN.3/2\ H_2O$: OCH_3, 20.4%. Found for the product, m.p. 100–102°C: OCH_3, 20.4, 20.2, 20.8%.

residue washed with hot water. The combined filtrate was acidified with sulphur dioxide gas but no precipitate formed. To recover any unreacted aldehyde, dilute sulphuric acid (7 ml.) was added and the solution boiled until the sulphur dioxide had been removed. After standing, a precipitate was removed and was shown to be starting material (35% recovery). The remaining filtrate was extracted with ether. This extract was dried and the excess solvent removed to leave a residue (1.0 gm.). Two recrystallizations from dilute acetic acid gave pale yellow crystals (0.6 gm.) m.p. 153–155°C. in good agreement with that of 155°C. reported by Levine (5). Calc. for $C_9H_9O_5Br$: C, 39.0; H, 3.28; OCH_3, 22.4%. Found: C, 39.2; H, 3.38; OCH_3, 22.2%.

Conversion of 2-bromosyringaldehyde to 2-bromo-3,4,5-trimethoxybenzoic acid.—To a suspension of 2-bromosyringaldehyde (4 gm.) in ether (300 ml.) was added an ethereal solution of diazomethane prepared from nitrosomethylurea (20.6 gm.). After 2.5 hr. stirring at around 0°C. a clear solution resulted after which the ether and excess diazomethane were allowed to evaporate at room temperature. The residual yellow oil was dissolved in ether (100 ml.) and this solution extracted with 5% sodium hydroxide (2 × 100 ml.). The ether layer, after drying, was concentrated to leave an orange-colored oil (4.3 gm.) which was used directly in the next step.

The method of Head and Robertson (4) for the oxidation of a substituted benzaldehyde to the corresponding acid was first tested by the successful conversion of veratraldehyde to veratric acid in 60% yield, after recrystallization from dilute acetone. To the methylated product (4.3 gm.) obtained above, dissolved in acetone (100 ml.), was added with swirling a solution of potassium permanganate (1.62 gm.) in water (50 ml.) over a period of one hour at 50–55°C. During the next hour, further permanganate (0.38 gm. in 10 ml. water) was added. The mixture was cooled to 0°C., cleared with sulphur dioxide, and the acetone evaporated. Some white crystals and a yellow oil separated, which, after decantation of the water, were treated with saturated sodium bicarbonate (50 ml.) which dissolved only the crystals. From this solution, after acidification, a white precipitate (0.8 gm.) was obtained. Reoxidation of the oil resulted in a further amount (0.2 gm.) of product. These were combined and after recrystallization from dilute ethanol gave the required product, m.p. 146–148°C. A mixed melting point with synthetic V was undepressed. Calc. for $C_{10}H_{11}O_5Br$: C, 41.3; H, 3.81; OCH_3, 31.9%. Found: C, 42.1, 41.6; H, 3.94, 4.16; OCH_3, 31.6, 31.8%.

ACKNOWLEDGMENT

The authors wish to thank the Saskatchewan Research Council for the award of a Graduate Research Fellowship to one of them (K. R. K.). The Howard Smith Chemicals Limited, kindly donated the vanillin used in this investigation.

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OBSERVATIONS ON THE REACTION OF β,β'-DICHLORODIETHYL SULPHIDE WITH GLYCINE AND WITH GLYCYLGLYCINE[1]

By D. E. Douglas[2] and R. D. H. Heard

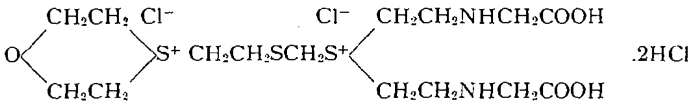
ABSTRACT

In the reaction of β,β'-dichlorodiethyl sulphide with glycine and with glycylglycine in dilute aqueous base, stable complex sulphonium chlorides are formed. One of these compounds has been isolated in a pure state from the H-glycine reaction and a tentative structure has been proposed.

INTRODUCTION

The reaction of β,β'-dichlorodiethyl sulphide (designated hereafter as "H") with glycine in aqueous alkaline solution at pH 10 has previously been described by Fleming, Moore, and Butler (4). As the main product was not characterized chemically, further investigation of the reaction was undertaken.

This product has been obtained in pure form and shown to be a nitrogen-containing sulphonium chloride. Nitrogen, sulphur, and chlorine values, and other data, admit of the following tentative structure.



The purification and chemistry of this compound and also a preliminary investigation of other products of the reaction of H with glycine are described in this communication. Because of their intractable nature many of the compounds were only obtained in an impure state.

EXPERIMENTAL

All the reactions of H with amino compounds described below were carried out at 37° C. in the presence of aqueous sodium hydroxide.

H-glycine (Compound I)

The preparation of this compound in impure form has been described by Fleming *et al.* (4). In the present investigation, 2 *N* sodium hydroxide was added through a simplified Hershberg funnel to the vigorously stirred mixture of glycine, water, and H in a round-bottomed flask fitted with a glass electrode

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Contribution from the Department of Biochemistry, McGill University. Project CW 557 of The Department of National Defence, Canada.

[2] *Present address: The Montreal General Hospital Research Institute, Montreal, P.Q.*

for pH measurement. The rate of addition of sodium hydroxide was adjusted to keep the pH close to 7.5.

Purification of the crude gum obtained from the reaction mixture by precipitation with hydrochloric acid was effected by solution of the gum in water with the aid of sodium hydroxide and continuous extraction of the concentrated aqueous solution with *n*-or *sec*-butanol for one to two hours. The aqueous phase, after acidification with hydrochloric acid to pH 2 was concentrated *in vacuo* on the steam bath, and the residue dissolved in methanol. The filtered methanol solution was poured into a large volume of acetone to precipitate the product. The solid was washed with acetone, and dried over magnesium perchlorate at 80–100° C. and 0.1 mm. The product was a white crystalline, hygroscopic solid, melting at 161° C. to a viscous liquid.
Found: N, 500; S, 17.0; Cl (Carius), 23.3, (with Hg $(NO_3)_2$) 24.4. Calc. for $C_{16}H_{34}O_5N_2S_3Cl_4$: N, 4.89; S, 16.8; Cl, 24.8.

The formation of complexes by compound I with heavy metal ions (Co^{++}, Cd^{++}, Ni^{++}, Cu^{++}) has been mentioned previously (2,4). Silver nitrate in dilute solution failed to yield an initial precipitate of silver chloride with this compound, although the chloride ion present was titratable with mercuric nitrate. Highly diluted cupric ion gave a greenish-blue color with compound I. Potentiometric titration of I failed to indicate the presence of an isoelectric region characteristic of compounds such as glycine, and showed, moreover, that the nitrogen atoms are practically uncharged above pH 8 (Fig. 1). The observed similarity in the titration curves of compound I and the other compounds described later in this communication seems to indicate a fundamental

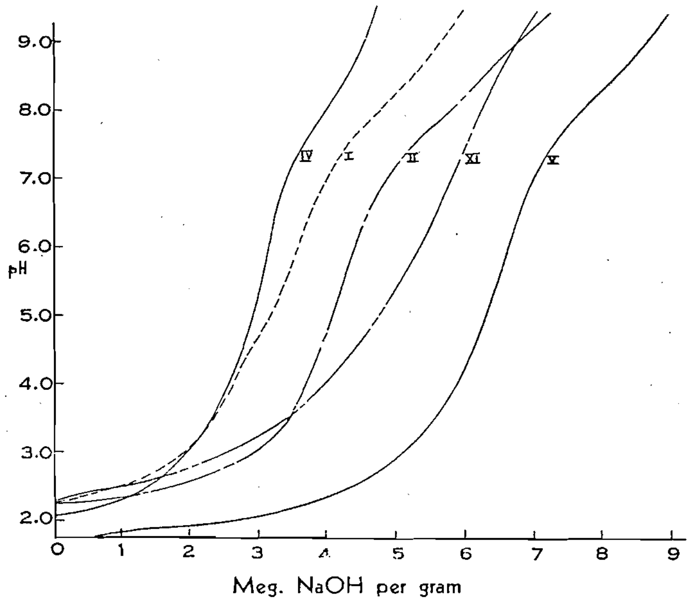
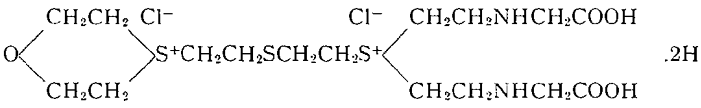


FIG. 1. Titration curves of compounds I, II, IV, V, and XI.

similarity in structure, probably the postulated presence of a sulphonium sulphur atom in the β-position to amino nitrogen. The absence of hydroxyl groups was indicated by failure of I to react with acetyl chloride or acetic anhydride. That vinyl groups adjacent to sulphonium sulphur are absent was shown by failure of I to react with thiosulphate in bicarbonate buffer (Stahmann, Fruton, and Bergmann (8)).

Analytical nitrogen, sulphur, and chlorine values and the observed properties admit of the following tentative structure:

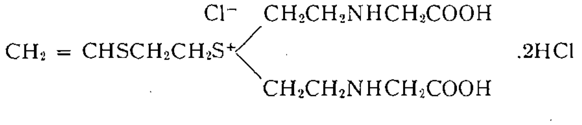


Evidence that sulphonium sulphur is present is furnished by the observed presence of chloride ion in excess of the calculated amount bound by the nitrogen atoms as hydrochloride. The assumed presence of the terminal thioxane ring seems to be the only conclusion possible in view of the indicated absence of hydroxyl or vinyl groups.

Fission of Compound I in Hydrochloric Acid

Two grams of I in 20 cc. of water refluxed with an equal volume of concentrated hydrochloric acid for one and a half hours. Some white material which formed during the reaction was filtered off. The filtrate was evaporated *in vacuo* on the steam bath to a small volume, and most of the remaining acid was neutralized with 2 *N* sodium hydroxide, giving a solution of pH 2. The sodium chloride which separated on further evaporation was filtered off, and the filtrate was put aside for seven months. The solution was then evaporated to dryness and the residue extracted with methanol. Precipitation with acetone yielded a white, hygroscopic solid (compound II) which was dried *in vacuo* at 80° C.

Electrometric titration of this compound yielded a curve similar to that obtained for compound I (Fig. 1). The presence of chloride ions in excess of that required by the two nitrogen atoms again strongly indicated the presence of sulphonium sulphur. To compound II has been assigned the following tentative structure:



Found: N, 6.60; S, 15.0; Cl, 26.0. Calc. for $C_{12}H_{25}O_4N_2S_2Cl_3$: N, 6.50; S, 14.9; Cl, 24.6.

Isolation of Compound IV From the H-glycine Reaction

The supernatant liquid, after the initial precipitation of compound I, was neutralized and extracted continuously with *n*-butanol for three hours. The filtered aqueous phase was taken to dryness *in vacuo*. The resulting residue was taken up in methanol, the sodium chloride filtered off, the filtrate partially evaporated and poured into a large volume of acetone. The gum which precipitated was separated by decantation, washed with acetone, and dried in a drying pistol at 80° C. This compound was a white amorphous, hygroscopic solid. Found: N, 5.90; S, 15.5; Cl, 14.2. Because of its physical properties, this substance as obtained was probably impure.

The large analytical chlorine value indicated that this compound was also a sulphonium chloride. The presence of glycylglycyl residues was indicated by elementary analysis, and from potentiometric titration only one titratable carboxyl group was present for every two nitrogen atoms.

Compound V

This compound, formed when H reacts with glycine in the presence of thiodiglycol, is similar to IV in its physical properties, but differs in N, S, and Cl content.

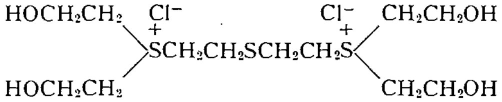
One-tenth mole each of H, thiodiglycol, and glycine were stirred together in 250 cc. of water in the presence of added 2 *N* sodium hydroxide. The pH was kept close to 7.5. The reaction mixture was evaporated *in vacuo* to a convenient volume, and was extracted continuously with *n*-butanol for two hours. Upon working up the aqueous phase as described for the isolation of compound IV, the product was obtained as hygroscopic, yellow gum, which softened on warming. Found: N, 7.00; S, 16.6; Cl, 4.62. Both IV and V gave similar, but not superimposable, titration curves, as illustrated in Fig. 1.

Reaction of Glycylglycine with H and Thiodiglycol

Reaction of tenth-molar quantities of H, glycylglycine, and thiodiglycol was carried out in dilute sodium hydroxide at pH 7.5. From the aqueous phase after continuous extraction with *sec*-butanol was obtained a gum soluble in ethylene chlorohydrin. Precipitation of the material from its ethylene chlorohydrin solution with ethanol yielded a brown, crystalline solid, which became amorphous on being dried at 40° C. in the oven. Yield 4.1 gm. Found for compound XI: N, 9.9; S, 12.8; Cl, 5.41. The titration curve of this compound was similar to those of the compounds previously described (Fig. 1).

DISCUSSION

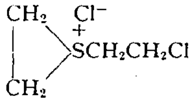
The tendency for H to form sulphonium salts in water and in the presence of thiodiglycol has been noted by several observers (Stein, Moore, and Bergmann (9), Herriott (5)). It appears that, in the initial absence of thiodiglycol, at least partial hydrolysis of some of the H molecules is necessary before sulphonium salts sufficiently stable to be isolated can be formed. The sulphonium chloride H2TG,



has been described by Stein, Moore, and Bergmann (9). It appears to be the most stable of the sulphonium chlorides derived from the hydrolysis of H, but can be decomposed further to the thiodiglycol, or converted back to H.

The nitrogen-containing sulphonium chlorides described in this communication in contrast, appear to be quite stable structures, and, by virtue of the proximity of sulphonium sulphur, amino nitrogen, and free carboxyl group, possess unique physical and chemical properties. One common property of all these sulphonium chlorides investigated is the characteristic shape of their titration curves.

If it is assumed that the initial stage in the reactions of H in aqueous media is the formation of the cyclic intermediate of Bartlett and Swain (1) the



tendency towards the formation of open chain secondary amines rather than thiazanes when H reacts with amino compounds such as glycine may be explained. This cyclic ion, by virtue of its labile structure is a powerful alkylating agent. Moreover, rearrangement of H to this structure takes place with a lower velocity than the subsequent hydrolysis or alkylation reaction (1). After alkylation of an amino group, e.g. of glycine, the remaining chlorine atom of the H residue becomes ionic, and another cyclic structure is formed, capable of alkylating a second amino group. This di-2-glycinoethyl sulphide apparently can undergo further alkylation by another H molecule to form a stable sulphonium chloride. This intermediate, which is still capable of forming a cyclic sulphonium ion, apparently reacts further with another hydrolyzed H residue or with thioxane, yielding compound I.

In aqueous media, the presence of buffers may influence the course of a reaction involving H, since ester formation has been shown to occur readily in the presence of many anions (1, 4, 6). Formation of thiodiglycol esters may occur with a greater velocity than alkylation of amino compounds which are present. Thus, in the presence of buffers, such as acetate or bicarbonate, the products of the reaction of H with amino compounds may be entirely different from those formed in the absence of buffers. In attempts to reproduce as closely as possible physiological conditions of pH *in vitro*, many investigators have employed rather high concentrations of buffer salts, and may thus have failed to obtain H derivatives of biochemical significance.

The possibility of the formation of sulphonium chlorides when H reacts with proteins has already been considered by several investigators (Ogston (7)). If stable sulphonium chlorides similar in type to compounds I, IV, V, and XI are formed in the H-protein reaction, with protein residues replacing the amino acid residues, an explanation is at once offered for some of the observed properties of the H-protein complexes. The strongly bound chlorine in these complexes (7) is in reality chloride ion associated with sulphonium sulphur, and the observed changes in the titration curves of the altered proteins may possibly be due in part to the influence of the strongly electropositive sulphonium sulphur, and not entirely to "covering" of the carboxyl groups of the proteins as postulated previously (7). Such complex protein sulphonium chlorides may be of significance in the reactions of H *in vivo* (3).

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CARBODIIMIDES

PART III.* (A) A NEW METHOD FOR THE PREPARATION OF MIXED ESTERS OF PHOSPHORIC ACID. (B) SOME OBSERVATIONS ON THE BASE-CATALYZED ADDITION OF ALCOHOLS TO CARBODIIMIDES[1]

By H. G. Khorana

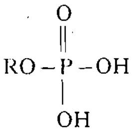
ABSTRACT

The preparation of a number of N,N′-di-*p*-tolyl-O-alkyl pseudourea ethers through the alkoxide catalyzed exothermic addition of alcohols to di-*p*-tolyl carbodiimide is described. Triethyl amine is not effective as a catalyst for such additions. Dicyclohexylcarbodiimide has been found not to undergo such additions at all.

The N,N′-diaryl-O-alkyl pseudourea ethers decompose in the presence of mono-and disubstituted hydrogen phosphates to form the diaryl urea and the neutral tertiary phosphates in excellent yield. Several mixed esters of phosphoric acid have been prepared by this method.

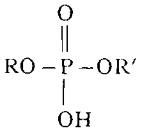
INTRODUCTION

Because of their importance in biological processes, esters of phosphoric acid, particularly those derived from carbohydrates, purine, and pyrimidine glycosides, have been the subject of extensive chemical investigations in recent years (1, 9, 12, 13, 18, 22). Chemical methods of phosphorylation have been developed which have been successfully applied to the synthesis of many naturally occurring monoalkyl esters of phosphoric acid (I) (9, 13). However, currently, great interest has been attached to the dinucleoside phosphates (dialkyl esters of phosphoric acid, II) which are the degradation products of nucleic acids (15, 17, 19).



$$RO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH$$

I, R = e.g. nucleoside residue.



$$RO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OR'$$

II, R, R′ = e.g., nucleoside residues.

The synthesis of these fragments is therefore important (cf. 7) in the development of the chemistry of nucleic acids (5).

The methods so far employed extensively for synthesis in the carbohydrate and the nucleotide field (1–4, 9, 12, 13, 17, 22) have used suitably protected phosphoric acid chlorides such as diphenyl and dibenzyl phosphorochloridates† (III, R and R′ = phenyl or benzyl). Some syntheses reported employ polyphosphoric acid (12) which also contains activated phosphate bonds.‡

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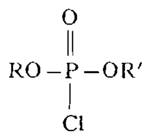
Contribution from the Chemistry Division of British Columbia Research Council, Vancouver 8, B.C., Canada. Presented before the Chemistry Section of the B.C. Academy of Sciences at its Seventh Annual Conference held on April 17 and 18, 1953.

* *Part II, Can. J. Chem. 31: 585. 1953.*

† *See new nomenclature of phosphorous compounds adopted by the International Union of Pure and Applied Chemistry. J. Chem. Soc. 5122. 1952.*

‡ *See also a recent patent by A. R. Todd and F. A. Atherton (Chem. Abstracts, 47: 6436. 1953), on the use of tetrabenzyl pyrophosphate in phosphorylation of alcohols.*

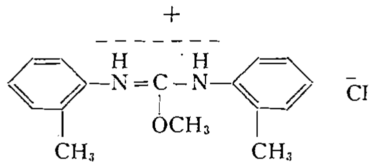


$$RO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}-OR'$$

III

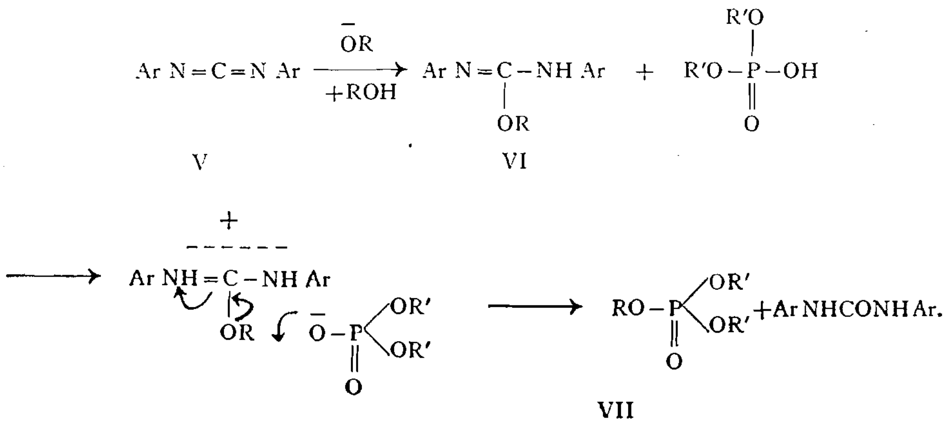
Another main approach which has found some application in the synthesis of biologically important substances is the heterogeneous reaction between a metallic (e.g. silver) salt of phosphoric acid and a halogen derivative (7 and the references cited therein). For the synthesis of the complex dialkyl esters of phosphoric acid, e.g. the dinucleoside phosphates mentioned above, a logical extension of the present methods would require the preparation of the intermediate nucleoside phosphorochloridates (III, R = nucleoside residue, R′, a protecting group, e.g. benzyl). As these intermediates are relatively inaccessible substances, the development of methods in which the well characterized mononucleotides (9) should serve directly for the phosphorylation of a second suitably protected nucleoside is clearly desirable. In the present communication we wish to report on a new method designed to achieve this purpose.

Dains recorded that the hydrochloride of di-O-tolyl-O-methyl pseudourea ether presumably (IV) decomposed on heating to form methyl chloride. This observation suggested the possibility of the synthesis of mixed esters of



IV

phosphoric acid by bringing a mono- or dialkyl hydrogen phosphate (I or II) into reaction with a pseudourea ether derived from the alcohol to be phosphorylated.



V VI VII

N,N′-diphenyl-O-ethyl pseudourea ether (VI; Ar = phenyl; R = ethyl) was first prepared by Lengfield and Stieglitz (14) by heating ethyl alcohol with diphenyl carbodiimide (V; Ar = phenyl) in a sealed tube. By this method Dains (6) prepared a number of pseudourea ethers derived from aromatic carbodiimides. Stieglitz (21) also discovered the exothermic sodium-ethoxide-catalyzed addition of ethyl alcohol to diphenyl carbodiimide. As far as we are aware this reaction has not been examined further.

We have confirmed and extended these findings of early workers and have prepared in practically quantitative yield a number of pseudourea ethers by the addition of alcohols to di-*p*-tolyl carbodiimide (V; Ar = *p*-tolyl). The choice of this carbodiimide was dictated by its easy preparation in a crystalline state (24, 25; see also experimental) and its stability over a period of several months. The preparation of pseudourea ethers through base catalysis is preferable to the sealed tube treatment because of a number of considerations. A useful modification appears to be the use of stoichiometric amounts of the alcohol and the carbodiimide in an anhydrous solvent, e.g. dioxane (see Experimental). Theoretical yield of N,N′-di-*p*-tolyl-O-*n*-butyl pseudourea ether was thus obtained. Further, it was clearly desirable to attempt to replace sodium by a tertiary base, e.g. triethylamine, as the catalyst for the production of alkoxide ions. No reaction was however observed between alcohols and di-*p*-tolyl carbodiimide in the presence of pyridine or triethylamine over a period of three days.

It was also of interest to examine the addition of alcohols to aliphatic carbodiimides. Using catalytic as well as two equivalents of sodium dissolved in *n*-butyl alcohol, it was found that dicyclohexyl carbodiimide is practically inert at room temperature. The presence of the unchanged carbodiimide was demonstrated by (*a*) strong absorption* at 4.75μ in the infrared spectrum; (*b*) evolution of carbon monoxide and carbon dioxide on the addition of oxalic acid (23); and (*c*) the formation of dicyclohexyl urea and tetrabenzyl pyrophosphate on the addition of dibenzyl hydrogen phosphate (11). More vigorous conditions to effect the addition of alcohols to dicyclohexyl carbodiimide have not been tried.

The observed stability of dicyclohexyl carbodiimide to the attack of alkoxide ions is presumably due to the high electron density at the central carbon of the twinned double bands, which is the point of attack in such reactions. Reaction occurs readily when, in place of the electron donating alkyl groups (e.g. cyclohexyl), aromatic residues are present, the latter resulting in increased conjugation of the two nitrogen–carbon double bands with the respective aromatic rings.†

For the preparation of phosphoric acid esters through the O-alkyl pseudourea ethers, we have found that a benzene solution of a mixture of N,N′-di-*p*-tolyl-O-alkyl pseudourea ethers and diesters of phosphoric acid, although quite stable at room temperature, deposits, on being refluxed, di-*p*-tolyl urea

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* *This band is characteristic of* $-N=C=N$*-stretching, cf. H. G. Khorana, ref. 10.*

† *In a recent paper, which was received after the completion of the above work, Hünig et al. (8) have advanced similar arguments to explain the differences in rate of reaction of cyanide ions with aromatic and aliphatic carbodiimides.*

and from the clear benzene solution tertiary esters of phosphoric acid (VII) can be isolated in excellent yield. In all cases studied, a reflux period of two and one-half to three hours was found to be sufficient for the completion of this reaction (VI → VII). In this way we have prepared several tertiary phosphates (see Table II) including a few which do not appear to have been previously obtained analytically pure (cf. 12).

The direct preparation of dialkyl esters, using monoesters of phosphoric acid (i.e. monoalkylation) was next attempted. The reaction between equimolar proportions of monophenyl dihydrogen phosphate and di-*p*-tolyl-O-ethyl pseudourea gave, however, in addition to di-*p*-tolyl urea, diethyl phenyl phosphate (20) and the unreacted acid as the only recognizable products. This result although disappointing from the present point of view was not surprising. As the dialkyl esters of phosphoric acid (e.g. II) are known to be, in general, stronger acids than the monoalkyl esters (e.g. I) the initial product of reaction (of the type II) would be expected to react preferentially with the pseudourea ethers, forming thus the completely esterified product.

The application of this method in the nucleotide field and to more complex cases will be reported in due course.

EXPERIMENTAL

A. PSEUDOUREA ETHERS

Preparation of Di-p-tolyl Carbodiimide (cf. 24, 25)

Finely powdered di-*p*-tolyl thiourea (60 gm.) and yellow mercuric oxide* (100 gm.) was added to carbon disulphide (500 cc.) and the reaction mixture was warmed gently and shaken for 30 min. Anhydrous calcium chloride (*ca.* 25 gm.) was then added and the mixture filtered under suction. The insoluble mercuric sulphide and admixed calcium chloride were washed thoroughly with ether. The combined washings and filtrate were evaporated under reduced pressure. Di-*p*-tolyl carbodiimide obtained as an oil solidified under prolonged suction. This was dissolved in petroleum ether (b.p. 30°–60°), filtered from traces of insoluble material and crystallized according to the directions of Zetzsche and Nerger (25). Yield in first crop, 40 gm. Mother liquor after being concentrated and standing at −20° deposited a further crop (*ca.* 5 gm.).

N,N′-di-p-tolyl-O-n-butyl Pseudourea Ether

(*a*) *Using Stoichiometric Amounts of Sodium*

A solution of di-*p*-tolyl carbodiimide (8.88 gm.; 0.04 moles) in anhydrous ether (15 cc.) was added rapidly to a solution of sodium *n*-butoxide (obtained by dissolving 1 gm. sodium) in anhydrous *n*-butyl alcohol (25 cc.). The mixture which became warm was kept for 15 min. with complete exclusion of moisture, then diluted with ether, washed thrice with water, and dried over anhydrous sodium sulphate. N,N′-di-*p*-tolyl,O-*n*-butyl pseudourea ether obtained as viscous oil after removal of ether and butyl alcohol under reduced pressure crystallized on prolonged suction. Yield, 11.8 gm.; theoretical. A portion was

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* *Baker and Adamson—reagent grade.*

recrystallized by keeping its petroleum ether (b.p. 30°–60°) solution at −20° and afforded clusters of fine needles. These were collected and washed with more chilled solvent, m.p. 34°. Found; C, 77.0; H, 8.1; N, 9.6%; $C_{19}H_{24}ON_2$ requires C, 77.0; H, 8.1; and N, 9.5%.

(*b*) *Using Catalytic Amounts of Sodium*

(*i*) *With excess of n-butyl alcohol.*—An ethereal solution of di-*p*-tolyl carbodiimide (2.22 gm.; 0.01 mole) was added to a solution of sodium butylate (from *ca.* 30 mgm. of sodium) in *n*-butyl alcohol (10 cc.). The reaction mixture was worked up as above, giving 2.9 gm. (theoretical yield) of the pseudourea ether.

(*ii*) *In dioxane, with stoichiometric amounts of n-butyl alcohol.*—Sodium (30 mgm.) was dissolved in a solution of anhydrous *n*-butyl alcohol (1 cc.; *ca.* 1.1 mole) in anhydrous dioxane (5 cc.). Di-*p*-tolyl carbodiimide (2.22 gm.; 1 mole) was then added. The warm reaction mixture was kept for 30 min. and then worked up as above. Yield of the pseudourea ether, 2.85 gm.

(*c*) *Attempted Preparation by Using Triethylamine as the Catalyst*

Triethylamine (0.2 cc.) was added to a solution of di-*p*-tolyl carbodiimide (1.11 gm.) in anhydrous *n*-butyl alcohol (6 cc.) and the mixture kept in a sealed flask at room temperature for three days. After evaporation of the alcohol and triethylamine *in vacuo*, the residual oil was taken up in petroleum ether. The solution afforded, on being kept at −20°, the unreacted carbodiimide, m.p. 54°–55°.

By using the conditions described above (*b*) (*i*) the pseudourea ethers listed in Table I were prepared.

TABLE I
N,N′-DI-*p*-TOLYL-O-PSEUDOUREA ETHERS

Name and formula of N,N′-di-*p*-tolyl-pseudourea ether	M.p. or b.p.*	Found %			Requires			Reference
		C	H	N	C	H	N	
O-methyl $C_{16}H_{18}ON_2$	120° at 2 mm.	75.6	7.1	10.8	75.5	7.2	11.0	6
O-ethyl $C_{17}H_{20}ON_2$	125° at 2 mm.	75.8	7.6	10.5	76.0	7.5	10.4	
O-ethoxyethyl $C_{19}H_{24}O_2N_2$	40°†	72.9	7.8	8.9	73.1	7.8	9	

* *The distillations were performed in bulb-tubes, with the bulbs containing the substance and a portion of the tube immersed in a heated air bath.*

† *Crystallized from petroleum ether (30°–60°) by keeping the solution at −20°.*

Attempted Preparation of N,N′-Dicyclohexyl-O-butyl Pseudourea Ether

(*a*) A solution of dicyclohexyl carbodiimide (2.06 gm.) in anhydrous ether (5 cc.) was added to dry *n*-butyl alcohol containing *ca.* 30 mgm. of dissolved sodium. No warming was observed and the oil obtained after working up in the usual manner was examined as described under (*b*) (see below).

(*b*) The above experiment was repeated employing 2 molar equivalents of sodium *n*-butylate solution in *n*-butyl alcohol. The oil obtained was treated as follows:

(1) An ethereal solution of dibenzyl hydrogen phosphate (280 mgm.) was added to a solution of the oil (110 mgm.). Dicyclohexylurea (50 mgm.; m.p. 225°–228°) separated soon and was collected after one hour.

(2) The addition of oxalic acid to an ethereal solution of the oil caused the liberation of carbon monoxide and carbon dioxide.

B. MIXED ESTERS OF PHOSPHORIC ACID

General Method: By Using Diesters of Phosphoric Acid

A benzene solution (15 cc.) of anhydrous disubstituted ester of phosphoric acid* (0.01 mole) and N,N′-di-*p*-tolyl pseudourea ether (0.01 mole) is refluxed for two and one-half to three hours. Crystals of di-*p*-tolyl urea begin to separate after 15–30 min. The reaction mixture after being allowed to cool is filtered and the urea washed with small amounts of benzene. The yield of urea is usually between 80–95% of theoretical. The clear benzene solution is washed thrice with sodium hydrogen carbonate† then with dilute hydrochloric acid and dried over anhydrous sodium sulphate. The neutral ester of phosphoric acid obtained as an oil after removal of benzene is distilled twice *in vacuo* in a bulb-tube immersed in a heated air bath. This step removes the small amounts of the urea retained by the esters. The esters prepared in this way are listed in Table II.

TABLE II
MIXED TERTIARY PHOSPHATES

Phosphate	B.p. (air bath temp.) at 2 mm.	Found %		Requires %		22_{25}^{D}*	Reference
		C	H	C	H		
Methyl, dibenzyl† $C_{15}H_{17}O_4P$	145–150°	62.6	6.8	61.6	5.9	1.5308	16
Ethyl, diphenyl $C_{14}H_{15}O_4P$	135–140°	60.5	5.5	60.4	5.4	1.5247	20
Ethyl, dibenzyl‡ $C_{16}H_{19}O_4P$	155–160°	62.6	6.2	62.6	6.2	1.5285	
n-Butyl, diphenyl‡ $C_{16}H_{19}O_4P$	140–145°	62.9	6.3	62.6	6.2	1.5229	
n-Butyl, dibenzyl‡ $C_{18}H_{23}O_4P$	170°	64.5	7.1	64.6	6.9	1.5233	

* *These were determined in an Abbé Refractometer.*
† *The analytical results show the contamination of the product with a substance, presumably di-p-tolyl urea, with higher C and H content. Alternatively the contaminant might be a disproportionation product, in view of the known occurrence of disproportionations of phosphates at elevated temperatures.*
‡ *New esters.*

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* *The hygroscopic esters, e.g. diphenyl hydrogen phosphate, can be dehydrated by azeotropic removal of water through repeated distillation of its benzene solution.*

† *At this stage some urea separates, if the separation is not complete earlier.*

Preparation of Diethyl Phenyl Phosphate (20) by Using Phenyl Dihydrogen Phosphate

A benzene solution (10 cc.) of monophenyl dihydrogen phosphate (1.75 gm.; 0.01 mole) and N,N′-di-*p*-tolyl-O-ethyl pseudourea ether (2.7 gm.; *ca.* 0.01 mole) was refluxed for two and one-half hours. The reaction mixture after being allowed to stand at room temperature for one hour was filtered and the urea (2 gm.) washed twice with benzene. The combined filtrate and washings were extracted thrice with sodium hydrogen carbonate solution (more urea separated at this stage) and then dried over anhydrous sodium sulphate. Phenyl diethyl phosphate obtained as a light colored oil was dissolved in petroleum ether (b.p. 30°–60°) and the solution on standing deposited traces of di-*p*-tolylurea which was removed. The tertiary phosphate was distilled twice, after removal of the solvent, at 2 mm. (air bath temp. 100°). Found: C, 52.3; H, 6.8; $C_{10}H_{15}O_4P$ requires C, 52.2; H, 6.6%. $n^{D}_{25} = 1.4773$.

The sodium hydrogen carbonate extracts obtained above were evaporated to a small volume, acidified with concentrated hydrochloric acid, and extracted thrice with ether. The ethereal solution was dried over sodium sulphate and evaporated. The residue which partly solidified was freed from last traces of water azeotropically by distillation of its chloroform solution. It was crystallized from a mixture of chloroform and petroleum ether. Yield 0.68 gm., m.p. 95°–97°; no depression on admixture with authentic monophenyl dihydrogen phosphate.

ACKNOWLEDGMENT

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17-HYDROXYLUPANINE AND 17-OXYLUPANINE[1]

BY O. E. EDWARDS, F. H. CLARKE,[2]
AND BRYCE DOUGLAS[3]

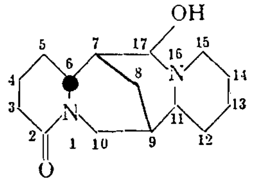
ABSTRACT

Silver oxide has been shown to oxidize lupanine to 17-hydroxylupanine. This base gives an anhydronium perchlorate identical with the "dehydrolupanine (NBS)" perchlorate of Marion and Leonard. 17-Oxylupanine is described, and, from the observation that it can be reduced catalytically to oxysparteine, the stereochemistry of aphylline and oxysparteine is deduced. The basic strength of tertiary carbinolamines is discussed.

Silver oxide has been observed to oxidize lycoctonine to hydroxylycoctonine (5, 8) and to dehydrogenate nicotine to nicotyrine (2). In an examination of the scope of the reaction of silver oxide with tertiary amines, we have now studied the action of the reagent on several lupine alkaloids.

Oxysparteine proved to be inert to silver oxide even at 90° in aqueous methanol. Sparteine was almost unattacked at room temperature but was oxidized at 60° giving products which have not been characterized. Lupanine is unaffected by the reagent at room temperature but is oxidized above 60° in aqueous methanol. From the mixture of products obtained in this reaction, a basic product was isolated as its perchlorate. This analyzed for $C_{15}H_{22}N_2O.HClO_4$ and proved identical (mixed melting point and comparison of infrared spectra) with the "dehydrolupanine (NBS)" perchlorate of Marion and Leonard (6). These workers treated lupanine with N-bromosuccinimide and obtained the above perchlorate in high yield from the product.

We have confirmed their observation that the new base is reduced to lupanine in the presence of platinum (Adams') in acetic acid solution. Since this reduction gave no change of configuration, Marion and Leonard concluded that the hydrogen on carbon 11 was not involved. On the assumption that N-bromosuccinimide introduced unsaturation α-β to the basic nitrogen, these authors suggested tentatively that their product was 14-dehydrolupanine. However, we have now been able to prove decisively that the new base is 17-hydroxylupanine.[4]



17-Hydroxylupanine

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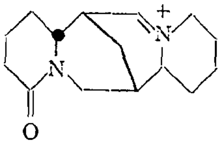
[4] *The authors are indebted to Dr. H. J. Vipond who first suggested this possibility in the course of discussion.*

The infrared spectrum (carbon disulphide solution) of the new base contained a hydroxyl band at 3380 cm.$^{-1}$ which was absent in the spectrum of lupanine in the same solvent. (Liquid films of this base and lupanine both showed bands near 3400 cm.$^{-1}$ and this confused the interpretation for a time.) An active hydrogen determination (Zerewitinoff) confirmed the presence of one hydroxyl group. Reduction of the base with sodium borohydride gave lupanine in high yield, which is consistent with the carbinolamine structure.

When the new base was oxidized with permanganate in acetone a neutral oxylupanine, $C_{15}H_{20}N_2O_2$, was obtained. Clemo and Leitch (3) described the oxidation of *dl*-lupanine to *dl*-oxylupanine. When this oxidation was repeated with *d*-lupanine an oxylupanine was obtained which was identical with that from the new base. Alkaline ferricyanide oxidation of lupanine also gave the same product.

Hydrogenation of this oxylupanine in 2 *N* hydrochloric acid with platinum catalyst (Adams') gave oxysparteine, identical with the product from ferricyanide oxidation of *l*-sparteine. These observations clearly locate the second lactam carbonyl in the above oxylupanine at position 17, and hence show the hydroxyl in the new base to be on that carbon atom.

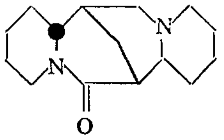
The perchlorate and picrate of 17-hydroxylupanine analyze for anhydro salts. The infrared spectrum of the perchlorate has a band at 1682 cm.$^{-1}$ which can be assigned to a $>C=\overset{+}{N}<$ group (9, 10). The pK's of lupanine and 17-hydroxylupanine in 50% aqueous methanol were found to be 8.4 and 10.5 respectively. This difference parallels the findings of Adams and Mahan (1) who showed that tertiary vinylamines which can form salts of quaternary ammonium character are stronger bases than the corresponding saturated amines. Thus the salts of 17-hydroxylupanine have the anhydronium salt form:

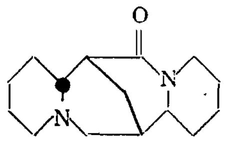


The carbinolamines hydrastinine and cotarnine form similar anhydronium salts. The former has a pK of 11, and the latter has been reported to be a strong base (4). However, pseudostrychnine, a carbinolamine which cannot give an anhydro salt (bridgehead double bond), is a weak base (7).

It appears that silver oxide can convert tertiary amines to the corresponding carbinolamines which in some cases can dehydrate to the vinylamine. The yield in the oxidation of lupanine with silver oxide was low when air was excluded, but in one run with exposure to air a high yield was obtained. It is possible that a silver catalyzed air oxidation was superimposed on the direct action of the reagent. N-Bromosuccinimide probably gives 17-bromolupanine which is later hydrolyzed to the carbinolamine.

Since the steric relation between lupanine and sparteine has been established (6), the preparation of oxysparteine from 17-oxylupanine is clear proof of the stereochemistry of the former. Thus aphylline and oxysparteine are:


Aphylline


Oxysparteine

The ultraviolet absorption spectrum of 17-hydroxylupanine perchlorate (Fig. 1) is noteworthy. The normal hypsochromic shift in going from an aliphatic amine to its salt is reversed. This strong absorption above 250 mμ must be due to the $>\mathrm{C} = \overset{+}{\mathrm{N}}<$ group. The intense end absorption due to the lactam function is illustrated in Fig. 2.

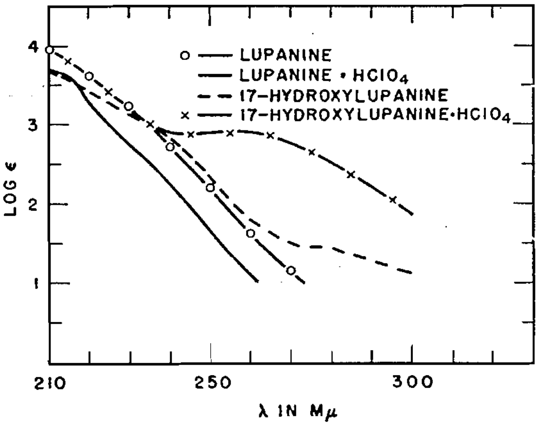


Fig. 1

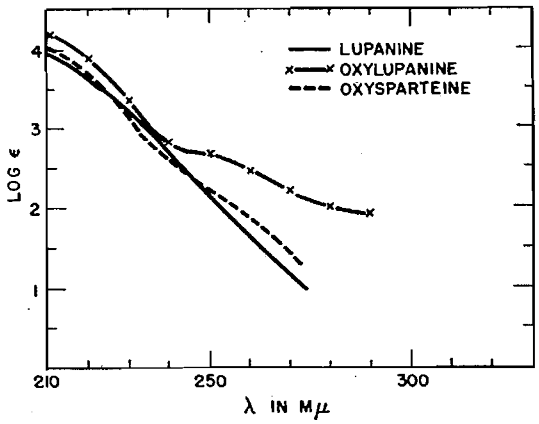


Fig. 2

EXPERIMENTAL

Melting points are corrected to ±1° C. The infrared spectra were determined on a Perkin-Elmer double beam model 21 instrument. They are reported by citing the position of the main peaks in cm.$^{-1}$ followed by percentage absorption, in parentheses. The ultraviolet spectra were determined on solutions in 95% ethanol using a Beckman D.U. spectrophotometer.

d-Lupanine Perchlorate

d-Lupanine perchlorate isolated in these laboratories from *Lupinus polyphyllus* L. and crystallized from methanol had m.p. 214–215° (immersed at 180°). $[\alpha]_D^{25} = +46.8 \pm 0.5°$ (*c*, 2.29 in water).

The pK of lupanine was found to be 8.4 (pH at half-titration) by titration of the perchlorate in 50% aqueous methanol. Calc. for $C_{15}H_{24}NO_2.HClO_4$: C, 51.61; H, 7.16; N, 8.02. Found: C, 51.54; H, 7.36; N, 7.84%. Infrared spectrum (nujol mull): 3500(31), 3240(42), 2680(35), 1617(91), 1455(77), 1425(68), 1377(31), 1346(44), 1334(38), 1314(51), 1281(31), 1250(52), 1225(20), 1192(25), 1170(68), 1100(98), 967(33), 929(25), 856(19), 820(11), 785(14), 725(15), 655(21), 607(24).

d-Lupanine

d-Lupanine base was obtained by treatment of *d*-lupanine perchlorate with aqueous sodium hydroxide, extraction with methylene chloride, removal of solvent after drying (sodium sulphate), and distillation of the oil at 117–120° at 0.3 mm. Infrared spectrum (3 mgm./ml. in carbon disulphide, 1 mm. cell): 2930(64), 2840(36), 1644(77), 1359(32), 1345(38), 1335(48), 1309(37), 1279(40), 1250(38), 1185(23), 1165(40), 1137(38), 1119(42), 1099(26), 1071(21), 1025(18), 1013(17), 965(12), 916(14), 842(11), 785(16).

17-Hydroxylupanine

Lupanine (1.614 gm.) dissolved in 50% aqueous methanol (40 cc.) was stirred for six hours at 60–70° with freshly prepared silver oxide (8.8 gm. dry weight) in a nearly closed system. Metallic silver was formed slowly. The solids were removed by filtration and washed thoroughly with hot methanol. The combined filtrate and washings were concentrated to remove solvent, made alkaline with aqueous sodium hydroxide, filtered, and extracted exhaustively with methylene chloride. The methylene chloride solution was extracted with 3 *N* sulphuric acid (twice) and once with water. The acid solution was made alkaline with sodium hydroxide, extracted with methylene chloride, the extract dried (sodium sulphate), and concentrated to yield an oil which was converted to perchlorate in methanol. The warm supernatant methanolic solution was removed from the deposited perchlorate (mainly *d*-lupanine perchlorate) and allowed to crystallize to yield crystals, m.p. 210–220°, which after three crystallizations from methanol had a melting point of 253° dec. (immersed at 210°) (100 mgm.). In other similar experiments yields of up to 15% of the theoretical were obtained. In one experiment in an open system (reflux condenser) a yield of 53% was obtained. Lupanine was nearly inert to air oxidation under similar conditions without a catalyst. A sample of the perchlorate prepared by the method of Marion and Leonard (6) also melted at 253° (dec.). $[\alpha]_D^{27} = -135.6°$ (c, 2.91 in water). Found: C, 51.56; H, 6.81; N, 7.72. Calc. for $C_{15}H_{22}N_2O.HClO_4$: C, 51.94; H, 6.68; N, 8.08%. Infrared spectrum (nujol mull): 1682(33), 1635(86), 1434(55), 1416(53), 1371(40), 1350(35), 1335(36), 1312(41), 1295(22), 1271(57), 1243(34), 1215(22), 1175(48), 1149(36), 1103(90), 1182(90), 1130(29), 1111(26), 975(30), 949(24), 921(27), 907(17), 880(14), 851(12), 830(14), 686(22), 650(20).

17-Hydroxylupanine obtained from pure perchlorate was converted to picrate in methanol, recrystallized from methanol–ether, m.p. 172–174°. Found: C, 53.22, 53.45; H, 5.79, 5.73; N, 14.65. Calc. for $C_{21}H_{25}N_5O_8$: C, 53.05; H, 5.30; N, 14.73%.

The pK of 17-hydroxylupanine was found to be 10.5 (pH at half titration) by titration of the perchlorate in 50% aqueous methanol.

The base liberated from the perchlorate had $[\alpha]_D^{25}$ 38.7 ± 0.5° (c, 3.72 in ethanol).

Active hydrogen (Zerewitinoff). Found: 0.443%. Calc. for one active hydrogen: 0.378%. Infrared spectrum (7.6 mgm./ml. in carbon disulphide, 1 mm. cell): 3540(15), 3380(18), 2930(84), 2850(70), 2050(12), 1643(91), 1346(71), 1329(67), 1310(65), 1292(44), 1280(40), 1255(64), 1203(34), 1175(48), 1165(64), 1128(60), 1119(62), 1090(53), 1078(60), 1047(43), 1034(50), 1018(48), 1001(37), 980(25), 963(39), 910(45), 840(30), 795(28), 685(12), 648(21).

Catalytic Reduction of 17-Hydroxylupanine

17-Hydroxylupanine (65 mgm.) dissolved in absolute ethanol (10 cc.) was treated with hydrogen at atmospheric pressure and room temperature in the presence of Adams' platinum oxide catalyst (50 mgm.). One mole of hydrogen was absorbed. The catalyst was removed by filtration, the solution made acid to Congo red with 70% perchloric acid and allowed to crystallize to give prisms, m.p. 210–211°, which showed no depression on admixture with authentic *d*-lupanine perchlorate. $[\alpha]_D^{27.5} = +46.1$ (c, 1.92 in water). The infrared spectrum, as a liquid film, of the base from the perchlorate was superposable on that of authentic lupanine.

Sodium Borohydride Reduction of 17-Hydroxylupanine

17-Hydroxylupanine perchlorate (30 mgm.) was dissolved in water (4 cc.) and the solution made faintly alkaline with sodium hydroxide. Sodium borohydride (50 mgm.) was added and the solution maintained at room temperature with occasional shaking for one hour. The alkaline solution was extracted exhaustively with methylene chloride, the extract dried (sodium sulphate), concentrated, and the resulting oil converted to perchlorate in methanol.The salt crystallized from methanol as needles (30 mgm.), m.p. 209–210°, which showed no depression on admixture with a specimen of authentic *d*-lupanine perchlorate.

d-Oxylupanine from 17-Hydroxylupanine

17-Hydroxylupanine (107 mgm.) dissolved in acetone (10 cc.), glacial acetic acid (1 cc.), and water (1 cc.) was treated portionwise with pulverized potassium permanganate (40 mgm.) during 40 min. The deposited manganese dioxide was filtered off and washed with acetone. The combined filtrate and washings were concentrated *in vacuo* to remove solvent, dissolved in methylene chloride (10 cc.), washed with dilute hydrochloric acid and water and dried (sodium sulphate). The solvent was removed to yield an oil which immediately crystallized. Sublimation at 170° at 0.4 mm. yielded a colorless crystalline product, m.p. 152–153°. Calc. for $C_{15}H_{22}N_2O_2$: C, 68.67; H, 8.45; N, 10.68. Found: C, 68.58; H, 8.52; N, 10.77%. Infrared spectrum (8.7 mgm./ml. in carbon disulphide, 1 mm. cell): 2940(85), 2860(71), 1640(96), 1348(85), 1330(69), 1320(51), 1308(73), 1275(89), 1260(87), 1231(51), 1185(57), 1173(63), 1163(66), 1150(53), 1136(53), 1124(51), 1098(51), 1082(36), 1040(27), 1020(38), 985(28), 966(33), 916(31), 835(20), 815(21), 771(23), 707(16).

d-Oxylupanine from Lupanine

d-Lupanine (532 mgm.) dissolved in acetone (50 cc.), glacial acetic acid (5 cc.), and water (5 cc.) was treated as described for 17-hydroxylupanine with pulverized potassium permanganate (859 mgm.) during 35 min. The mixture was filtered, the solvent removed *in vacuo*, the oil dissolved in methylene chloride (15 cc.), and extracted with 3 *N* sulphuric acid (two 15 cc. portions) and once with water. The dried (sodium sulphate) methylene chloride solution was concentrated to yield a crystalline solid (319 mgm.) which was sublimed at 168–170° at 0.4 mm. After two recrystallizations from acetone–ether the compound melted at 154°. It showed no depression on admixture with *d*-oxylupanine obtained by oxidation of 17-hydroxylupanine. $[\alpha]_D^{23} = +138.9°$ (*c*, 2.86 in absolute ethanol).

Oxidation of Lupanine with Alkaline Ferricyanide

Lupanine (1.333 gm.) was shaken with potassium ferricyanide (10 gm.) and sodium hydroxide (1.75 gm.) in water (25 cc.) for 40 min. The solution was extracted with three portions of methylene chloride, the extracts washed twice with 3 *N* sulphuric acid and with water, dried (sodium sulphate), and concentrated to yield an oil (300 mgm.) which partially crystallized. This product was crystallized twice from boiling petroleum ether (b.p. 30–60°) to yield colorless needles, m.p. 150–151°, which showed no depression on admixture with specimens of oxylupanine prepared from lupanine or 17-hydroxylupanine.

The infrared spectrum in carbon disulphide was superposable with the corresponding spectrum of the oxylupanine prepared from lupanine or 17-hydroxylupanine.

Catalytic Reduction of Oxylupanine

Oxylupanine (200 mgm.) dissolved in 2 *N* hydrochloric acid (15 cc.) was treated with hydrogen at 26° and atmospheric pressure in the presence of platinum catalyst (200 mgm.) for 24 hr. The catalyst was removed by filtration and the filtrate extracted with methylene chloride. The acidic solution was made alkaline, extracted exhaustively with methylene chloride, dried (sodium sulphate), and concentrated to yield a crystalline product, m.p. 83–85°. After recrystallization from petroleum ether (b.p. 30–60°) it melted at 86°.

This showed no depression on admixture with authentic oxysparteine. The infrared spectra in carbon disulphide of the two specimens were superposable (10 mgm./ml. in carbon disulphide; 1 mm. cell): 2930(91), 2860(78), 2760(69), 1640(92), 1363(82), 1355(73), 1335(63), 1315(74), 1298(57), 1286(54), 1274(88), 1260(87), 1247(50), 1233(45), 1192(71), 1185(62), 1166(56), 1150(71), 1136(69), 1120(76), 1108(59), 1086(55), 1061(43), 1026(37), 1115(48), 985(18), 965(35), 932(20), 905(16), 842(25), 805(14), 769(22), 749(45), 690(15).

Hydrastinine

The pK of hydrastinine was found to be 11 by titration of the chloride with sodium hydroxide in 50% aqueous methanol.

ACKNOWLEDGMENT

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SYNTHESIS AND INFRARED SPECTRA OF GUANYLUREAS[1]

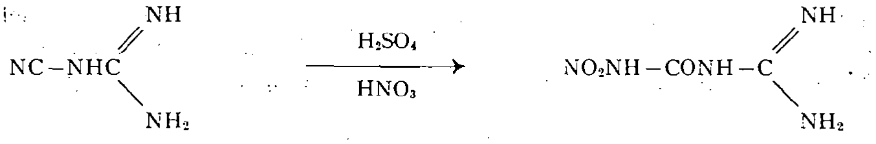
By Paul A. Boivin, W. Bridgeo,[2] and Jean L. Boivin

ABSTRACT

When 1-amidino-3-nitrourea is reacted in aqueous solutions of amines, nitrous oxide and carbon dioxide are eliminated and guanylureas are formed, together with disubstituted ureas as by-products. The infrared absorption spectra of some disubstituted ureas and nitrates of guanylureas are discussed with tentative assignment of bands to some groups.

INTRODUCTION

1-Amidino-3-nitrourea (II) is prepared in good yield by nitration of dicyandiamide (I) in mixed nitric–sulphuric acid:

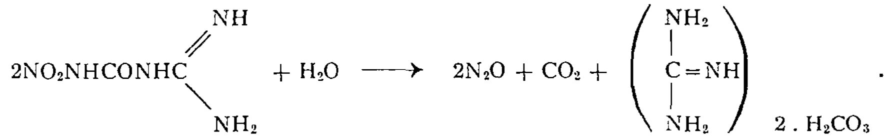


(I) (II)

According to its configuration, it is a mixed derivative of nitrourea and guanidine. As a nitrourea derivative, it is not expected to be a stable compound in aqueous solution. Davis and Blanchard (5) have shown that nitrourea decomposed into nitrous oxide, carbon dioxide, and water.

The rate of decomposition is increased by alkaline catalysts such as amines. The isocyanic acid formed in the decomposition of nitrourea reacts with amines to yield substituted ureas. Moreover the substituted ureas (6) are transformed in aqueous solution into either a primary amine and isocyanic acid or an isocyanate and ammonia.

The decomposition of 1-amidino-3-nitrourea in aqueous solution is known to yield guanidine carbonate, nitrous oxide, and carbon dioxide according to the following equation:



Since nitrous oxide is formed, this gas might come from the decomposition of nitramide which should be present at some stage of the decomposition. 1-Amidino-3-nitrourea could therefore decompose as suggested by T. L. Davis for nitrourea according to the following equation:

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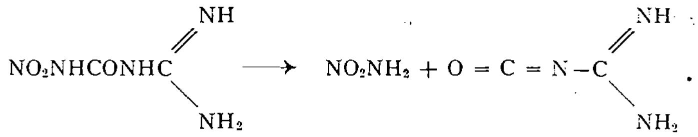
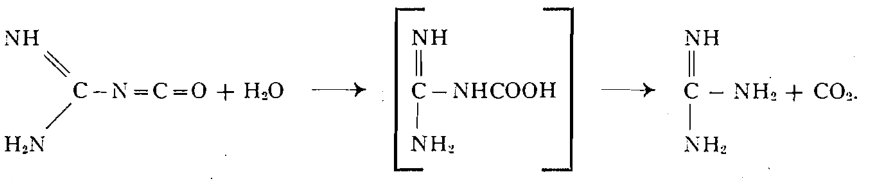
Contribution from the Department of Chemistry of the University of Ottawa, and the Organic Section of Canadian Armament Research and Development Establishment, Valcartier, Que.

[2] *Graduate Student.*



$$\mathrm{NO_2NHCONHC({=}NH)NH_2} \longrightarrow \mathrm{NO_2NH_2} + \mathrm{O = C = N{-}C({=}NH)NH_2}$$

This implies the formation of nitramide and guanylisocyanate (7). Nitramide decomposes in the normal way into water and nitrous oxide, and guanylisocyanate like alkyl isocyanate according to the following equation:

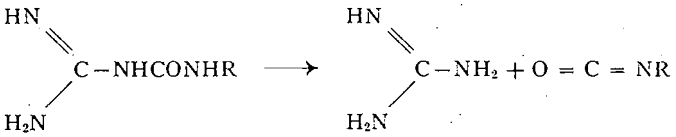


$$\mathrm{HN{=}C(H_2N){-}N{=}C{=}O} + \mathrm{H_2O} \longrightarrow \left[\mathrm{HN{=}C(NH_2){-}NHCOOH}\right] \longrightarrow \mathrm{HN{=}C(NH_2){-}NH_2} + \mathrm{CO_2}.$$

Thus the intermediate formed, guanylcarbamic acid, will decarboxylate rapidly into guanidine and carbon dioxide.

Since guanylisocyanate cannot be isolated, its presence is shown, however, by its reaction with amines. When aniline was boiled with 1-amidino-3-nitrourea in the presence of water, N-phenyl-N′-guanylurea was formed together with diphenylurea as by-product (8).

The formation of diphenylurea indicates a further transformation of N-substituted-N′-guanylurea which can decompose like N-substituted ureas (6). Therefore the guanylurea formed can react with another mole of amine to yield disubstituted ureas according to the following equations:



$$\mathrm{HN{=}C(H_2N){-}NHCONHR} \longrightarrow \mathrm{HN{=}C(H_2N){-}NH_2} + \mathrm{O = C = NR}$$

$$\mathrm{O = C = NR + RNH_2} \longrightarrow \mathrm{RNHCONHR}.$$

Several N,N′-disubstituted ureas were prepared from 1-amidino-3-nitrourea as a by-product of the synthesis of guanylureas. They are shown in Table I.

TABLE I
N,N′-DISUBSTITUTED UREAS

N,N′-Substituents	M.p., °C.	Ref.
Phenyl	241–242	(4)
Benzyl	170	(10)
o-Tolyl	252	(2)
p-Tolyl	267–268	(1)
p-Bromophenyl	292–293 decomp.	(3)
p-Anisyl	237–239	(9)

In all cases disubstituted ureas were obtained. N-substituted-N′-guanylureas were prepared by refluxing 1-amidino-3-nitrourea with amines in aqueous solution. After removing insoluble disubstituted ureas, nitric acid was added and a solid came out which was the nitrate of N-substituted-N′-guanylureas. They are listed in Table II. All their salts are slightly soluble, the nitrate being most insoluble. Qualitative measurements showed that their sulphate and hydrochloride were also slightly soluble. The nitrate of N-phenyl-N′-guanylurea is as insoluble as nitron nitrate, but is not suitable for the estimation of nitrate.

TABLE II
NITRATES OF N-SUBSTITUTED-N′-GUANYLUREA

N-Substituent	M.p., °C.	Analysis % HNO_3	
		Found	Calc.
Propyl	160–162	30.1	30.4
Amyl	142–143	26.9	26.8
Hexyl	148–150	25.2	25.3
Isobutyl	168–169	28.2	28.5
Hydroxyethyl	153–155	30.3	30.1
Phenyl*	212–213 decomp.	Ref. (8)	
Benzyl	183–184	24.4	24.7
o-Tolyl	180–181 decomp.	25.0	24.7
p-Tolyl	220 decomp.	24.7	24.7
p-Bromophenyl	207–209 decomp.	20.0	19.7
p-Anisyl	213–214 decomp.	23.6	23.3
Morpholinyl	124–125	26.9	26.8

**Phenylguanylurea was also isolated as a free base, m.p. 143°–144°C. (8).*

If an excess of amine is used, disubstituted ureas are the main products while guanylureas are formed in low yield. 1-Amidino-3-nitrourea is no more stable in water than nitrourea itself. The fact that it gives off one fourth of its nitrogen in the DuPont Nitrometer also explains its similarity to nitrourea (5).

INFRARED SPECTRA

Since guanylureas are mixed compounds of urea and guanidine it was of interest to determine their infrared spectra in order to correlate them with those of guanidine and urea.

The spectra of these compounds are reported in Tables III and IV. Only the more intense bands are reported as wave numbers (cm^{-1}).

TABLE III
INFRARED SPECTRA OF N,N′-DISUBSTITUTED UREAS

N,N′-Substituents	Band frequencies in $cm.^{-1}$								
Phenyl	695	750	900	1230	1310	1500	1600	1650	3330
Benzyl	695	765	900	1240		1570	1630		3330
o-Tolyl		750	900	1240	1300	1650			3030
p-Tolyl		750	816	1240	1310	1570	1650		3330
p-Bromophenyl		750	820	1240	1560	1630			3310
p-Anisyl		750	825	1240	1570	1630			3330

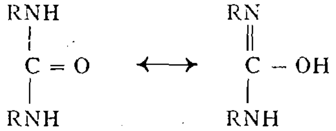
TABLE IV
INFRARED SPECTRA OF N-SUBSTITUTED-N′-GUANYLUREAS

N-Substituent	Band frequencies in cm.$^{-1}$													
Propyl	788	820	890	965	1020	1050	1250	1580	1630	1710	1730	3140	3330		
Amyl	728	820	890	950	1010	1060	1240	1270	1350	1570	1630	1710	3140	3330	
Hexyl	722	821	890	960	1050	1230	1270	1570	1620	1630	1710	3140	3330		
Isobutyl		821	885		1020	1260	1340	1580	1630		1710	1730	3140	3330	
Hydroxyethyl	732	821	880	958	1030	1060	1100	1160	1280	1320	1470	1630	1730	3140	3330
Phenyl (base)	695	752	1240	1300	1320	1440	1520	1600	1620	1640	1710	1730	3360	3500	
Phenyl	821		1580	1670	1780	3220	3480								
Benzyl	695	721	821	1230	1570	1650	1720	3140	3330						
o-Tolyl	748	821	1210	1260	1310	1360	1560	1600	1620	1630	1710	1740	3160	3400	
p-Tolyl	724	818	1210	1220	1510	1560	1620	1630	1700	1730	3180	3250	3330		
p-Bromophenyl	724	734	818	858	1210	1510	1560	1600	1620	1710	1730	3130	3250	3330	
p-Anisyl	724	734	818	860	1030	1240	1510	1570	1620	1710	1730	3130	3250	3330	
Morpholinyl	710	734	740	848	1120	1240	1380	1620	1680	1710	3100	3270	3330		
Guanidine nitrate		844	1580	1670	1780	3130	3380								
Urea nitrate		734	815	1580	1680	1710	3270	3380							

N,N′-Disubstituted Ureas

The infrared spectrum of urea itself is not fully explained. Although urea gives a strong absorption band in the keto region, it has not been possible to establish definitely the vibration frequency of the carbamido group. It was thought that the symmetric disubstituted ureas isolated in the course of this work might be of value to elucidate the spectra of urea type compounds.

They all show a sharp and strong absorption band at 3300 cm.$^{-1}$ which is indicative of OH or NH bands. Since —OH groups in these compounds, which are formed by tautomerization, are not likely to occur, the bands are attributed to unassociated NH groups.



$$\mathrm{RNH{-}C({=}O){-}NHR} \longleftrightarrow \mathrm{RN{=}C({-}OH){-}NHR}$$

In the double bond region, several absorption bands occur. One which is sharp and shows strong absorption is present at 1620–1639 cm.$^{-1}$ and should be due to the amide group. Other bands at 1330–1590 cm.$^{-1}$ indicate the presence of a phenyl ring. It was observed that compounds such as diphenylurea and dibenzylurea show a strong band at 695 cm.$^{-1}$ whereas such a band is absent when the aromatic ring bears a substituent as does N,N′-di-*p*-tolylurea. Also worth mentioning are the bands falling at 750 cm.$^{-1}$ for *o*-phenyl substituted compounds and other bands at 816, 820, and 825 cm.$^{-1}$ which are shown for *p*-phenyl substituted ureas.

Guanylureas

In the case of N-substituted-N′-guanylureas, strong hydrogen stretching vibration bands should be expected in the neighborhood of 3300 cm^{-1}.

Like guanidine and urea nitrates which show NH vibration bands at about 3270 and 3380 cm.$^{-1}$, most guanylureas exhibit two bands at nearly the same frequencies. Absorption bands of higher frequencies are due to NH groups and the band at lower frequencies is probably associated with NH_2 groups which can occur in the guanidine part of the nitrate of guanylurea.

In the double bond absorption region, several bands of different intensities occur which are due either to C = O or C = NH. In the case of nitrates of alkylguanylureas, two strong bands occur, one at 1700–1710 cm.$^{-1}$ and the other at 1620–1630 cm^{-1}. In the disubstituted ureas, the band at 1630–1650 cm.$^{-1}$ has been tentatively attributed to the carbonyl group of urea. On the basis of this observation the carbonyl band of the nitrate of alkylguanylureas would fall in this region whereas with arylguanylureas the band would occur at slightly lower frequencies 1600–1630 cm^{-1}.

Between 1670–1710 cm.$^{-1}$ a strong sharp band occurs with all the nitrates of guanylurea examined; this band would be due to the C = NH group which is shown by guanidine compounds at 1670–1690 cm^{-1}.

The second band in the double bond region showed by guanidine nitrate and urea nitrate is due to the vibration of N = O, which band is present in most nitrates of guanylurea whereas it is absent in the case of N′-phenyl-N′-guanylurea, which is free base. It falls at 1310–1380 cm^{-1}.

A band of good intensity at 800–825 cm.$^{-1}$ is attributed to nitrate ion; such a band is formed by inorganic nitrates such as ammonium nitrate (3).

At 695 cm.$^{-1}$, the phenyl and benzyl derivatives show the band characteristic for monosubstituted benzene ring. Weak bands are obtained at 890 cm.$^{-1}$ with nitrates of alkylguanylurea which are indicative of a hydrocarbon chain on a nitrogen atom; they are absent, however, with aromatic substituents.

In conclusion, it can be said that the infrared absorption spectra of guanylureas and disubstituted ureas are in conformity with their chemical structure although it is difficult to distinguish C = O and C = NH owing to the many resonating structures of the guanidine molecule as an ion.

EXPERIMENTAL

Decomposition of 1-Amidino-3-nitrourea in Water

1-Amidino-3-nitrourea (7.35 gm., 0.05 mole) and water (200 ml.) were boiled under reflux. Gases were evolved,—mainly carbon dioxide and nitrous oxide. The latter was collected over a solution of sodium hydroxide. The volume of gas collected measured 1200 ml. at 30°C. at 755 mm. The theoretical value under identical conditions is 1210 ml. The alkaline solution was titrated with standard acid using phenolphthalein as indicator and 0.0258 mole carbon dioxide was found. The theoretical value is 0.025 mole.

In the aqueous solution, which was mainly guanidine carbonate, there was found 2.5 gm. of guanidine estimated as its picrate. Guanidine was found in 85% yield from 1-amidino-3-nitrourea.

Preparation of the Nitrate of N-Substituted-N′-Guanylureas

1-Amidino-3-nitrourea (0.034 mole) was reacted with amines (0.034 mole) in aqueous solution (50 ml.). The solution was boiled until the evolution of nitrous oxide ceased. Then it was evaporated at 60°C. and filtered. The residues were identified as N,N′-disubstituted ureas. The remaining solutions were acidified with nitric acid and yielded the nitrates of N-substituted-N′-guanylurea which were recrystallized from water. Results are listed in Tables I and II.

With a large excess of amines, only disubstituted ureas were formed, as was the case with aniline, which failed to yield N-phenyl-N′-guanylurea.

Estimation of 1-Amidino-3-nitrourea by Nitrometer

Using standard procedure to determine nitrate in a DuPont Nitrometer, 1-amidino-3-nitrourea gave 9.50% of nitro-nitrogen. Calc. for $C_2H_5O_3N_5$: N, 47.6%. Found N, 47.5%.

Infrared Spectra Measurements

The infrared spectra were taken on a Perkin Elmer Spectrophotometer Model 21R. The instrument recorded the spectrogram automatically. All the samples were shaken in mineral oil into a uniform emulsion and placed between rock salt plates at a suitable thickness in order to obtain a good spectrogram. The bands are tabulated in Table III and IV in wave numbers (cm^{-1}). Only those of good intensity are reported.

ACKNOWLEDGMENTS

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THE ORTHO–PARA CONVERSION OF HYDROGEN AND DEUTERIUM ON INHOMOGENEOUS PARAMAGNETIC SURFACES[1]

By Y. L. Sandler[2]

ABSTRACT

The kinetics of the magnetic ortho–para conversion of hydrogen and deuterium on neodymium oxalate and hemin crystals has been determined over a wide temperature range in a static system. In these cases a similar type of rate curve is obtained: at high and at low temperatures the rate decreases with temperature, while in the intermediate region the rate increases with temperature. The behavior is explained in terms of an energetic surface heterogeneity. In case of neodymium oxalate two distinctly different groups of sites appear to be active having energy barriers to migration of the adsorbed hydrogen at considerably different height. The conversion mechanism of the "trapped" gas is assumed to be similar to the mechanism in liquids where repeated collisions are also assumed to occur.

INTRODUCTION

The ortho–para conversion of hydrogen is catalyzed by molecular inhomogeneous magnetic fields (6,14). This type of conversion has been observed to take place in the presence of paramagnetic gases, ions and molecules in solution (6) and when hydrogen is adsorbed on solids (1,13,7,2). The conversion on paramagnetic solids generally proceeds appreciably faster than on diamagnetic solids (13). In the latter case, when a conversion was found* it has been attributed to "surface paramagnetism" (1).

When the fraction of gas adsorbed is small, generally a negative temperature coefficient (negative "apparent activation energy") of the conversion has been found. This has been explained as due to a decrease in coverage of the solids with temperature; the negative activation energy found was approximately equal to the expected heat of adsorption of hydrogen on these solids (1). However, Eley (2) reported that with hemin the conversion is approximately temperature independent between +185°C. and −80°C. He suggested that the adsorbed hydrogen might require an activation energy for approaching the paramagnetic center, in this case fortuitously equal to the heat of adsorption. On the other hand, L. Farkas and the present author (7) at the same time reported that with neodymium oxalate the conversion appears to have the normal temperature dependence above 0°C., while below this temperature the apparent activation energy becomes strongly positive.

In order to obtain more information on the nature of the activation energies in these two interesting cases it seemed desirable to investigate the kinetics of the conversion on hemin and neodymium oxalate more thoroughly than has been done heretofore.

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Contribution from Division of Pure Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 3167.

[2] *Present address: Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Mass.*

**No cases are considered here in which the solid may also be partly chemically active.*

EXPERIMENTAL

Hemin was prepared by the same method as used by Eley (2). The surface area was about 0.2 sq. meter/gm., determined by microscopic measurement. One gram of substance was used, leaving a gas volume of 2.43 cc. in the reaction vessel. The crystals were outgassed at 200°C. for three hours. Neodymium oxalate hydrate "Nd I" was prepared from the same stock of nitrate and in the same manner as the material used in the previous paper (7), however the crystals were not fractionated to produce a uniform size. A spectrographic analysis in the region between 3800 Å and 5000 Å showed no impurities beyond 0.3% praseodymium. Neodymium oxalate hydrate "Nd II" was prepared from a pure sample of the oxide, kindly supplied by Mr. D. S. Russel. His method of purification has been described elsewhere (10). The crystals had a surface area of 2.3 sq. meters/gm., determined by the BET method with nitrogen. Three grams were used in the reaction vessel, leaving a gas space of 7.3 cc. The powder was outgassed for three hours at 25°C. Small U-shaped traps of 3 mm. diameter were placed between the reaction vessels and their stopcocks. They were attached closely to the reaction vessels and kept at the same temperature as the vessels; a constant temperature over practically the entire volume is thus assured, and the gas space can be kept small. This system proved entirely satisfactory in the present case although the traps cannot be effective above room temperature.*

The two vessels with hemin and Nd II were kept together in the same temperature bath and the conversion was measured in one vessel while in the other vessel the hydrogen was allowed to equilibrate at the chosen temperature by allowing the gas to remain in contact with the powder for more than seven times the half-life of the powder. Measurements were generally made at a time near the expected half-life τ, and t was evaluated assuming a first order law $u = u_0 \exp[-kt]$, where u is the excess paraconcentration (or orthoconcentration for D_2) over the equilibrium concentration at the time t, and u_0 the excess concentration at $t = 0$. In all cases the admitted gas was 68% parahydrogen or 83% orthodeuterium. The analysis of the ortho-para compositions was carried out by the Farkas micromethod (3). The points on the half-life versus temperature curves were measured in random sequence and each point was determined at least twice. The activity of the powders remained constant to within the error of measurement throughout the period of measurement. The points were reproducible to within about 4% for H_2 and about 6% for D_2.

All rates were measured at a pressure of 20 mm. Hg, except where stated otherwise.

RESULTS

In Fig. 1 the results for hemin with H_2 and D_2 are given. The measured half-lives at 20 mm. pressure are plotted against temperature, for 1 gm. of substance and a gas volume of 2.43 cc., in the temperature range between

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**Neodymium oxide, catalyzing also the $H_2 + D_2$ reaction, became rapidly poisoned under the same conditions. This can be considered additional evidence that no chemical process is involved in the present cases.*

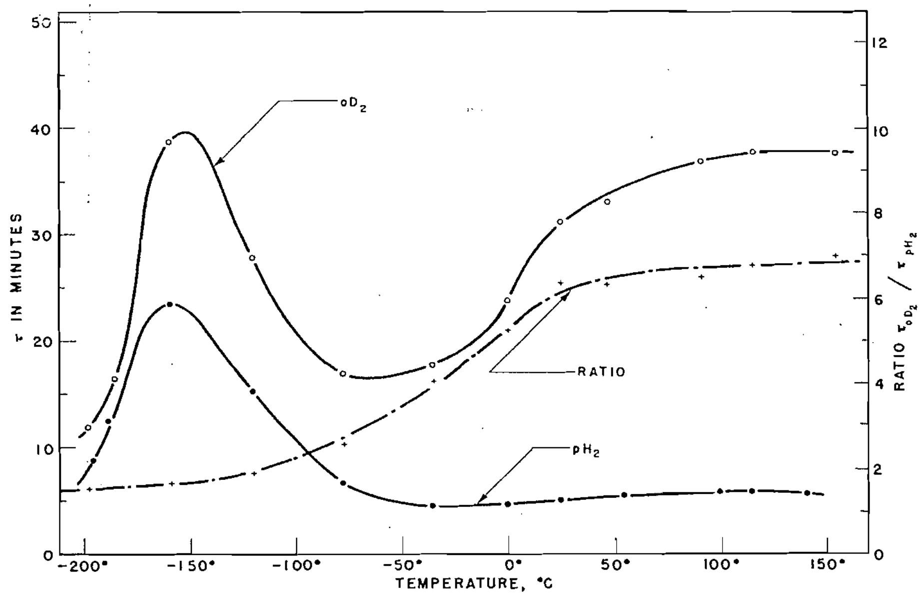

FIG. 1. Observed half-lives τ for hemin at 20 mm. pressure with H_2 and D_2, and ratio τ_{D_2}/τ_{H_2}.

+150°C. and −195°C. It is seen that the rate of the H_2 conversion changes very little with temperature in the high temperature region within a range of 200°, in good agreement with Eley's findings (2); also the absolute rates are practically the same.* The half-life is seen to increase only little between −35°C. and +100°C. while the corresponding increase for deuterium is considerably larger.

We shall express our results in terms of a constant weight of catalyst and a total number of gas molecules N independent of temperature. We define a half-life τ_N as the half-life for 1 gm. of catalyst and a quantity of gas equal to the amount present in 1 cc. at 0°C. at the chosen pressure (1.18×10^{-6} mole at 20 mm.).

For evaluating τ_N it was assumed here that the amount of gas adsorbed N_S is small compared with the total amount of gas N, so that $N = N_{gas}$. Thus

$$\tau_N = \tau\,(W/V)\,(T/273), \tag{1}$$

and the rate constant $k_N = \ln 2/\tau_N$, where V is the gas volume in cc., W the weight of catalyst in grams, and T the absolute temperature. This seems justified except perhaps for the lowest temperatures; the calculated values of τ_N in this region may be a little too high.

In Fig. 2 the logarithm of τ_N is plotted against $1/T$ for hemin. The curves for H_2 and D_2 are of similar shape. The apparent activation energy is negative

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On a basis of equal surface area and gas volume the found half-lives agree within a factor 2. The microscopic estimates of the surface area of the needle shaped crystals necessarily are rather unreliable. For equal weights and volumes we find, in both cases, τ = 2 min. gm./cc.

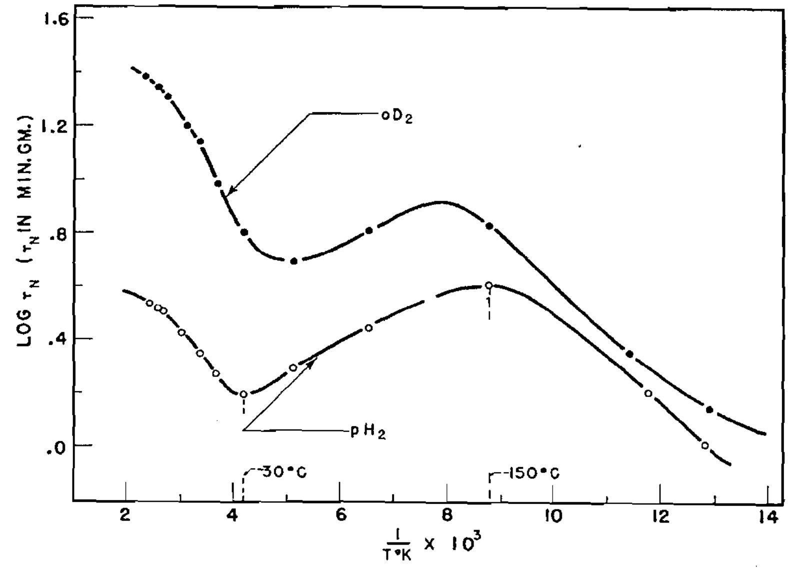

FIG. 2. Plots of log τ_N against $1/T$ for hemin.

in the high temperature and in the low temperature region, but positive in the intermediate region. The high degree of constancy of the conversion rate at high temperatures in Fig. 1 is thus fortuitous; but the change of the rate over the entire temperature range is still relatively small.

Fig. 3 gives the results with the new sample of neodymium oxalate Nd II; here the half-lives τ_N for D_2 are plotted on a 10 times smaller scale. For comparison, in Fig. 4, the previous results (7) with neodymium oxalate are reproduced for H_2 (drawn out curve), and the curve of 1/10 τ for D_2 has been constructed from the ratios τ_{D_2}/τ_{H_2} previously given. The curves in Figs. 3 and 4 appear to show a completely different behavior. However measurements made at 25°, −80°, and −183°C. with two samples of Nd I, produced from the same starting material as the crystals used in the previous investigation, showed that the previously implicit assumption that τ continues to increase with the decreasing temperature was unjustified. The approximate shape of the conversion curve at low temperatures is indicated by the dotted line in Fig. 4. On comparing Figs. 3 and 4 at high temperatures, it is evident, especially from the rising ratio curve in Fig. 3, that also for Nd II the half-life would increase again at high temperatures. The measurements could not be extended here above 50°C. owing to rapidly changing activity of the catalyst above this temperature.

Summing up, we see that the general shape of the neodymium oxalate curves appears to be similar, though differing in detail. With all three materials investigated here, including hemin, we find a similar type of temperature dependence: at high and at low temperatures the apparent activation energy is negative, while in the intermediate temperature region it is positive.

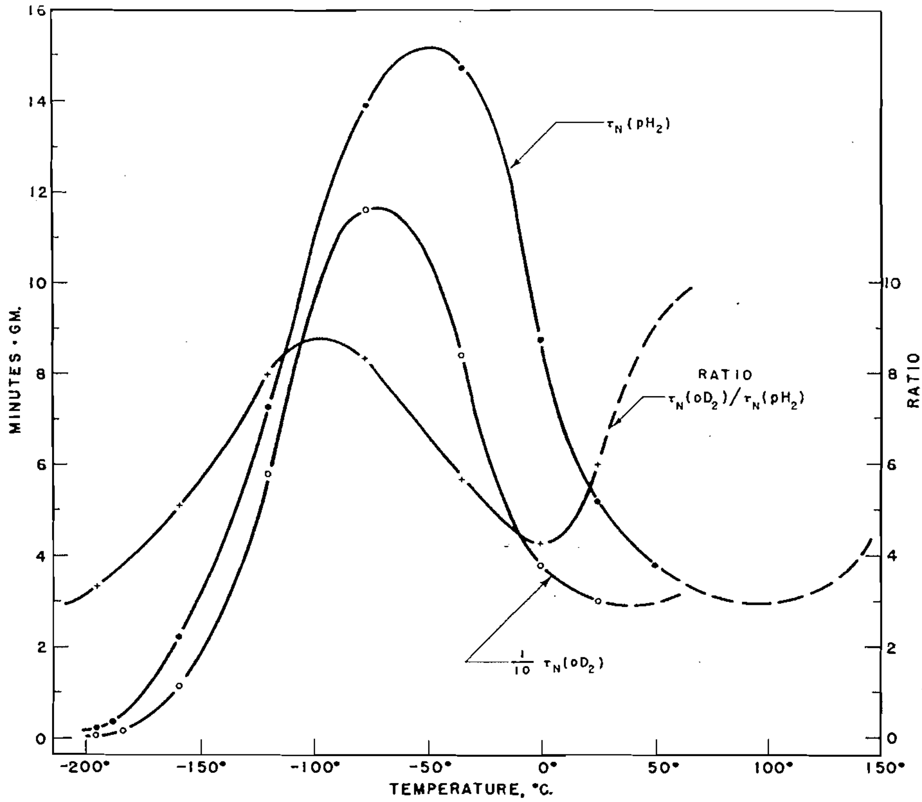

FIG. 3. Temperature dependence at 20 mm. for Nd II:—τ_N with H_2, 1/10 τ_N with D_2 and ratio τ_{D_2}/τ_{H_2}.

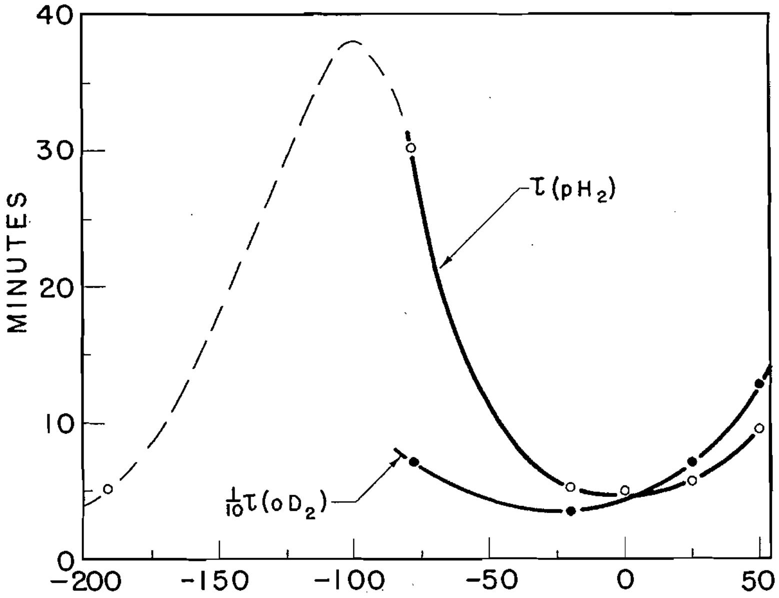

FIG. 4. Temperature variation of observed half lives for Nd I:—τ_{H_2} and 1/10 τ_{D_2}.

In Table I selected values for the apparent activation energy are given, together with the apparent kinetic orders n_k. n_k is defined by the equation (12)

$$n_k = [\partial \log (\text{rate})/\partial \log p]_T. \qquad [2]$$

TABLE I

APPARENT ACTIVATION ENERGIES E AND REACTION ORDERS n_k

Catalyst	Temperature, °C.	Gas	$E_{\text{cal.}}$ (const. N)	n_k
Hemin	+ 50	H_2	−1000	1.00
	+ 50	D_2	−1200	
	−120	H_2,D_2	+ 500	
	−188	H_2,D_2	− 800	
	−188	H_2		0.64
	−195	D_2		0.52
Nd II	0	H_2	+3600	1.0
	− 35	D_2	+3100	
	− 80 to −195	H_2	−1050	
	− 80 to −195	D_2	−1300	
	−188	H_2		0.6
	−195	D_2		0.6
Nd I	0 to + 50	H_2	−3000	1.00
	+ 50	H_2	−5300	
	+ 50	D_2	−5900	
	− 80			0.95

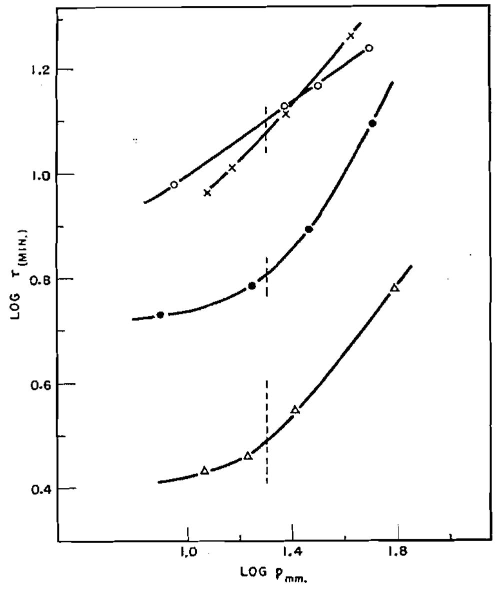

FIG. 5. Plots of log τ against log p:
× Hemin, −195.5°C. with D_2
○ Hemin, −188°C. with H_2
● Nd II, −195.5°C. with D_2
△ Nd II, −188°C. with H_2.
The vertical dotted line indicates a pressure of 20 mm.

As the adsorbed fraction N_S/N has been assumed to be small, n_k can be calculated from the equation

$$[3] \qquad n_k = 1 - [\partial \log \tau / \partial \log p]_T.$$

In the high temperature regions the conversion was found completely pressure independent between 3 mm. and 50 mm. pressure, therefore $n_k = 1$. The order rapidly decreases on the low temperature branches with decreasing temperature. In Fig. 5 a few examples of the change of log τ with log p at low temperatures are given. The vertical dotted line indicates the pressure of 20 mm.

The high ratio τ_{D_2}/τ_{H_2} found at high temperatures indicates that no chemical reaction is involved in the observed conversions. Nd II was contacted with $H_2 + D_2$ at -37°C. (in the region of positive apparent activation energy) for a period equal to six half-lives of the parahydrogen conversion. Analysis by mass spectrograph showed that no HD was formed in the mixture within 1% (cf. also (2)).

DISCUSSION

In the present paper the rate data have been reduced to a constant number of molecules in the reaction vessel. The observed activation energy is then strictly related (12) to the activation energy of the surface reaction E^s at constant coverage ("true" activation energy) by the equation

$$[4] \qquad E = E^s - n_k Q,$$

where n_k is the apparent reaction order (equation 2) as determined in the present experiments and Q is the isosteric heat of adsorption.

A number of cases have been reported in which, when the fraction of gas adsorbed was small, the observed conversion rate decreased uniformly with temperature over a wide range (4,2). The values of $-E$ in these cases lie approximately between 500 and 2500 cal. and agree with the order of magnitude of the heat of adsorption of hydrogen on these solids. This has generally been assumed to mean that the rate of the surface reaction does not vary considerably with temperature ($E^s \approx 0$).

As the isosteric heat Q should be positive, the positive apparent activation energy E, found in the present experiments in the intermediate temperature region, proves the existence of a strong temperature dependence of the surface reaction. From equation 4 we see that E^s in this region must be greater than n_kQ. For H_2 in the case of Nd II at 0°C. we find $E^s = 3600 + n_kQ$ cal.; in case of hemin at -120°C., $E^s = 500 + n_kQ$ with n_k near to 1, and Q probably between 500 and 2500 cal.

This rapidly changing conversion rate in the intermediate temperature range might be explained as due to some resonance acting in this region and thus increasing the ortho–para transition probability. In view of the similarity of the curves found for H_2 and D_2, however, this possibility is practically excluded. A possible existence of a physical transition in the solid in this region would not appear to provide a satisfactory explanation, because such changes would be expected to take place in a much narrower temperature interval.

Neodymium Oxalate

In the previous communication (7) we assumed that the temperature dependence found with Nd I at high temperatures (Fig. 4) is of the "normal" type, i.e., the change of the observed rate is essentially due to a change of coverage and E^s is small. The sharp decrease of the rate on lowering the temperature (positive E) was suggested to indicate that another process becomes rate determining in this region. This also seemed clearly indicated by the sharp decrease of the ratio τ_{D_2}/τ_{H_2}. At temperatures above 0°C. this ratio is above 10, the value found for the conversions in presence of paramagnetic gases (5,9). No process other than the magnetic conversion is so far known that would lead to such high ratios in this temperature region. But at −78°C. the ratio is only two. A similar decline to a value 4 at 0°C. was found in the present experiments with Nd II in the intermediate temperature region.

It was originally suggested (7) that the desorption of the gas from the surface becomes rate determining in the region of positive E. The fact now found that the rate increases again when further lowering of the temperature, seems to contradict this explanation. This apparent contradiction can be removed by assuming the existence of two distinctly different sets of paramagnetic sites. The conversion due to one set predominates at high temperatures. In the intermediate temperature region then desorption from these sites becomes slow. This will occur when the mean adsorption life of a hydrogen molecule on these sites becomes greater than its mean conversion life. In the low temperature region the conversion is solely due to the second set of sites and the temperature dependence of the observed rate again shows the "normal" slope. Desorption from the first set of sites in this region has become so slow that the conversion due to these sites no longer masks the conversion due to the second set of sites. In this region also the ratio τ_{D_2}/τ_{H_2} again assumes high values, characteristic of the magnetic conversion (as further discussed below).

If we would assume that the paramagnetic ions are all freely approachable, a simple numerical estimate shows (2) that desorption from the surface could not become rate determining anywhere in the measured temperature interval, because the mean contact time with the surface would be roughly 10^{10} times smaller than the mean conversion life of a molecule. This difficulty can be resolved by assuming that the paramagnetic centers active in the high temperature region are not freely approachable, but a high energy barrier may have to be overcome by a hydrogen molecule to reach these centers and similarly also to leave them. The presence of such barriers does not necessarily slow down the reaction. The decreased chance of a molecule of reaching a paramagnetic site will be counteracted by an increased conversion probability due to a longer time of sojourn near a paramagnetic center. Each "collision" with these centers within the narrow cage will cause an ortho–para transition with a certain probability γ. Probably the value of γ for the trapped molecule is not of a very different order of magnitude than the γ for paramagnetic gases (10^{-12} to 10^{-13}). Thus the conversion rate may be of a similar order of magnitude as in case of a freely approachable ion. This seems to be the reason why previous estimates based on a free collision mechanism appeared to lead to reasonable results. The "cage mechanism" proposed here is somewhat similar to the conversion mechanism in liquids where repeated collisions are also assumed to occur (11). The rates found in paramagnetic solutions are nearly equal to those found with paramagnetic gases (8).

In a more quantitative manner, the state of affairs can be described as follows:

The observed rate for a nonuniform surface can be written as,

[5] $$\text{rate } r = k\,N = \sum k_i\,N_i,$$

where N is the total number of hydrogen molecules in the reaction vessel and N_i is the number adsorbed on sites of type i. In case of neodymium oxalate we have essentially two types of site, "1" and "2", 1 referring to the sites active at high temperatures. In the high temperature region $N_2\,k_2$ is 10^2 to 10^3 times smaller than $N_1\,k_1$, as found by extrapolating the low temperature branch of the rate curves to high temperatures.

As long as the magnetic conversion itself completely determines the observed rate, each k_i is given by,

[6] $$k_i(\text{conversion}) = C_i\,\gamma_i \approx \nu_i\,\gamma_i,$$

where C_i is the number of coordinations per unit time with a paramagnetic center for a hydrogen molecule trapped near this center. It is of the same order as the vibration frequency ν_i of the hydrogen molecule in the trap. γ_i is the conversion probability at each such coordination. Then k_i (conversion) $\approx 10^{13} \times 10^{-12} = 10 \text{ sec}^{-1}$.*

Equation 6 is only valid as long as the rate constants for desorption from any site i are large compared with the corresponding conversion rate constants. The desorption rate constants are roughly given by,

[7] $$k_i\,(\text{desorption}) \approx \nu_i \exp\,[-E_i/RT],$$

where E_i is the energy barrier to desorption from site i. Thus with decreasing temperature, when $k_1\,N_1$ (desorption) becomes of the same order as $k_1\,N_1$ (conversion), a change in sign of the observed activation energy will be found. For Nd I (Fig. 4) this occurs at 273°K. From equations 6 and 7 we find that in this temperature region $\gamma_1\,\nu_1 \approx \nu_1 \exp\,[-E_1/RT]$, giving $E_1 = 16$ kcal./mole as the approximate barrier to desorption from the high temperature sites.

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* *Note to be added in proof: For a two-dimensional gas the rate r can be estimated from the equation* $r = (v/d)\,\gamma N_s$; *here v is the velocity of the adsorbed molecules, d is their mean path between the paramagnetic sites, and* N_s *is the* total *number of adsorbed hydrogen molecules. Then* $r \approx (10^5/10^{-7})\;10^{-12}\;N_s$. *This gives an order of magnitude for the "true" rate constant* k_s $(= r/N_s)$ *of 1 sec.*$^{-1}$. *For a synthetic paramagnetic surface composed of oxygen molecules adsorbed on a diamagnetic surface, the value* $d = 10^{-7}$ *cm. chosen for the Nd surface would correspond to about* 2×10^{14} *oxygen molecules per cm.*^{2} *surface. For this concentration one actually finds a* k_s *of about 0.5 sec.*$^{-1}$ *(cf. Sandler, Y. L. J. Phys. Chem. 58: 56. 1954).*

We tentatively assume that the model of a completely localized hydrogen (as assumed above for the estimate of k_i*) and of a completely mobile hydrogen would lead to the same order of magnitude for the conversion rate. The relation* $r = \Sigma k_i N_i = k_s N_s$ *then leads to a fraction adsorbed on the paramagnetic sites* $\Sigma N_i/N_s \approx \Sigma 10^{-1}$. *This appears to be a reasonable order of magnitude which unfortunately cannot be checked independently.*

This calculated figure seems larger than the maximum true activation energies E^s in the intermediate temperature region. However, apart from the approximations involved in the equations and the uncertainties in the data used, the maximum of E^s found in the intermediate temperature range must be smaller because this region constitutes only a relatively narrow transition range between the high temperature and low temperature regions. Also, both the high temperature and low temperature sites may not be completely uniform, as has been assumed here.

There are thus two distinctly different groups of sites in the case of neodymium oxalate; one group requiring a high activation energy for approach, the other a relatively low, or no activation energy.

In the regions in which the conversion is rate determining, these activation energies of migration in the surface layer are, of course, not to be confused with the "true" activation energy E^s. The latter quantity is derived from the temperature dependence of the "true" rate of the surface reaction (at constant coverage). We have seen that the height of the migration barriers may have little effect on the reaction rate in a region in which the rate is controlled by the repeated collision mechanism.

Hemin

In the case of hemin the existence of a true activation energy E^s again indicates the requirement of an activation energy for approaching and leaving the paramagnetic sites. In this case the change of E^s with temperature is much smaller and a more or less continuous decrease of the ratio τ_{D_2}/τ_{H_2} with decreasing temperature was found. There is therefore no such distinct division into two temperature regions in which two different groups of sites are active as found for Nd. The changing true activation energy can be explained by a more continuous energy distribution of sites and barriers.

It is difficult to decide how far an analogy with the much clearer case of Nd exists. We may, by analogy, assume that desorption increasingly determines the over-all reaction with decreasing temperature. However, in the present case the observed changes of E^s are not large and a certain variation with temperature may always be expected with a heterogeneous surface due to a changing distribution of the gas amongst different types of sites with temperature and coverage.

The H_2/D_2 Ratio

A complete discussion of the behavior of the ratio τ_{D_2}/τ_{H_2} cannot be given owing to the complexity of this problem.

For the conversion in presence of oxygen at 300°K. the ratio is 10, while at 83°K. it is about 5.4 (5). This change can be explained on the basis of the difference in the rotational energy levels and statistical weights of H_2 and D_2. Neglecting factors which on the basis of simple classical considerations would be expected to be approximately equal for H_2 and D_2, the temperature dependence for each isotope will be given by (9),*

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*In formula (6) of ref. 9 the subscripts "even" and "odd" should be exchanged.

$$[8]\ f(T) = \frac{\sum_{\text{all } J} J \exp[-E_J/RT]}{\sum_{\text{para}} (2J+1)\exp[-E_J/RT]} + \frac{I}{I+1} \cdot \frac{\sum_{\text{all } J} J \exp[-E_J/RT]}{\sum_{\text{ortho}} (2J+1)\exp[-E_J/RT]}.$$

(E_J is the energy of the rotational state J, and I is the resultant nuclear angular momentum of H $(=1/2)$ and D $(=1)$. The para states for H_2 are the even states, for D_2 the odd states.)

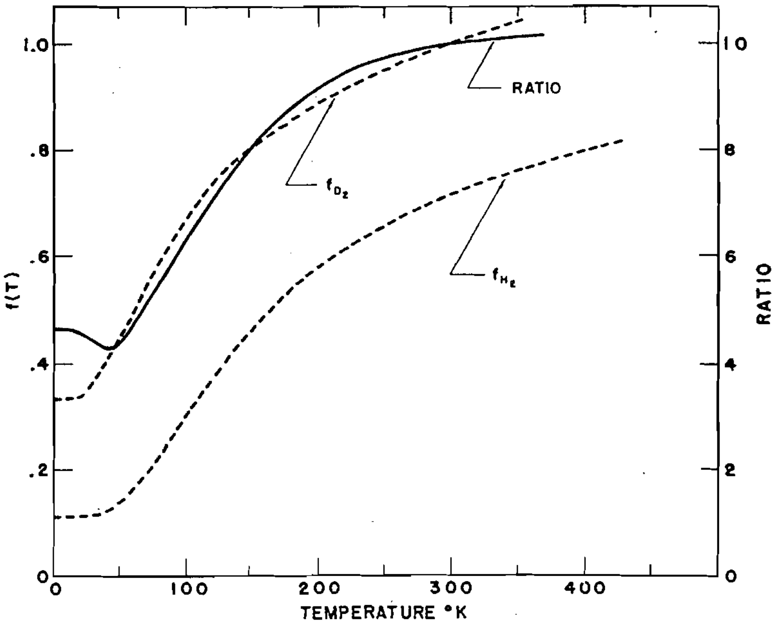

FIG. 6. The function $f(T)$ (equation 8) for H_2 and D_2 (dotted lines) and the ratio f_{H_2}/f_{D_2} normalized to 10 at 300°K. (solid line).

In Fig. 6 the function $f(T)$ is plotted for H_2 and D_2 (dotted curves). Their ratio, normalized to 10 at 300°K., is also given (solid line). At 83°K. we obtain from the curve a ratio 5.65, which is in agreement with the value above for O_2 within experimental accuracy.*

For solid surfaces the state of affairs should be considerably more complicated—owing to the effect of the differences in zero-point energies and energy levels of H_2 and D_2 on a variety of other factors. However, it might be worth while recording a certain trend recognizable in the present measurements, although the detailed explanation for the behavior does not seem to be the same in all cases. It seems that a high positive true activation energy, at least in the present cases, leads to a depression of the H_2/D_2 ratio, while low, or even negative, true activation energies lead to a relatively high ratio. For

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**According to Kalckar and Teller (Proc. Roy. Soc. A, 150: 520. 1935.) a comparison of the rates, as given here, may be objectionable owing to the difference in translational momenta of H_2 and D_2. It is, however, seen that this does not lead to serious errors, at least as far as the change of the ratio below 300°K. is concerned.*

example, for Nd I a highly negative apparent activation energy E of 5000 to 6000 cal. was found at +50°C. (Table I, Fig. 4). As the heat of Van der Waals adsorption is unlikely to be as high as 5000 to 6000 cal., it follows that E^s must be negative. The H_2/D_2 ratio at this temperature is as high as 13.5, even higher than the expected value 10 found with paramagnetic gases. With decreasing temperature E^s rapidly increases while the ratio rapidly decreases to low values (2 at −80°C.); similarly for Nd II (Fig. 3) in the corresponding region the ratio falls off to 4 (at 0°C.) from some higher value. At low temperatures, the ratio for Nd II has the approximately normal value 9 at −100°C. (falling off towards lower temperatures somewhat faster than expected). In this region indeed the true activation energy seems to be small. This can be seen by applying equation 4, setting $E^s \approx 0$. Then $E = -n_k Q$, with an average $n_k = 0.8$ and $E = -1050$ cal. (Table I). This leads to a value for Q of about 1300 cal., which is at least a reasonable order of magnitude for the heat of adsorption.

In the case of hemin the small change of the rate throughout the entire temperature range indicates that E^s is high (of the order of magnitude of Q). Correspondingly the ratio values (Fig. 1) are low throughout with respect to the normal values. The ratio in this case decreases, more or less uniformly, from a value 7 at +150°C. (instead of about 10) to 1.5 at −190°C. (instead of 5.6).

ACKNOWLEDGMENT

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CARBODIIMIDES

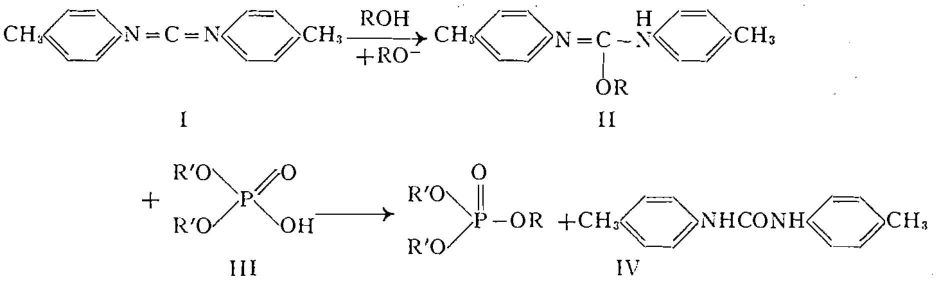
PART IV. THE FISSION OF N,N'-DI-*p*-TOLYL-O-BENZYL AND-O-ALLYL PSEUDOUREA ETHERS IN THE PRESENCE OF ACIDS[1]

By H. G. Khorana

ABSTRACT

N,N'-di-*p*-tolyl-O-benzyl pseudourea ether has been shown to form, in the presence of acids, a mixture of the corresponding benzyl ester and unchanged acid, di-*p*-tolyl urea and an isomer of the urea ether which is concluded to be N-(2-benzyl-*p*-tolyl)-N'-*p*-tolyl urea. The transient coloration (to orange red) of the reaction mixture affords strong evidence for the intermediate formation of benzyl cations. The fission of N,N'-di-*p*-tolyl-O-allyl pseudourea ether follows an analogous course.

In Part III (10) of this series the preparation of a number of N,N'-di-*p*-tolyl O-alkyl pseudourea ethers (II, R = alkyl) and their subsequent decomposition with mono- and di-esters of phosphoric acid (e.g. III to form tertiary phosphates (IV) was described.



It was of interest to extend this method to the preparation of benzyl esters* of phosphoric acid derivatives through the easily prepared N,N'-di-*p*-tolyl-O-benzyl pseudourea ether (II, R = benzyl). The benzyl group has proved to be a suitable protecting group as shown by its extensive use in the synthesis of biologically important phosphates by Todd and collaborators (3, 9). In this communication we report on the behavior of the above mentioned O-benzyl ether in attempts to prepare benzyl phosphates. The results provide a further demonstration of the well-known reactivity of the benzyl group. N,N'-di-*p*-tolyl-O-allyl pseudourea ether was also shown to react in an analogous manner.

The O-benzyl and O-allyl ethers (II, R = benzyl and allyl respectively) were prepared in quantitative yield (I→II) as described earlier (10), the former being a highly crystalline substance. When to a benzene solution of the O-benzyl ether a stoichiometric amount of dibenzyl hydrogen phosphate was

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* *Phenyl diazomethane, an unstable and rather difficultly prepared substance, has been used for the preparation of benzyl esters (2, 4).*

added and the solution was warmed, it began to color immediately. The orange red color which developed faded again, as a practically colorless reaction mixture containing a white crystalline precipitate resulted in approximately 15 min. The same sequence of reactions was found to occur when dibenzyl hydrogen phosphate was replaced by diphenyl hydrogen phosphate, *p*-toluene sulphonic acid, or glacial acetic acid. Similar reactions were also observed in the course of a few hours when a benzene solution of the O-benzyl ether and dibenzyl hydrogen phosphate was kept at room temperature. From the reaction mixtures using dibenzyl hydrogen phosphate, 30–50% of the acid was recovered and some tribenzyl phosphate, the expected benzyl ester, could also be isolated. The benzene-insoluble neutral reaction product was a mixture which was separated by fractional crystallization into di-*p*-tolyl urea (m.p. 265°) and a substance (m.p. 206°–207°). The latter substance was isolated also from the products of fission of the O-benzyl ether in the presence of *p*-toluene sulphonic acid. The yield of this substance appeared to be in direct proportion to the amount of the acid recovered from the reaction products. (If the O-benzyl pseudourea ether (m.p. 85°) was heated alone at 160° for 15 min., none of the transformation product (m.p. 206°–207°) was formed, the starting material being recovered. Use of 10% of stoichiometric amount of acid was also not satisfactory in effecting the fission of the O-benzyl ether.) A procedure which was found to be particularly favorable to the formation and isolation of the substance (m.p. 206°–207°) consisted of the addition of a hot dilute solution of the benzyl ester to a very dilute boiling solution of *p*-toluene sulphonic acid. Analytical data showed this substance to be an isomer of the O-benzyl pseudourea ether. The fission of N,N′-di-*p*-tolyl-O-allyl pseudourea ether in the presence of acids gave similarly a substance ($C_{18}H_{20}ON_2$; m.p. 200°–202°) isomeric with the O-allyl ether.

From the general properties of these substances ($C_{22}H_{22}ON_2$ m.p. 206°–207°, and $C_{18}H_{20}ON_2$, m.p. 200°–202°), it is concluded that they are derivatives of di-*p*-tolyl urea, carrying respectively a benzyl and an allyl group in one of the two symmetrically substituted rings (e.g. VI). Infrared absorption spectra of di-*p*-tolyl urea and the "rearrangement products" which are reproduced in Fig. 1 confirmed these structures for the latter compounds. All the three compounds have a strong absorption band around 3290 cm. (3.2 μ) characteristic of N–H stretching. The absorption bands in the region (1700–1520^{-1} cm.), where bands characteristic of NHCONH grouping are known to occur (13), as found in urea, and related urea derivatives including the above mentioned substances (Fig. 1), are listed in Table I. The bands at 6.12 and 6.4 μ in di-*p*-tolyl urea, at 6.12 and 6.47 μ in the substance $C_{22}H_{22}ON_2$, and at 6.11 and 6.41 μ in the substance $C_{18}H_{20}ON_2$ can clearly be ascribed to –NHCONH– grouping in all these compounds. The common band at 6.27 μ may also be due to the same grouping although weak bands in this region have been ascribed to phenyl group vibration (12, 13). The extra band in the substance ($C_{18}H_{20}ON_2$, allyl-di-*p*-tolyl urea) at 6.21 μ is obviously due to $-CH = CH_2$ stretching (12, 13), a similar band being present in the infrared spectra of compounds containing allyl grouping (13, p. 110; 15). The absorptions in the

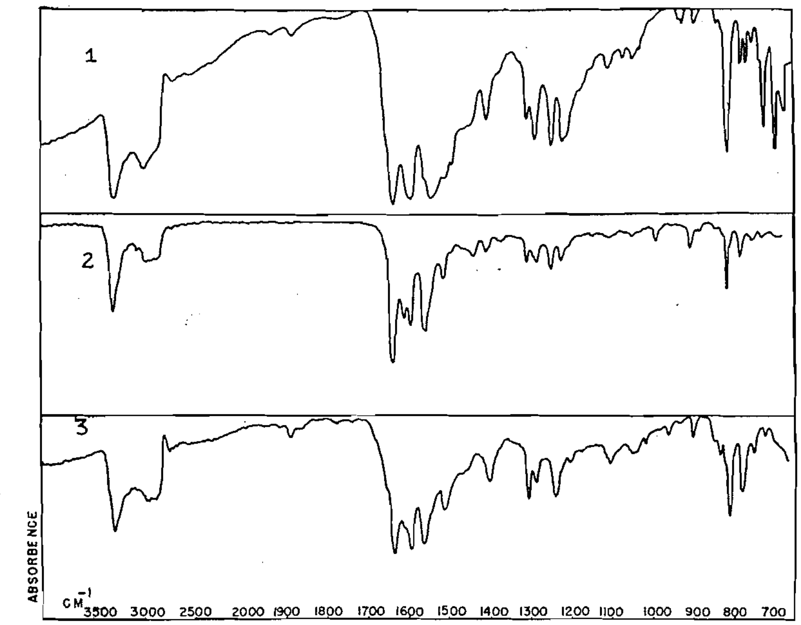

FIG. 1. Infrared spectra of (1) N,N′-di-*p*-tolyl urea; (2) $C_{18}H_{20}ON_2$, m.p., 200–202°; (3) $C_{22}H_{22}ON_2$, m.p., 206–207°. The spectra were taken in a Perkin–Elmer double beam spectrophotometer Model 21B, using nujol paste.

TABLE I

	Substance									
	Urea	S-diethyl-urea	S-dicyclohexyl urea		S-di-*p*-tolyl urea		$C_{22}H_{22}ON_2$		$C_{18}H_{20}ON_2$	
	μ	μ	cm.$^{-1}$	μ	cm.$^{-1}$	μ	cm.$^{-1}$	μ	cm.$^{-1}$	μ
I.R. absorption	5.92	6.18	1629	6.14	1635	6.12	1635	6.12	1637	6.11
	6.12	6.29	1575	6.35	1595	6.27	1595	6.27	1611	6.21
	6.21		1537	6.51	1563	6.4	1545	6.47	1595	6.27
									1560	6.41
Reference	(13, p. 169)	(13, p. 170)	(7)							

most sensitive, "the finger print," region (below 1350 cm.$^{-1}$), which are mainly due to skeletal vibrations (8) (di- and tri-substituted benzene nuclei; see for example (12)), are not discussed here but would appear to support the assigned structures.

The formation of the reaction products discussed above points collectively to the following mode of decomposition of, for example, the benzyl ether. The first step is the formation of the cations of the type V in the presence of acids. Whereas the fission of such cations derived from other alkyl pseudourea ethers (10) was bimolecular,* involving nucleophilic attack of an acid anion

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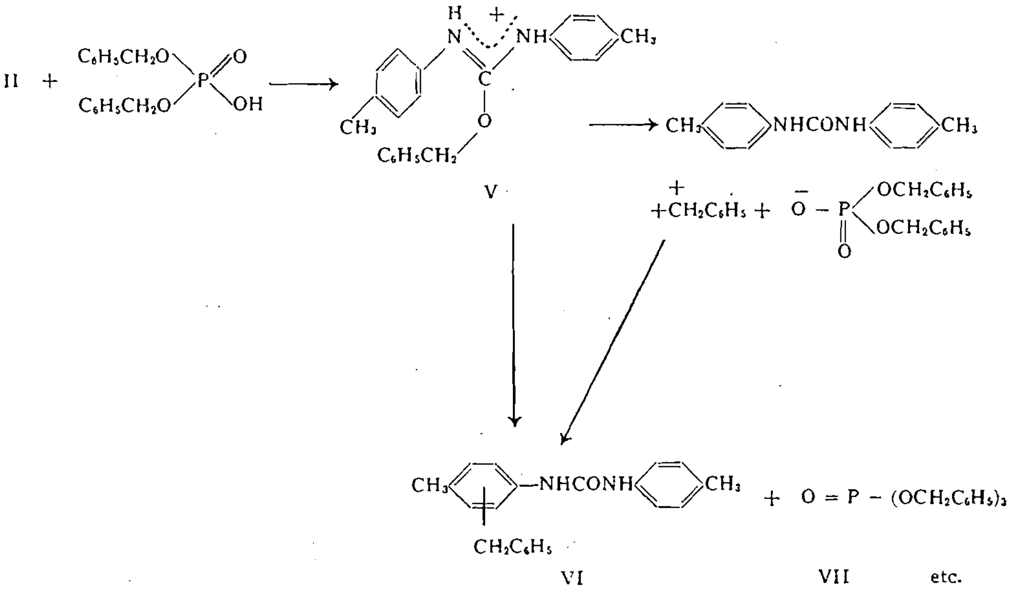
* *Although no quantitative studies were made, increased rate of reaction was observed with increased concentration of the reactants.*

on the alkyl group, the cation V itself is unstable and decomposes unimolecularly to form the colored benzyl cations.*



The latter on combination with the acid anions would form the benzyl ester, e.g. VII. Alternatively, they could attack the aromatic nuclei of di-*p*-tolyl urea to form VI. As the reaction was carried out in benzene, diphenylmethane would also be expected to be formed.† Although traces of this substance might have escaped detection it was not formed in any appreciable amount. This could be explained by assuming high reactivity of the aromatic nuclei of di-*p*-tolyl urea compared with the weakly nucleophilic benzene molecules. This, however, might also be regarded as evidence in favor of an intramolecular rearrangement‡ of V, via a six-membered ring transition complex, to VI. Further work involving fission of V in the presence of a reactive substance (from the point of view of electrophilic attack by benzyl cations), for example, phenol, is necessary to decide finally in favor of one of the two possible mechanisms discussed above.

It remains to comment on the point of attachment of the benzyl or allyl group to one of the benzene rings in the final compounds (e.g. VI). Intramolecular cyclization as discussed above would of course form the ortho substituted (to the NHCO— grouping) ureas. If free benzyl and allyl cations

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* *The intermediate formation of colored benzyl ions was postulated by Roberts and Hammett (14) in kinetic studies on benzyl halides and more recently (6) in some debenzylation reactions. The present work affords strong evidence for the formation of the colored cations.*

† *For reactions of organic cations and fission of benzyl ethers see Ref. 5.*

‡ *This mechanism was favored by Dr. Streitwieser of the Department of Chemistry, University of California, Berkeley, during a seminar given by the author in the above department on "Chemistry of carbodiimides". We are indebted to Dr. Streitwieser and Dr. Noyce for a discussion on the work described here.*

were formed, their attack on the aromatic nuclei of di-*p*-tolyl urea would also be expected to give the same (ortho-substituted) products. Although no direct studies on nucleophilic substitutions in such systems appear to have been made there is abundant evidence on orienting effects (supporting substitution ortho to the NH-$COCH_3$ group) in *p*-acyl toluidines (see for example Ref. 1, p. 244, and the references cited there).

EXPERIMENTAL

Preparation of N,N'-di-p-tolyl-O-benzyl Pseudourea Ether

Sodium* (*ca.* 40 mgm.) was dissolved in anhydrous benzyl alcohol (2.4 cc., 0.023 moles). Anhydrous dioxane (10 cc.) was added to the clear solution, followed by the addition of di-*p*-tolyl carbodiimide (4.44 gm.; 0.02 moles). The mixture which became warm was allowed to stand for 15 min., then diluted, largely with ether, and the ethereal solution extracted thrice with water. Removal of ether from the dried solution gave a viscous oil which soon crystallized. This product was recrystallized from petroleum ether (b.p. 30°–60°) at 0° C. Yield of the first crop 5.35 gm., 81%; m.p. 84°–85°, no change on further crystallization. Mother liquor after concentration gave a second small crop of the same substance. For analysis† a sample was recrystallized from petroleum ether (b.p. 30°–60°). Found: C, 79.64, 79.57; H, 6.77, 6.68; N, 8.67%. $C_{22}H_{22}ON_2$ requires C, 80.0; H, 6.7; N, 8.5%.

N,N'-di-p-tolyl-O-allyl Pseudourea Ether

Sodium (40 mgm.) was dissolved in anhydrous allyl alcohol‡ (10 cc.) and an ethereal solution (10 cc.) of di-*p*-tolyl carbodiimide (4.45 gm.; 0.02 moles) was added with exclusion of moisture. After 15 min., the O-allyl pseudourea ether was isolated as described for the O-benzyl compound. Thus obtained, it was a viscous oil (5.6 gm.; 97%) which distilled at 135°–140° (air bath temperature) at 2 mm. Found: C, 77.16; H, 7.1; N, 10.1%. $C_{18}H_{20}ON_2$ requires C, 77.1; H, 7.2; N, 10.0%.

Fission of N,N'-di-p-tolyl-O-benzyl Pseudourea Ether in the Presence of Acids Using Dibenzyl Hydrogen Phosphate

(*a*) Dibenzyl hydrogen phosphate (1.4 gm.; 0.005 moles) and N,N'-di-*p*-tolyl-O-benzyl pseudourea ether (1.65 gm.; 0.005 mole) were dissolved in benzene (15 cc.). The solution, practically colorless at first, developed on heating yellow, orange, and finally orange red color. On being refluxed for 15 min., the solution lost color and a white precipitate separated.

After being kept overnight the mixture was filtered and the precipitate washed twice with small amounts of benzene. Yield 0.75 gm., melting point unsharp, 195°–200° with previous shrinkage (m.p. of pure di-*p*-tolyl urea, 265°). The combined filtrate and the washings were extracted thrice with sodium bicarbonate solution. The bicarbonate extracts were acidified with

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* *As observed earlier (10) sodium could not be replaced by triethylamine as a catalyst in this reaction.*

† *Analyses were carried out by Mr. W. Manser of Zurich, Switzerland.*

‡ *Allyl alcohol was refluxed over calcium oxide and distilled. It was then refluxed in presence of sodium and diallylphthalate and distilled.*

hydrochloric acid and extracted exhaustively with ether. The dried ethereal extracts afforded, on evaporation and prolonged suction, 0.71 gm. of dibenzyl hydrogen phosphate (m.p. and mixed m.p. 79°–80°). The benzene solution was dried over anhydrous sodium sulphate and evaporated to a sirup, which was dissolved in a few cubic centimeters of 95% ethyl alcohol. The solid which separated was removed (0.202 gm.; m.p. after recrystallization from alcohol, 195°–205°). The mother liquor was concentrated to an oil which was extracted repeatedly with hot petroleum ether (b.p. 30°–60°). The extracts deposited first an oil and then on prolonged standing clusters of fine needles. These were collected and washed with chilled ether – petroleum ether mixture, m.p. 64°–65°, which is identical with that reported for tribenzyl phosphate* (p. 260 in Ref. 11).

(*b*) *At Room Temperature*

A solution of the O-benzyl ether (3.3 gm.; 0.01 mole) and dibenzyl hydrogen phosphate (2.78 gm.; 0.01 mole) in 30 cc. of benzene was kept at room temperature. The color changes (orange → orange red → orange → light yellow) were slower. After approximately two hours the color began to lighten and a solid separated. The practically colorless solution was worked up after three hours as described under (*a*) above. Yield of dibenzyl hydrogen phosphate recovered 1.12 gm. (40%). The insoluble solid material (1.84 gm.) collected in two crops from the benzene solution had an unsharp melting point, 190° to 220°. Fractional crystallization from ethyl alcohol gave a sample melting at 235°–240°.

(*c*) *Isolation of the "Rearrangement Product" Using p-Toluene Sulphonic Acid in High Dilution*

To a boiling anhydrous benzene solution† (120 cc.) of *p*-toluene sulphonic acid (0.95 gm.; 5 mM.) was added with agitation a benzene solution (10 cc.) of the benzyl ether (1.65 gm.; 5 mM.). A very transient orange color developed immediately. The final (after 10 min.) colorless benzene solution was concentrated to *ca.* 30 cc. and kept at room temperature for 40 hr. The crystalline deposit (0.5 gm.; m.p. 230°–250°) was removed and the mother liquor was concentrated to an oil which was dissolved in alcohol (5 cc.). The solid which separated was collected and washed with a fresh portion of alcohol. After recrystallization from aqueous ethyl alcohol (90%) the material (380 mgm.) had a melting point of 205–206°. Further recrystallization from alcohol without appreciable loss gave a sample with constant melting point 206°–207°. Found on a twice crystallized sample, C, 79.8; H, 6.8; N, 8.4; $C_{22}H_{22}ON_2$ requires C, 80.0; H, 6.7; N, 8.5%.

(*d*) *Attempted Degradation Using Catalytic Amounts of Dibenzyl Hydrogen Phosphate*

A benzene solution (10 cc.) of the O-benzyl pseudourea ether (1.65 gm.; 5 mM.) and dibenzyl hydrogen phosphate (0.14 gm.; 0.5 mM.) was brought to the boiling point; at this temperature it developed a persistent yellow color

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* *Dr. R. H. Hall (private communication) confirmed this melting point of the substance.*

† *Prepared by azeotropic removal of water.*

and deposited a solid after approximately fifteen minutes. After being refluxed for eight and one-half hours the yellow reaction mixture was allowed to stand at room temperature overnight. The collected precipitate (244 mgm.) had a melting point of 190°–200°. The light yellow mother liquor was evaporated and the residual oil taken up in 15 cc. of ethyl alcohol. On the addition of a few drops of water, an oil separated which soon crystallized; the melting point of the crystals was 82°–83°, undepressed on admixture with the O-benzyl pseudourea ether. Recovery, 0.85 gm. (51%).

Stability of N,N′-di-p-tolyl-O-benzyl Pseudourea Ether to Heat

The ether (0.2 gm.) was heated in an oil bath at 160° for 15 min. when the colorless melt developed light yellow color. After being allowed to cool to room temperature, the solid was crystallized from ethyl alcohol. Melting point 85°, undepressed on admixture with the starting material.

Isolation of the "Rearrangement Product" of N,N′-di-p-tolyl-O-allyl Pseudourea Ether

A hot benzene solution (5 cc.) of the O-allyl ether (14 gm.; 5 mM.) was added to an anhydrous benzene solution (150 cc.) of *p*-toluene sulphonic acid (0.95 gm.; 5 mM.). The solid (0.65 gm.; mostly di-*p*-tolyl urea), which separated on concentration of the benzene solution to approximately 50 cc., was removed and the clear filtrate was evaporated *in vacuo* to an oil. A solution of the residual oil in ethyl alcohol (8 cc.) containing a small amount of water gave, on standing, a crop of crystals (0.25 gm.; m.p. 230°–240° after shrinkage at 195°). Fractional crystallization from ethyl alcohol gave a crop (100 mgm.) with m.p. 195°–198°. One more crystallization of this material from 90% ethyl alcohol gave rosettes of fine needles, m.p. 200°–202°. Found: C, 77.1; H, 7.2; N, 10.1%; $C_{18}H_{20}ON_2$ requires C, 77.1; H, 7.2; N, 10.0%.

ACKNOWLEDGMENTS

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ANNOTININE: THE REACTIONS OF THE CYCLIC ETHER FUNCTION[1]

By H. L. Meier[2], P. D. Meister[3], and Léo Marion

ABSTRACT

Treatment of annotinine chlorohydrin with chromous chloride has been found to produce not only the already reported unsaturated lactone A ($C_{16}H_{21}O_2N$), but also a second unsaturated lactone B ($C_{16}H_{21(23)}O_2N$), and a hydroxylactone ($C_{16}H_{23}O_3N$). Under the action of a concentrated solution of the same reagent the hydroxylactone is converted to the unsaturated lactone B. On hydrogenation the latter gives a dihydrolactone B which seems to contain a secondary amino group. Annotinine hydrate on treatment with thionyl chloride gives an unsaturated chlorolactone ($C_{16}H_{20}O_2NCl$) which can be hydrogenated and subsequently dechlorinated to produce a third lactone C, different from either of dihydrolactones A or B, but which like the latter seems to contain an imino group. Oxidation of annotinine hydrate with chromic acid produces a hydroxyketone which can be converted into an oxime and, therefore, one of the hydroxyls of the hydrate is secondary while the other is probably tertiary. On the other hand, oxidation of annotinine with potassium permanganate gives rise to a lactam which by the Clemmensen reduction is converted to a mixture of lactam chlorohydrin and dihydrolactone A.

In a previous study (5) it has been shown that the three oxygens of annotinine ($C_{16}H_{21}O_3N$), the major alkaloid of *Lycopodium annotinum* L. (4), are present in a lactone structure and in a cyclic ether. Further support for the presence of a lactone has also been found in the occurrence of a strong absorption peak at 1776 cm.$^{-1}$ in the infrared spectrum of the alkaloid (6), and the position of this peak is characteristic of five-membered lactones. The cyclic ether is cleaved by halogen acids to form halohydrins, and also by the action of alcoholic potassium hydroxide to give annotinine hydrate ($C_{16}H_{23}O_4N$) (5). Since annotinine could not be hydrogenated catalytically and annotinine had been found to be inert towards periodic acid, the ether oxygen was assumed to be part of a five- or six-membered ring (5). Recently MacLean and Prime (3) suggested that the ether was an epoxide notwithstanding the failure of annotinine hydrate (which would then be a 1:2 diol) to react with periodic acid. They also pointed out that the product of the oxidation of annotinine with potassium permanganate was not a base, as mentioned by Manske and Marion (5), but a neutral lactam, and because of the influence of the lactamic carbonyl on the ether, assigned to this carbonyl a position between the nitrogen and the ether ring. The present study was undertaken to gain further insight into the nature of the functional groups of annotinine. In the course of this work most of the degradation reactions described so far have been reinvestigated.

The product of the oxidation of annotinine with potassium permanganate contained two hydrogens less and one oxygen more than the base itself. It was neutral and its infrared absorption spectrum contained besides the usual

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lactone band (1768 cm.$^{-1}$) a new strong peak at 1640 cm.$^{-1}$ which is characteristic of a $-CO.N<$ group present in a six-membered ring. Hence, as already observed by MacLean and Prime (3) the oxidation product is not a base (5) but a lactam, and it follows that annotinine must contain a methylene group next to the nitrogen. The further observation of MacLean and Prime (3) that boiling hydrochloric acid converted annotinine lactam into a lactam chlorohydrin ($C_{16}H_{20}O_4NCl$) arising from the cleavage of this cyclic ether has also been confirmed. The infrared spectrum of this chlorohydrin contained, besides the absorption bands attributable to the lactone carbonyl (1760 cm.$^{-1}$) and the lactam carbonyl (1624 cm.$^{-1}$), a sharp peak at 3330 cm.$^{-1}$ indicative of the presence of a hydroxyl group. This lactam chlorohydrin could also be obtained, although in small yield only, by the oxidation of annotinine chlorohydrin.

It has been reported previously that the Clemmensen reduction of annotinine lactam gives rise to a base $C_{16}H_{23}O_2N$, also obtainable via a different route (5). This work has been repeated and the formation of the base (dihydrolactone A) confirmed although a second product was also found which was identical with the lactam chlorohydrin described above. Dihydrolactone A no longer contained the ether oxygen nor the lactam carbonyl which had been reduced back to a methylene, although it still contained the lactone ring (its characteristic absorption in the infrared was in the usual position). The formation of the chlorohydrin is to be expected, but the reduction of the amide group under these conditions can be understood only if a strong activation of the lactam carbonyl by the close proximity of one of the other functional groups is assumed. In contrast, as already reported (5) annotinine when kept for two hours under the conditions of the Clemmensen reduction was only affected by the hydrochloric acid and converted to a chlorohydrin. It has now been found that only if the reaction was prolonged for 10 hours did it go further and give rise to unsaturated lactone A and hydroxylactone (see Fig. 1). Hence, as well as the lactam carbonyl having an increased reactivity, as shown by the results of the Clemmensen reduction, it also enhances the reactivity of the cyclic ether.

Annotinine chlorohydrin is known to react with chromous chloride to produce an unsaturated lactone (5). On reinvestigation this reaction proved to be more complex. The reaction did not only produce the lactone already reported (now designated unsaturated lactone A), but depending particularly on the solvent used and also on the concentration of hydrochloric acid, various other compounds as well. Treatment of annotinine chlorohydrin hydrochloride with an alcoholic solution of chromous chloride and hydrochloric acid yielded a mixture of products which by chromatography was separated into the unsaturated lactone A, $C_{16}H_{21}O_2N$, m.p. 132°, amounting to about two-thirds of the product, and a hydroxylactone, $C_{16}H_{23}O_3N$, m.p. 174° (about one-third). But when annotinine chlorohydrin was treated with an aqueous solution of chromous chloride and hydrochloric acid the product consisted of hydroxylactone (34.6%), unsaturated lactone A (33.2%), and an unsaturated lactone B (3.8%) apparently isomeric with A but possibly containing two

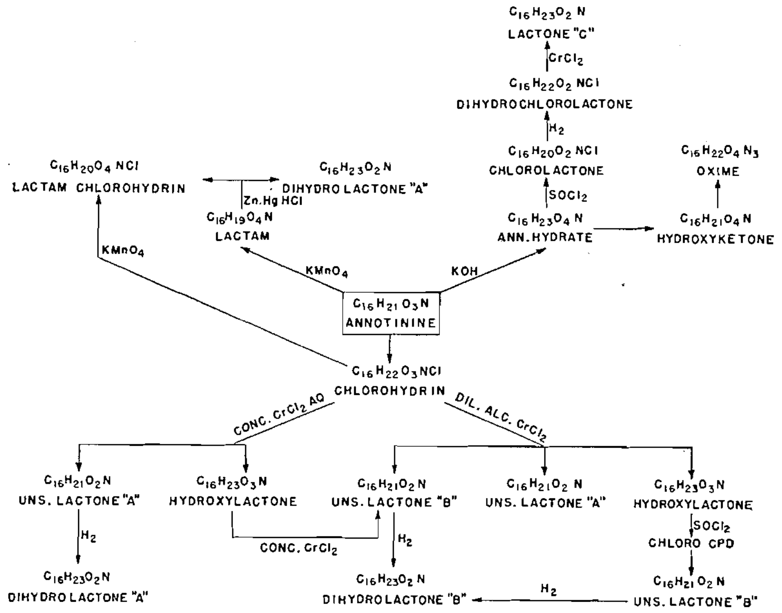

FIG. 1

more hydrogens. There was also left an uncrystallized residue still to be examined. The hydroxylactone is the compound that one would expect to obtain from the action of a dehalogenating agent such as chromous chloride on annotinine chlorohydrin. The formation of unsaturated lactone B can be considered as a secondary reaction. This view seemed justified since the hydroxylactone on treatment with a dilute aqueous acid solution of chromous chloride remained unchanged whereas on refluxing in a more concentrated solution of the reagent it was transformed into the unsaturated lactone B in good yield. None of the unsaturated lactone A was obtained from the hydroxylactone and it can be concluded that unsaturated lactone A must have arisen from the chlorohydrin directly by a different mechanism of dehalogenation and dehydration.

With the idea of gaining more information on this point many attempts were made to dehydrate annotinine chlorohydrin and also to obtain the hydroxylactone directly from it by catalytic removal of chlorine, but all proved fruitless. Negative results were also obtained in the attempted catalytic hydrogenation of the corresponding bromohydrin and iodohydrin. In contrast, MacLean and Prime (3) have reported that lactam chlorohydrin is converted by catalytic hydrogenation over Adams' catalyst to a hydroxy compound $C_{16}H_{21}O_4N$ and to a compound $C_{16}H_{21}O_3N$. The latter is reduced in small yield by the Clemmensen reaction to the dihydrolactone A (3) and is probably the corresponding lactam. In this product the ether is no longer present and has been replaced by hydrogen, but the lactamic carbonyl is still affected by the proximity of an activating group since it is still reduced, albeit in poor yield, in the Clemmensen reaction. The only activating group left in this compound is the lactone.

The hydroxyl group in annotinine chlorohydrin and in the hydroxylactone were then studied. Both resisted oxidation with chromic acid; neither gave an acetyl derivative. Thionyl chloride did not react with the chlorohydrin even under drastic conditions, nor did phosphorus halides although treatment with phosphorus pentachloride resinified some of the starting material. Boiling thionyl chloride converted the hydroxylactone into an intractable product. When, however, the hydroxylactone was left in contact with thionyl chloride at room temperature for a few minutes only, and care was taken to avoid heat in working up the mixture, a yellow oil was obtained which after chromatography on alumina was colorless. The Beilstein test showed that it contained chlorine. It decomposed if dissolved in any solvent or on heating. On treatment with a dilute solution of chromous chloride (which would not have affected the hydroxylactone) it gave rise to the unsaturated lactone B. The presence of the chlorine in the chlorohydrin therefore appears to stabilize the hydroxyl group. Unsaturated lactone B proved to be quite different from unsaturated lactone A. Whereas on catalytic hydrogenation the latter yielded a dihydro derivative having the expected properties, the former gave a product, dihydrolactone B, the infrared absorption spectrum of which contained a sharp absorption band at 3325 cm.$^{-1}$ in the NH region. The presence of an imino group, however, has not yet been confirmed chemically.

A survey of the infrared absorption spectra of annotinine and its derivatives shows that in some of them the absorption band of the lactone carbonyl is slightly shifted towards lower frequencies. This shift is particularly noticeable in the spectra of unsaturated lactone B, of its hydrogenation product, and of annotinine chlorohydrin. This could be attributed to a structural change near the lactone carbonyl, or to a possible relactonization with a different hydroxyl group than the original. The fact that these three compounds are prepared under acid conditions that are not likely to cause hydrolysis of the lactone seems to favor the first of these alternatives. To gain information on this point annotinine hydrate was prepared again and reinvestigated. This hydrate is the product of the action on annotinine of alcoholic potash which also hydrolyzes the lactone ring. Hence the chances of relactonization with one of the new hydroxyls arising from the hydrolytic cleavage of the cyclic ether seemed considerable. The reaction yielded only one product and the infrared absorption spectrum of the pure annotinine hydrate contained the lactone carbonyl band in the same position that it occupied in the spectrum of annotinine. It is difficult to draw a definite conclusion from this result, since, should relactonization have occurred exclusively with a different hydroxyl with formation again of a five-membered lactone, the carbonyl frequency in the infrared would probably have remained unchanged.

Annotinine hydrate was converted by chromic acid oxidation into a new compound $C_{16}H_{21}O_4N$. The infrared absorption spectrum of this product contained besides the usual lactone carbonyl absorption band at 1779 cm.$^{-1}$ a band at 1714 cm.$^{-1}$ indicating a new carbonyl group and a peak at 3390 cm.$^{-1}$

in the hydroxyl region. The product was therefore a hydroxyketone and showed that of the two hydroxyls in annotinine hydrate one was certainly secondary and the second probably tertiary. The presence of the keto group in this product was confirmed by the preparation of an oxime. Attempts to reconvert the new carbonyl function to a secondary alcohol by hydrogenation over a platinum catalyst failed.

Annotinine hydrate reacted with phosphorus halides to give unidentifiable resins, but by the action of thionyl chloride at room temperature it was converted into an unsaturated chlorolactone, $C_{16}H_{20}O_2NCl$, in which one of the hydroxyls had been replaced by chlorine while the other had been eliminated with formation of a double bond. This chlorolactone took up one mole of hydrogen when reduced catalytically and produced a dihydrochlorolactone which on treatment with chromous chloride was converted to a dihydrolactone C which like dihydrolactone B has an infrared absorption spectrum containing an absorption band at 3355 cm.$^{-1}$ indicative of an imino group.

The hydrogenolysis of chlorine and the hydroxyl in the catalytic hydrogenation of the lactam chlorohydrin described by MacLean and Prime (3) is the main evidence for the presence of an epoxide next to a $-CH_2-N<$ group in annotinine. The failure of annotinine hydrate to undergo oxidation with periodic acid militates against such a structure although, admittedly, a few α-glycols are known to be inert towards this reagent (1,2,7). The other reactions described above could possibly be accommodated by an epoxide, although the impossibility so far of reforming the epoxide from the chlorohydrin except in the lactam would be difficult to account for. It is probable that the reactions described could also be accommodated by a 1,3-oxide. The cleavage of the ether by lithium aluminum hydride (see following paper) seems to preclude a 1,4- or 1,5-oxide in a completely saturated molecule. The present state of our knowledge does not make it possible yet to state definitely what type of cyclic ether is present in the base.

EXPERIMENTAL

All melting points are corrected. All solvents were purified before use. The aluminum oxide (Merck) used for chromatographic separations was washed with hot dilute hydrochloric acid, then with distilled water (at least fifteen times). It was then dried, activated to grade O, and subsequently deactivated to grades I, II, III, and IV according to the Brockmann scale. If not otherwise stated the column was made up in benzene; its length was 8–10 times its diameter. Usually the weight of aluminum oxide employed was 30 times that of the substance. The substance was repeatedly taken up in benzene and the solvent evaporated to remove the last traces of other solvents before the final concentrated solution was brought on to the column. The fractions drawn were of 50 ml. and the solvent was removed by distillation under reduced pressure.

Most of the derivatives obtained could be sublimed and this operation was carried out *in vacuo* (10^{-4} mm. Hg) in glass tubes mounted in an electrically heated block at a temperature of 20–30° below the melting point of each sample.

When not otherwise specified the infrared absorption measurements were made on nujol mulls with a Perkin–Elmer double beam instrument, model 21, with a sodium chloride prism. The other measurements were made on a Perkin–Elmer single beam instrument, model 12B, using a chloroform solution and a calcium fluoride prism. The frequencies, given in wave numbers, are followed by a number in brackets indicating the percentage absorption.

Annotinine Lactam

As described previously (5) annotinine (1 gm.) was oxidized in aqueous solution with potassium permanganate. The product (380 mgm., m.p. 234°) was neutral and showed in its infrared spectrum a band at 1768 cm.$^{-1}$ (85) characteristic of the lactone carbonyl and a new band at 1640 cm.$^{-1}$ (91) attributable to a lactam carbonyl. In admixture with the product previously obtained ($C_{16}H_{19}O_4N$) (5) the melting point was unchanged.

Action of Hydrochloric Acid on Annotinine Lactam (Chlorohydrin Lactam)

Annotinine lactam (100 mgm.) was heated on the steam bath for two hours with 1: 1 hydrochloric acid (10 ml.). The cooled solution was extracted with chloroform and the extract on evaporation left a crystalline residue which could be recrystallized from methanol, 103 mgm., m.p. 295°. The sample was sublimed for analysis. Calc. for $C_{16}H_{20}O_4NCl$: C, 58.98; H, 6.19; N, 4.30; Cl, 10.88. Found: C, 58.84; H, 6.32; N, 4.19; Cl, 10.51%. The infrared absorption spectrum showed a strong band (3330 cm.$^{-1}$ (86)) in the OH region and bands at 1760 cm.$^{-1}$ (92) and 1624 cm.$^{-1}$ (98) indicative of the lactone and lactam carbonyls, respectively.

Clemmensen Reduction of Annotinine Lactam

Annotinine lactam (200 mgm.) was refluxed for six hours with an excess of amalgamated zinc in 30 ml. of 10% hydrochloric acid. The compound dissolved fairly quickly. The cooled acidic solution was extracted with chloroform, and the extract on evaporation left a crystalline residue (65 mgm.) which after recrystallization from methanol melted at 295° either alone or in admixture with annotinine chlorohydrin lactam. The acidic aqueous liquor was then alkalized with ammonia and extracted with chloroform. On evaporation the extract yielded 110 mgm. of a compound that crystallized slowly. It was partly soluble in benzene. On chromatographic purification it yielded 66 mgm. of a compound eluted with benzene which crystallized when seeded with saturated lactone A (see below). After recrystallization from heptane it melted at 108–110° either alone or in admixture with saturated lactone A. Both compounds had superimposable infrared absorption spectra, with a strong carbonyl band at 1768 cm.$^{-1}$ (84).

Annotinine Hydrate

Annotinine (1 gm.) was dissolved in absolute ethanol (30 ml.) and potassium hydroxide (1 gm.) was added to the solution. The resulting solution was refluxed for three hours on the steam bath, water was added, and the liquor evaporated to half volume. Water was again added up to the original volume and the solution again evaporated. This was repeated until the last traces had been removed. The cooled solution was acidified with sulphuric acid, heated for one hour on the steam bath, and left overnight at room temperature. The solution was cooled, alkalized with ammonia, and extracted with chloroform. Evaporation of the extract yielded 400 mgm. of a crystalline residue which was chromatographed on alumina No. III and eluted with acetone. Annotinine hydrate thus purified melted at 228°. Its infrared spectrum in a mull showed only one OH absorption peak (3500 cm.$^{-1}$) (73) and a carbonyl band at 1762 cm.$^{-1}$ (91), whereas in chloroform solution two peaks were present in the OH region, a sharp one (3625 cm.$^{-1}$) and a broad bonded one (3465 cm.$^{-1}$) besides the carbonyl absorption. It contained two active hydrogens. Repeated relactonization did not improve the yield.

Unsaturated Chlorolactone

Annotinine hydrate (200 mgm.) was dissolved in benzene (30 ml.) and thionyl chloride (5 ml.) added to the solution which was kept overnight at room temperature. The reaction mixture was then gently heated (70°) for five minutes and the solvent and excess thionyl chloride removed under reduced pressure. Ammonia was added to the residue and the mixture extracted with chloroform. The extract on evaporation yielded a slightly yellow oily residue which crystallized slowly. Colorless needles, m.p. 136°. A sample was sublimed for analysis. Calc. for $C_{16}H_{20}O_2NCl$: C, 65.45; H, 6.85. Found: C, 65.37; H, 6.99%. The infrared absorption spectrum of unsaturated chlorolactone showed no absorption in the hydroxyl region, but contained an absorption band at 1758 cm.$^{-1}$ (91) due to the lactone function.

Dihydro Chlorolactone

Unsaturated chlorolactone (160 mgm.) dissolved in absolute ethanol (3 ml.) was added to a suspension of pre-reduced Adams' catalyst in glacial acetic acid and shaken in an atmosphere of hydrogen for 12 hours, during which 1.1 moles of hydrogen was absorbed. The catalyst was filtered off and the filtrate evaporated to dryness. The residue was shaken with chloroform and ammonium hydroxide. The chloroform solution was separated and evaporated to dryness. A yellow oil remained which was dissolved in benzene and chromatographed on alumina (No. II–III). The colorless benzene eluates on concentration crystallized readily. The product when recrystallized from low-boiling petroleum ether consisted of long needles, m.p. 146–147°, wt. 195 mgm. A sample was sublimed for analysis. Calc. for $C_{16}H_{22}O_2NCl$: C, 64.96; H, 7.49; N, 4.73; Cl, 11.98. Found: C, 65.05; H, 7.39; N, 4.61; Cl, 11.21%. The infrared absorption spectrum showed the absorption band at 1756 cm.$^{-1}$ (92) of the lactone carbonyl.

Action of Chromous Chloride on the Dihydro Chlorolactone

Dihydro chlorolactone (100 mgm.) was refluxed for two hours with a solution of chromous chloride made from chromic chloride hexahydrate (5 gm.), concentrated hydrochloric acid (5 ml.), water (40 ml.), and amalgamated zinc (5 gm.). The cooled solution was alkalized with ammonium hydroxide and extracted with ether. The extract on evaporation yielded a colorless oil which was dissolved in benzene and chromatographed on alumina (No. II–III). The benzene eluates, when concentrated, crystallized spontaneously and the product (dihydro lactone C) after recrystallization from low boiling petroleum ether melted at 119–120°. A sample was sublimed for analysis. Calc. for $C_{16}H_{23}O_2N$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.81; H, 8.94; N, 5.46%. The infrared absorption spectrum of saturated lactone C contained an absorption band at 1772 $cm.^{-1}$ (89) indicative of the lactone carbonyl and a band at 3355 $cm.^{-1}$ (29) which may indicate an imino group.

Oxidation of Annotinine Hydrate

Annotinine hydrate (875 mgm.) was dissolved in glacial acetic acid (10 ml.) and to this solution chromic oxide (200 mgm.) dissolved in glacial acetic acid (5 ml.) was added dropwise. With each drop of the oxidizing agent a green-brown complex was formed which was allowed to dissolve before the addition was continued. The temperature throughout was kept at 10°. After the oxidizing agent had all been added the mixture was allowed to stand at room temperature for six hours. A few drops of ethanol were added to the green solution to destroy the excess chromic acid and the solution evaporated to dryness under diminished pressure. The residue was shaken with chloroform and dilute ammonium hydroxide, the chloroform layer separated, dried, and evaporated to dryness under reduced pressure. The residue crystallized for the bigger part. A little benzene (4 ml.) was added which dissolved hardly any of the crystals. It was decanted and chromatographed on alumina (No. III). The benzene eluates did not contain any material but two combined fractions of the benzene–ether (10: 1) eluates gave 135 mgm. of a crystalline compound identical with the above crystalline product. Recrystallized from ether, it melted at 159–160°. Calc. for $C_{16}H_{21}O_4N$: C, 65.96; H, 7.27; N, 4.81; one act. H, 0.35. Found: C, 66.16; H, 7.11; N, 4.81; act. H, 0.42%. The infrared spectrum of this hydroxyketone contained one absorption band at 3390 $cm.^{-1}$ (57) in the hydroxyl region, one at 1768 $cm.^{-1}$ (88) attributable to the lactone carbonyl and one at 1712 $cm.^{-1}$ (85) due to the newly introduced keto group.

Hydroxyketone Monoxime

A mixture of hydroxyketone (125 mgm.) dissolved in absolute ethanol (5 ml.), hydroxylamine hydrochloride (70 mgm.), and anhydrous sodium acetate (90 mgm.) was refluxed for four hours. The solvent was evaporated *in vacuo* and the residue dissolved in water and extracted with chloroform. The dried extract was evaporated to dryness. It left a crystalline residue, wt. 104 mgm., which after recrystallization from methanol–ether melted at 260–262°. A sample for analysis was dried for 24 hr. at 90° at 10^{-3} mm. Calc. for $C_{16}H_{22}O_4N_2$: C, 62.72; H, 7.24; N, 9.15. Found: C, 62.90; H, 7.02; N, 9.25%.

Action of Chromous Chloride on Chlorohydrin

In a previous publication (5) no details concerning the concentration of hydrochloric acid or chromous chloride used in this reaction were given. The reaction has therefore been reinvestigated.

(*a*) *In Alcoholic Solution*

Chlorohydrin hydrochloride (5.5 gm.) prepared as previously described (5) was refluxed for four hours with an alcoholic solution of chromous chloride prepared from chromic chloride hexahydrate (40 gm.), absolute ethanol (200 ml.), concentrated hydrochloric acid (50 ml.) reduced under nitrogen with metallic zinc (30 gm.). After cooling, the solution was alkalized with ammonium hydroxide and extracted with ether. The extract on evaporation yielded a crystalline residue (4.04 gm.) which after recrystallization from ethanol–ether consisted of colorless needles, m.p. 174°, and on admixture with the starting material, m.p. 140–150°. Calc. for $C_{16}H_{23}O_3N$: C, 69.28; H, 8.36; N, 5.05; one act. H: 0.36. Found: C, 69.33, 69.41; H, 8.60, 8.30; N, 5.29%, act. H, 0.63%. The infrared absorption spectrum of this hydroxylactone contained a broad band (3100 cm.$^{-1}$) (60) in the hydroxyl region and the usual band (1767 cm.$^{-1}$) (89) attributable to the lactone carbonyl.

Chlorohydrin (1.15 gm.) was refluxed for four hours with an alcoholic solution of chromous chloride prepared from chromic chloride hexahydrate (10 gm.), absolute ethanol (50 ml.), concentrated hydrochloric acid (10 ml.), and zinc (10 gm.). Most of the ethanol was then removed under reduced pressure and the chilled residual solution alkalized with ammonium hydroxide and extracted with ether. On evaporation of the solvent the extract left 980 mgm. of a light yellow oil which partly crystallized on standing. The product was dissolved in a few milliliters of benzene and chromatographed on alumina. The benzene eluates yielded 360 mgm. of a crystalline substance, m.p. 128–130°, the ether eluates, 180 mgm. of a second crystalline product, m.p. 172–174°, consisting of hydroxylactone which after recrystallization from ether or heptane melted at 174°, while the ether–methanol eluates yielded 410 mgm. of an oil that did not crystallize. A second chromatographic purification of this last fraction gave an additional 40 mgm. of hydroxylactone, m.p. 174°, but the remainder remained oily.

The first fraction (benzene eluates) was recrystallized from heptane from which it separated as colorless aggregates, m.p. 130–132°, identical with the unsaturated lactone previously reported (5) and now designated unsaturated lactone A. If kept overnight in the solvent, the surface of the crystals turned yellow. It was even more sensitive in ether solution. On each recrystallization a considerable quantity of material remained in solution. Its infrared absorption spectrum contained a strong peak at 1762 (84).

(*b*) *In Aqueous Solution*

Chlorohydrin hydrochloride (1.3 gm.) was refluxed under nitrogen for three hours with an aqueous solution of chromous chloride prepared from chromic chloride hexahydrate (8 gm.), amalgamated zinc (4 gm.), and concentrated hydrochloric acid (5 ml.) diluted with water (50 ml.). After cooling, the solution was diluted to 150 ml. with water, alkalized with ammonium hydroxide, and extracted with ether. The extract on evaporation left a colorless oil (1.1 gm.) which crystallized from absolute ether (5 ml.) as long needles, m.p. 174° either alone or in admixture with hydroxylactone, wt. 380 mgm.

The mother liquor was evaporated to dryness, the residue dissolved in a few milliliters of benzene and chromatographed on alumina (No. III). The first two benzene eluates when combined and concentrated yielded 365 mgm. of a crystalline substance, m.p. 128–130°, which on recrystallization from heptane melted at 132° either alone or in admixture with unsaturated lactone A. The subsequent benzene eluates gave 42 mgm. and 18 mgm. of a new crystalline product, m.p. 130°. Recrystallization from heptane increased this melting point to 135°. Admixture with unsaturated lactone A produced a melting point depression of 35°. Calc. for $C_{16}H_{21}O_2N$: C, 74.10; H, 8.16; N, 5.40. Calc. for $C_{16}H_{23}O_2N$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.97; H, 8.36; N, 5.31%. This product will be designated unsaturated lactone B. Its infrared absorption spectrum showed a strong peak at 1752 cm.$^{-1}$ (86) due to the lactone carbonyl. Further elution of the chromatogram with ethylene dichloride yielded other compounds that have not yet been characterized.

Reaction of Thionyl Chloride with Hydroxylactone

Hydroxylactone (200 mgm.) was treated with thionyl chloride (5 ml.) in the cold. After 30 min. the solution turned yellow and the excess thionyl chloride was removed under reduced pressure. The residue was shaken with chloroform and ammonium hydroxide. The chloroform extract was separated and evaporated under reduced pressure at a temperature below 40°. An oily residue remained that did not crystallize from any of a number of solvents. The oil was dissolved in benzene and chromatographed on alumina (No. II–III). The benzene eluates did not contain any substance, but benzene–ether (10: 1) eluted a substance which after evaporation of the solvent (below 40°) consisted of a colorless oil, 185 mgm. This oil could not be induced to crystallize and when heated on the steam bath was altered immediately and afterwards no longer dissolved readily in benzene. When, however, the colorless oil was refluxed for three hours with an aqueous solution of chromous chloride prepared from chromic chloride hexahydrate (10 gm.), concentrated hydrochloric acid (10 ml.), amalgamated zinc (5 gm.), and water (30 ml.) and the cooled solution alkalized with ammonium hydroxide and extracted with ether, the extract yielded a crystalline residue. This, when recrystallized from heptane, melted at 134–135° either alone or in admixture with unsaturated lactone B.

Action of Chromous Chloride on Hydroxylactone

Hydroxylactone (100 mgm.) was refluxed for three hours with an aqueous solution of chromous chloride prepared from chromic chloride hexahydrate (5 gm.), concentrated hydrochloric acid (5 ml.), and amalgamated zinc (5 gm.). The cooled mixture was diluted with water (50 ml.), alkalized with ammonium hydroxide, and extracted with ether. The extract on evaporation left a crystalline residue, wt. 65 mgm., which after recrystallization from heptane melted at 134–135° either alone or in admixture with unsaturated lactone B.

Oxidation of Annotinine Chlorohydrin

Annotinine chlorohydrin (600 mgm.) was dissolved in acetone (30 ml.) and finely powdered potassium permanganate added gradually under constant stirring until the pink color persisted. The manganese dioxide was filtered off, washed with acetone, and the combined filtrate and washings evaporated to dryness. The residue was dissolved in chloroform and the solution shaken with dilute hydrochloric acid. The chloroform layer was separated, washed with water, dried, and evaporated. There was left a white crystalline compound, wt. 290°, which after recrystallization from methanol melted at 295° either alone or in admixture with the chlorohydrin lactam obtained by the action of hydrochloric acid on annotinine lactam.

The acidic aqueous layer obtained above was alkalized with ammonium hydroxide and extracted with chloroform. The extract yielded 45 mgm. of an oil which was not further investigated.

An attempt to oxidize annotinine chlorohydrin with chromic acid in acetic acid failed and yielded practically quantitatively the unchanged chlorohydrin.

Dihydro Lactone A

A pure recrystallized sample of unsaturated lactone A (175 mgm.) was dissolved in absolute ethanol (5 ml.) and shaken in the presence of hydrogen over pre-reduced Adams' catalyst. The hydrogenation was completed in 40 min. when one mole of hydrogen had been absorbed. The catalyst was removed by filtration and the filtrate evaporated to dryness. A colorless crystalline residue was left which after recrystallization from heptane melted at 110°. Calc. for $C_{16}H_{23}O_2N$: C, 73.53; H, 8.87; N, 5.36. Found: C, 73.61; H, 8.74; N, 5.38%. The infrared absorption spectrum of saturated lactone A contained a strong band at 1768 cm.$^{-1}$ (84) atrributable to the lactone carbonyl, but contained no absorption in the OH–NH region.

Dihydro Lactone B

Unsaturated lactone B (120 mgm.) was dissolved in ethanol (5 ml.) and shaken over Adams' catalyst in an atmosphere of hydrogen. The reduction was complete in 40 min. in the course of which one molecular equivalent of hydrogen was absorbed. The catalyst was filtered off and the filtrate evaporated to dryness. The residue crystallized spontaneously. It was recrystallized from heptane and sublimed *in vacuo* at 100°, m.p. 135°. In admixture with unsaturated lactone B, the melting point was depressed by 30°. Calc. for $C_{16}H_{23}O_2N$: C, 73.53; H, 8.87; N, 5.36. Calc. for $C_{16}H_{25}O_2N$: C, 72.96; H, 9.57; N, 5.32. Found: C, 73.81; H, 8.65; N, 5.43%. The infrared absorption spectrum of saturated lactone B contained besides the absorption at 1755 cm.$^{-1}$ (89) due to the lactone carbonyl, a sharp absorption band at 3325 cm.$^{-1}$ (42) indicating the presence of an NH grouping.

ACKNOWLEDGMENT

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ANNOTININE: THE LACTONE RING[1]

By H. L. Meier[2] and Léo Marion

ABSTRACT

The action of lithium aluminum hydride in dioxane solution on annotinine reduces the lactone and gives rise to a dihydroxy ether while the same reaction in tetrahydrofuran causes scission of the cyclic ether as well and produces a trihydroxy compound. The same trihydroxy compound is also obtainable by the similar reduction of annotinine chlorohydrin. Treatment of the trihydroxy compound with thionyl chloride converts it to a chlorine-containing sulphite ester which under the action of chromous chloride yields an unsaturated dihydroxy compound A, while under the conditions of the Clemmensen reaction, it yields an isomeric unsaturated dihydroxy compound B. Annotinine reacts with phenyl-lithium to give what seems to be a tetrahydroxy compound ($C_{28}H_{35}O_4N$) which is oxidized by chromic acid to $C_{28}H_{33}O_4N$. These reactions lead to two conclusions: (*a*) that hydrochloric acid and lithium aluminum hydride open the cyclic ether of annotinine in the same way, and (*b*) that the hydroxyl involved in the lactone is tertiary.

It has already been established from the chemical behavior of the base that two of the three oxygens of annotinine ($C_{16}H_{21}O_3N$) are present in a lactone ring (3) and the third bridges a secondary carbon and a tertiary carbon in a cyclic ether (3, 5). From the position of the carbonyl absorption band in the infrared spectrum of the alkaloid it appears that the lactone is probably five-membered (4). Nothing is known, however, concerning the way in which this ring is attached to the rest of the molecule, nor of its position relative to the nitrogen or the cyclic ether. A study of the reactions to be described was undertaken in an attempt to gain more information about these points.

It has been stated by Bertho and Stoll (2) that annotinine is inert towards lithium aluminum hydride in ether solution. It has been shown by the present work, however, that a limited quantity of lithium aluminum hydride in dioxane solution reduced the lactone function to give a dihydroxy ether ($C_{16}H_{25}O_3N$) I, in which the cyclic ether remained intact. Moreover, the action of an excess of the same reagent in tetrahydrofuran gave rise to a trihydroxy compound ($C_{16}H_{27}O_3N$) III, in which not only had the lactone been reduced, but the ether ring had also been opened (cf. flowsheet).

It was found also that annotinine chlorohydrin ($C_{16}H_{22}O_3NCl$), a substance arising from the cleavage of the cyclic ether with hydrochloric acid (3), underwent reaction with lithium aluminum hydride in ether solution to produce the same trihydroxy compound III obtainable directly from annotinine. Hence in the chlorohydrin the hydroxyl group arising from the cyclic ether must have occupied the same position as the hydroxyl group in the trihydroxy compound which was derived from the same function. It can be concluded that both hydrochloric acid and lithium aluminum hydride open this cyclic ether in the same way. It is known that a secondary oxide linkage is attacked

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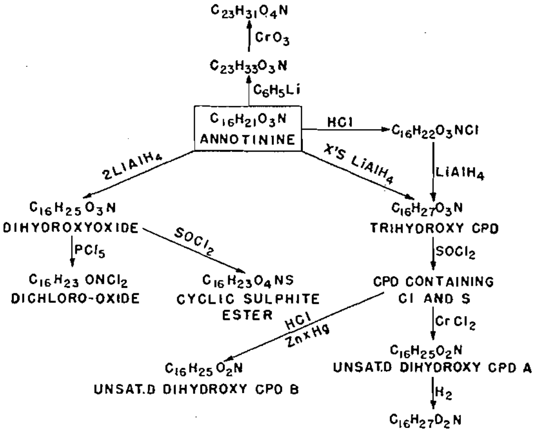
by lithium aluminum hydride in preference to a tertiary (6) and, therefore, in annotinine the ether must be cleaved between the secondary carbon and the oxygen. Since the lactone ring in the chlorohydrin is reduced in ether solution whereas annotinine is not affected under those conditions (2), it appears that the lactone is more stable when the cyclic ether is intact, and this observation prompts the surmise that the two functions may well be in close proximity to each other.



Flowsheet

The dihydroxy ether I was converted by phosphorus pentachloride to the corresponding dichloro ether, but the yield was small. Thionyl chloride, on the other hand, did not effect chlorination, but gave rise to a cyclic sulphite ester II. The infrared absorption spectrum of this derivative showed no absorption in the hydroxyl region nor in the carbonyl region, but contained a strong absorption band at 1206 cm.$^{-1}$, characteristic of the S–O frequency (1). The only difference in the behavior of the trihydroxy compound III in this reaction was due to the hydroxyl derived from the ether. When treated with thionyl chloride the trihydroxy compound was converted into an uncrystallizable product IV. Qualitative tests showed the presence of both sulphur and chlorine. Since the product IV could not be purified either by crystallization or distillation these tests might not be considered entirely significant, but the presence of sulphur (in a sulphite ester grouping) was confirmed by the subsequent reactions. The presence of chlorine was likely since the hydroxy lactone (one of the products of the reaction of annotinine chlorohydrin with chromous chloride) in which the hydroxyl formed from the cyclic ether was carried by the same tertiary carbon as in the trihydroxy compound III, was converted by thionyl chloride into an unstable chloro lactone (5). When the product IV was refluxed with chromous chloride and hydrochloric acid, it gave rise to an unsaturated dihydroxy compound A ($C_{16}H_{25}O_2N$). This unsaturated product when reduced catalytically absorbed one mole of hydrogen and gave a dihydro-dihydroxy compound A which failed to crystallize but was converted by thionyl chloride to an unstable crystalline sulphite ester. When, on the other hand, the reaction product IV was refluxed with amalgamated zinc and hydrochloric acid instead of chromous chloride, sulphur was liberated and an isomeric unsaturated dihydroxy compound B ($C_{16}H_{25}O_2N$) was produced. It is unlikely that more than two hydroxyls would have the required configuration for the facile formation of a sulphite ester. Therefore, by analogy with the formation of the unsaturated lactones described previously (5), it can be assumed that it is the hydroxyl group arising from the cyclic ether that is chlorinated and eventually eliminated with formation of a double bond. Attempts to remove the elements of water from unsaturated dihydroxy compound A failed. Treatment with thionyl chloride resulted in the formation of a sulphite ester.

The lactone ring of annotinine was also opened by a different method. Treatment of the base with phenyl-lithium[3] produced a derivative yielding analytical figures in agreement not with the expected $C_{28}H_{33}O_3N$, but with $C_{28}H_{35}O_4N$. The reaction mixture had been poured onto ice, and it is probable that the lithium hydroxide cleaved the ether with resulting formation of a glycol. The infrared absorption spectrum of this derivative contained several absorption peaks in the hydroxyl region, but showed no absorption in the carbonyl region. Oxidation of the derivative with chromic acid in acetic acid caused the loss of two hydrogens with no increase in the oxygen content. The oxidation product, $C_{28}H_{33}O_4N$, was still basic and its infrared absorption spectrum still contained several absorption bands in the hydroxyl region and a strong peak at 1720 cm.$^{-1}$ indicating the presence of a keto group. Hence the oxidation must have converted a secondary alcoholic into a keto group. In the similar oxidation of annotinine hydrate, a substance in which the cyclic ether has been converted to a glycol, it is one of these glycol hydroxyls which is secondary that is converted to a ketone group with the formation of a hydroxy ketone (5). In the present oxidation of the phenyl-lithium reaction product, since the same secondary hydroxyl arising from the ether was present, it can be assumed that it was this group that was oxidized to a ketone. It appeared probable, therefore, that the free hydroxyl that was originally esterified in the lactone was tertiary.

EXPERIMENTAL[4]

When not otherwise specified the infrared absorption measurements were made on nujol mulls with a Perkin–Elmer double beam instrument, model 21. The other measurements were made on a Perkin–Elmer single beam instrument, model 12B, and the solvent and prism used are mentioned in each case.

Annotinine and Lithium Aluminum Hydride (Incomplete Reaction)

Annotinine (3.0 gm.) was dissolved in purified dioxane and a 7% solution of lithium aluminum hydride in ether (7 ml.) added through a separatory funnel. The reaction mixture was refluxed under nitrogen for two hours. After cooling the excess lithium aluminum hydride was destroyed by the

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[3] *Dr. D. B. MacLean when working in Dr. R. H. Manske's laboratory carried out a preliminary investigation of this reaction. We are most grateful to them for making their results available and wish to acknowledge our indebtedness.*

[4] *Unless otherwise mentioned the melting points are corrected.*

addition of water (2 ml.) in methanol (20 ml.). The mixture was filtered and the clear filtrate extracted with chloroform. The evaporated extract yielded a partly crystalline residue that proved to be mostly unchanged annotinine, m.p. 232°, either alone or in admixture with an authentic sample.

When the aqueous filtrate which had been extracted by hand was again extracted with chloroform in a continuous liquid–liquid extractor, the extract yielded 2.65 gm. of an oily extract which was chromatographed on alumina (No. II). The chloroform–benzene (10: 1) eluate contained a compound (1.9 gm.) which formed a crystalline hydrochloride, m.p. 213–214°, after drying *in vacuo* for three hours at 80°. Found: C, 60.70, 60.84; H, 8.37, 8.28; N, 4.07. Calc. for $C_{16}H_{25}O_3N.HCl$: C, 60.86; H, 8.27; N, 4.44%. The free base liberated from the hydrochloride was crystallized from acetone, m.p. 220°. For analysis a sample was sublimed at 165° at 10^{-4} mm. Found: C, 68.78; H, 9.12; N, 5.13; active H, 0.79% (Zerewitinow). Calc. for $C_{16}H_{25}O_3N$: C, 68.78; H, 9.02; N, 5.01; 2 active H, 0.72%. The infrared absorption spectrum of this dihydroxyoxide contained two peaks at 3455 cm.$^{-1}$ (61.5)[5] and 3375 cm.$^{-1}$ (73) indicating two hydroxyl groups, and no longer contained absorption in the carbonyl region. The ether–methanol eluate yielded 450 mgm. of an oil which formed a crystalline hydrochloride, m.p. 254–255°. This salt yielded unsatisfactory analytical results, however, and was probably not homogeneous.

Annotinine and Lithium Aluminum Hydride (*Complete Reaction*)

Carefully dried annotinine (1.0 gm.) was dissolved in purified tetrahydrofuran (50 ml.) and added dropwise to saturated lithium aluminum hydride in ether (5 ml.) diluted with ether (100 ml.). A white precipitate separated immediately. The mixture was refluxed gently for two hours and the excess reagent destroyed with aqueous ether and methanol. The solvents were distilled off at 40° under reduced pressure and the solid residue dissolved in dilute hydrochloric acid. The solution was alkalized with ammonium hydroxide and extracted with chloroform in a continuous liquid–liquid extractor for 36 hr., the extract being removed and replaced by fresh chloroform every four to six hours. The combined chloroform extract on evaporation yielded an oily base, wt. 900 mgm., which crystallized from methanol. The product contained solvent of crystallization since on drying at 100° the crystalline form was altered and it lost weight (wt. 730 mgm. after drying). It melted at ca. 165–170°, solidified again, and melted at 214–215°. After sublimation in high *vacuo* at 170°, it melted at 215°. Found: C, 68.03; H, 9.54; N, 4.89. Calc. for $C_{16}H_{27}O_3N$: C, 68.29; H, 9.67; N, 4.98%. The infrared spectrum of this trihydroxy derivative determined in a mull on a single beam Perkin–Elmer spectrometer contained three absorption bands (3394 cm.$^{-1}$, 3298 cm.$^{-1}$, 3173 cm.$^{-1}$) indicating three hydroxyl groups. On the double beam instrument, only two absorption bands at 3305 cm.$^{-1}$ (75) and 3230 cm.$^{-1}$ (69.5) appeared.

Annotinine Chlorohydrin and Lithium Aluminum Hydride

Annotinine chlorohydrin (500 mgm.) was dissolved in absolute ether (50 ml.)

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[5] *The figures in brackets following wave numbers indicate per cent absorption.*

and added dropwise to an ethereal solution of lithium aluminum hydride (made up of 5 ml. of a saturated solution in 30 ml. of absolute ether). A white precipitate separated immediately. After the addition was complete the mixture was refluxed gently for one hour. The excess reagent was destroyed by the addition of ether–methanol and the mixture evaporated to dryness. The residue was dissolved in 2 *N* hydrochloric acid (20 ml.), the solution made alkaline with ammonium hydroxide, and extracted with chloroform in a continuous liquid–liquid extractor. The chloroform extract was concentrated and allowed to stand overnight at room temperature when long prismatic needles separated. The compound recrystallized from methanol, melted at ca. 165–180°, solidified, and melted again at 212–214°. On drying at 100° it lost weight. The dried material melted at 214–215° either alone or in admixture with the trihydroxy compound obtained by the reduction of annotinine with lithium aluminum hydride.

Dihydroxy Oxide and Phosphorus Pentachloride

The dihydroxy oxide (671 mgm.) was dissolved in dry chloroform (10 ml.) and refluxed for one hour with phosphorus pentachloride (1.0 gm.). The solvent was evaporated off, the residue made alkaline with sodium carbonate, and extracted with chloroform. The extract on evaporation left an oily residue, wt. 692 mgm., which was dissolved in benzene and chromatographed on alumina No. II. The benzene eluates were combined. After evaporation of the solvent they yielded 183 mgm. of a substance which was converted to the hydrochloride. This salt, after recrystallization from methanol, melted at 290–292° (uncorr.). For analysis a sample was dried for 12 hr. at 50° at 10^{-1} mm. Found: C, 54.44, 54.26; H, 6.44, 6.43; N, 3.96. Calc. for $C_{16}H_{23}ONCl_2.HCl$: C, 54.48; H, 6.86; N, 3.97%.

Dihydroxy Oxide and Thionyl Chloride

To the dihydroxy oxide (125 mgm.) thionyl chloride (3 ml.) was added and the mixture heated at 60° for five minutes. The excess thionyl chloride was distilled off under reduced pressure and the residue shaken with ammonium hydroxide and chloroform. The chloroform extract was separated and evaporated to dryness. There was left a yellow oil which was dissolved in benzene and chromatographed on alumina (No. II–III). The benzene eluate yielded a crystalline product which was recrystallized from heptane from which it separated as colorless needles, m.p. 147° (dec.). The product was sensitive to heat and on warming in a solvent there always formed a flocculent precipitate that had to be filtered. It could not be sublimed. Found: C, 58.72; H, 7.39; N, 4.11. Calc. for $C_{16}H_{23}O_4NS$: C, 59.05; H, 7.12; N, 4.30%. That this product was a sulphite ester was also indicated by its infrared absorption spectrum which no longer showed absorption in the hydroxyl region, but contained the absorption band at 1206 $cm.^{-1}$ (87.5) typical of S–O bonds (1).

When a small sample of this sulphite ester was treated with aqueous hydrochloric acid (1: 2) a yellowish precipitate was formed which proved to be elemental sulphur. Reduction with chromous chloride caused the evolution of hydrogen sulphide, but owing to paucity of material the main product of this reaction was not isolated.

Action of Thionyl Chloride on the Trihydroxy Compound

The trihydroxy compound (300 mgm.) (obtained by the complete reduction of annotinine with lithium aluminum hydride) was mixed with thionyl chloride (10 ml.) and the mixture kept at room temperature for one hour. The excess thionyl chloride was distilled off under reduced pressure and the residue shaken with ammonium hydroxide and chloroform. The chloroform extract on evaporation yielded 245 mgm. of a yellow oil which was dissolved in benzene and chromatographed on alumina (No. II–III). The benzene eluates contained 165 mgm. of an oil which crystallized slowly. All attempts to recrystallize this substance failed, since it decomposed rapidly on heating with solvents. Qualitative tests showed that the compound contained both sulphur and chlorine but since it could not be purified the tests may not be significant. Presumably the compound contained a sulphite ester group bridging the same two oxygens as in the ester obtained from the dihydroxyoxide and may have contained a chlorine replacing the third hydroxyl group.

The product was refluxed for three hours with chromous chloride prepared from chromic chloride hexahydrate (10 gm.), hydrochloric acid (10 ml.), amalgamated zinc (5 gm.), and water (50 ml.). The reduction mixture, after cooling, was extracted with ether. On evaporation, the extract left 95 mgm. of an oil which crystallized partly. Recrystallization from heptane yielded 60 mgm. of crystalline material, m.p. 169°. A sample was sublimed for analysis. Found: C, 73.05; H, 9.46; N, 5.21. Calc. for $C_{16}H_{25}O_2N$: C, 72.96; H, 9.57; N, 5.32%. The infrared absorption spectrum of this unsaturated dihydroxy compound A in chloroform solution on a single beam instrument with a calcium fluoride prism showed two absorption bands in the hydroxyl region, one free at 3615 cm.$^{-1}$ and one banded at 3379 cm.$^{-1}$.

The experiment was repeated with 480 mgm. of the trihydroxy compound and 15 ml. of thionyl chloride; the product on treatment with chromous chloride as above yielded 245 mgm. of the crystalline product, m.p. 169° after recrystallization from heptane. The oily material recovered from the heptane mother liquors was chromatographed on alumina and eluted first with benzene and then with ether. The combined benzene and ether eluates contained 195 mgm. of an oil which slowly decomposed on exposure to air, and could not further be characterized.

A third experiment was carried out slightly differently. The trihydroxy compound (205 mgm.) and thionyl chloride (10 ml.) were left at room temperature for one hour. The excess thionyl chloride was removed *in vacuo* and the residual product refluxed with 2 *N* hydrochloric acid and a small quantity of amalgamated zinc. A precipitate of elementary sulphur soon separated. After one hour of refluxing the mixture was cooled, filtered, and the filtrate alkalized with ammonia and extracted with chloroform. On evaporation of the combined extract an oily residue was left, 170 mgm., which was dissolved in benzene and chromatographed on alumina (No. III). The benzene–ether (5:2) eluate yielded a colorless oil which crystallized slowly. After recrystallization from ether the product melted at 146–147°. Found: C, 72.86; H, 9.29; N, 5.21. Calc. for $C_{16}H_{25}O_2N$: C, 72.96; H, 9.57; N, 5.32%. This unsaturated dihydroxy compound B, which was isomeric with the above dihydroxy derivative A (m.p. 169°), had an infrared absorption spectrum containing a number of absorption peaks in the OH–NH region, i.e., a double peak, 3360 (60), 3315 (59) and 3180 (56.5), 3060 (53).

Catalytic Reduction of Unsaturated Dihydroxy Compound A

The unsaturated dihydroxy compound (95 mgm.) was dissolved in ethanol (3 ml.) and hydrogenated over Adams' catalyst. The uptake of hydrogen was exactly one mole. After removal of the catalyst by filtration the solvent was evaporated and the residual colorless oil which failed to crystallize was chromatographed on alumina (No. III). The recovered product was still an oil and repeated attempts to crystallize it from various solvents were ineffective, nor was it possible to prepare a crystalline salt.

The oily product was allowed to stand at room temperature for 10 minutes with thionyl chloride (2 ml.). The product of this reaction, worked up as described above, was a yellowish oil which was chromatographed on alumina (No. III). The benzene eluate yielded a fraction that crystallized slowly. It was very unstable and no definite melting point could be observed. A qualitative test showed that it contained sulphur and therefore was probably a sulphite ester.

Action of Thionyl Chloride on Unsaturated Dihydroxy Compound A

The unsaturated dihydroxy compound (105 mgm.) was treated with thionyl chloride at room temperature and the product worked up in the usual way. It consisted of a colorless oil which crystallized from heptane as long colorless needles, m.p. 130–150° (dec.), which decomposed on attempted sublimation. Treatment of the substance with chromous chloride liberated hydrogen sulphide.

Reaction of Annotinine with Phenyl-lithium

Annotinine (800 mgm.) was dissolved in ether (50 ml.) and added dropwise to an ethereal solution of phenyl-lithium (made from 0.3 gm. of lithium). After being refluxed for one hour the reaction mixture was cooled and poured into a separatory funnel containing cracked ice. The milky mixture was alkalized with ammonia and extracted repeatedly with ether. The combined extract was distilled on the steam bath to remove the solvent and the oily residue dissolved in benzene and chromatographed on alumina (No. III). The benzene eluate contained some diphenyl and a few milligrams of unchanged annotinine. The ether eluate yielded an oily product which on treatment with heptane was converted into an amorphous solid. The product was sublimed at 190° at 10^{-4} mm. after which it melted at 236–239°. Yield, 800 mgm. Found: C, 74.89; H, 7.22; N, 3.07. Calc. for $C_{28}H_{35}O_4N$: C, 74.80; H, 7.85; N, 3.12%. The infrared absorption spectrum showed absorption bands in the hydroxyl region, but no absorption in the carbonyl region.

Oxidation of the Diphenyl Derivative of Annotinine

The diphenyl derivative (700 mgm.) was dissolved in glacial acetic acid (3 ml.) and to the solution a mixture of chromic acid (400 mgm.) in glacial acetic acid (3 ml.) was slowly added. A greenish brown precipitate separated which gradually dissolved again. The mixture was left standing for five hours and a few drops of ethanol were added to reduce excess chromic acid. The solvents were evaporated under reduced pressure at a temperature no higher than 40°, and the residue dissolved in chloroform. After shaking with hydrochloric acid the chloroform solution was washed with water, dried, and evaporated. There was left an oily residue (610 mgm.) that was dissolved in benzene and chromatographed on alumina (No. III). The benzene eluate yielded a product which was crystallized from a mixture of dichlorethylene and heptane from which it separated as fine small needles, m.p. 250–251°. Found: C, 75.67; H, 6.82; N, 3.12. Calc. for $C_{28}H_{33}O_4N$: C, 75.14; H, 7.43; N, 3.13%. The infrared absorption spectrum contains absorption bands in the hydroxyl region and a new absorption band at 1720 cm.$^{-1}$ attributable to a keto group.

ACKNOWLEDGMENT

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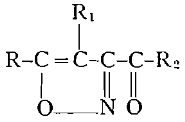
THE SYNTHESIS AND REACTIONS OF 1-CHLORO-2-ISONITROSODIBENZOYLETHANE[1]

By A. Beelik[2] and W. H. Brown

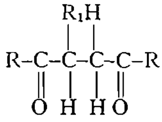
ABSTRACT

The addition of nitrosyl chloride to *trans*-dibenzoylethylene produces only the *syn*-benzoyl isomer of 1-chloro-2-isonitrosodibenzoylethane. This compound contains a hydrogen bond. It forms two isomeric mono-2,4-dinitro-phenylhydrazones. When boiled with hydrochloric acid it is converted into 3-benzoyl-4-chloro-5-phenylisoxazole. The reactions and derivatives of this latter compound are discussed.

In Cusmano's (16, 17, 13, 14) general synthesis of 3-ketoisoxazoles (I) by the action of boiling nitric acid on saturated 1,4-diketones (II), a 2-isonitroso-1,4-diketone (III) is the hypothetical and unisolated intermediate. III may be considered to be the monoxime of a 1,2,4-triketone, a compound with an interesting combination of functional groups

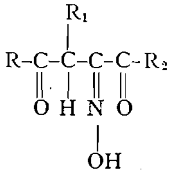


I



$R{-}C({=}O){-}C(R_1)H{-}CH_2{-}C({=}O){-}R_2$

II



$R{-}C({=}O){-}C(R_1)H{-}C({=}N{-}OH){-}C({=}O){-}R_2$

III

$R,R_2 = CH_3$ or C_6H_5
$R_1 = H$ or C_6H_5

The aim of the present investigation was the synthesis of a stable analogue of III and the study of its configuration. The synthesis has been achieved by the addition of nitrosyl chloride to *trans*-dibenzoylethylene (IV), which was prepared by the method of Lutz (20). A modification of the classical (19, 23, 24) amyl nitrite – hydrochloric acid method gave a 72% yield of the addition product, a white crystalline solid (V), melting at 133°C. Though the primary addition product in this reaction is the nitroso chloride, in most known cases (19, 24) the primary or secondary nitroso compounds rearrange to the more stable isonitroso chlorides. Thus V was assumed to be 1-chloro-2-isonitrosodibenzoylethane (III: $R,R_2 = C_6H_5$, $R_1 = Cl$). The physical and chemical properties of V have been shown to agree with this structure.

Red solutions result when V is dissolved in pyridine and cold aqueous sodium hydroxide. In the latter reagent, decomposition of V into benzaldehyde and resinous condensation products occurs. Hot dilute nitric acid oxidizes V to two molecules of benzoic acid.

V is unaffected by phosphorus pentachloride under the usual conditions for the Beckmann rearrangement of oximes. When V is treated with benzoyl

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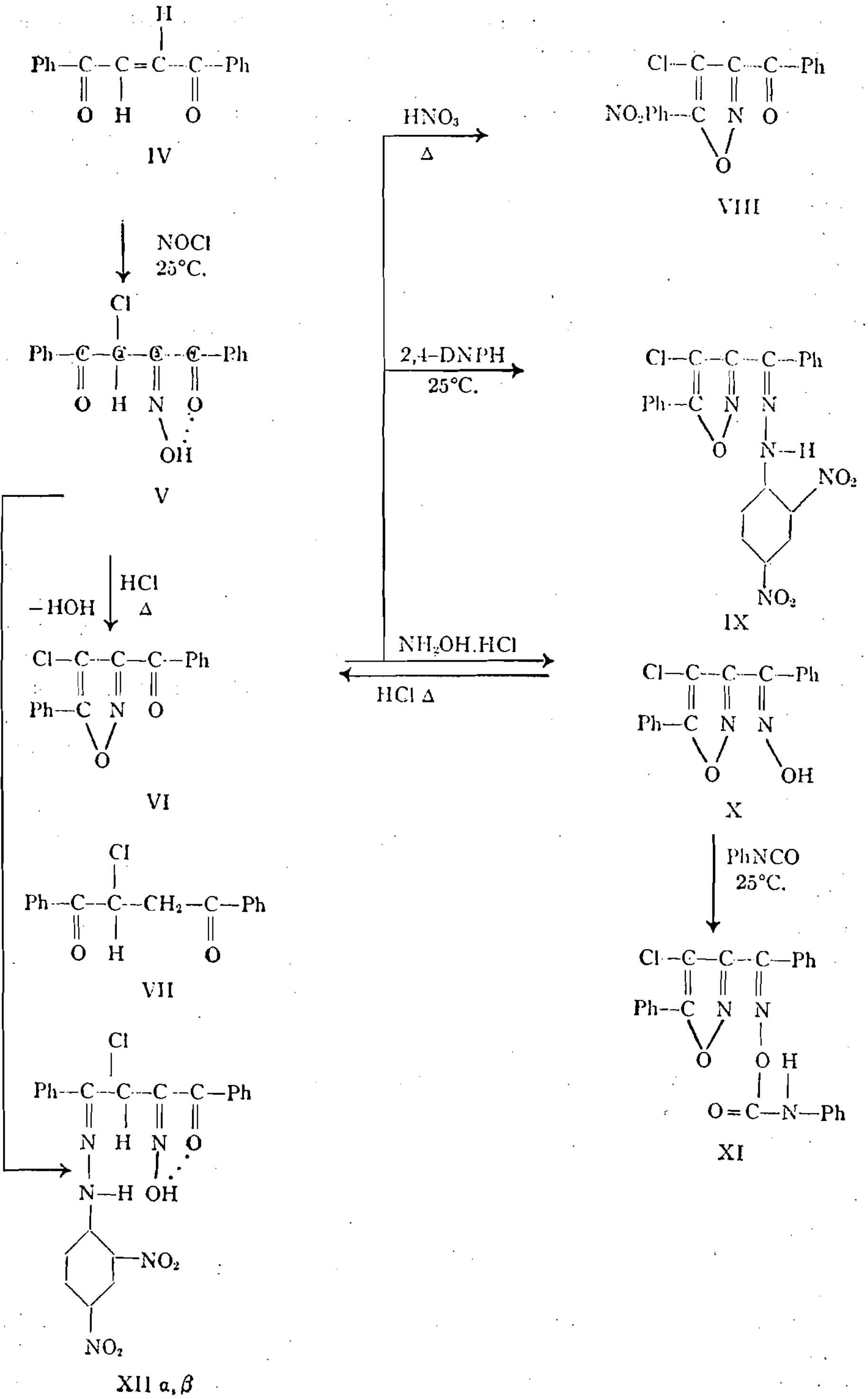
IV
NOCl
25°C.
V
HCl
−HOH
Δ
VI
VII
XII α, β
HNO₃
Δ
VIII
2,4-DNPH
25°C.
IX
NH₂OH.HCl
HCl Δ
X
PhNCO
25°C.
XI

chloride according to the method of Rheinboldt (22) benzoylation does not occur. No reaction has been observed when V is treated with phenyl isocyanate according to Schmidt (23).

Treatment of V with 2,4-dinitrophenylhydrazine in sulphuric acid according to Brady (8) gives two isomeric mono-2,4-dinitrophenylhydrazones. This result was unexpected, since the *bis*-2,4-dinitrophenylhydrazones are formed very readily by dicarbonyl compounds (6).

The existence of a hydrogen bond between the oxime hydroxyl and one of the carbonyl oxygens in V could account for the failure to form derivatives at these two functional groups. The *syn*-benzoyl form of V, indeed, fulfils all the theoretical requirements of intramolecular hydrogen bonding (25). The existence of a hydrogen bond has been established by infrared spectroscopy. Strong absorption due to hydrogen bonding usually occurs in the infrared from approximately 3500 cm^{-1}. to 3200 cm^{-1}. It may be seen in Figs. 1 and 2 that V exhibits absorption in this region while 1-chlorodibenzoylethane (VII) does not.

This in itself does not prove chelation in V, as simple oximes, which are only capable of intermolecular hydrogen bonding, are also known to absorb weakly in the same region. The chemical behavior of V, however, makes the existence of an intramolecular hydrogen bond in the molecule more than probable.

When V is treated with hot concentrated hydrochloric acid, loss of water occurs and a new compound (VI) is formed. The loss of water can only occur between the oxime hydroxyl and the enolized carbonyl group in position 1. The same reaction occurs in Claisen's (11) synthesis of isoxazoles by oximation of 1,3-diketones. Thus V corresponds to Claisen's intermediate mono-oxime and VI must be 3-benzoyl-4-chloro-5-phenylisoxazole. Like other aryl-substituted isoxazoles (12, 18, 26), VI resists oxidation by hot concentrated nitric acid, but is nitrated by this reagent. The product is, by analogy with work of Cusmano (18), probably, 3-benzoyl-4-chloro-5-*p*-nitrophenylisoxazole (VIII).

The configuration of oximes is frequently established through their conversion to cyclic compounds. The formation of VI would seem to support the *anti*-benzoyl configuration for V, contradicting previous considerations. However, the conflicting evidence may be reconciled by the assumption that the stable *syn*-benzoyl form isomerizes to the labile *anti*-benzoyl form prior to cyclization. Isomerization by hydrochloric acid in this direction is not common, but a similar conversion has been reported by Meisenheimer (21).

Two carbonyl derivatives of VI have been prepared, the 2,4-dinitrophenylhydrazone (IX) and the oxime (X). Ajello (1, 2, 3, 4) and Cusmano (17, 13) have found that on oximation, 3-ketoisoxazoles easily undergo ring fission and furazan derivatives may be formed. The extent of this transformation apparently depends on the nature of the substituents on the isoxazole nucleus, but does vary for a given isoxazole with the reagents and conditions employed (1). Some of their results are contradictory (4, 13) and the problem has not been wholly clarified. The reverse transformation has been reported by Cusmano (15) in a recent paper: 3-phenyl-4-desylfurazan was converted by boiling concentrated hydrochloric acid into 3-benzoyl-4,5-diphenylisoxazole,

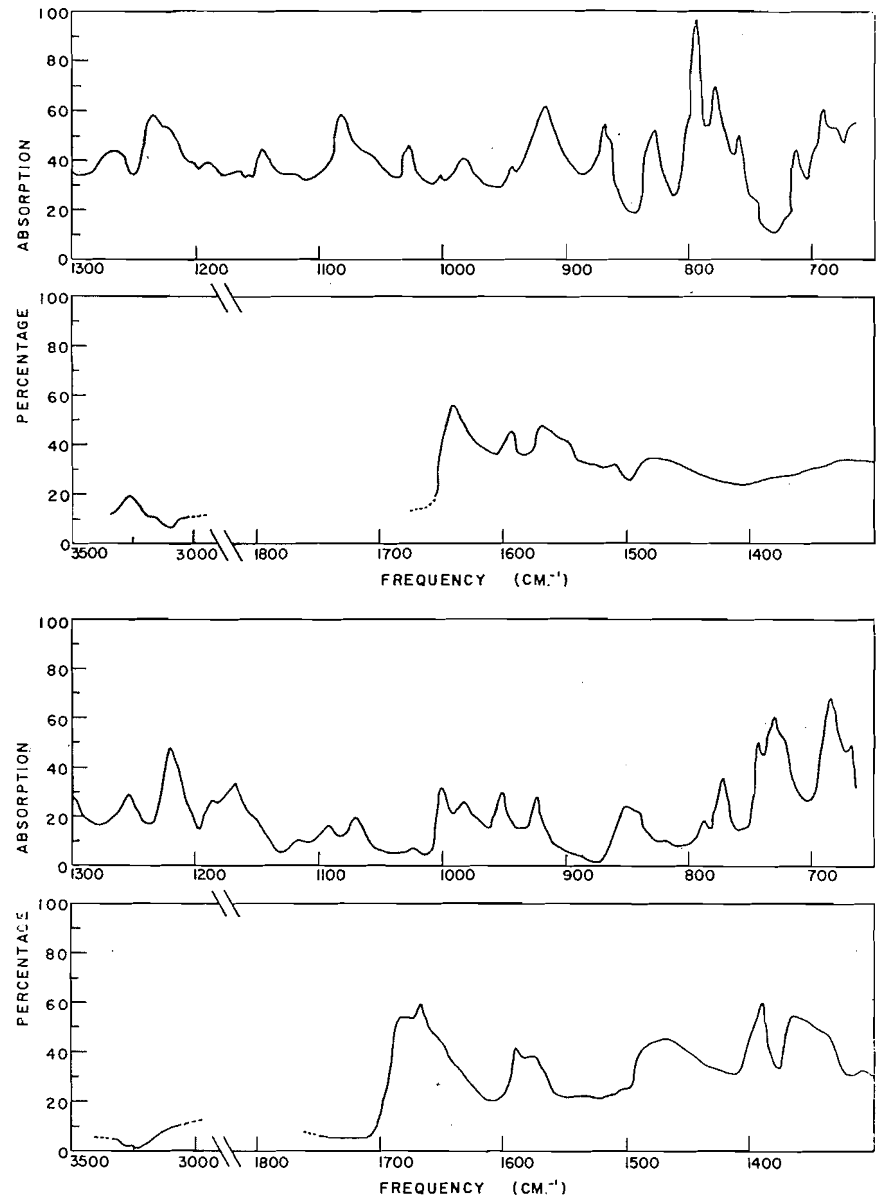

FIG. 1. Infrared spectra of 1-chloro-2-isonitrosodibenzoylethane (top), and 1-chlorodibenzoylethane (bottom), measured in a Nujol mull on a Perkin–Elmer 12C single beam spectrophotometer with sodium chloride prism, 0.025 mm. cell.

with liberation of hydroxylamine. In the light of these reports, X could have either an isoxazole structure or a furazan structure. However, it has been found that X fails to react with either hydroxylamine or 2,4-dinitrophenylhydrazine but does form a derivative (XI) with phenyl isocyanate. This establishes that the isoxazole structure for X is correct. The oximation of VI has been repeated under a variety of conditions simulating those employed by Cusmano and

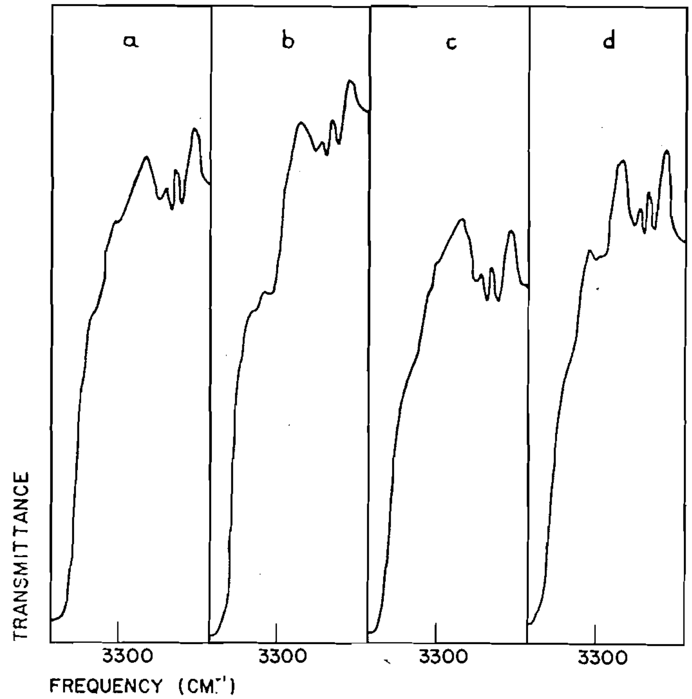

FIG. 2. Sections of the infrared spectra of (*a*), 1-chlorodibenzoylethane; (*b*) 1-chloro-2-isonitrosodibenzoylethane; (*c*), alpha-2,4-dinitrophenylhydrazone of (*b*); and (*d*), beta-2,4-dinitrophenylhydrazone of (*b*); as recorded by a Perkin–Elmer 12C single beam spectrophotometer. All four compounds in Nujol mull, sodium chloride prisms, cells vary 0.025, 0.10, 0.20, 0.20 in above order.

Ajello (1, 2, 3, 13). In all cases X was the only product, indicating that the nucleus of VI resists cleavage in this reaction.

Attention may now be turned to the two isomeric mono-2,4-dinitrophenylhydrazones (XII) of V. Of these, the α-isomer, melting at 211–212°C., is formed at low temperatures (4°C.) and the β-isomer, melting at 183°C. with decomposition, is obtained at room temperature. Repeated boiling in different solvents did not change these melting points. The α-isomer of XII as well as compound IX are unaffected by hot concentrated hydrochloric acid, but the β-isomer of XII is converted into the α-isomer by this reagent. In these isomers, the 2,4-dinitrophenylhydrazine group may be attached to the same or to different carbon atoms of V. Attachment to different positions would require simultaneous hydrolysis and recondensation for the interconversion. This process is ruled out after consideration of the stability of 2,4-dinitrophenylhydrazones (5, 6). An isomer with attachment at position 4 should be convertible by hot concentrated hydrochloric acid into IX through formation of the isoxazole nucleus. Failing this, attachment has to be at position 1 in both isomers, which agrees with the theory of the hydrogen bond. Thus geometric isomerism seems to be a logical explanation. The close correspondence over the fingerprint region (1350–600 cm^{-1}.) in the infrared spectra of the α and β-isomers also favors this assumption. A marked band due to bonded OH is present in the spectrum of the β-isomer at 3330 cm^{-1}. (see Fig. 2*d*). The absence of this band in the spectrum of the α-isomer (see Fig. 2*c*) could be due to the overlapping of the NH stretching frequency.

Two double bonds in XII could be involved in geometrical isomerism. A shift at the oxime double bond would conform to a similar shift, caused also by hot concentrated hydrochloric acid, in V. The infrared evidence would not contradict this assumption. Accordingly, the α-isomer would have an *anti*-benzoyl, the β-isomer a *syn*-benzoyl oxime structure. A shift at the hydrazone double bond would produce the rare type of geometrically isomeric 2,4-dinitrophenylhydrazones, of which the most outstanding example is found in the work of Bredereck (9, 10). He reported two forms of furfural 2,4-dinitrophenylhydrazone melting at 212–214°C. and 230°C., respectively, with a mixed melting point of 185°C. For an excellent discussion on the occurrence of geometrical isomerism, polymorphism, mixed crystal formation, and structural rearrangements of 2,4-dinitrophenylhydrazones see Braddock *et al.* (7).

The simple procedure and good yield in the synthesis of V and its almost quantitative conversion to VI offer a convenient method for the preparation of 3-keto-4-chloroisoxazoles from symmetrical unsaturated 1,4-diketones.

EXPERIMENTAL*

1-Chloro-2-isonitrosodibenzoylethane

To a solution of 10.0 gm. (0.0424 mole) of *trans*-dibenzoylethylene in 100 ml. of dioxane was added 10.0 gm. (0.0853 mole) of freshly prepared *n*-amyl nitrite. The solution was stirred at room temperature at a moderate speed, while 8.0 ml. (0.099 mole) of concentrated hydrochloric acid (37%) was introduced dropwise from a separatory funnel, over a period of twenty minutes. The solution turned golden brown. Stirring was continued.† After a lapse of two hours the addition of *n*-amyl nitrite and concentrated hydrochloric acid was repeated, again using the same quantities and procedure. Stirring was continued for another half hour, and then the reaction mixture was allowed to stand for 48 hr. at room temperature. The mixture separated into two layers and some gas development was observed. Subsequently, the reaction mixture was diluted with 600 ml. of water. A yellowish oil separated at the bottom of the vessel. Most of the water was decanted, and the oil slowly crystallized into a white solid on standing. The solid was filtered off and purified from benzene–hexane and methanol–water, yielding 9.27 gm. (73%) of white crystals melting at 131–133°C.

Anal. Calc. for $C_{16}H_{12}O_3NCl$ (301.5): C, 63.70; H, 4.01; N, 4.65.
Found: C, 63.86; H, 4.05; N, 4.62. Mol. wt. Found: 299.

3-Benzoyl-4-chloro-5-phenylisoxazole

A suspension of 5.0 gm. (0.0166 mole) of 1-chloro-2-isonitrosodibenzoyl-

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**All melting points have been corrected against reliable standards. The molecular weights were determined by the Rast camphor method.*

†The reaction mixture usually does not warm up significantly. With greater quantities, however, the temperature may rise, and when it passes 40°C. it is advisable to cool the mixture back to room temperature.

ethane in 50 ml. of concentrated hydrochloric acid (37%) and 15 ml. of water was refluxed over a low flame for five hours. At the end of this period the organic material was present in the reaction mixture as an oil, and solidified overnight at room temperature. The off-white solid was separated from the clear acid liquor by filtration, washed with several lots of water, and was crystallized from ethanol–water. The purified product, fine white needles, weighed 4.32 gm. (92%) and melted at 56–57°C.

Anal. Calc. for $C_{16}H_{10}O_2NCl$ (283.5): C, 67.69; H, 3.52; N, 4.94.
Found: C, 67.59; H, 3.45; N, 4.85. Mol. wt. Found: 265, 259.

1-Chloro-2-isonitrosodibenzoylethane Mono-2,4-dinitrophenylhydrazone (α-Isomer)

The reagent solution was prepared by dissolving 0.38 gm. (0.0019 mole) of 2,4-dinitrophenylhydrazine in 0.8 ml. of hot concentrated sulphuric acid (d. 1.84, 95%) and by adding 6 ml. of 95% ethanol to this solution. A solution of 0.60 gm. (0.002 mole) of 1-chloro-2-isonitrosodibenzoylethane in 14 ml. of 95% ethanol and the reagent solution were mixed at room temperature. The resulting clear red solution was stored overnight at 3–4°C. A copious orange precipitate formed. It was filtered off and crystallized from benzene–hexane, yielding 0.44 gm. of an amorphous solid, melting at 186–197°C. with decomposition. This product was recrystallized from acetone–water and again from benzene–hexane, finally yielding 0.31 gm. of an amorphous orange solid melting at 211–212°C.

Anal. Calc. for $C_{22}H_{16}O_6N_5Cl$ (482): N, 14.52.
Found: N, 14.64, 14.48. Mol. wt. Found: 467.

1-Chloro-2-isonitrosodibenzoylethane Mono-2,4-dinitrophenylhydrazone (β-Isomer)

The same quantities of 2,4-dinitrophenylhydrazine, 1-chloro-2-isonitrosodibenzoylethane, concentrated sulphuric acid and 95% ethanol were used to prepare the final clear red solution as in the preparation of the high melting isomer. This solution, however, was stored overnight at room temperature. An orange precipitate formed. It was filtered off and crystallized from ethanol–water and benzene–hexane. The purified product, fine orange needles, weighed 0.45 gm., and melted at 182–183°C. with decomposition.

Anal. Calc. for $C_{22}H_{16}O_6N_5Cl$ (482): N, 14.52.
Found: N, 14.59, 14.49.

3-Benzoyl-4-chloro-5-phenylisoxazole 2,4-Dinitrophenylhydrazone

This derivative was prepared as above and crystallized from acetone–water and ethyl acetate – ethanol. The yield was 0.35 gm. of an amorphous orange solid melting at 203–204°C.

Anal. Calc. for $C_{22}H_{14}O_5N_5Cl$ (464): N, 15.09.
Found: N, 15.06.

Conversion of β-Isomer of 1-Chloro-2-isonitrosodibenzoylethane Mono-2,4-dinitrophenylhydrazone to the α-Isomer

A suspension of 0.100 gm. of the β-mono-2,4-dinitrophenylhydrazone of 1-chloro-2-isonitrosodibenzoylethane in 3 ml. of concentrated hydrochloric acid (37%) was heated on the steam bath, with occasional stirring, for seven hours. The orange solid was filtered off and washed with water. After drying, this crude product weighed 0.092 gm. and melted at 194–202°C. This was crystallized twice from benzene–hexane, yielding 0.062 gm. of an amorphous orange solid melting at 211–212°C. A mixed melting point with a pure sample of the α-isomer showed no depression.

3-Benzoyl-4-chloro-5-phenylisoxazole Oxime

To a suspension of 2.5 gm. (0.00877 mole) of 3-benzoyl-4-chloro-5-phenylisoxazole in 50 ml. of 95% ethanol was added a solution of 1.7 gm. (0.0245 mole) of hydroxylamine hydrochloride in the minimum amount of water. The resulting mixture was refluxed on the steam bath for four hours. All the solid dissolved after the first few minutes of heating. The colorless clear solution was concentrated to a sixth of its original volume, and then cooled. An off-white solid separated from the solution. It was filtered off and triturated with several lots of water on the filter. This crude solid was dried by suction. It weighed 2.59 gm. and melted at 148–150.5°C. By crystallization from acetic acid – water 1.95 gm. (75%) of white needles was obtained, melting at 151–153°C. Further purification from acetic acid – water and toluene – hexane narrowed the range to 152–153°C. Oximation in the presence of pyridine or potassium hydroxide gave the same product.

Anal. Calc. for $C_{16}H_{11}O_2N_2Cl$ (298.5): C, 64.35; H, 3.71; N, 9.37; Cl, 11.89. Found: C, 64.86, 64.50; H, 3.72, 3.66; N, 8.76, 8.70; Cl, 12.19, 12.27.

Hydrolysis of 3-Benzoyl-4-chloro-5-phenylisoxazole Oxime

To 2 ml. of concentrated hydrochloric acid (37%) was added 0.2 gm. (0.00067 mole) of 3-benzoyl-4-chloro-5-phenylisoxazole oxime. The resulting suspension was refluxed over a low flame for three hours. The solid was converted to a yellow oil. This oil thickened overnight, and was filtered off. The sticky crude solid was crystallized from ethanol–water, and 0.07 gm. of fine white needles was obtained, melting at 56–57°C. A mixed melting point with 3-benzoyl-4-chloro-5-phenylisoxazole showed no depression. The clear reaction liquor was evaporated to dryness, the yellowish residue was taken up in 2 ml. of water, and the presence of hydroxylamine in this solution was demonstrated by the hydroxamate test.

Reaction of 3-Benzoyl-4-chloro-5-phenylisoxazole Oxime with Phenyl Isocyanate

A solution of 0.23 gm. (0.00078 mole) of 3-benzoyl-4-chloro-5-phenylisoxazole oxime and 0.12 gm. (0.001 mole) of phenyl isocyanate (EK 533) in 2 ml. of absolute ether was stored for two days in a well-stoppered bottle, in the dark at room temperature. A minor quantity of colorless prisms formed during this period. Removed from the solution they proved to be *sym*-diphenylurea. The ether solution was evaporated to dryness. The residue, a pale brown oil, solidified in a short time. This solid was crystallized from toluene–ether–hexane, yielding 0.15 gm. of product, melting at 147–149°C. Two further crystallizations from ethanol–water narrowed the melting range to 148–149°C.

The purified product, long white needles, weighed 0.11 gm. A mixed melting point with 3-benzoyl-4-chloro-5-phenylisoxazole oxime showed a marked depression.

Anal. Calc. for $C_{23}H_{16}O_3N_3Cl$ (417.5): N, 10.04.
Found: N, 9.87, 9.83.

Nitric Acid Oxidation of 1-Chloro-2-isonitrosodibenzoylethane

A suspension of 0.5 gm. (0.00165 mole) of 1-chloro-2-isonitrosodibenzoylethane in 7 ml. of dilute nitric acid (d. 1.15, 25%) was heated on the steam bath for seven hours. The evolution of brown fumes began after the first few minutes and ceased after six hours of heating. The cooled reaction mixture yielded an alkali soluble, white solid which weighed 0.264 gm. and melted at 122–123°C. A mixed melting point with an authentic sample of benzoic acid showed no depression; 0.264 gm. (0.00216 mole) of benzoic acid corresponds to a yield of 1.31 mole per mole of 1-chloro-2-isonitrosodibenzoylethane.

Nitration of 3-Benzoyl-4-chloro-5-phenylisoxazole

When 0.5 gm. (0.00176 mole) of 3-benzoyl-4-chloro-5-phenylisoxazole was added to 7 ml. of concentrated nitric acid (d. 1.42, 70%), the white solid changed into a yellowish oil which spread out over the surface of the acid in a thin film. The mixture was heated on a steam bath, and evolution of brown fumes began after a few minutes. In the second hour of heating a white solid started to crystallize from the brown liquor. Heating was continued for a total of seven hours. A considerable amount of the crystalline white solid collected at the bottom of the vessel, and was separated from the hot brown acid liquor by filtration. This solid was crystallized from acetic acid – water, yielding two crops of white crystals: 0.19 gm. melting at 182–185°C. and 0.064 gm. melting at 167–180°C. The first crop was recrystallized three times from acetone–water and once from dioxane–water, yielding 0.06 gm. of pure product melting at 190–191°C. A qualitative test for the nitro group was positive.

Anal. Calc. for $C_{16}H_9O_4N_2Cl$ (328.5): N, 8.52.
Found: N, 8.45, 8.28.

Alkaline Hydrolysis of 1-Chloro-2-isonitrosodibenzoylethane to Give Benzaldehyde

When 1.14 gm. (0.00378 mole) of 1-chloro-2-isonitrosodibenzoylethane was added to a solution of 0.4 gm. (0.01 mole) of sodium hydroxide in 14 ml. of water (2.8% aqueous sodium hydroxide) a red suspension formed immediately. The suspension was steam distilled and 50 ml. of distillate was collected. The presence of benzaldehyde in the distillate was demonstrated through formation of the 2,4-dinitrophenylhydrazone.

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We are indebted to Canadian Industries Limited for determining the infrared spectra and also for providing a scholarship for one of us (A.B.).

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THE KINETICS OF THE PYROLYSIS OF TOLUENE[1]

By H. Blades,[2] A. T. Blades,[3] and E. W. R. Steacie

ABSTRACT

The pyrolysis of toluene has been studied in an attempt to verify the findings of Szwarc (2). The major products have been confirmed but styrene and isomeric dimethyl diphenyls have also been detected. First order rate constants for the decomposition have been found to depend on the condition of the surface of the reactor, the contact time, and, to a lesser degree, on the pressure. Some preliminary studies on the mechanism of the formation of the dimethyl diphenyls are also recorded.

INTRODUCTION

Recently Szwarc (3) and his co-workers have determined the bond dissociation energy for a number of compounds by means of the toluene carrier gas technique. In this technique compounds are decomposed thermally in the presence of a large excess of toluene which, at the relatively high temperatures involved, acts as a very good inhibitor to free radical chain reactions.

Many of the compounds so studied have been toluene derivatives and, in the calculations of standard heats of formation of radicals which follow from the kinetics data, it is necessary that the standard heat of formation of the benzyl radical be known. It has been customary to obtain a figure for this from the kinetic measurements of the pyrolysis of toluene itself.

Szwarc (2) studied the pyrolysis of toluene by passing the vapor through a fairly large (about 450 cc. in volume) reaction cell, the temperature of which was adjusted to produce from 0.01 to 1.25% decomposition. These low conversions help to assure the inhibiting properties of the toluene. The products identified were bibenzyl, benzene, methane, hydrogen, and large proportions of the undecomposed toluene. The quantities of hydrogen and methane were determined accurately and the bibenzyl was weighed for a limited number of runs.

The basic reactions postulated were

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2 + H \qquad [1]$$

$$H + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2 \qquad [2]$$

$$2C_6H_5CH_2 \rightarrow C_6H_5CH_2CH_2C_6H_5. \qquad [3]$$

The presence of methane and benzene was explained by the following set of reactions

$$H + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3 \qquad [4]$$

$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2. \qquad [5]$$

Reactions [2] and [4] thus compete for hydrogen atoms. Support for the exis-

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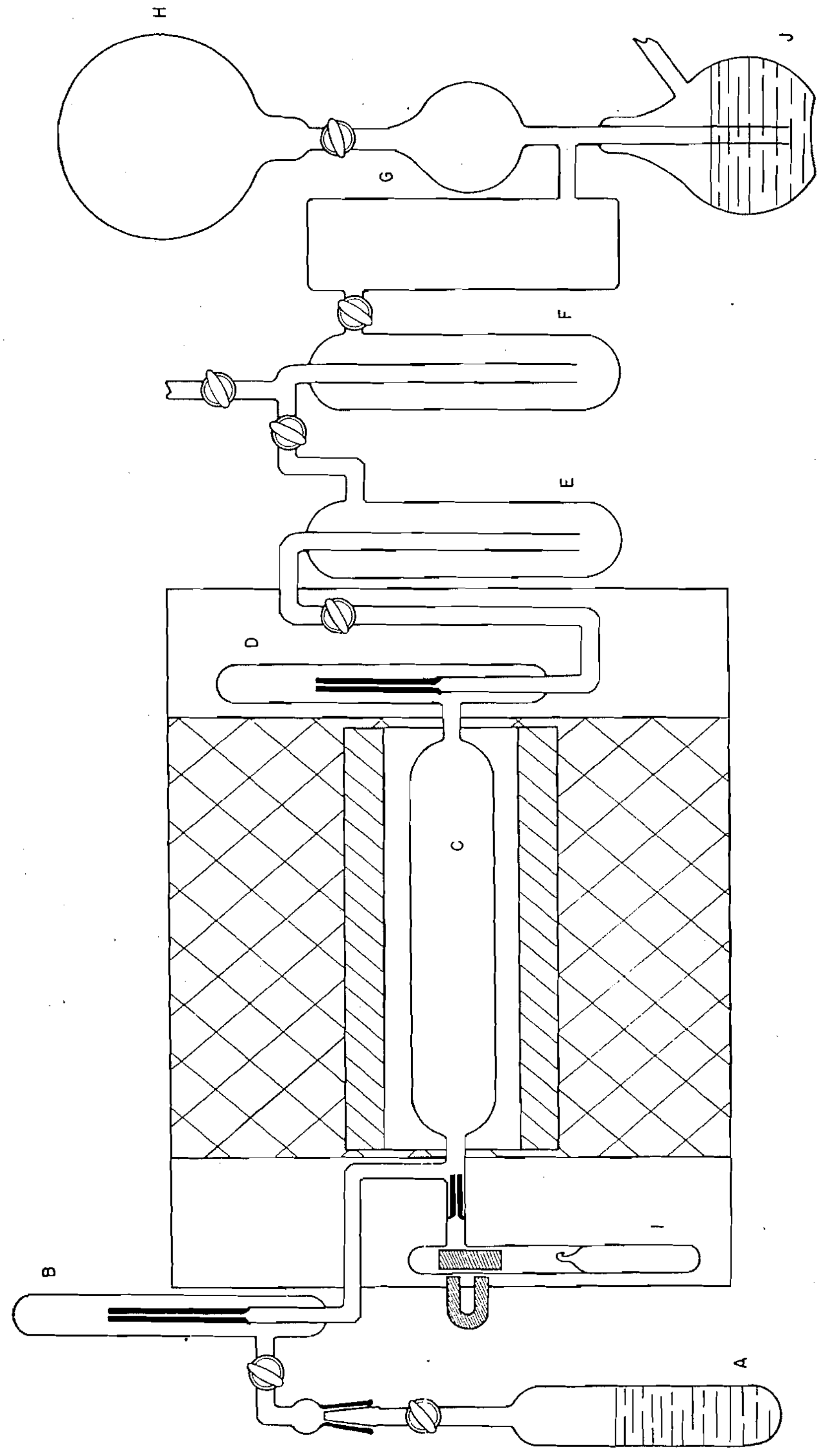


FIG. 1. The pyrolysis apparatus.

tence of these reactions has been obtained by studying the decomposition of other compounds (1) which produce hydrogen atoms in the presence of an excess of toluene.

The relative proportions of hydrogen, methane, and dibenzyl were found to be consistent with the above scheme. In addition, the hydrogen to methane ratio was found to be independent of temperature and conversion.

The pressure of toluene was varied from 2.7 mm. to 13.7 mm. and the time of reaction from 0.235 to 0.905 sec. To test for first order behavior of the data, the rate constants were calculated assuming a first order rate and these values plotted on the usual Arrhenius plot. The data lay on a straight line with no systematic deviations with either pressure or reaction time. From this it was concluded that the reaction was first order. Homogeneity was demonstrated by packing the reaction cell with silica wool, thereby increasing the surface area 15 times.

From the kinetics data, Szwarc calculated the following rate expression

$$k = 2.1 \times 10^{13}\ e^{-77,500/RT}\ \text{sec}^{-1}.$$

The activation energy was identified with the bond dissociation energy of the first hydrogen in toluene, and this was then used to calculate the standard heat of formation of the benzyl radical.

In the present study the work of Szwarc on the pyrolysis of toluene has been repeated and extended in an attempt to assess the uncertainty in the figure for the heat of formation of the benzyl radical derived from measurements on the rate of this reaction.

Apparatus and Procedure

The flow type apparatus shown in Fig. 1 is similar to that used by Szwarc. Toluene was evaporated from *A*, which was held at constant temperature, through the capillary *B* into the reaction chamber *C* in a furnace, and then into traps *E* and *F* which were immersed in acetone – dry ice mixture and liquid air respectively. Noncondensable gases were compressed by the diffusion pump *G* and collected by the Toepler pump in the measured volume *H* where the pressure was measured with a McLeod gauge.

The pressure in *C* was regulated by the capillary at *D* and measured with a wide diameter manometer, using a cathetometer for measurements. Throughout the work several reaction chambers were used, varying in size from a few cubic centimeters to 450 cc. The chamber used for the rate experiments listed below was 1.7 cm. in diameter and 24 cm. long.

To prevent condensation of material not volatile at room temperature, the capillary *D* was surrounded by a box thermostated at 100°C. The line leading from this box to the trap *E* was heated to 100° also.

For experiments where dibenzyl and other compounds were introduced into the toluene stream, a fine capillary and reservoir were connected as shown at *I*. This assembly was all glass and was surrounded by a thermostated box, thus making it possible to raise the vapor pressure of material, such as bibenzyl, high enough so that the flow could be easily regulated.

At the conclusion of a run the contents of traps *E* and *F* were combined. Solid material, such as bibenzyl, which had collected in the stem of trap *E* was washed down by refluxing the liquid in *E*. The trap was then cooled to 0°C. and everything volatile at this temperature transferred by distillation to a high efficiency vacuum still. Experience showed that this provided a sharp separation of the high and low molecular weight material. The residue from this distillation will be termed 'nonvolatile material'.

The low molecular weight material consisting of toluene, etc., was subjected to fractionation in the vacuum still. Here it was found possible to remove dissolved gases quantitatively. When present, these were characterized by the mass spectrometer.

This still also permitted the concentration and determination of the benzene and the removal of the excess toluene from the higher boiling residue.

To obtain the nonvolatile material, the trap was removed, weighed, and the contents washed out with a suitable solvent. The trap was then weighed again. Samples of dibenzyl passed through a warm furnace were completely recovered, thus proving the reliability of the method.

Materials

In all the work reported here, Phillips Research Grade toluene was used. Bibenzyl was supplied by Brickman and was purified by recrystallization from ethanol.

Qualitative Observations

Szwarc found that when toluene was pyrolyzed to about one per cent conversion and then distilled and pyrolyzed again, the rate had decreased the second time and products which had appeared the first time were not present in the second experiment. Moreover, he found that he could get consistent rate data from toluene obtained from different sources only by using the above procedure. He concluded that the first pyrolysis removed interfering impurities and hence purified all his toluene for rate measurements by this method, and named it prepyrolysis.

In some pyrolytic reactions, such as that of butane, inhibiting materials are produced which are difficult to remove by distillation. The possibility that such materials may be produced in toluene, however, is not important because toluene itself is an excellent inhibitor at these temperatures and would be present in overwhelming proportions. From this point of view, prepyrolysis appears to be a valid way of removing impurities which are less stable thermally than toluene. Four repeat experiments were performed at constant temperature and contact time using distilled toluene from the preceding experiment each time. The data for these experiments are given in Table I.

Noncondensable gases were formed in pyrolysis and collected and measured as indicated above. These were consistently a mixture of methane and hydrogen. It will be seen from Table I that the rate of production of these gases was higher in fresh toluene than in the prepyrolyzed material. At the temperatures used in the above experiments, it reached a stable value after one pyrolysis, but in other experiments where the conversion was lower, two or three successive passes were needed to reach a steady value. These observations are consistent with the belief that an impurity is being removed.

Analysis of the methane–hydrogen ratio for the experiments in Table I was made on a mass spectrometer, and it was found that the uncertainty in the determination was larger than for a combustion analysis. The apparent increase in the methane production with successive pyrolysis as indicated in Table I is probably not real. Subsequent combustion analysis for a number of experiments showed the hydrogen content in the noncondensable gas to be 69% and this figure was essentially independent of reaction parameters such as temperature and contact time.

TABLE I

Expt. No.	Molar ratios of products						
	Hydrogen + methane / Toluene $\times 10^2$	Hydrogen / Toluene $\times 10^2$	Methane / Toluene $\times 10^2$	Benzene / Toluene $\times 10^2$	Styrene / Toluene $\times 10^4$	Anthracene / Toluene $\times 10^4$	Non-volatile / Toluene $\times 10^2$
1	1.71	1.11	0.60	0.65	7.6	—	—
2	1.50	1.03	0.47	0.55	7.0	—	—
3	1.49	0.99	0.50	0.55	6.5	—	—
4	1.48	0.95	0.53	0.53	6.8	—	—
Average 2–4	1.49	0.99	0.50	0.55	6.8	3.4	1.10

When the contents of the dry ice trap were distilled, four distinct fractions were obtained. The first fraction was made up of gaseous material which was shown by analysis on the mass spectrometer to contain numerous hydrocarbons with two to four carbon atoms. These materials did not appear in prepyrolyzed toluene and were not investigated further.

The second fraction in the distillation was shown to contain benzene. This was characterized by its boiling point, freezing point, and ultraviolet absorption spectrum. Since it was very desirable to obtain a quantitative estimate of the benzene, the following procedure was developed.

The fractional distillation was carried on until the vapor pressure indicated in the still head at 0°C. was that of pure toluene. The fraction so obtained was weighed and was found to contain between 15 and 50% benzene in toluene. The exact quantity was determined by spectrophotometric analysis. Tests with prepared solutions of comparable concentrations to those expected from pyrolysis showed that by this method of concentration the quantity of benzene produced could be estimated within 10%. This estimation was carried out only for the experiments listed in Table I, where the values found are recorded.

The third fraction in the distillation was the toluene left over from reaction. No evidence of any other material was found in this.

The fourth fraction or residue of the distillation was the one or two cubic centimeters left when the distillation was stopped. This was examined spectro-

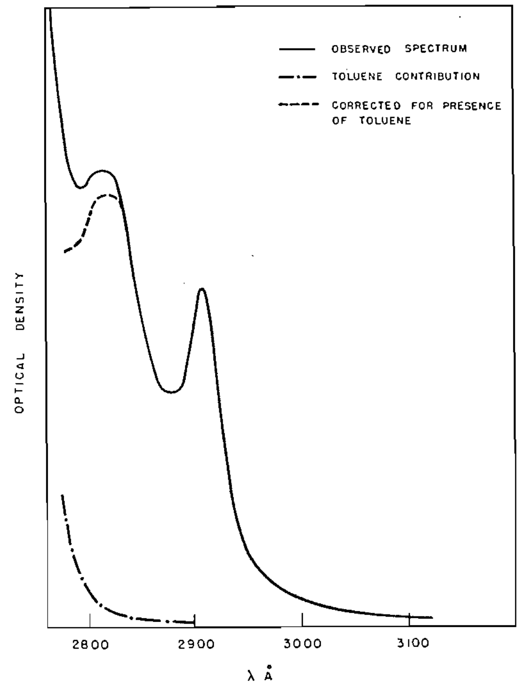


FIG. 2. Absorption spectrum of the distillation residue.

photometrically and, as shown in Fig. 2, there was distinct evidence of the presence of styrene. Most of the styrene spectrum is masked by the toluene which is present in large excess, but this one peak allowed its characterization and estimation. Again, this determination was carried out only for those experiments listed in Table I and the values found are shown there. In spite of their constancy, the absolute values are not reliable since no attempt was made to determine the amount of polymerization which might take place.

It was observed that the nonvolatile material was an oil rather than the crystalline solid expected. Its ultraviolet absorption spectrum indicated a compound containing the diphenyl nucleus. A sample was distilled and a combustion, performed on a portion of the fraction having the strongest ultraviolet absorption, indicated a carbon to hydrogen ratio of unity. From this it was suspected that one or more isomers of dimethyl diphenyl were present.

An oxidation produced a crystalline material which, when titrated with sodium hydroxide proved to have two acid groups per molecule, assuming the molecular weight of diphenic acid. The absorption spectrum of the oxidized material was stronger than that of the original, a fact which would be expected of diphenic acid but not benzoic acid. Thus it was established that the acid as titrated was not benzoic acid and hence could not have arisen from the oxidation of bibenzyl.

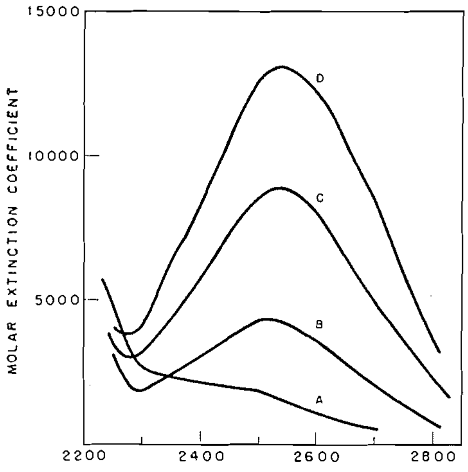
A 1 gm. sample of the nonvolatile fraction was separated into several fractions chromatographically, and their boiling points and physical appearance indicated in Table II.

TABLE II
DESCRIPTION OF CHROMATOGRAPHIC FRACTIONS INTO WHICH THE NONVOLATILE MATERIAL WAS DIVIDED

Fraction	Physical appearance	B.p., °C.	Weight, gm.
A	Colorless liquid	271	0.272
B	Moist solid	280	0.490
C	Liquid	288	0.035
D	Moist crystals		0.027
E	Solids (identified as anthracene)		

The melting and boiling points of the various isomers of dimethyl diphenyl are shown in Table III.

In Fig. 3 are shown absorption spectra characteristics of the various fractions of the chromatogram. In Fig. 4 are shown the absorption spectra for the symmetrical isomers of dimethyl diphenyl.



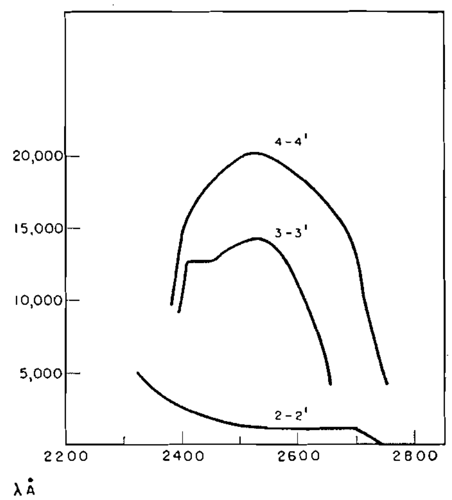


FIG. 3. Absorption spectra of the various fractions of the chromatogram of the nonvolatile fraction.

FIG. 4. Absorption spectra of the symmetrical isomers of dimethyl diphenyl.

In addition to the above information, it was found, by making up synthetic mixtures, that in a chromatographic separation bibenzyl and 33′ dimethyl diphenyl are eluted together.

From this information, it was concluded that fraction A probably was a mixture of 22′ and 23′ dimethyl diphenyl, fraction B was probably bibenzyl and 24′ and 33′ dimethyl diphenyl, while fractions C and D may be mixtures of the more strongly absorbing isomers such as 33′, 34′, and 44′.

Finally, bibenzyl was separated from fraction B by fractional crystallization from alcohol at 0°C. It was characterized by its infrared spectrum.

From the chromatogram it may be concluded that the nonvolatile material contains more than one of the isomers of dimethyl diphenyl and that bibenzyl may make up as little as fifty per cent of the nonvolatile material.

TABLE III
MELTING AND BOILING POINTS OF THE ISOMERS OF DIMETHYL DIPHENYL AND OF BIBENZYL

Isomer	M.p., °C.	B.p., °C.
22′ Dimethyl diphenyl	17	258
23′ Dimethyl diphenyl		270–276
24′ Dimethyl diphenyl		273–288
33′ Dimethyl diphenyl		283–288
34′ Dimethyl diphenyl	15	295–296
44′ Dimethyl diphenyl	122	288–289
Bibenzyl	52	284

Rate Studies

For studies on the rate of pyrolysis of toluene, Szwarc's procedure of measuring the sum of hydrogen plus methane was adopted. These two products are easy to collect and estimate and it has been demonstrated that the relative proportions of products do not vary with various conditions of pyrolysis.

A series of experiments where the production of hydrogen plus methane was measured as a function of contact time, pressure, and surface conditions in the reactor, all at a fixed temperature of 1121°K., were performed. The data are recorded in Table IV as per cent decomposition assuming the Szwarc mechanism. Calculated values of the first order rate constant are also listed. A plot of these data is shown in Fig. 5 where the calculated first order rate constant k (sec.$^{-1}$) is plotted against the contact time t(sec.).

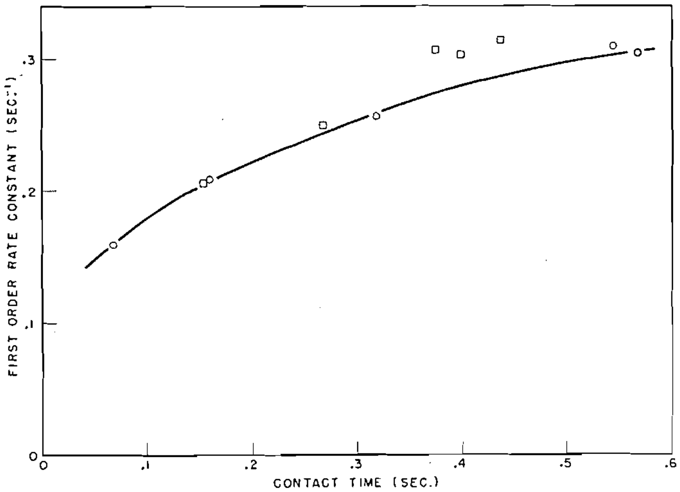


FIG. 5. The variation of the first order rate constant with contact time.
○ Pressure about 1.2 cm. Hg.
☐ Pressure about 2.0 cm. Hg.

For experiments 5 to 9, the pressure was held constant and the contact time varied by changing the rate of flow; the results are indicated by the circles in Fig. 5. It will be noted that there is a definite variation of k with contact time.

Experiments 10 to 14 were performed with varying pressures and contact times. The results are represented by squares in Fig. 5, and it is possible there to separate the effect of the two variables. At low contact times the pressures were comparable with those of experiments represented by the circles. However, at larger contact times, i.e. around 0.4 sec., the pressures in the experiments, represented by the squares, were higher and it will be noted that this has affected the rates, making them somewhat greater.

TABLE IV

EFFECT OF CONTACT TIME, PRESSURE, AND SURFACE ON THE RATE OF FORMATION OF H_2 AND CH_4 AT 1121°K.

Expt. No.	Pressure, cm. Hg	Contact time, sec.	% Decomposition	k_1, sec.$^{-1}$
5	1.05	.068	0.11	.0159
6	1.17	.159	0.33	.0208
7	1.24	.319	0.82	.0256
8	1.16	.544	1.7	.0309
9	1.21	.568	1.7	.0304
10	1.90	.154	0.32	.0206
11	1.63	.267	0.66	.0249
12	2.26	.375	1.15	.0306
13	2.28	.398	1.20	.0303
14	2.36	.436	1.37	.0314
15	1.15	.164	0.603	.0367
16	1.17	.164	0.544	.0332
17	1.20	.164	0.522	.0318

For experiments 15 to 17, a piece of silica tubing was inserted in the reaction chamber. Experiment 15 was performed in the fresh clean chamber and it is comparable in pressure and contact time with experiment 6. It will be noted that the rate of decomposition has nearly doubled. Experiments 16 and 17 were performed after the chamber had been subjected to conditions suitable to carbonizing, i.e. several experiments were conducted and toluene vapor allowed to stand in contact with the chamber for some time. It will be noted that this conditioning of the surface does affect the rate and presumably a steady value would eventually be reached. Experiments 5 to 17 were performed after many previous runs in the same reactor, and it is unlikely that there would be any variation in the surface conditions of the reactor throughout the series reported here.

These experiments do indicate, however, that the calculated first order rate constant does vary with pressure, contact time, and the condition of the surface reactor.

A series of experiments was performed in which the contact time was kept constant at .068 sec., and the temperature was varied. The first order rate constants were calculated; a plot of log k vs $1/T$ is shown in Fig. 6. An activation energy of 90 kcal. is indicated for the process.

Note: This paper was prepared prior to the publication of Anderson, Scheraga, and Van Artsdalen, J. Chem. Phys. 21: 1258. 1953 in which they claim a value of 89.5 kcal./mole for the bond dissociation energy of the first hydrogen in toluene. The correspondence is coincidental as is shown by arguments presented here.

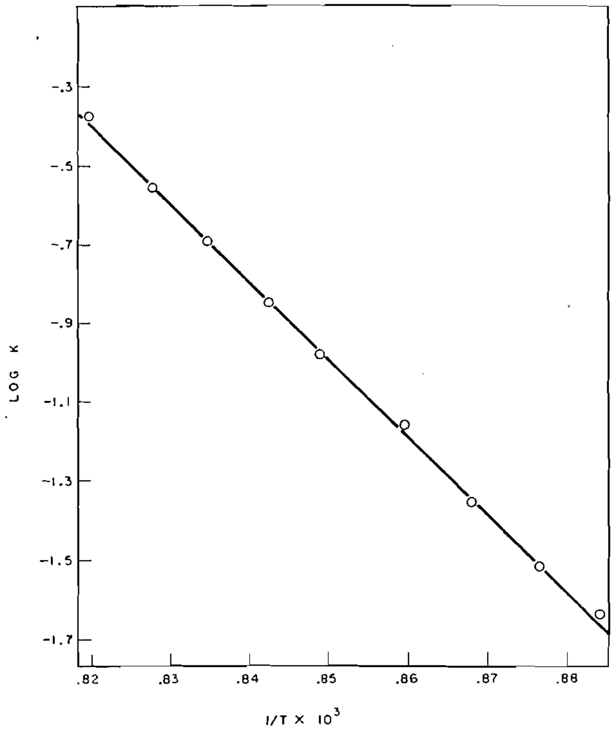


FIG. 6. The Arrhenius plot at constant contact time.

GENERAL DISCUSSION

The findings in the present work differ in some details from those reported by Szwarc, notably the identification of dimethyl diphenyl, the value for the activation energy, and the failure to obey a first order rate law.

At first it was thought that the presence of dimethyl diphenyl indicated a possible imperfection in the reaction mechanism suggested by Szwarc. However, from work done on the pyrolysis of bibenzyl, which is reported in an appendix at the end of this paper, it was found that bibenzyl undergoes reactions in the furnace at the temperatures used which produce hydrogen and dimethyl diphenyl. Thus it might reasonably be assumed that dimethyl diphenyl is produced by side reactions of either benzyl or bibenzyl in the toluene pyrolysis.

In Table I it will be seen that the amount of bibenzyl collected is significantly less than that predicted by the Szwarc mechanism. If, however, we refer to Fig. 8 of the appendix, we see that in the reactions of bibenzyl or benzyl a significant quantity of bibenzyl is lost also. In fact, for the bibenzyl to toluene ratios found in the experiments in Table V, the amount of bibenzyl lost is almost exactly the difference between the amounts found and the amount predicted by the Szwarc mechanism. Thus, it seems reasonable to assume that the loss of bibenzyl can be ascribed to side reactions of benzyl or bibenzyl in the toluene pyrolysis.

The above side reactions were not observed by Szwarc and in anticipation of the criticism that unsuitable reaction conditions were used, it might be pointed out that in the course of this work reaction vessels varying in size from about 450 cc. (the size used by Szwarc) to a few cubic centimeters were used. Conversions from 0.075% to 3% were obtained and in no instance was the nonvolatile material found free of dimethyl diphenyl. Contact times were varied from 10^{-3} sec. to several seconds without marked effect on the production of dimethyl diphenyl.

Szwarc introduced reaction [4]

$$H + C_6H_5CH_3 \rightarrow CH_3 + C_6H_6 \qquad [4]$$

to explain the production of benzene and methane. This reaction has not been confirmed by any other system where a reliable source of hydrogen atoms existed under conditions of the toluene pyrolysis experiments. However, in the reactions of benzyl or bibenzyl to produce hydrogen as reported in the appendix, it is difficult to postulate a mechanism not involving hydrogen atoms because so little stilbene is formed. No methane is formed and the conclusion would seem to be that reaction [4] does not occur.

If, in fact, the bond dissociation energy for $C_6H_5CH_2$–H is significantly higher than the value suggested by Szwarc, it would then be reasonable to postulate reaction [6] as proceeding concurrently with reaction [1] and this would explain the occurrence of methane.

$$C_6H_5CH_3 \rightarrow C_6H_5 + CH_3 \qquad [6]$$

The fact that the reaction has been shown to deviate from a first order rate expression makes it impossible to assign the observed activation energy to a specific step in the process.

CONCLUSION

The present observations on the products of the toluene pyrolysis are consistent with the basic mechanism suggested by Szwarc. However, the mechanism of the production of benzene and methane is not well established.

The first order rate constants are greatly increased by an increase in contact time but seem to be only slightly influenced by increased pressure. The condition of the reactor surface also affects the rate of decomposition.

In view of these major complications in the kinetics of this pyrolysis and the uncertainties in the mechanism, it seems premature to assign any definite value to the bond dissociation energy of toluene.

APPENDIX

Pyrolysis of Bibenzyl in the Presence of Toluene

The identification of dimethyl diphenyls in the products of the toluene pyrolysis brings up the question of their origin. In order to determine whether or not they were products of reactions of benzyl radicals or bibenzyl, bibenzyl was pyrolyzed in toluene under conditions similar to those where toluene pyrolysis has been studied.

These experiments were carried out in the same apparatus used for the toluene studies but modified so that bibenzyl could be added to the toluene stream in controlled amounts. This was done as shown in Fig. 1. Bibenzyl was degassed in a sample tube with a delicate internal seal which could be broken with the help of a magnet and a sealed-in armature. This arrangement eliminated the use of grease for joints and could be heated to a high enough temperature so that an appreciable vapor pressure of bibenzyl was produced. The whole assembly was enclosed in a thermostated box, and flow rates of bibenzyl were regulated by manipulating the temperature of the box.

Products of reaction were analyzed as above. Since the amount of bibenzyl introduced was known it was possible to determine the amount lost in reaction.

Only a limited number of experiments were done and these are reported in Table V. Experiments 1 to 4 were performed at the same temperature but with varying concentrations of bibenzyl. At this particular temperature and contact time, toluene is pyrolyzed to the extent of 0.73%. Blank runs with toluene were made and the contribution of toluene to the products has been subtracted for all products listed in Table V.

TABLE V
DATA FOR THE PYROLYSIS OF BIBENZYL

Expt. No.	BB/T $\times 10^2$	Pressure, mm.	Temp., °K.	H_2/BB	Stilbene/BB $\times 10^2$	Anthracene/BB $\times 10^2$	Loss/BB	Contact time $\times 10^2$ sec.	Optical density per mgm./l. $\times 10^2$
1	0.315	9.90	1170	0.103	2.14	0.86	0.47	7.08	0.68
2	0.631	9.80	1170	0.156	2.98	1.05	0.114	7.03	1.33
3	1.72	9.80	1169	0.199	1.82	1.25	0.243	6.98	1.95
4	5.46	9.98	1169	0.203	2.38	1.25	0.386	7.07	2.81
5	0.776*	12.4	1170	0.155*	42.0*	0.88*	0.387*	7.23	2.54
6	0.283	10.6	1098	0.113			0.0	7.21	0.78
7	1.33	9.8	1118	0.065			0.184	7.28	1.03
8	1.33	9.8	1150	0.19			0.180	7.28	1.55

Toluene was replaced by carbon dioxide.

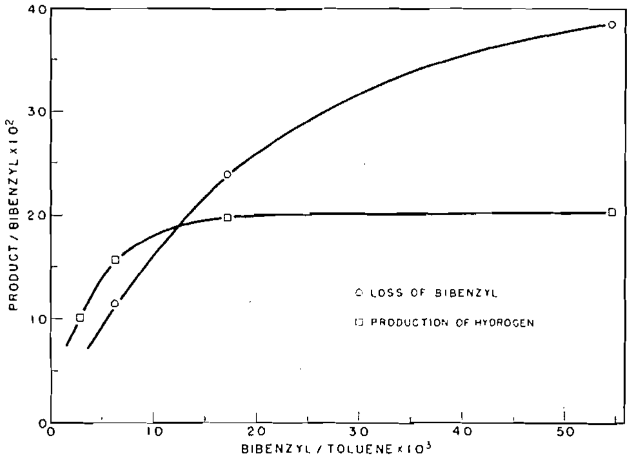


FIG. 7. The effect of the bibenzyl to toluene ratio on the production of hydrogen and the loss of bibenzyl.

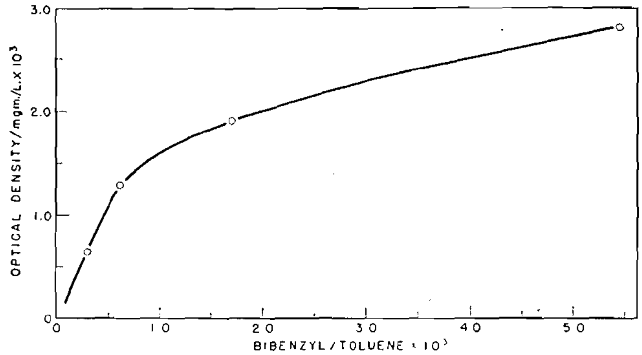


FIG. 8. The effect of the bibenzyl to toluene ratio on the optical density of the nonvolatile fraction at 2515 Å.

Experiment 5 was performed substituting carbon dioxide for toluene. The carbon dioxide was collected in a liquid air trap instead of the dry ice acetone used for toluene.

Experiments 6 to 8 were performed at lower temperatures to give some indication of the effect of temperature on the various products.

The various conversions are plotted as a function of the bibenzyl to toluene ratio in Figs. 7 and 8.

Observations

It will be noted that no methane is formed in the reactions involving benzyl and bibenzyl.

Hydrogen is formed in relatively large quantities compared to stilbene and anthracene. Also the presence or absence of toluene has little effect on the hydrogen produced. The production of hydrogen appears to reach a limit of about 20%. If the production for experiments 3 and 8 is compared, this figure does not seem to be much affected by temperature. However, the data are too sparse to draw any definite conclusions here.

The production of stilbene, which was determined by its ultraviolet absorption spectrum, does not seem to be much influenced by the ratio of bibenzyl to toluene in the range investigated. However, in the absence of toluene as shown in experiment 8, the yield is increased many times.

Anthracene production, also determined by its ultraviolet absorption spectrum, does not seem to be affected by any of the reaction parameters studied.

The disappearance of bibenzyl, presumably in the form of toluene or benzene, is interesting and the magnitude of this loss is of special interest in deciding on a mechanism for the toluene pyrolysis. In Fig. 7 the result for experiment 1 is ignored since it is so far out of line with the other observations. There was, in fact, some difficulty in the measurement of this particular value.

The loss seems to increase as the proportion of bibenzyl increases. When the ratio of bibenzyl to toluene is about 0.01, the loss of bibenzyl is about 15%. In the absence of toluene, the loss is much greater as indicated by experiment 5.

The determination of the absorption spectrum showed that the same optically active species produced in toluene pyrolysis was present, i.e. dimethyl diphenyl. A relative measure of its proportion can be obtained by expressing the optical density of a solution of the nonvolatile fraction of fixed concentration in ethanol. This has been done, as shown in Table V, the units chosen being 1 mgm./liter for concentration and a wave length of 2515 Å, which is the peak in the absorption curve.

From Fig. 8 it can be seen that the optical density of the nonvolatile product increases steadily with increasing proportions of bibenzyl. Experiment 5 shows the production of dimethyl diphenyl to be increased in the absence of toluene. Experiments 6 and 8 show it to be definitely affected by temperature.

The optical density of bibenzyl at this wave length is about 1.2×10^{-3} which is one order smaller than the figures found for the nonvolatile material.

Discussion

The data are too meager to permit detailed discussions, but some points have been established.

1. No methane was formed in the presence of toluene, although considerable hydrogen was produced. In view of the fact that there was more hydrogen than stilbene, it seems likely that hydrogen atoms were in existence at some time in the reaction. This would seem to cast some doubt on the feasibility of the reaction

$$H + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3.$$

2. Benzyl radicals or bibenzyl can take part in secondary reactions at the temperatures where toluene pyrolysis takes place. This results in the loss of bibenzyl and the production of hydrogen and dimethyl diphenyls.

3. Some reactions such as stilbene formation and loss of bibenzyl are difficult to explain without assuming the presence of bibenzyl molecules in the system.

4. We are indebted to Dr. M. Szwarc for the suggestion that styrene and dimethyl diphenyl might arise by an intramolecular hydrogen transfer in bibenzyl.

ACKNOWLEDGMENT

The authors are indebted to Miss F. Gauthier for the mass spectrometer analyses, Mr. R. Pilon for the gas analyses, and to Dr. C. Sandorfy for the ultraviolet spectra. We would also like to thank Dr. M. Szwarc for the interest shown throughout the research.

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ESTIMATION OF CARBOXYL, ALDEHYDE, AND KETONE GROUPS IN HYPOCHLOROUS ACID OXYSTARCHES[1]

BY MARY E. MCKILLICAN[2] AND C. B. PURVES

ABSTRACT

Purified wheat starch was oxidized at room temperature in approximately 0.05 to 0.09 *M* hypochlorous acid, preferably buffered to pH 4.0 or 4.2 with calcium acetate – acetic acid. The chemical efficiency of the oxidant was at least 56%. The fractions of oxystarch, insoluble and soluble in water, were isolated in a combined yield of 93% to 95%.

So prepared, the water-soluble fraction (about 75% of the oxystarch) contained 45 to 58 mM. of carboxyl groups per anhydroglucose unit, probably all as uronic acid. Carbonyl groups amounted to 52 to 54 mM., 65% to 80% being aldehydes in the primary alcohol positions, and roughly 9% being ketone groups in the second positions. Between 80% and 90% of the total oxidation therefore concerned primary alcohol groups. Various estimations for carboxyl, total carbonyl, and aldehyde groups were compared.

INTRODUCTION

Although technical information is readily available about the use of chlorine water and aqueous hypochlorite for the preparation of valuable starch dextrins (16, 17, 21), knowledge concerning the detailed chemistry of the oxidations is still scanty. According to Craik (5), Fletcher and Taylor (10), and Samec (23, 24), chlorine water or hypochlorous acid oxidized starch granules or "beta-amylose" (the "branched chain" fraction) at 10° to 25°C. very slowly and after induction periods of varying length. The viscosity and the osmotic molecular weight of the starch decreased, but the lability toward alkali, the reducing power, and the acidity increased. The rate of oxidation was greatest in a neutral system; the reducing power sometimes passed through a maximum (10, 16), and about half of the carboxyl groups were of the uronic acid type (15). Oxidations with alkaline hypochlorite yielded less viscous dextrins of smaller reducing power and with fewer carboxyl groups (7, 15, 22, 25), probably because the alkali cleaved the oxystarch molecules at their reducing units to readily soluble substances.

The object of the present research was to prepare in a reproducible way a highly reducing, hypochlorous acid oxystarch with a minimum amount of degradation and to study the product by methods already described in detail for chromic acid oxystarch (6). It was therefore considered advisable to avoid the use of heterogeneous systems containing unbroken starch granules, to use the shortest practical time of oxidation, and to carry out the reaction on the acid side of neutrality at a controlled pH. The last-named factor appeared particularly important, because the equilibria

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$$Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl$$
$$HOCl \rightleftarrows H^+ + OCl^-$$

contained three oxidants that might not have the same chemical action. According to the review by Green (13), at 25°C. the equilibria contained 20% of molecular chlorine at pH 2, at least 95% of undissociated hypochlorous acid between pH 4 and 5, and even greater amounts of the dissociated hypochlorite ion in the alkaline range.

A purified, thin-boiling wheat starch was accordingly oxidized in an apparently homogeneous, dilute dispersion with an excess of hypochlorous acid, and the reduction of the acid was followed with concordant results either iodometrically or by the arsenite method. The fact that blank oxidizing solutions containing no starch decreased in titer when kept on the acid side of pH 5 (Table I) created an ambiguity in the calculation of the millimoles of hypochlorite reduced (or of oxygen atoms consumed) per anhydroglucose unit in the starch. Neglect of the change in the blank, which led to the first figure in column 4, was equivalent to the assumption that the presence of the starch prevented the spontaneous decomposition of the hypochlorite, just as the presence of cellulose seemed to stabilize solutions of hydroxylamine hydrochloride (12) and of sodium cyanide (4). The second figure in column 4, which took account of any decrease in the blank, occasionally led to the erroneous conclusion that the oxidation *decreased* with time (e.g. Expt. 6). The first figure was probably a better approximation than the second to the true extent of the oxidation. Although only one example is quoted for each oxidation, duplicate or triplicate experiments were performed in each case with results that in general agreed to within ±5%.

The oxystarches described in Table I were isolated as calcium salts insoluble (column 5), and soluble (column 6) in water, the latter fraction being precipitated by the addition of two volumes of ethanol to the mother liquor. Although the total yield at pH 1 was high (column 7), the blanks were very unstable and the oxidation was slow. Oxidations with unbuffered hypochlorous acid were less reproducible than the others; a suspension of calcium carbonate proved inadequate as a buffer, and phosphate buffers were rejected because no satisfactory way was found of eliminating the phosphate ion from the product. Details of these oxidations have been omitted from the Experimental portion. Calcium acetate – acetic acid buffers at pH 4 to 4.2 were found to be most convenient; the oxidation proceeded rather rapidly, the blanks were fairly stable, and the products were readily isolated. Such oxidations gave 93% to 95% yields of oxystarch near pH 4, but, near pH 5.5, were extensive enough to diminish the total yield to 78%. When the water-insoluble products from oxidations at pH 4.2 and 4.0 were reoxidized under the original conditions, the new yields were 48% and 52% of water-soluble, and 16% and 17% of water-insoluble oxystarch, corresponding to over-all recoveries of 64% and 69%, respectively. In these cases about one-third of the oxystarch became soluble in 60% ethanol when reoxidized.

Since the water-soluble fractions from the oxidations had been kept in the form of calcium salts, incineration left a residue of calcium oxide the weight

TABLE I

OXIDATION OF 0.123 *M* STARCH SOLUTION WITH HYPOCHLOROUS ACID NEAR 20°C.

Expt.	Hours	Millimoles HClO		Oxystarch, %[c]		
		Blank[a]	Consumed[b]	Insol.	Sol.	Total
Hydrochloric acid: pH 1; initial blank 73.5 mM[d].						
1	18	55.4	283–152	45.2	46.9	92
Unbuffered: pH 3.3 to 1.4; initial blank 62 mM.						
2	2 18 24 66	61 59 59 59	43– 34 43– 17 52– 26 330–300	—	78[e]	—
Calcium carbonate: pH 6.1 to 3.4; initial blank 67 mM.						
3	9 12	62.5 62.5	250–215 254–220	5.4	49.5	55
Calcium acetate: pH 4.0; initial blank 124 mM.						
4	6 9 12	119 118 118	160–120 220–170 220–170	18.5	77	95
Calcium acetate: pH 4.2; initial blank 105 mM.						
5	9 12	91.5 91.0	275–165 278–165	17.5	75.5	93
Sodium phosphate: pH 5.2[f]*; initial blank 49.3 mM.*						
6	16 24 36	47.4 39.5 30.2	265–250 300–220 340–185	79[g]	60[h]	—
Calcium acetate: pH 5.5 to 5.2; initial blank 70 mM.						
7	6 9	70 70	300 390	6	72	78

[a] *In millimoles of hypochlorous acid per liter.*

[b] *Milliatoms of oxygen per glucose residue.*

[c] *Fraction insoluble in water, and fraction soluble in water, insoluble in 60% ethanol.*

[d] *Solution 0.137 M in starch.*

[e] *Contained 10.3% of ash. Insoluble fraction not isolated.*

[f] *Disodium hydrogen phosphate, 0.6 M, plus phosphoric acid.*

[g] *Nondialyzable fraction.*

[h] *Soluble fraction from a duplicate experiment. Ash content 30%.*

of which was equivalent to the total carboxyl content of the oxystarch (8). An alternative estimation, in which the calcium was precipitated as the oxalate (2, 11) gave concordant results (Table II). A comparison of columns 4 and 5

TABLE II

CARBOXYL AND CARBONYL CONTENTS OF OXYSTARCH FRACTIONS SOLUBLE AND INSOLUBLE IN WATER

Expt.	Fraction	% Ca^{b}	Millimoles COOH^{a}		Millimoles CO^{a}	
			Total	Uronic^{e}	$NH_2OH.HCl$	HCN
1	*Hydrochloric acid, pH 1*					
	Soluble	0.40	33		20	—
	Insoluble		23^{d}		14	—
3	*Calcium carbonate, pH 6.1–3.4*					
	Soluble	1.21	100		144	—
	Insoluble		62^{d}		70	—
4	*Calcium acetate, pH 4.0*					
	Soluble	0.545 0.530^{c}	45 44	58	52.3	50.8
	Insoluble		32^{d}		11.2	—
5	*Calcium acetate, pH 4.2*					
	Soluble	0.715 0.700^{c}	59 57	76	54	54.4
	Insoluble		47^{d}		57	—
7	*Calcium acetate, pH 5.5–5.2*					
	Soluble	1.44	118	—	58	—
	Insoluble	—	62^{d}		0	—

[a] *Per anhydroglucose unit (mol. wt., 162) of starch.*
[b] *By ashing sample. Corrected for 0.11% ash in original starch.*
[c] *As oxalate.*
[d] *By calcium acetate method.*
[e] *Analyses by A. S. Perlin. Corrected for 0.4% of apparent uronic acid groups in original starch.*

suggested that most, if not all, of the carboxyl groups were of the uronic acid type. Little importance was attached to the 30% discrepancy between the figures for total carboxyl and for uronic acid, because the latter estimation was often inaccurate when applied to plant materials (28) and to oxycelluloses (19). The insoluble fractions were converted to the acidic oxystarches, whose carboxyl content was measured by the amount of acetic acid that they liberated in a calcium acetate solution.

The total carbonyl content of the oxystarches was determined by condensation with hydroxylamine hydrochloride (liberation of hydrochloric acid), and also by the saponification of the cyanohydrin to ammonia (4). Since the agreement was good (Table II, columns 6 and 7), it appeared that the hydroxylamine hydrochloride estimation was valid for hypochlorous acid oxystarches, whereas this estimation gave low results with chromic acid products (6). Table II shows that the soluble fraction was usually more highly oxidized than the insoluble fraction of the oxystarch, and that the latter fraction was practically nonreducing when prepared at pH 5.5.

If it was assumed that all of the carboxyl groups originated from primary alcohol units in the starch, each group represented the consumption of two atoms of oxygen from the hypochlorous acid. The data in column 4 of Table II, when multiplied by the corresponding fractional yields of the soluble and insoluble portions of the oxystarches (Table I, columns 5 and 6), gave the results shown in column 3 of Table III. In the same way, column 4 of Table III denoted the amount of oxidant corresponding to the carbonyl contents, each carbonyl group requiring the expenditure of one atom of available oxygen. The total expenditure for each oxidation was then expressed as a percentage of the hypochlorous acid reduced (column 6), the range in percentage being created by the range of values noted in Table I, column 4. These percentages show that much of the hypochlorous acid was expended in oxidizing a relatively small portion of the starch to substances soluble in 60% ethanol (7, 10).

TABLE III

RECOVERY OF OXIDANT IN HYPOCHLORITE OXYSTARCHES

Expt.	Fraction	Milliatoms, oxygen recovered[a]			Milliatoms, oxygen expended[e]	Oxidant recovered, %
		As COOH[b]	As CO[c]	Total[d]		
1	*Hydrochloric acid, pH 1*					
	Soluble	31	9.4	68.4	280–150	24–47
	Insoluble	21.7	6.3			
3	*Calcium carbonate, pH 6.1–3.4*					
	Soluble	100	72	182	254–220	72–83
	Insoluble	6.2	3.5			
4	*Calcium acetate, pH 4.0*					
	Soluble	70	40	124	220–170	56–73
	Insoluble	12	2			
5	*Calcium acetate, pH 4.2*					
	Soluble	87.6	40.8	145	278–165	52–88
	Insoluble	16.5	10			
7	*Calcium acetate, pH 5.5–5.2*					
	Soluble	170	41.8	219	390	56
	Insoluble	7.4	0			

[a] *Multiplied by fraction yields of soluble and insoluble portions (Table I).*
[b] *Two atoms of oxygen assumed to produce one carboxy group (Table II).*
[c] *One atom of oxygen assumed to produce one carbonyl group (Table II).*
[d] *Per anhydroglucose unit in oxystarch.*
[e] *From Table I.*

Even so, the efficiency of 52% to 88% noted in the oxidations at pH 4.0, 4.2, and 5.5 compared favorably with the values of 35% to 55% found for similar oxidations of cellulose (18).

As already noted, the total carbonyl contents of the water-soluble oxystarch fractions made at pH 4 and 4.2 were 54 and 52 mM. per glucose unit, respectively. When reoxidized with alkaline hypoiodite in an attempt to determine the aldehyde groups selectively, no less than 109 and 92 mM. of apparent aldehyde were found. Thus hypochlorite oxystarches, unlike chromic acid products (6), were too sensitive toward alkali to be examined satisfactorily in this way. Titrations of the amount of sodium bisulphite solution "bound" by the oxystarch fractions, however, showed that 30 mM. of apparent aldehyde was present in each oxystarch fraction. The best method found was to reoxidize the starch fractions in almost quantitative yield with excess chlorous acid and to assume that the remaining carbonyl groups were all ketone groups. Hydroxylamine hydrochloride estimations made on the calcium salts then showed that 16, 21, and 19.3 mM. of ketone groups, or 30 ±5% of the total carbonyl groups, were present in the starch originally oxidized with hypochlorous acid at pH 4. Ketone groups amounting to 10, 12, and 13 mM. per glucose unit, or 22 ±3% of the total carbonyl content, were found in the sample oxidized with hypochlorous acid at pH 4.2. Since there was evidence that most, if not all, of the 45 and 58 mM. of carboxyl groups in the two oxystarches were derived from aldehydes, 80 to 90% of the entire oxidation of starch with hypochlorous acid had occurred in the sixth or primary alcohol positions of the anhydroglucose units. The assumption, of course, was that hypochlorous acid did not oxidize starch to the 2,3-dialdehyde structure produced by highly selective agents like periodic acid.

The previous adaptation (20) of Kiliani's classic method of locating the ketone group in fructose was used to determine the position of some of these groups in the above oxystarches. A large, composite sample, averaging about 16 mM. of ketone per anhydroglucose unit, was condensed with aqueous sodium cyanide, and the nonreducing adduct was hydrolyzed to glucose and sugar acids with dilute sulphuric acid. The reducing power of the hydrolyzate corresponded to an 84.5% yield of glucose when estimated by Hassid's (14) method employing alkaline ferricyanide. Since the theoretical yield from unoxidized starch was 105%, about one-fifth of the oxystarch adduct probably consisted of difficultly hydrolyzable aldobiuronic or aldotriuronic acids. These acids were isolated as light-brown, amorphous barium salts in 23.6% yield by weight, and their barium content of 17.2% was in the expected range. The barium in the salts amounted to 4.06% (17.2% × 23.6%) of the oxystarch, in fair agreement with the value of 4.4% calculated from the original carboxyl plus carbonyl substitution.

The barium salts were then reduced with red phosphorus and constant-boiling hydriodic acid to partially iodinated substances, which were further reduced with caustic soda and Raney nickel – aluminum to hydrocarbon acids and lactones. The resulting pale yellow oil (2.6% of the oxystarch) when fractionally distilled gave 14% of a fragrant, colorless oil with a composition close to that of a heptanoic lactone. The boiling point, density, and refractive index of this product diverged clearly from those recorded for the isomeric lactones of 2-ethyl 4-hydroxypentanoic and 4-hydroxy-*n*-heptanoic acid (expected from 3-keto and 6-aldehydo units, respectively, in oxystarch), but agreed well with the constants for the lactone of 2-methyl 4-hydroxyhexanoic acid. This identification was completed by preparing a crystalline hydrazide from the oil. Since an oxystarch averaging 16 mM. of ketone groups could theoretically yield 1.24% of the above lactone, and (2.6% × 14%) 0.364% was actually recovered, about 30% of the ketone groups were in the second positions of the anhydroglucose units. This estimate was a minimum because the recovery of the lactone from pure fructose was only 70%, and the proper value was probably near 40%. On the other hand, the latter figure would be excessive if the lactone isolated from the oxystarch was not as pure as it seemed to be.

EXPERIMENTAL

Materials

The starch used was prepared from wholly unbleached and untreated top patent wheat flour, milled from a hard red spring wheat mixture, comprised of No. 2 and No. 3 Northern grades, and containing about 13.5% of protein. Extraction at room temperature with changes of 97% acetic acid (6) removed any fats, modified the starch to a thin-boiling state, and altered the analyses from N, 0.09, 0.10; ash, 0.19, 0.19% to N, 0.03, 0.03; ash, 0.11, 0.12% for the purified product.

Hypochlorous acid was prepared by adding 40 gm. of calcium hypochlorite, or the equivalent amount of the sodium salt, to 2 liters of cold water saturated with chlorine gas (27). When distilled under diminished pressure and at pH 5, the mixture yielded about 600 ml. of 0.09 to 0.12 *N* acid. The reagent grade acetic acid used in the buffers was freed of any readily oxidizable impurities by being boiled with 2% of chromium trioxide before it was redistilled.

Analytical Methods

Hypochlorous acid was estimated by acidifying a 5 ml. aliquot, adding 5 ml. of 10% potassium iodide, and titrating the liberated iodine with 0.1 *N* sodium thiosulphate. When any chlorite or chlorate was to be excluded from the estimation, the 5 ml. aliquot was added to 20 ml. of standard 0.1 *N* arsenious oxide in neutral solution. An excess of sodium bicarbonate was added, and the excess arsenite was titrated with 0.05 *N* iodine (1). A starch oxidized at pH 4 (Table I) consumed 15 to 18 mM. of hypochlorous acid per anhydroglucose unit as estimated iodometrically, and 16 to 18 mM. by the arsenite method. The results for a sample oxidized at pH 4.2 were 14 to 22, and 18 to 21 mM., respectively.

To determine the carboxyl content of calcium salts of the oxystarches, 0.2 gm. to 0.5 gm. samples were ignited to constant weight at 750°C. (about 5.5 hr.). The ash was weighed as calcium oxide, the result was corrected for the 0.1% of ash in the original starch, and one mole of the oxide was assumed to correspond to two carboxyl groups. An alternative procedure was to digest a 1.0 gm. sample in nitric and perchloric acids (11), precipitate the calcium as the oxalate, and titrate a solution of the latter in sulphuric acid with standard potassium permanganate (2) (Table II).

Estimations for free carboxylic acid groups were made as described by Yackel and Kenyon (29) and for total carbonyl, aldehyde, and ketone groups according to Ellington and Purves (6).

Preparation of the Oxystarches (Table I)

Before each oxidation, the purified starch (10 gm.) was suspended in 50 ml. of cold water and was dispersed by adding 100 ml. or 150 ml. of boiling water. The mixture was heated on a steam bath for 10 min. and was cooled before use. All oxidations were carried out at room temperature in the dark.

Buffered at pH 1

A dispersion of 10 gm. of starch in 150 ml. of water was mixed with 25 ml. of concentrated hydrochloric acid diluted 1 : 1 by volume with water, and with 275 ml. of approximately 0.1 *M* hypochlorous acid. The mixture was therefore 0.137 *M* in starch and about 0.06 *M* in hypochlorous acid.

After 18 hr. an excess of aqueous calcium acetate was added to form the calcium salts of the oxystarch, and the mixture was poured into two volumes of ethanol. The precipitate was removed on the centrifuge, was extracted with water, and the water-insoluble portion was isolated by centrifuging again. The addition of two volumes of ethanol to the mother liquor precipitated the water-soluble portion, which was washed in succession with alcohol and ether and was dried *in vacuo* over phosphorus pentoxide. Average yield 47% by weight. The water-insoluble portion was freed of ash by immersion in 0.1 *N* hydrochloric acid at 0°C. for 30 min., and was recovered by pouring the suspension into cold ethanol. The precipitate was washed with ethanol until free of the chloride ion, then with ether, and was dried *in vacuo* over phosphorus pentoxide. Average yield, 45%.

Calcium Acetate Buffers, pH 4.0, 4.2, and 5.5

The buffer for the oxidations at pH 4.0 was prepared by mixing 500 ml. of aqueous calcium acetate (132 gm., 2.7 *N*) with 250 ml. of glacial acetic acid; those at pH 4.2 required 125 ml. of the acid, and those at pH 5.5 only 5 ml. Ten grams of the starch, dispersed in 150 ml. of water, was mixed with 100 ml. of the buffer and with 250 ml. of the hypochlorous acid. The final dispersions, which were 0.123 *M* in starch and 0.07 *M* to 0.085 *M* in hypochlorous acid, retained their original pH for at least 12 hr.

The oxystarches were isolated by adding two volumes of ethanol to the dispersions, and were separated into water-soluble and water-insoluble fractions as described for the oxidation at pH 1.

Reduction of Oxystarch Cyanohydrin to 2-Methyl 4-Hydroxyhexanoic Lactone

About 150 gm. of the water-soluble calcium salts of starch oxidized at pH 4 or pH 4.2 with hypochlorous acid was thoroughly mixed and analyzed. This oxystarch averaged 53 mM. each of carboxyl and carbonyl groups per anhydroglucose unit, and about 30% of the latter were ketones. The published method (20) was followed, with the exceptions noted below.

Ten grams of the oxystarch was kept dispersed in 300 ml. of aqueous 0.38 *N* sodium cyanide at pH 9.5 for 24 hr. at room temperature. The resulting solution of the cyanohydrin, which was almost completely nonreducing to Hassid's (14) alkaline ferricyanide reagent, was freed from ammonia and hydrogen cyanide, and was hydrolyzed with boiling 0.5 *N* sulphuric acid for 5.5 hr. After eliminating sodium and calcium ions as the sulphates, the sulphuric acid and the sugar acids were neutralized with barium carbonate and the clarified filtrate was cautiously evaporated under diminished pressure to a thick sirup. Considerable difficulty was experienced in removing sugars from this sirup, because the barium salts of the sugar acids also present tended to precipitate as a sirup from 70% ethanol. These salts (2.36 gm.) were eventually isolated as a light brown, reducing, powder. Found: Ba (as sulphate), 17.1, 17.3%. Calc. for a barium aldobiuronate, $(C_{12}H_{19}O_{12})_2Ba$: Ba, 16.8%.

An accumulation of 20 gm. of the above barium salts was heated for three hours under gentle reflux with 160 ml. of constant-boiling hydriodic acid and 4 gm. of red phosphorus. Water (75 ml.) was then added through the condenser and after being cooled the liquor was saturated with ammonium sulphate and was thoroughly extracted with ether. The dried extract was filtered through glass wool to remove particles of phosphorus and was allowed to evaporate at room temperature and atmospheric pressure, since the product was found to be quite volatile. This product was dissolved in 160 ml. of 2 *N* sodium hydroxide and was freed from combined iodine by the gradual addition of 3 gm. of Raney nickel – aluminium alloy (26). When the strongly acidified filtrate was continuously extracted for three hours with ether, the extract yielded 2.25 gm. (11.3%) of a clear, pale yellow oil.

A part of this oil (1.28 gm.) was fractionally distilled from a semimicro apparatus (3) specially built by N. Allentoff, of Science Service, for distillations under diminished pressure. The first fraction, 0.181 gm. (14%), boiled at 44° to 49°C. at 2 mm. pressure, or at 50° to 54°C. at 4 mm.; the refractive index was η_D^{23}, 1.4320, and the density, d^{25} 0.9801. Found: C, 59.9; H, 8.6%; mol. wt. (Rast), 136; neutralization equivalent, 132. Calc. for a heptolactone $C_7H_{12}O_2$: C, 65.6; H, 9.4%; mol. wt., 128. Synthetic 2-methyl hexanoic lactone-1,4 boiled at 48° to 49°C. (2 mm.), had η_D^{23}, 1.4332 and d^{25} 0.9806 (20). The boiling point and density of *n*-heptolactone were 61° to 67°C. (2 mm.) and *d*, 0.9948, respectively, while the density of the isomeric 2-ethyl pentanoic lactone-1,4 was *d*, 0.992 (9). A sample of the first fraction yielded a crude hydrazide, which after recrystallization melted at 114° to 120°C., undepressed by admixture with an authentic sample of 2-methyl 4-hydroxyhexanoic hydrazide, m.p. 119° to 121°C., kindly supplied by A. S. Perlin.

The second fraction from the above distillation, 0.192 gm. (15%), boiled at 70° to 75°C. (4 mm.), and had a refractive index, η_D^{23}, 1.4405. Found: C, 57.1; H, 8.3%; neutralization equivalent, 148. Calc. for the lactone of a dihydroxyheptanoic acid, $C_7H_{12}O_3$: C, 58.3; H, 8.2%; neutralization equivalent, 144. Apparently the reduction with hydriodic acid had not been quite complete.

ACKNOWLEDGMENTS

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IRRADIATION OF AQUEOUS CHLORAL HYDRATE SOLUTIONS WITH Co^{60} GAMMA-RAYS:

AVERAGE LIFETIME OF THE FREE RADICAL CHAINS[1]

By G. R. Freeman, A. B. Van Cleave,
and J. W. T. Spinks

ABSTRACT

When aqueous one molar chloral hydrate solutions are irradiated with X rays or gamma-rays, hydrochloric acid is produced. The reaction appears to be a chain reaction. The average free radical chain lifetime, as determined using a rotating sector, is approximately 0.1 sec.

INTRODUCTION

When aqueous one molar chloral hydrate solutions are irradiated with X rays or gamma-rays, hydrochloric acid is produced. The reaction appears to be a chain reaction, and it has been suggested that the average free radical chain lifetime is greater than 1/180 sec. (3). The present paper describes the determination of the average free radical chain lifetime using a rotating sector.

The use of intermittent illumination to measure the lifetime of the active particles in photochemical chain reactions was suggested by Chapman, Briers, and Walters (2). Modifications and extensions of the theory have been made by Melville (5) and Dickinson (6). The theory can be applied directly to the use of intermittent radiation in radiation chemistry.

The effect of intermittency has been worked out for a simple four step mechanism in Noyes and Leighton (6, p. 203), and a simplification of this has been elaborated by Burnett and Melville (1). They state that the theory is applicable to all chain reactions in which the rate varies directly with the square root of the light intensity.

The average lifetime of the chains, τ, is defined as

$$\tau = \frac{\text{No. free radicals per unit volume}}{\text{No. free radicals disappearing per unit volume per unit time}}.$$

This average lifetime varies with the temperature and with the light intensity (1,5).

For very high rates of sector rotation, the reaction rate is independent of the rate of rotation. As the rotation velocity of the sector decreases, the value of b, the ratio of the length of the period of illumination to the average lifetime of the chains under steady illumination of the same intensity, increases, and when b is approximately equal to one, the reaction rate begins to decrease. When b is approximately one hundred, the reaction rate has reached its lower steady value, and is again independent of sector speed. The value of b at

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

which the reaction rate begins to decrease depends upon the ratio

$$\frac{\text{length of dark period}}{\text{length of light period}}.$$

The factor b decreases as this ratio increases. When the ratio of dark to light is two, the reaction rate begins to decrease when b is about one (6).

Thus, to determine the average lifetime of the chains in a chain reaction which obeys the square-root law, it is only necessary to measure the reaction rates at a series of different sector speeds and determine the speed at which the rate begins to decrease. From this speed the length of the illumination period may be determined, and hence the average lifetime of the chains.

MATERIALS AND METHODS

The one molar chloral hydrate solutions were prepared using May and Baker's reagent grade chloral hydrate and triple distilled water (for preparation of water see (3)). Fresh solutions were made up for each run. The procedure for cleaning glassware and titrating samples was the same as in the previous work (3).

The irradiation source used was the 1100 curie Co^{60} bomb at the University Hospital.

The rotating sector was a solid steel cylinder, 6 in. in diameter and 1 ft. long, with two 60° sectors cut out on opposite sides. It was connected through a series of multiple pulleys to a variable speed motor (4).

During irradiation the test tubes containing the samples were placed in a lucite block which was fastened to the sector apparatus.

All dose determinations were made with a Victoreen Model 70 25-r. chamber.

All samples were given a dose of about 1100 roentgens. The steady dose rate with the sector stationary was about 1260 roentgens per hour. A pair of samples was irradiated for 55 min. with the sector stationary, and immediately afterwards, another pair of samples was irradiated for 165 min. with the sector rotating. This was done for each different sector speed. The amounts of acid produced in the samples were then compared by titration.

EXPERIMENTAL RESULTS

The solutions received 2.5 % more irradiation, as measured with the Victoreen, with the sector stationary for one hour than with it rotating for three hours. Therefore the amount of acid produced in 55 min. with the sector stationary was multiplied by 0.975 and compared with the amount of acid produced in 165 min. with the sector rotating. The results are reported as:

% difference =

$$\frac{(\text{acid formed with sector rotating}) - (\text{acid formed with sector stationary})}{(\text{acid formed with sector stationary})} \times 100$$

(see Table I and Fig. 1).

The total observed difference in the amount of acid produced between the slowest and fastest sector speeds is 32%.

The temperature of the samples was held constant during each run, but did vary a few degrees from run to run. The average temperature was 25° C.

TABLE I

VARIATION OF ACID PRODUCTION WITH SECTOR SPEED

Sector speed (r.p.m.)	Length of light period (sec.)	% Difference between acid produced with sector stationary and with sector rotating
1.1	9.0	− 5.7
2.3	4.5	− 6.9
6.7	1.5	− 2.9
23	0.45	+18.3
360	0.028	+26.4
820	0.012	+24.2
1330	0.0075	+26.6
2000	0.005	+25.4

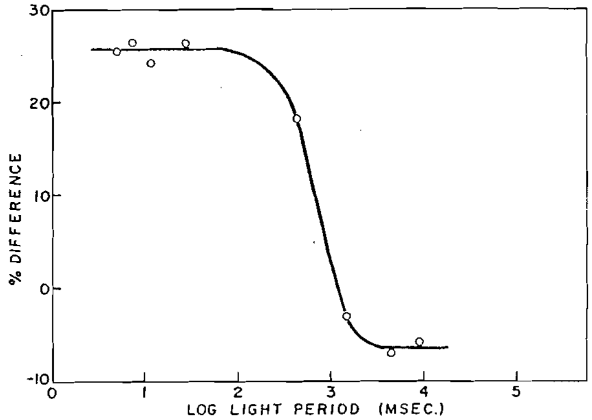

FIG. 1. Variation in percentage difference in acid produced with sector rotating and stationary for different sector speeds. All results referred to samples given the same dose continuously at the rate of 1260 r./hr.

From Fig. 1 it is seen that the average chain lifetime under these conditions is approximately 0.1 sec.

DISCUSSION

Since the dark to light ratio for the sector is two, and the dose rate in each pulse is 1260 roentgens/hr., the irradiation at high sector speeds should correspond to continuous irradiation at 420 roentgens/hr.

Twenty-six per cent more acid is produced at high sector speeds and six per cent less acid is produced at low sector speeds than when the solution is given the same dose continuously at the rate of 1260 roentgens/hr. Ordinarily one would expect no difference between the yields for low sector speeds and for continuous irradiation. One possible explanation for the negative difference observed is that there may be a small induction period at the beginning of the reaction. Since at slow sector speeds, say 1 r.p.m., the free radical concentration drops virtually to zero during each dark period, the induction period would occur at the beginning of each light period. Thus, for a 165 min. irradiation with a sector speed of 1 r.p.m. there would be 330 induction periods, but for continuous irradiation for 55 min. there would be only one induction period. This induction period may be related to the one observed with solutions which were three or four days old (see reference (3)), in which case an inhibitor is probably generated in a dark reaction. The induction period would have a negligible effect upon the yield at high sector speeds, since under these circumstances the free radical concentration remains approximately constant. Therefore, the actual observed difference in yield caused by the dose rate effect appears to be 26%.

Using the inverse square-root variation of yield with dose rate shown in Fig. 2 (Fig. 4 of Reference (3)), and extrapolating the Co^{60} line to a dose rate of 0.42 kr./hr., one finds that the expected percentage difference between the yields at 0.42 kr./hr. and 1.26 kr./hr. is 51%. However, using the semilog plot (μmoles acid/l./kr. vs. dose rate) shown in Fig. 3, the expected percentage difference between the yields for these two dose rates is 29%. Thus it appears that the semilog relationship holds at these low dose rates. It is seen from the graphs that the semilog relationship begins to fail at dose rates greater than about 9 kr./hr., and that the inverse square-root relationship is not adequate for dose rates below about 1 kr./hr. Between 1 and 9 kr./hr. both relationships hold reasonably well. This seems to indicate that more than one mechanism is operative in the production of acid, and that the relative importance of the different mechanisms depend upon the dose rate. At low dose rates acid is produced mainly by a certain mechanism (or mechanisms) and at higher dose rates a different mechanism (or mechanisms) become(s) more important.

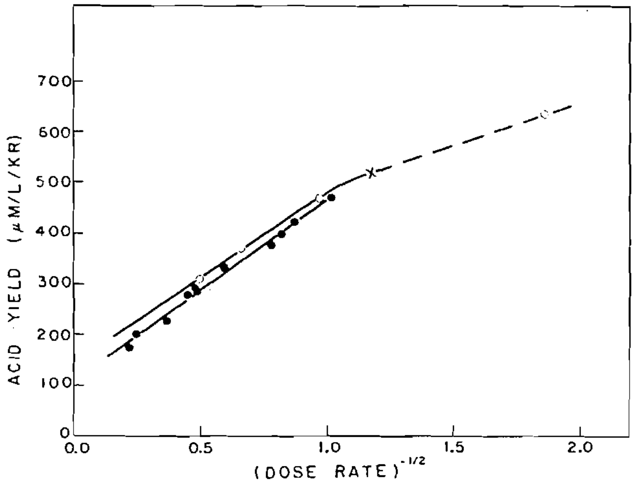

FIG. 2. Variation of specific yield of acid with square root of the dose rate in kr./hr. for Co^{60} gamma-rays (○) and (×) and for betatron X rays (●).

An additional experiment was carried out to determine the specific acid yield at a dose rate below 1 kr./hr. to check the observation that the inverse square-root relationship falls off below 1 kr./hr. At the dose rate of 0.727 kr./hr. the specific acid yield was 516 μ moles/l./kr. This point fell on the semilog plot but not on the inverse square-root plot (see point × in Figs. 2 and 3). It should perhaps be mentioned that when the data in Fig. 1 are replotted as

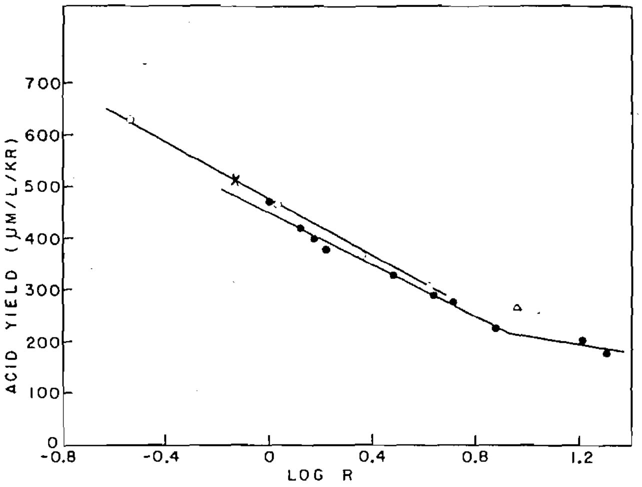

FIG. 3. Variation of specific yield of acid with logarithm of the dose rate in kr./hr. for Co^{60} gamma-rays (○) or (×) and for betatron X rays (●).

in Reference 6, p. 207, the asymptote of the curve at high sector speeds is 0.73 rather than the theoretical 1.0. Experimental sector curves which exhibit asymptotes at high sector speeds which are lower than those predicted by simple theory have been observed in photochemical systems. They have been attributed to a second rate termination step, linear in the chain carrier (7).

It thus appears that the reaction mechanism is quite complicated and does not correspond to any of the relatively simple cases proposed by Noyes and Leighton (6), so only a rough average lifetime may be determined for the free radical chains. Under the conditions of these experiments it is approximately 0.1 sec.

Since the betatron at this University has a dark to light ratio of about 1400 and a light period of about four microseconds, the effect of the pulsed nature of the beam on the production of acid in chloral hydrate solutions is negligible.

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NOTE

THE ISOTOPE EFFECT IN THE SYNTHESIS OF 3,3′-METHYLENE-C^{14}-*bis*(4-HYDROXYCOUMARIN)

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

A majority of the isotope effect studies recorded in the literature involve the breaking of the C^{12}-C^{14} bond. A wide range of values for the effect have been reported (9). By contrast, the synthesis of 3,3′-methylene-C^{14}-*bis*(4-hydroxycoumarin) from 4-hydroxycoumarin and formaldehyde-C^{14} (7,8) affords a convenient reaction for an isotope-effect study involving formation of the C^{12}-C^{14} bond. Recently Downes (4) has developed a method for the determination of ϵ, the ratio of the specific rate constant of the labeled reactant molecules to that of the unlabeled reactant molecules, by fractional isolation of the product. The equation derived was

$$S_{xy}/S_{01} = [(1-\gamma_x)^\epsilon - (1-\gamma_y)^\epsilon]/(\gamma_y - \gamma_x)$$

where S_{xy} is the specific activity of the product formed between any two stages, γ_x and γ_y; and S_{01} is the specific activity of the total product. When the interval between γ_x and γ_y is small but finite, a useful approximation is

$$S_{xy}/S_{01} = \epsilon(1-\gamma_m)^{\epsilon-1}$$

where γ_m is the mean of γ_x and γ_y. A plot of log S_{xy} vs. log $(1-\gamma_m)$ would then give a straight line with a slope equal to $\epsilon - 1$. Extrapolation of this line to $\gamma = 0$ would give an intercept equal to ϵS_{01} from which another value of ϵ could be obtained. In this way, Downes (4) found ϵ for the reaction of formaldehyde-C^{14} with dimedon to be 0.927 ± 0.005. This method is used in the present study.

A solution of 0.3136 gm. of formaldehyde-C^{14} (determined by the method of Yoe and Reid (11)) in 200 ml. of distilled water was heated under reflux to its boiling point (99.5° C. in our laboratory). Powdered 4-hydroxycoumarin (300–350 mgm.) was added. The mixture was refluxed for 20 min. and then cooled in an ice-bath. The product was collected in a sintered-glass funnel and dried to constant weight. The filtrate was quantitatively recovered and treated again with 300–350 mgm. of 4-hydroxycoumarin, the process being repeated until no more product could be obtained. After recrystallization from cyclohexanone, the activities of the various fractions of 3,3′-methylene-C^{14}-*bis*(4-hydroxycoumarin) were measured in a windowless "Q-gas" counter. Duplicate experiments were carried out. The results are given in Table I. Since the samples were "infinitely thick", the observed activity could be taken as the specific activity, S_{xy}. Each value of S_{xy} recorded in Table I was the average of six separate determinations, each of which was counted sufficiently long to give a total of at least 10000 counts. Little changes in S_{xy} after repeated crystallization indicated that the samples were of good radiochemical purity.

TABLE I

ACTIVITY OF FRACTIONALLY ISOLATED 3,3′-METHYLENE-C^{14}-*bis*(4-HYDROXYCOUMARIN)

Fraction	Weight (gm.)	γ_m	S_{xy}(counts/min.)
Expt. 1 1	0.3197	0.0455	2981
2	0.3265	0.1375	2982
3	0.3355	0.2317	3019
4	0.3282	0.3262	3076
5	0.3333	0.4205	3124
6	0.3318	0.5152	3126
7	0.3254	0.6087	3171
8	0.2802	0.6948	3198
9	0.3298	0.7816	3315
10	0.3270	0.8752	3413
11	0.0790	—	—
Expt. 2 1	0.2722	0.0388	2978
2	0.2850	0.1181	3002
3	0.3303	0.2051	2986
4	0.3323	0.3000	3026
5	0.3298	0.3943	3051
6	0.3272	0.4878	3119
7	0.3308	0.5814	3132
8	0.3347	0.6782	3197
9	0.3300	0.7708	3251
10	0.3330	0.8652	3407
11	0.0915	—	—

A plot of log S_{xy} vs. log $(1 - \gamma_m)$ gave a straight line with a slope, determined by the method of the least squares, equal to $-0.068 \pm 0.003 = \epsilon - 1$. Hence $\epsilon = 0.932 \pm 0.003$. The intercept at $\gamma = 0$ corresponded to a S_{xy} value of

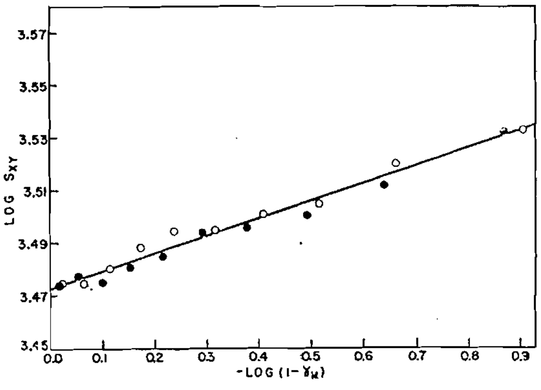


FIG. 1. Graphic determination of ϵ.
● Experiment 1. ○ Experiment 2.

2968 ± 4 counts/min. The total product from reacting 31.4 mgm. of formaldehyde-C^{14} with 400 mgm. of 4-hydroxycoumarin gave an over-all specific activity, S_{01}, of 3195 ± 23 counts/min. Thus from the intercept, $\epsilon = (2968 \pm 4)/(3195 \pm 23) = 0.929 \pm 0.007$.

Recently, Stevens and co-workers (10) discussed the application of isotope effect observations as evidence in the elucidation of mechanisms of reaction. When the rate-determining step in a reaction involved the rupture or formation of the C^{12}-C^{14} bond, an isotope effect should be expected. The mechanism for the synthesis of 3,3'-methylene-*bis*(4-hydroxycoumarin) has been postulated by Ikawa and Link (6) to involve: (*a*) an aldol condensation between formaldehyde and 4-hydroxycoumarin, (*b*) dehydration of the aldol to an α,β-unsaturated ketone, and (*c*) a Michael condensation between the α,β-unsaturated ketone with a second mole of 4-hydroxycoumarin to give the final product. Although it would be difficult to decide whether any one of the three processes are rate-controlling or whether they proceed at comparable rates, it is of interest to note that with appropriate assumptions, one can give theoretical grounds for supposing that the dehydration step may be rate-determining.

In 1949, Bigeleisen (1) developed an equation for the theoretical calculation of isotope effects which has given results in remarkable agreement with experiment.

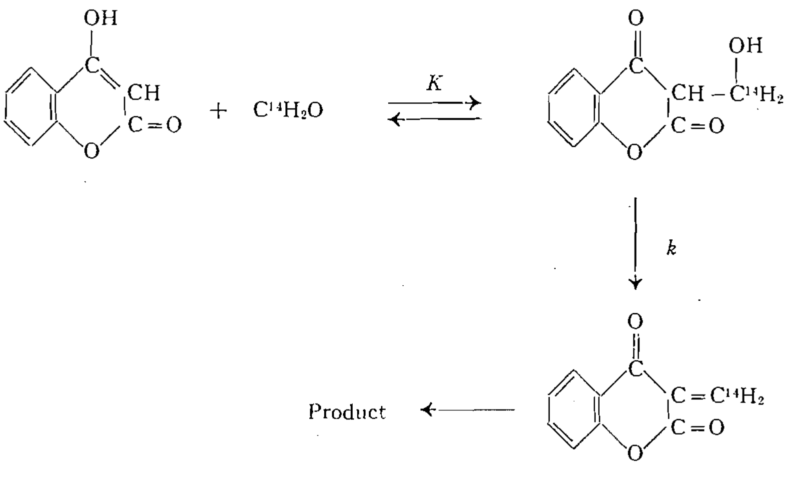
$$\frac{k_{12}}{k_{14}} = \left(\frac{\overset{*}{m}_{14}}{\underset{*}{m}_{12}}\right)^{\frac{1}{2}} \left[1 + \sum_i^{3n-6} G(u_i)\,\Delta u_i - \sum_i^{3n'-6} G(u_i\ddagger)\,\Delta u_i\ddagger\right]$$

where the m^*'s are the effective masses of the activated complex along the reaction co-ordinate and are calculated as the reduced mass across the bond being broken or formed, $\Delta u_i = hc/kT(\omega_{1i} - \omega_{2i})$, where the ω's are the vibrational frequencies in cm.$^{-1}$, $G(u_i)$ is a function defined previously by Bigeleisen and Mayer (3), and ‡ refers to the activated complex. If the assumption is made that in going from the initial state to the activated complex, the vibrational frequency of only the bond actually being formed or broken is appreciably changed, one may say that in bond formation,

$$\sum_i^{3n'-6} G(u_i\ddagger)\,\Delta u_i\ddagger > \sum_i^{3n-6} G(u_i)\,\Delta u_i$$

and the opposite is true in bond rupture because in the initial state, the atoms of the bond being formed are completely separated whereas in bond rupture, these atoms are joined by a covalent bond. It follows that the square bracket term in the Bigeleisen equation must be less than unity for bond formation, and accordingly, the ratio k_{12}/k_{14} would be less than the reduced mass term, $(m_{14}/m_{12})^{\frac{1}{2}}$, which for C^{12} and C^{14} is 1.04. Since the isotope effect observed for the synthesis of 3,3'-methylene-C^{14}-*bis*(4-hydroxycoumarin) is about 7%, quite different from k_{12}/k_{14}, equalling 1.04, one may assume that the rate-determining step is not one of bond formation.

The following interpretation can then be shown to fit the observed facts.



If the dehydration is rate-determining, the over-all isotope effect is given by

$$\frac{k_{12\text{obs}}}{k_{14\text{obs}}} = \frac{K_{12}k_{12}}{K_{14}k_{14}}.$$

The ratio k_{12}/k_{14} for the rupture of C^{12}-O^{16} and C^{14}-O^{16} bonds would be approximately 1.10 according to Eyring and Cagle (5). For the aldol type of reaction of the carbonyl group, Bigeleisen (2) has shown that K_{12}/K_{14} is of the order of 1/1.03 to 1/1.05. The over-all effect, $k_{12\text{obs}}/k_{14\text{obs}}$, will therefore be 1.05 to 1.07 which is in reasonable agreement with the experimental value.

The 7% isotope effect thus indicates that the rate-determining step is not one of bond formation and suggests a prior equilibrium between formaldehyde and the aldol followed by a slow dehydration. One must emphasize, however, that such qualitative conclusions are based on much simplified calculations. The Ikawa-Link mechanism is really too complicated to be confirmed or denied by isotope effect data alone.

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THE PHOTOLYSIS OF ACETONE ABOVE 300° C.[1]

BY L. MANDELCORN[2] AND E. W. R. STEACIE

ABSTRACT

Acetone has been photolyzed at temperatures above 300° C. The formation of ethylene becomes of increasing importance at higher temperatures. The normal kinetics of the reaction are followed, however, and ethylene does not appear to be formed at the expense of ethane or methane.

INTRODUCTION

The production of methane and ethane in the acetone photolysis at temperatures below 300° C. is well accounted for by the reactions (3, 4)

$$2CH_3 \rightarrow C_2H_6 \qquad [2]$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2. \qquad [3]$$

On this basis

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}}[CH_3COCH_3]}.$$

It has, however, been found that ethylene becomes a product at higher temperatures (1, 5). It appeared to be desirable to determine if the formation of ethylene at higher temperatures complicated the kinetics of the photolysis.

EXPERIMENTAL

The apparatus and procedure were the same as in a previous investigation (2), with the reaction cell isolated by a mercury cutoff (reaction volume = 195 cc.). To get sufficient amounts of ethane the full intensity of a Hanovia S-100 lamp was used. Methane and carbon monoxide were separated from a trap cooled with solid nitrogen to ensure that ethylene was retained. Ethane and ethylene were determined by mass spectrometric analysis of the C_2 fraction.

RESULTS

The results are given in Table I. They include two experiments at reduced light intensity, and one experiment in which water vapor was added in an

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TABLE I

PRODUCTS OF PHOTOLYSIS OF ACETONE

Temp., ° C.	Time, sec.	$[CH_3COCH_3]$ $\times 10^6$ M./cc.	R_{CH_4}	$R_{C_2H_6}$	$R_{C_2H_4}$	R_{CO}	$\frac{k_3}{k_2^{\frac{1}{2}}} \times 10^{13} \left\{\frac{\text{cc.}}{\text{molecules-sec.}}\right\}^{\frac{1}{2}}$
			$\times 10^5$ cc. N.T.P./sec.				
284*	3600	1.77	8.47	0.44	0.05	6.15	136
318	1500	1.73	33.9	2.30	0.41	26.1	250
332	1500	1.77	37.7	1.72	0.50	28.1	313
344	1800	1.76	35.2	1.29	0.52	25.4	338
352	1200	1.75	42.1	1.46	0.64	29.1	387
375	1380	1.78	49.5	1.17	1.00	30.9	500
408	1200	1.74	59.8	0.88	2.12	38.7	705
434	1500	1.75	66.1	0.88	3.41	41.9	850
439	900	1.75	73.3	0.82	4.88	41.5	890
271	1800	0.86	10.3	3.20	0.11	11.2	129
291	1800	0.91	13.2	2.44	0.16	12.7	181
309	1800	0.83	13.8	1.76	0.16	12.2	242
325	1500	0.86	16.7	1.48	0.22	13.8	310
341	1500	0.94	20.9	1.33	0.27	16.2	374
342**	7800	0.86	5.81	0.14	0.09	4.09	358
343	1800	0.86***	17.5	1.03	0.30	13.3	388
362	1500	0.91	23.4	0.97	0.48	17.2	512
374	1200	0.89	26.5	1.00	0.48	18.9	575
392	1200	0.87	27.7	0.77	0.77	18.9	708

* *Corning No. 9863 filter.*
** *Two No. 9863 filters.*
*** *Plus* $[H_2O] = 0.38 \times 10^{-6}$ *M./cc.*

attempt to detect ketene by the formation of acetic acid. The test was negative.

An Arrhenius plot of the results is given in Fig. 1. The equation of the line is

$$13 + \log \frac{k_3}{k_2^{\frac{1}{2}}} = 6.03 - \frac{2.13 \times 10^3}{T},$$

corresponding to $E_3 - \frac{1}{2}E_2 = 9.8$ kcal., $P_3/P_2^{\frac{1}{2}} = 25 \times 10^{-4}$ (at 350° C.). These values are in good agreement with previous work, including the tendency for the ratio $k_3/k_2^{\frac{1}{2}}$ to increase somewhat with decreasing acetone concentration. It is evident, therefore, that the formation of ethylene is independent of the mechanism of formation of ethane and methane. The reaction follows the normal kinetics in spite of the considerable formation of ethylene. The source of the ethylene is uncertain. In the photolysis of diethyl ketone ethylene is formed at high temperatures by the decomposition of the pentanonyl radical

$$C_2H_4COC_2H_5 \rightarrow C_2H_4 + CO + C_2H_5.$$

It is possible that ethylene in the present case arises from hydrogen abstraction from methyl ethyl ketone, followed by the breakup of the resulting radical

$$CH_3COC_2H_4 \rightarrow CH_3 + CO + C_2H_4.$$

This would give the reaction chain characteristics, but the total amount of ethylene formed is quite small, and the effect on the quantum yield of CO formation would be very slight.

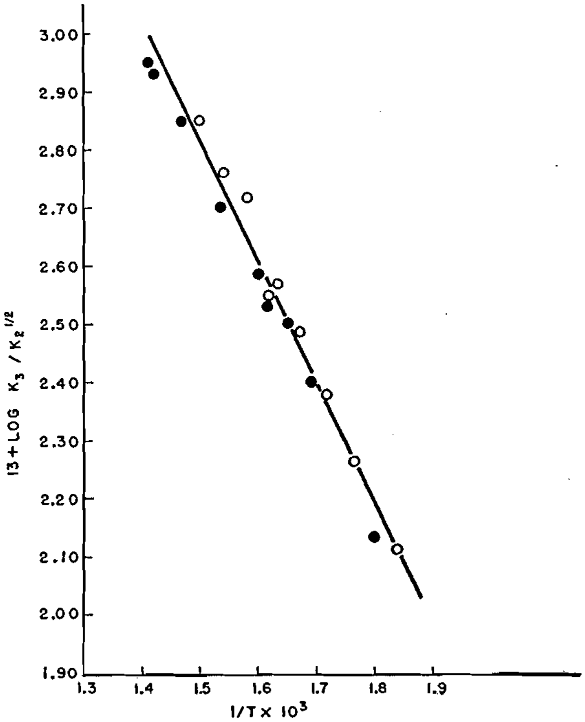

FIG. 1. Arrhenius plot for the abstraction of hydrogen from acetone by methyl radicals.
Filled circles—acetone conc. = 1.76×10^{-6} M./cc.
Open circles—acetone conc. = 0.88×10^{-6} M./cc.

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PREPARATION OF 1-C^{14} PENTONIC ACIDS BY THE CYANHYDRIN SYNTHESIS[1]

By A. C. Neish

ABSTRACT

Solutions of pure D-threose and D-erythrose, buffered with bicarbonate (0.82 moles) plus carbonate (0.18 moles), were treated with an equimolar amount of C^{14}-labeled KCN. The aldonic acids were isolated as salts, using carrier technique, in yields of 90–95% based on the radioactive carbon. D-Erythrose gave 1.89 times as much arabonic as ribonic acid while D-threose gave 2.36 times as much lyxonic as xylonic acid. Despite the unfavorable ratio in the latter case it was found that D-xylose could be obtained in an over-all yield of 22%, based on the cyanide.

Interest in the metabolism of pentoses by bacteria has prompted an investigation on the cyanhydrin synthesis as a method for preparing 1-C^{14}-labeled pentoses. L-Arabinose-1-C^{14} has been made, in yields of about 3% (12), by the nitromethane synthesis while D-xylose-1-C^{14} (13) has been prepared from glucose-1-C^{14}. As far as the present writer knows pentonic acids have never been prepared by the cyanhydrin reaction, so there is no information on the yields of isomers to be expected. The ratio of epimers would be expected to vary with the pH of the cyanide reaction mixture (10) and a complete investigation should include a study of this important factor. The present paper gives information on the yields of pentonic acids obtained from D-erythrose and D-threose under one set of conditions. Since the results indicate that the cyanhydrin reaction is a convenient route for preparing C^{14}-labeled pentoses this information may be of value to other workers.

Deionized solutions of threose or erythrose, prepared by the Ruff degradation, contained at least one other reducing substance so they were not used. D-Erythrose was obtained from 4,6-ethylidene-D-glucitol (9), the intermediate 2,4-ethylidene-D-erythrose being purified by distillation. D-Threose was prepared from 1,3-benzylidene-D-arabitol. The intermediate 2,4-benzylidene-D-threose crystallized, unexpectedly, so it was not necessary to convert it to the isopropylidene derivative for purification. The solutions of tetroses obtained by these methods were pure as far as could be ascertained by paper chromatography.

The cyanhydrin reaction and hydrolysis of the amides was done following the work of Isbell *et al.* (10) on preparation of D-glucose-1-C^{14}. The aldonic acids were separated using methods developed for epimerization studies (3, 4). Since high specific activities were not required, these separations were simplified by the use of carriers. The yields were good, 90–95% of the C^{14} being recovered as aldonic acids. D-Erythrose gave arabonic and ribonic acids in the ratio of 1.89: 1 while D-threose gave lyxonic and xylonic acids in the ratio of 2.36: 1 respectively.

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The conversion of these acids to the aldoses has not been thoroughly investigated. It has been pointed out by Isbell *et al.* (10) that there is no universal procedure for the sodium amalgam reduction of lactones which will give maximum yields with all lactones. They found that glucono-δ-lactone gave excellent yields in an oxalate buffered medium while mannonic-γ-lactone gave better yields in a benzoate buffered medium and required more amalgam. We have investigated the reduction of xylono lactone and obtained better yields in an oxalate buffered medium than in a benzoate buffered one but it required twice as much amalgam as glucono-δ-lactone. The yield of xylose was about 80%, based on the cadmium D-xylonate cadmium bromide double salt. Presumably the other aldonic acids could be converted to pentoses in similar yields under the best conditions. D-Arabinose-1-C^{14} could then be used for preparation of D-glucose-2-C^{14} in good yields, by addition of inactive cyanide (10). In both of the cyanhydrin reactions, starting with D-erythrose, the epimer needed for this synthesis is formed in the highest yield.

EXPERIMENTAL

Methods

Unless stated otherwise evaporations were carried out in a Craig evaporator (2) using a bath temperature of 40–45° C. and the full vacuum of a filter pump (20–25 mm.). The aldose content of the solutions was determined by hypoiodite oxidation (8). Measurements of radioactivity were made using a windowless counter operating in the proportional region. The samples were plated on aluminum disks and were so small that self absorption was negligible. The counting assembly was calibrated against the U.S. National Bureau of Standards carbon-14 standard; a sodium carbonate solution rated at 1280 disintegrations per second/ml. The results were expressed as millicuries. Paper chromatography of the tetrose solutions was carried out with Whatman No. 1 paper using the descending technique. Methyl ethyl ketone saturated with water was the only developing solvent used. Spots of reducing substances were detected by three spray reagents; molybdate (1), alkaline dinitrosalicylate (11) and triphenyl-tetrazolium chloride (15). The tetrazolium spray is much more sensitive for tetroses than glucose, whereas the other sprays are about equally sensitive for glucose and the tetroses.

Preparation of Tetroses by the Ruff Degradation

Ruff degradation (5) of Ca-D-arabonate and Sr-D-xylonate gave solutions of D-erythrose and D-threose. Analysis of the deionized solutions for aldose indicated yields of 36% and 40% of the theoretical, respectively. However, paper chromatography showed at least two reducing substances to be present in each solution, both being detected by all three sprays as spots of about equal intensity. One component migrated at the same rate as the tetroses, and the other at about half the rate. A pure tetrose fraction could probably be obtained by chromatographic fractionation of these solutions. However the tetrose solutions used in the cyanhydrin reactions were prepared by other methods, described below, which gave chromatographically pure solutions directly.

*2,4-Ethylidene-*D*-Erythrose*

4,6-Ethylidene-D-glucitol (10.4 gm., 50 mM.) (9) was dissolved in 150 ml. of ice-cold water and treated with an ice-cold solution containing 23.94 gm. (105 mM.) of H_5IO_6 in 150 ml. of water. After 10 min. the mixture was neutralized to the phenolphthalein end point by a warm concentrated solution of strontium hydroxide. The precipitate was filtered out and the filtrate evaporated to dryness. The residue was extracted with alcohol, the alcohol evaporated, and the sirup distilled through a short column, under reduced pressure, to give 1.5 gm. of 2,4-ethylidene-D-erythrose, b.p. 98° C. at 8 mm., as the only fraction. This material was a colorless glass; $[\alpha]_D^{22}$ $-41.36°$ (c, 2.5, water). It gave 91.2% of the expected amount of acetaldehyde on hydrolysis by 0.5 N sulphuric acid, followed by distillation, as measured by the bisulphite binding capacity of the distillate. This rotation is a somewhat higher than the value $[\alpha]_D$ 36, reported for the L-isomer (12).

D-*Erythrose*

A solution of 1.08 gm. (7.4 mM.) of 2,4-ethylidene-D-erythrose was dissolved in 45 ml. of water and 6–8 ml. of IR-120-H Amberlite cation-exchange resin added. This mixture was distilled at constant volume for 1.5 hr. to effect hydrolysis and removal of the acetaldehyde. The residue was treated with charcoal and filtered. The colorless solution thus obtained was found to contain 5.71 mM. of aldose. A portion was chromatographed on paper as described above and found to give only one spot with an R_f of 0.21 (glucose had R_f of 0.055 on same sheet). An aliquot of this solution was used for the cyanhydrin synthesis described below.

Reaction of C^{14}-labeled Cyanide with D-*Erythrose*

A solution containing 2 mM. of $KC^{14}N$ (1 millicurie) and 0.36 mM. of KOH in 10 ml. of water was frozen solid in a 50 ml. glass stoppered Erlenmeyer flask immersed in a dry ice bath. An aliquot of the D-erythrose solution (14.1 ml., 2 mM.) containing 2 mM. of $NaHCO_3$ was added, the stoppered flask allowed to stand two days at room temperature, and then 1.64 ml. of N NaOH added. After two more days at room temperature the mixture was heated to 60° C. and aerated to remove the ammonia released by hydrolysis of the amides. This ammonia was caught in standard acid and measured by back titration. A total of 1.85 m.e. (92.5%) was recovered in five hours, at which time the volume had decreased to about one-third and the hydrolysis was complete. The residue was transferred to a beaker containing 25 ml. of IR-120-H Amberlite cation-exchange resin, stirred, and then transferred to a column containing an additional 25 ml. of the resin. The effluent was treated with 2 gm. of Ca-D-arabonate carrier and the mixture warmed with 0.3 gm of calcium carbonate, filtered, and the filtrate concentrated to about 8 ml and crystallization induced by addition of methanol. The Ca-D-arabonate which separated (2.3 gm., 0.635 mc.) was recrystallized from methanol–water to constant specific activity to give 2.25 gm. (0.590 mc.). The mother liquors were combined, concentrated to remove methanol, diluted with water, passed through an IR-120-H column to remove the calcium ions, boiled with 0.4 gm of cadmium carbonate in the presence of 2 gm. of Cd-D-ribonate carrier, filtered, and the filtrate concentrated and crystallized from methanol–water. After recrystallizing to constant specific activity, 1.97 gm. (0.312 mc.) of Cd-D-ribonate was obtained. Thus the ratio of arabonate: ribonate was 1.89, and a total of 90.2% of the C^{14} added as cyanide was found in the aldonic acids.

*2,4-Benzylidene-*D*-Threose*

A solution of 5 gm. of 1,3-benzylidene-D-arabitol (7) in 150 ml. of warm water was cooled to 30° C. and mixed with 50 ml. of 9.45% $NaIO_4$. After one hour at room temperature, 14.5 ml. of molar barium acetate was added. The mixture was filtered and the filtrate concentrated in a flask containing 1 gm. of $BaCO_3$. The residue was dehydrated by three successive evaporations with 25 ml. portions of absolute ethanol, then dissolved in ethanol and filtered. The filtrate was concentrated to a sirup and allowed to stand one hour at room temperature. This was treated with 100 ml. of water, and a crystalline residue formed, which was filtered out and washed with water giving 2.4 gm. melting at 160–161° C. This melting point was raised to 165.5° C. by recrystallization from ethanol. Found: $[\alpha]_D^{22}$ 77.6° (*c*, 2, pyridine), C, 63.32; H, 5.82. Calculated for $C_{11}H_{12}O_4$: C, 63.45, H, 5.81. This compound was obtained only as a sirup by previous workers (14), who carried out this oxidation using lead tetraacetate. However, a crystalline benzylidene-L-threose hemihydrate, m.p. 119–120° C., has been reported (6).

D-*Threose*

A solution of 1.7 gm. of 2,4-benzylidene-D-threose in 40 ml. of 10% acetic acid was refluxed for one hour, concentrated to a sirup, and the residue, after addition of 20 ml. of water, was extracted three times with ether to remove the last traces of benzaldehyde. The aqueous phase was again evaporated to a sirup and dissolved in 20 ml. of water to give a clear colorless solution, pH 5.0, containing 7.22 millimoles (88%) of aldose. Paper chromatography as described above showed the presence of only one reducing substance with an R_f of 0.22 (glucose had R_f of 0.055 on the same sheet). A portion of this solution was used in the cyanhydrin synthesis described below.

Reaction of C^{14}-labeled Cyanide with D-*Threose*

This reaction was carried out with 2 mM. (1 mc.) of cyanide as described for D-erythrose. The yield of ammonia on hydrolysis was 1.8 m.e. (90%). The solution of aldonic acids obtained, after removal of the cations, was warmed with 2 mM. of cadmium hydroxide and 5 mM. of cadmium carbonate, then treated with 10 m.e. of aqueous HBr and filtered. Inactive cadmium-D-xylonate cadmium bromide double salt (2 gm.) was dissolved in the filtrate, which was then concentrated until crystallization started. After this was allowed to stand overnight at 3° C., 1.98 gm. of the double salt was obtained. Recrystallization to constant specific activity from water, and reworking of the mother liquors, gave a total of 2.17 gm. (0.273 mc.) of cadmium xylonate cadmium bromide. Addition of more carrier to the combined mother liquors, followed by reisolation, gave only 0.011 mc. more. Thus a total of 28.4% of the C^{14} was present as D-xylonic acid.

The combined mother liquors from the double salt were passed through an IR-120-H column containing 50 ml. of resin. The effluent was stirred one hour with 4 gm. of silver carbonate, filtered, and the bromide-free filtrate treated with 2 gm. of D-lyxono lactone and passed through a 25 ml. column of IR-120-H resin, to remove the silver ions. The effluent was concentrated to a sirup which was dehydrated by three evaporations with glacial acetic acid, giving finally 3 gm. of sirup. This was dissolved in 2 ml. of glacial acetic acid and cooled. Crystallization of the lactone was rapid. The product was recrystallized twice from acetic acid – ethyl acetate (about equal proportions) to give 1.73 gm. (0.260 mc.) of D-lyxono lactone. The mother liquors still contained a considerable amount of C^{14}, possibly because equilibrium had not been reached between the carrier lactone and the active lyxonic acid. In order to confirm this supposition another 2 gm. of inactive D-lyxono lactone was added to the mother liquors, the acetic acid removed by evaporation with water, and the aqueous solution titrated with N KOH to the phenol red end point until all the lactone was converted to the K salt. The potassium ions were then removed by an IR-120-H column and the effluent concentrated to a sirup and crystallized from glacial acetic acid as before. This time the crystallization required four days. After purification to constant specific activity 1.1 gm. (0.210 mc.) of D-lyxono lactone was obtained. The residue from this was rather gummy so another gram of carrier was added and reisolated by rapid crystallization giving another 1.1 gm. (0.100 mc.) of pure D-lyxono lactone. A total of 0.570 mc. of pure lactone was isolated and it was calculated, from the amounts of carrier added and recovered, that another 0.1 mc. was present in the residue. From these data about 67% of the C^{14} added as cyanide was converted to D-lyxonic acid. The ratio of lyxonic: xylonic acids was thus 2.36 and about 95% of the cyanide was converted to aldonic acids.

D-*Xylose-1-*C^{14}

Cadmium D-xylonate cadmium bromide (2.17 gm., 0.273 mc.) was dissolved in 125 ml. of warm water and the solution passed through a 50 ml. column of IR-120-H resin. The effluent was treated with 3.5 gm. of silver carbonate, filtered, and the bromide-free filtrate passed through a 35 ml. column of IR-120-H resin to remove silver ions. The effluent was evaporated to a sirup which was heated in a drying pistol, containing phosphorus pentoxide, at 100° C. (2 mm.) for 24 hr. to effect lactonization. The mixture of sirup and crystals thus obtained was dissolved in 120 ml. of water containing 4.2 gm. of oxalic acid dihydrate and 4.8 gm. of sodium oxalate. The mixture was stirred vigorously and 14 gm. of 5% sodium amalgam added. The temperature was maintained at 5–10° C. (ice-alcohol bath) and powdered oxalic acid added from time to time to keep the pH from rising above 4. After 30 min. another 14 gm. portion of the amalgam was added. When this was used up (about 45 min.) the mixture was filtered to remove mercury and excess sodium acid oxalate, the filter cake being washed with ice water. The filtrate was concentrated to about 50 ml., treated with 100 ml. of methanol, filtered again, diluted with an equal volume of water and neutralized by N NaOH, to the phenol red end point, to convert any residual lactone to the sodium salt. Ordinary D-xylose (3 gm.) was dissolved in the solution which was then deionized by 50 ml. columns of IR-120 and IR-4B Amberlite resins in the acid and base forms, respectively. The deionized solution was concentrated to a sirup which was dehydrated by three evaporations with absolute ethanol and then crystallized from ethanol containing a little isopropanol. The first crop of crystalline D-xylose was 3.17 gm. (0.194 mc.). It was recrystallized by solution in 1 ml. of hot water followed by addition of 2 ml. of methanol and 4 ml. of ethanol. This gave 2.97 gm. with unchanged specific activity. A further 4 gm. of carrier was added to the mother liquors and another 3.52 gm. (0.027 mc.) of pure D-xylose isolated. The pure xylose isolated contained about 77% of the activity present in the cadmium double salt, another 3–4% remaining in the mother liquors.

Some glyoxylic acid, isolated as the 2,4-dinitrophenyl-hydrazone, was formed from the oxalate during reduction by sodium amalgam. It was necessary to remove this aldehyde-acid by deionization of the solution before the yield of aldose could be determined by the hypoiodite method. Experiments on the reduction of a sample of crystalline D-xylono lactone using acetic acid or benzoic acid as buffers gave only 35–40% yields of aldose. These yields were not increased by addition of an extra portion of sodium amalgam.

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A CHEMICAL SYNTHESIS OF D-TREHALOSE[1]

BY R. U. LEMIEUX AND H. F. BAUER

ABSTRACT

Chromatographic separation of the products formed on heating a mixture of the anomers of 2,3,4,6-tetra-*O*-acetyl-D-glucose and tri-*O*-acetyl-D-glucosan ⟨1,5⟩ α ⟨1,2⟩ at 100° C. afforded D-trehalose and the *neo*-D-trehalose of Haworth and Hickinbottom. Evidence was obtained to show that the latter compound is in fact α-D-glucopyranosyl β-D-glucopyranoside.

Three diastereoisomeric D-glucopyranosyl D-glucopyranosides are theoretically possible. The α,α-, β,β-, and α,β-forms have been termed trehalose (7), *iso*-trehalose (3, 7), and *neo*-trehalose (6), respectively. D-Trehalose occurs naturally in many lower plants and trehala (5). The substance has not previously been synthesized by chemical means. Leloir and Cahib (8) have recently reported an enzymic synthesis. *iso*-D-Trehalose (12) was first obtained by Fischer and Delbrück (3) as a by-product in the preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucose. The identity of *neo*-D-trehalose is obscure. Vogel and Debowska-Kurnicka (19) obtained a substance, m.p. 68–70°, $[\alpha]_D$ +68.1 (chloroform), by condensing 2,3,4,6-tetra-*O*-acetyl-D-glucose in the presence of zinc chloride and phosphorus pentoxide. The product was assumed to be *neo*-D-trehalose octaacetate since the rotation was that expected on the basis of Hudson's rules of isorotation (7). Haworth and Hickinbottom (6) reacted 2,3,4,6-tetra-*O*-acetyl-β-D-glucose in benzene solution with Brigl's anhydride (2) to form the heptaacetate of a disaccharide termed *neo*-trehalose. The octaacetate melted at 140–141° C. with specific rotation +82° (chloroform). Sharp and Stacey (18) have recently questioned the identity of this substance and have reported the preparation of *neo*-D-trehalose octaacetate, m.p. 120°, specific rotation, +67° (chloroform), both by reaction of β-acetofluoroglucose with silver carbonate, "anhydrone", and iodine in chloroform and by treating 2,3,4,6-tetra-*O*-acetyl-α-D-glucose with phosphorus pentoxide in chloroform. More recently, Micheel and Hagel (14) reacted acetobromoglucose in acetone with about 0.4 moles of water in the presence of mercuric cyanide to form *iso*-trehalose octaacetate and a *neo*-trehalose octaacetate, m.p. 140°, $[\alpha]_D$ +80° (chloroform). These constants are in close agreement with those reported by Haworth and Hickinbottom (6). Since the present work was completed, a paper has appeared wherein Bredereck, Höschele, and Ruck (1) report melting 2,3,4,6-tetra-*O*-acetyl-β-D-glucose with zinc chloride to form *iso*-trehalose octaacetate and a *neo*-trehalose octaacetate, m.p. 140° C., $[\alpha]_D$ +64.4° (chloroform). We have reinvestigated the reaction of Brigl's anhydride with the anomeric 2,3,4,6-tetra-*O*-acetyl-D-glucoses.

A mixture of the anomeric 2,3,4,6-tetra-*O*-acetyl-D-glucoses (about 65% α-anomer) was heated in a small amount of benzene with an equimolar amount

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of tri-*O*-acetyl-D-glucosan ⟨1,5⟩ α ⟨1,2⟩ (Brigl's anhydride) (2) for 36 hr. at 100° C. The product was deacetylated and the disaccharides were isolated by preparative paper chromatography (15). This fraction was acetylated and the resulting mixture of sugar acetates was subjected to chromatographic separation on a column of Magnesol-Celite (5: 1) according to the general procedure of McNeely, Binkley, and Wolfrom (13). Two crystalline substances were isolated. One of the materials was identified as D-trehalose octaacetate. The other substance possessed the melting point and rotation reported by Haworth and Hickinbottom (6) for *neo*-D-trehalose octaacetate. Deacetylation of these substances afforded D-trehalose and a substance with the physical constants reported by Haworth and Hickinbottom for *neo*-trehalose (6).

Lemieux (9) has reviewed the previous experience in the preparation of α-D-glucopyranosides by reaction of alcohols with Brigl's anhydride and prepared β-D-maltose octaacetate by heating 1,2,3,6-tetra-*O*-acetyl-β-D-glucose with the anhydride and acetylating the product. Lemieux and Huber (11) have synthesized sucrose by reaction of the anhydride with 1,3,4,6-tetra-*O*-acetyl-D-fructose and deacetylation of the product. These syntheses as well as the synthesis of D-trehalose reported herein show that Brigl's anhydride has a strong tendency to form α-D-glucopyranosides when reacted with the secondary alcoholic or hemiacetal hydroxyl groups of partially acetylated sugars. Therefore, it is to be expected that Haworth and Hickinbottom (6) did in fact prepare an α-D-glucopyranoside on reacting Brigl's anhydride with 2,3,4,6-tetra-*O*-acetyl-β-D-glucose. There can be little doubt that the substance we have isolated is identical with the *neo*-D-trehalose reported by Haworth and Hickinbottom (6). A sample was hydrolyzed and paper chromatography showed the hydrolyzate to contain only glucose. Therefore, the nonreducing substance must be a D-glucosyl-D-glucoside. Periodate oxidation of the trehalose-type molecule should liberate two moles of formic acid and no formaldehyde. The new technique developed by Perlin (16) to measure the amount of formic acid liberated in periodate oxidations was used to study the periodate oxidation both of trehalose and of the *neo*-trehalose of Haworth and Hickinbottom. In each case, two moles of formic acid were liberated per mole of disaccharide and no appreciable amount of formaldehyde was formed. Therefore, the *neo*-trehalose of Haworth and Hickinbottom must be a D-glucopyranosyl D-glucopyranoside. The rotation in chloroform of the octaacetate, +82°, when compared (7) to those of D-trehalose octaacetate, +163°, and *iso*-D-trehalose octaacetate, −18.4° (12), leaves no doubt that the substance is in fact α-D-glucopyranosyl β-D-glucopyranoside.

EXPERIMENTAL

Octaacetates of D-*Trehalose and neo*-D-*Trehalose*

A solution of 2,3,4,6-tetra-*O*-acetyl-β-D-glucose (4), 4 gm., in 50 ml. of 96% ethanol was kept at 50° C. for 40 hr. The solution was concentrated *in vacuo* to a dry sirup which was dissolved in 50 ml. of dry ether. Skellysolve F was added to a slight turbidity and after seeding with starting material the solution was kept overnight at 0° C. The crystals which separated were removed by filtration and the filtrate was evaporated *in vacuo* to a sirup $[\alpha]_D^{22}$ +93° (chloroform). The substance (about 65% α-anomer), 2.15 gm., was dissolved in 25 ml. dry benzene. The solution was concentrated by distillation at atmospheric pressure to about 5 ml. volume and transferred to a tube which contained 1.90 gm. of Brigl's anhydride (2). The tube was sealed and heated at 100° C. for 36 hr. in a temperature-controlled oil bath. The product was deacetylated in methanolic ammonia and a 20% aqueous solution of the free sugars was applied as uniform streaks to 50 × 50 cm. sheets of Schleicher-Schuell No. 470A filter paper for chromatographic separation. About one milliliter of the solution was applied to each sheet. The sheets were attached to strips of Whatman No. 1 filter paper for downward irrigation (15) with butanol–pyridine–water (6: 4: 3). The band in the resulting chromatogram which was expected to contain disaccharides was readily detected on strips cut from the sheets by the periodate–permanganate spray reagent (10). After isolation by extraction with water and solvent removal, the disaccharides were acetylated with acetic anhydride and sodium acetate in the usual manner. The sirupy sugar acetates were dissolved in about 5 ml. of benzene and added to the top of a 160 × 35 mm. (in diam.) column of Magnesol-Celite (5: 1) (12) wetted with benzene. The chromatogram was developed with 1.5 liter of 60: 1 benzene – tertiary butanol mixture, the column was extruded and a streak was applied to the length of the column by spraying a freshly prepared aqueous solution of 1% potassium permanganate in 2.5 *N* aqueous sodium hydroxide through a 2 mm.-wide slit cut from a sheet of plexiglass. A diffuse zone extended from 8 to 60 mm. from the top of the column and a sharp zone from 65 to 90 mm. from the top of the column. Elution of the top zone with acetone gave 10 mgm. of a substance, m.p. 141–142° C., $[\alpha]_D^{25}$ + 81.8° (*c*, 0.4 in chloroform), after two crystallizations from ethanol. Haworth and Hickinbottom (6) have reported *neo*-D-trehalose octaacetate to melt at 140–141° C. with $[\alpha]_D$ +82° (*c*, 5 in chloroform). The bottom zone was eluted with acetone to yield, after two crystallizations from ethanol, 15 mgm. of a substance, m.p. 100–101° C., $[\alpha]_D^{25}$ +163° (*c*, 0.1 in chloroform). The melting point was undepressed by authentic D-trehalose octaacetate, m.p. 100–101° C. The infrared spectrum of the synthetic substance pressed with potassium bromide (17) into a window and measured with a Perkin–Elmer Model 21 spectrometer was identical to the spectrum of the authentic sample of D-trehalose octaacetate obtained under the same conditions.

D-*Trehalose*

The synthetic D-trehalose octaacetate was deacetylated in methanolic ammonia and the product was recrystallized from aqueous ethanol. The melting point of the substance, m.p. 97–98° C., was unaffected by mixture with an authentic sample of D-trehalose dihydrate of the same melting point.

neo-D-*Trehalose*

The synthetic *neo*-D-trehalose octaacetate was deacetylated with methanolic ammonia. The product obtained on crystallization from 90% ethanol sintered at 141–145° C. and melted in the range 195–210° C. All attempts to obtain a sharply melting product were unsuccessful. Haworth and Hickinbottom (6) had the same difficulty and reported *neo*-trehalose to melt at 210–220° C. with sintering at 145–150° C. A sample was hydrolyzed in *N* hydrochloric acid. Paper partition chromatography using butanol–ethanol–water (5: 1: 4) and butanol–pyridine–water (6: 4: 3) detected only glucose in the hydrolyzate.

Periodate Oxidations

The disaccharides, 0.004 mM., were oxidized at 16° C. in 3.2 ml. of solution containing 0.05 mM. sodium periodate and 0.042 mM. sodium bicarbonate and saturated with carbon dioxide according to the procedure developed by Perlin (16) using a Warburg apparatus to follow the liberation of carbon dioxide. The results of typical runs are plotted in Fig. 1. Only negligible amounts of formaldehyde could be detected in the oxidation mixture after 24 hr. reaction time using the chromotropic acid reagent.

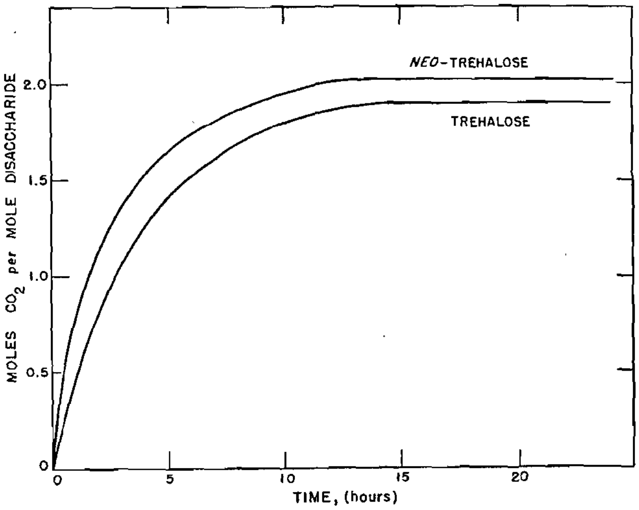

FIG. 1. The rates of liberation of formic acid on periodate oxidation of trehalose and *neo*-trehalose measured by the method of Perlin (16).

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SULPHUR ISOTOPE EFFECTS IN THE BISULPHITE ADDITION REACTION OF ALDEHYDES AND KETONES

II. BOND-FORMATION EFFECT[1]

BY W. A. SHEPPARD,[2] R. F. W. BADER,[3] AND A. N. BOURNS

ABSTRACT

The relative rates of formation of C^{12}–S^{32} and C^{12}–S^{34} bonds in the bisulphite addition reaction of heptanal, benzaldehyde, anisaldehyde, and 2-heptanone have been measured and found to approximate unity. This result has been interpreted in terms of the Bigeleisen treatment of isotope effects in unidirectional processes.

INTRODUCTION

During the past few years a number of papers have appeared dealing with the fractionation of the isotopes of the lighter elements, other than hydrogen, due to differences in reaction rates. Attention has been given chiefly to reactions in which a bond associated with the isotopic atom is broken in the rate-determining step, although a simultaneous bond-rupture and bond-formation mechanism has been proposed to account for the isotope effects observed in the deammonation of phthalamide (9) and the pyrolysis of barium adipate (3). Certain complex reactions in which the initial step is probably a reversible bond-formation process have also been investigated (10, 6), but as yet no isotope effect studies have been reported for a simple one-step bond-formation reaction.

In a previous communication from this laboratory (8), equilibrium constants of 1.010 to 1.021 were reported for the S^{32} : S^{34} isotopic exchange reaction between bisulphite ion and the bisulphite-addition products of a number of aldehydes and ketones. These results were considered as evidence in support of the sulphonic acid structure of the addition compounds. The present paper deals with an extension of these studies in which the isotopic fractionation arising from the difference in reaction rates of light and heavy sulphur in the forward reaction *alone* has been determined. If, as seems likely, the rate-determining step of the addition reaction is the attack of bisulphite ion on the carbonyl carbon, the results give a measure of the sulphur isotope effect in the formation of a carbon–sulphur bond.

The bisulphite-addition reaction is readily reversible and isotopic equilibrium between bisulphite ion and the addition product is quite rapidly established. Although it was possible to reduce the contribution of the reverse reaction to the observed fractionation by removing the precipitated addition product as rapidly as possible from the reaction system, conditions which give a strictly unidirectional process could not be achieved. However, the isotope effect for the addition reaction could be determined with reasonable accuracy by

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measuring the fractionation after varying short reaction periods and extrapolating to zero time.

Bisulphite ion was used in a very large excess in all experiments and no significant change in the isotopic ratio of this reactant, therefore, occurred during the addition reaction. It follows that the extent of fractionation at any time t is given, to a very close approximation, by the quotient $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} \Big/ \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$, where $\left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$ is the ratio of the two sulphur isotopes in the original sodium bisulphite reactant and $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}}$ is the corresponding ratio in the addition product removed from the reaction system at time t. Extrapolation to zero time of the plot of this quotient against time gives the specific rate constant ratio, k^{32}/k^{34}, for the reaction of light and heavy species of bisulphite ion.

RESULTS

In Fig. 1 are shown $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} \Big/ \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$ values for four bisulphite ion–carbonyl systems determined at 25°C. and plotted as a function of time. Equilibrium values previously reported (8) are also indicated.* The standard deviation of the isotopic ratios represented by the individual points in this figure was of the order of 0.1%.

The extrapolated values for the isotopic ratios shown in the figure are subject to considerable uncertainty owing to limitations in the precision of the mass spectrometer analyses and the experimental difficulty in obtaining points at very short reaction times. Nevertheless, in the heptanal, anisaldehyde, and 2-heptanone systems, the conclusion that the reaction rates of the two isotopic species of bisulphite ion differ by no more than 0.2% would appear to be justified. With benzaldehyde, the isotope effect is somewhat larger and it can definitely be concluded that the reaction of $HS^{32}O_3^-$ is favored.

It should be noted that the addition reaction was very rapid under the conditions used in obtaining these results, particularly in the case of heptanal and benzaldehyde. In fact, with these compounds, almost complete precipitation of the addition product usually occurred in less than one minute. The possibility, therefore, that the rate-determining process might be the diffusion of bisulphite ion through the aqueous solution to the droplets of the insoluble carbonyl compound must not be overlooked. For this reason, a number of experiments with heptanal were made in which the rate of reaction was greatly reduced by diluting the aldehyde with benzene. From the results given in Table I, it is apparent that, even under these conditions, isotopic fractionation was extremely small. It may therefore be concluded that for the reaction of heptanal with sodium bisulphite the rate constant ratio, k^{32}/k^{34}, is close to unity and probably falls within the range 0.999–1.001.

**In order to compare the fractionation observed under equilibrium conditions with the rate-constant ratios, k^{32}/k^{34}, the equilibrium values are expressed as the reciprocals of the equilibrium constants previously reported.*

TABLE I
ISOTOPE EFFECT IN THE REACTION OF SODIUM BISULPHITE WITH HEPTANAL DILUTED WITH BENZENE (25°C.)
(20 ml. saturated sodium bisulphite, 20 ml. benzene)

Run No.	Heptanal, ml.	Reaction time, sec.	% yield (based on RCHO)	$\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} \Big/ \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$
D_{I}	1.5	30	1.4	0.9996
D_{II}	1.5	30	1.4	0.9982
B_{III}	3.0	15	7.3	0.9982
C_{I}	3.0	30	19.5	0.9995
C_{IV}	3.0	300	38.6	1.0008

EXPERIMENTAL

Reagents

The source and purity of all reagents were as previously reported (8).

Preparation of the Addition Compounds

A. *Without Diluent*

To a saturated aqueous solution of sodium bisulphite, containing 5.15 moles of bisulphite per liter of solution, was added the carbonyl compound in the quantity necessary to give a bisulphite to carbonyl molar ratio of 10 : 1. The mixture was shaken vigorously from the time of mixing for periods ranging from the point of first precipitation of the addition product up to a total reaction time of four to six minutes. With the exception of the product from anisaldehyde, the addition compounds started to separate within one-half minute and, in the case of heptanal and benzaldehyde, the reaction was essentially complete a few seconds after the appearance of the first precipitate. The product was rapidly removed by suction filtration, washed with ethanol and then with ether, and dried.

B. *With Benzene Diluent*

Heptanal (1.5 or 3.0 ml.) was diluted with 20 ml. of thiophene-free benzene and the solution then mixed with 20 ml. of saturated aqueous sodium bisulphite. After vigorous shaking for the desired reaction period, the addition product was removed, washed, and dried.

Determination of Isotopic Ratios

Sulphur dioxide samples for mass spectrometric analysis were prepared from the addition compounds by the method previously described (8).

The samples from the addition product obtained in the reaction carried out in the absence of the diluent were analyzed in a 90° direction focusing Nier type mass spectrometer. The same instrument, but equipped for simultaneous collection, was used for the samples prepared from the product of the benzene diluted reaction medium. Details of the mass spectrometer measurements are found in the earlier paper (8).

DISCUSSION

The effect of isotopic substitution on rates of chemical reactions has recently been treated theoretically by Bigeleisen (1, 2), who has developed the following equation for the calculation of rate constant ratios:

$$\frac{k_1}{k_2} = S\left(\frac{m_2{}^*}{m_1{}^*}\right)\left[1 + \sum_i^{3n-6} G(u_i)\,\Delta u_i - \sum_i^{3n'-7} G(u_i{}^{\ddagger})\,\Delta u_i{}^{\ddagger}\right]$$

where the subscripts 1 and 2 refer to the light and heavy isotopic molecules, respectively, S is a statistical factor, m^* is an effective mass of the molecule along the reaction coordinate, $\Delta u_i = (hc/kT)(\omega_{1i} - \omega_{2i})$, $G(u_i)$ is a function previously defined by Bigeleisen and Mayer (4), and ‡ refers to the activated complex. S is unity except in reactions in which there are two or more identical atoms of the isotope in question in the molecule. The factor $(m_2{}^*/m_1{}^*)^{\frac{1}{2}}$, which gives the ratio of the number of molecules in the transition state undergoing reaction per unit time, may be calculated as the reduced mass of the two atoms connected in the bond being broken or formed. The quantity in the square brackets describes quantitatively the zero point energy effects.

In reactions involving the rupture of a bond connected with the isotopic atom, the molecule is more "tightly bound" in the initial state than in the activated complex,

i.e., $$\sum_i^{3n-6} G(u_i)\,\Delta u_i > \sum_i^{3n'-7} G(u_i{}^{\ddagger})\,\Delta u_i{}^{\ddagger}.$$

The zero point energy term is therefore greater than unity and its effect on the relative reaction rates is in the same direction as the reduced mass term.

For reactions in which the isotopic atom forms a new bond without any appreciable weakening of other bonds involving this atom, however, one would expect this atom to be more tightly bound in the activated complex than in the initial state, i.e.,

$$\sum_i^{3n'-6} G(u_i{}^{\ddagger})\,\Delta u_i{}^{\ddagger} > \sum_i^{3n-6} G(u_i)\,\Delta u_i.^*$$

The zero point energy term of the Bigeleisen expression would then be less than unity and would tend to cancel the term involving the reduced masses. This interpretation would appear to account qualitatively at least for the approximately zero sulphur isotope effect in the bisulphite addition reaction.

It is of interest to attempt a more quantitative theoretical analysis of the isotope effect in this bond formation reaction. If one assumes that the vibrational frequencies of all bonds other than the bond being formed are unchanged in going from initial state to activated complex, then the reaction can be treated as the formation of the hypothetical C–S molecule from separated atoms. The term

$$\sum_i^{3n-6} G(u_i)\,\Delta u_i$$

is then zero. Some model must be assumed for the activated complex in order to evaluate

$$\sum_i^{3n'-6} G(u_i{}^{\ddagger})\,\Delta u_i{}^{\ddagger},$$

On the other hand, isotope effect studies on the hydrolysis of esters (10) *and reaction of dimedon with formaldehyde* (7) *suggest that the initial state term is greater than the activated complex term in bond formation at the carbonyl carbon. In these reactions, however, bond formation is clearly accompanied by the weakening of other bonds; a π bond is broken and the hybridization of carbon in the three σ bonds is changed from sp^2 to sp^3.*

and it is convenient to consider that the new bond is completely formed, in other words, that the vibrational frequencies of the C–S bond in the activated complex are the same as in the product. Using a wave number of 760 cm.$^{-1}$ for the C^{12}–S^{32} bond (5, 7) and 754 cm.$^{-1}$ for the C^{12}–S^{34} bond (calculated from the relation of the reduced masses), one obtains a k^{32}/k^{34} ratio of 1.001 at 25°C., compared to the experimental values of approximately 0.999 to 1.003 for the four systems studied (see Fig 1).

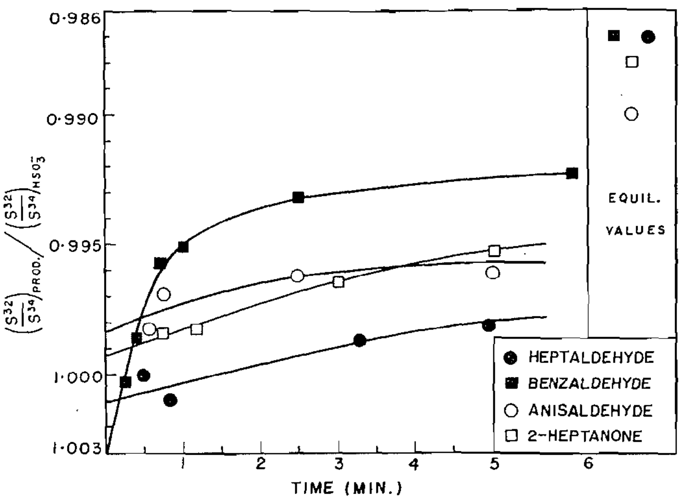

FIG. 1. Variation of $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} \Big/ \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$ ratios with reaction time.

Somewhat poorer agreement between calculated and experimental values would be anticipated for the reaction of bisulphite ion with lower molecular weight carbonyl compounds such as acetone. Although the unidirectional effect could not be determined experimentally for such systems owing to the much greater solubility of the addition product in saturated sodium bisulphite, their lower equilibrium values, $1/K$, for isotopic exchange (8) would suggest a k^{32}/k^{34} ratio of several tenths of a per cent less than unity. The agreement with the calculated value, nevertheless, is as good as could be expected bearing in mind the assumptions made in the calculations and the model chosen for the transition state.

The results demonstrate that this treatment permits a semiquantitative prediction of the magnitude of isotope effects in simple bond-formation processes.

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THE REACTION OF ACTIVE NITROGEN WITH PROPANE[1]

By M. Onyszchuk,[2] L. Breitman,[3] and C. A. Winkler

ABSTRACT

The reaction of nitrogen atoms with propane has been found to produce hydrogen cyanide as the main product, together with smaller amounts of acetylene, ethylene, and ethane, which were recovered at all propane flow rates. Complete consumption of nitrogen atoms was not attained at any propane flow rate used at 63°C., but was attained at 250°C. for ratios of propane to nitrogen atoms greater than 1.3. An activation energy of 5.6 ± 0.6 kcal. and a steric factor between 10^{-2} and 10^{-3} was estimated from second order rate constants.

The reaction of active nitrogen with propane has been discussed briefly in a recent review of active nitrogen – hydrocarbon reactions (13). A detailed examination of the reaction products and their dependence on propane flow rate is reported in the present paper. As before, it is assumed that the chemically reactive species in active nitrogen is atomic nitrogen (3, 4).

EXPERIMENTAL

The apparatus used in this investigation was similar to that described in earlier papers from this laboratory (3, 4). Preliminary experiments showed that hydrogen cyanide was the major product, and that ethylene, acetylene, ethane, and methane were formed in much smaller quantities.

The vapor pressure – temperature relations for acetylene and propane are not sufficiently different at low temperatures to allow their fractionation in the LeRoy distillation apparatus used (6). Therefore, a portion of the unreacted propane was codistilled with ethylene and acetylene at −140°C. until the equilibrium vapor pressure decreased from that of the mixture to that of propane at this temperature. Analysis with a mass spectrometer gave the composition of this combined C_2–C_3 hydrocarbon fraction.

The remaining propane fraction, containing only a trace of acetylene, was separated from hydrogen cyanide by distillation at −120°C. Hydrogen cyanide was distilled at −70°C. and condensed on the surface of 10 ml. of 1 *N* potassium hydroxide which had been previously degassed and frozen in a detachable trap immersed in liquid nitrogen. The trap, closed with a stopcock, was removed and its bottom end plunged into hot water. This melted the alkali solution, which then dissolved the hydrogen cyanide before it could melt and polymerize. Titration of the resulting solution with standard silver nitrate gave the cyanide content.

Analysis of noncondensable products, methane and hydrogen, was not made.

The molecular nitrogen flow rate was maintained constant at 5.83×10^{-5} mole per sec.; this gave a pressure of 1.35 ± 0.02 and 1.42 ± 0.01 mm. of

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mercury at 63 ± 3° and 250 ± 5°C. respectively. Experiments were made at each temperature with propane flow rates ranging from 5×10^{-7} to 2×10^{-5} mole per sec.

From 15 experiments with ethylene at 100° and at 260°C., under experimental conditions corresponding to complete removal of the available nitrogen atoms (11), the atomic nitrogen flow rate was estimated to be $5.20 \pm 0.50 \times 10^{-6}$ mole per sec.

RESULTS AND DISCUSSION

The results of the investigation are summarized in Fig. 1. Hydrogen cyanide accounted for 90–97% of the propane consumed and the remainder was recovered as ethylene, acetylene, and ethane. The average carbon and hydrogen balances were 101% and 92% respectively.

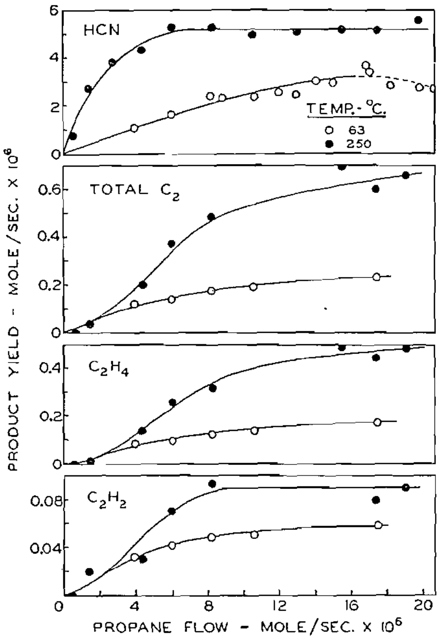

FIG. 1. Rate of formation of various products in the nitrogen atom – propane reaction, as a function of propane flow rate.

The yield of hydrogen cyanide from the reaction at 63°C. increased gradually with increasing propane flow rate, and appeared to pass through a maximum without complete consumption of the nitrogen atoms available. The presence of the maximum may result, in part, from dilution effects which reduce the reaction time significantly at high propane flow rates. Moreover, under these conditions the reaction flame was localized at the top of the reaction vessel where the surface to volume ratio is relatively large and loss of nitrogen atoms or nitrogen atom – propane complexes at the surface might lead to the observed decrease in hydrogen cyanide production.

For the reaction at 250°C., on the other hand, the yield of hydrogen cyanide remained constant at 5.2×10^{-6} mole per sec. beyond a critical propane flow rate of about 7×10^{-6} mole per sec. This value corresponds to the average atomic nitrogen flow rate determined from the ethylene experiments. It may be concluded that when the flow rate of propane exceeds the nitrogen atom flow rate by a factor of 1.3 or greater, the reaction proceeds to complete removal of the available atomic nitrogen.

The curves representing production of C_2 hydrocarbons (mainly ethylene and acetylene) offer further support to the conclusion that nitrogen atoms are completely consumed at 250° but not at 63°C. Since ethylene and acetylene react rapidly with nitrogen atoms, a continued increase in the amounts of these hydrocarbons would be expected above the critical propane flow rate. This was realized experimentally for ethylene, but only at the high reaction temperature. On the other hand, if nitrogen atoms are available for reaction at all propane flow rates, the curve for C_2 hydrocarbon production should parallel that for hydrogen cyanide formation. This appears to be true for the reaction at 63°C.

Of particular significance was the recovery of ethylene and acetylene in the region of incomplete consumption of nitrogen atoms. The reaction of nitrogen atoms with these unsaturates is about ten times more rapid than the reaction with propane, if it is assumed that the initial attack of a nitrogen atom on a hydrocarbon molecule is rate controlling. Since ethylene, acetylene, and propane would be expected to compete for nitrogen atoms according to their relative reactivities, the recovered unsaturates should represent only a fraction of the total amounts formed. Conservative calculations indicate that most of the hydrogen cyanide was probably derived from ethylene and acetylene formed by the primary attack of nitrogen atoms on propane.

The general reaction mechanism which has been tentatively suggested for the paraffin hydrocarbon – nitrogen atom reaction (13), and which appears to be satisfactory for the ethane reaction (3), cannot adequately explain the presence of ethylene and acetylene among the products of the propane reaction. The recovery of these unsaturates in appreciable amounts in the region of excess nitrogen atoms implies their formation in a primary reaction step, rather than from secondary reactions involving hydrogen atoms and free radicals. A number of possible reactions might be suggested, but many of these are energetically unfavorable while others involve the improbable formation of "hot" radicals from the collision complex. A thermochemically favorable reaction of a type by which ethylene might be formed by decomposition of the propane–nitrogen atom collision complex would be

$$N + C_3H_8 \rightarrow \text{Collision complex} \rightarrow HCN + CHCH_3 + H_2 + H. \qquad [1]$$

The ethylidene radical previously postulated in the nitrogen atom – propylene reaction (10) and in other reactions (1, 2) is thought to transform rapidly to ethylene,

$$CH_3CH \rightarrow CH_2{=}CH_2$$

An alternative primary step might produce acetylene directly by a similar exothermic reaction,

$$N + C_3H_8 \rightarrow \text{Collision complex} \rightarrow HCN + C_2H_2 + 2H_2 + H. \qquad [2]$$

Nitrogen atom reaction with the ethylene and acetylene produced by reactions [1] and [2] could occur as outlined in previous papers (11, 12).

Both reactions [1] and [2] are admittedly incompatible with the Rice–Teller principle of least motion (8). However, this principle has been applied to processes that involve energies of about 100 kcal. or less, while in the nitrogen atom reactions, the high energy of formation of the $C{\equiv}N$ bond (170–200 kcal.) is effectively released within the reaction complex and might result in considerably more intracomplex rearrangement than would otherwise be expected.

The small quantities of ethane detected only in the experiments at 250°C. probably resulted from the hydrogenation of ethylene by atomic hydrogen (7).

Second order rate constants were calculated for the propane–nitrogen atom reaction in a manner similar to that previously outlined for the ethane reaction (3). In Table I are recorded the data obtained for experiments corresponding to incomplete consumption of nitrogen atoms and used for the calculation of second order rate constants when both streamline and turbulent flow conditions are assumed. The average values of the rate constants, together with the corresponding activation energies, E, and steric factors, P, in the expression $k = PZe^{-E/RT}$ are shown in Table II. The collision number, Z, was calculated using collision diameters of 3.0 Å and 4.2 Å for atomic nitrogen (5) and pro-

TABLE I

DATA USED FOR THE CALCULATION OF SECOND ORDER RATE CONSTANTS

Propane flow	HCN formed	Reaction time, sec.	Ratio of propane* consumed to at. N	k, l.mole.$^{-1}$sec.$^{-1}$ $\times 10^{-5}$	
Mole.sec.$^{-1}$ $\times 10^{6}$				Streamline flow	Turbulent flow
Temperature = 63 ± 3°C.					
3.92	1.12	0.322	0.375	0.772	2.46
5.97	1.64	0.312	0.391	0.880	2.89
8.21	2.44	0.302	0.381	1.12	4.33
8.83	2.37	0.299	0.378	1.00	3.83
10.6	2.42	0.292	0.387	0.915	3.43
12.0	2.58	0.286	0.357	0.844	3.09
13.0	2.48	0.282	0.385	0.820	3.52
14.1	3.07	0.278	0.378	1.05	4.68
15.5	3.03	0.273	0.375	0.961	4.23
16.7	3.45	0.269	0.378	1.16	5.75
16.8	3.74	0.268	0.381	1.41	7.50
Temperature = 250 ± 5°C.					
0.473	0.777	0.230	0.333	10.2	50.0
1.42	2.77	0.227	0.341	19.9	150
2.73	3.83	0.222	0.352	16.8	133
4.43	4.37	0.217	0.381	13.8	129

**The amount of propane consumed was calculated from the total amount of HCN and C_2 hydrocarbons produced.*

TABLE II

KINETIC CONSTANTS FOR THE NITROGEN ATOM – PROPANE REACTION

Flow condition assumed	Temp., °C.	k, l.mole.$^{-1}$sec.$^{-1}$	P	E, kcal.
Streamline	63	9.94×10^{4}	9.1×10^{-4}	5.1
	250	1.52×10^{6}		
Turbulent	63	4.16×10^{5}	2.1×10^{-2}	6.2
	250	1.16×10^{7}		

pane (9) respectively. Actual flow conditions within the reaction vessel probably lie somewhere between the two extremes assumed.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to Dr. R. A. Back, who concurrently investigated the nitrogen atom reaction with the butanes, for many helpful discussions of the reaction mechanism. The authors are also indebted to Dr. H. I. Schiff of this department for mass spectrometer analyses.

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ADDITION COMPOUNDS OF THE MOLECULAR HALIDES

III. THE TRICHLORIDES AND PENTACHLORIDES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH WITH TRIETHYLAMINE[1]

By W. R. Trost

ABSTRACT

Monoaminates of the trichlorides and pentachlorides of phosphorus, arsenic, antimony, and bismuth have been prepared, as well as triaminates of the trichlorides of phosphorus and arsenic and mixed polyaminates of the remaining chlorides. The co-ordinate valences and possible structures of the compounds are related to a model that depends on the geometry of the molecular halide and on the outer orbitals of the atoms in it.

INTRODUCTION

The possibility that the $(n+1)s$, nd, $(n+1)p$ orbitals are significant bonding factors carries with it definite implications concerning the structures and the reactions of inorganic compounds. The systems provided by saturated molecular halides with independent donor groups are particularly suited to a study of the role and function of these outer orbitals. Addition reactions between the Group V halides and tertiary amines would be expected if outer orbitals are effective electron acceptors. Differences from the Group IV tetrahalides (1), because of the lone-pair on the Group V atoms and the less symmetrical structures of the tri- and pentachlorides, may occur.

EXPERIMENTAL

The liquid chlorides (PCl_3, $AsCl_3$, $SbCl_5$) were purified by fractionation; the solid chlorides (PCl_5, $SbCl_3$, $BiCl_3$) by sublimation; and triethylamine, after treatment with anhydrous potassium hydroxide, by fractionation. Measured volumes of individual liquid chlorides and triethylamine were mixed together by consecutive condensation into a flask, at −78°C. The mixtures were brought to room temperature, while being magnetically stirred. Then volatile products were removed from the mixture by condensation into a volumetric flask, at −78°C. The vapor pressure of the mixture, at 16°C., was plotted with reference to the mole fraction remaining in the mixture. When the vapor pressure had fallen to zero, at 16°C., the temperature of the mixture was steadily raised until phase change or thermal decomposition began. The products above 16°C. were collected separately from the liquid condensates recovered at 16°C.

All operations, from purification to thermal decomposition, were carried out in an all glass vacuum system that had been flamed, and was filled with dried nitrogen when a procedure required it. The solid chlorides were weighed outside the vacuum system, the procedure with them being otherwise the same.

Mole ratios in the mixtures were calculated from density and volume for the liquids. Liquid volumes were measured directly in the vacuum system in

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the graduated tubes that were used to supply to, and to receive from, the mixture. The products recovered from the mixtures were identified, when they were unchanged chloride or amine, by vapor pressure or melting point. The products of the thermal decomposition, however, were not identified, if they were neither amine, chloride, nor amine hydrochloride, although qualitative tests for amine, chloride, and Group V element were generally completed.

RESULTS

The Trichlorides

The condensation of phosphorus trichloride, or arsenic trichloride, into excess triethylamine at −78° immediately produces a white solid substance. When one mole of trichloride has been added to six moles of amine, no free liquid can be observed in the mixture. The vapor pressure of the mixture, 48 mm. at 16°C., is, however, normal for that of liquid amine at the same temperature. As the vapor is condensed out of the mixture, the white solid cracks and shrinks, and the vapor pressure falls slowly (Table I), until very nearly three moles of amine have been recovered. Then the vapor pressure abruptly vanishes, even though the temperature of the mixture is raised from 16° to 200°C. The composition of the mixtures from which all volatile amine has been removed are shown in Table II. They correspond to the triaminates, $PCl_3.3ET_3N$, $AsCl_3.3ET_3N$, and are stable, white, powders at room temperature. They begin to decompose, in vacuum, at 50° to 60°, a colorless liquid with no measurable vapor pressure condensing out of the solid mixture, which is itself developing yellow colors. At about 150°, white solids begin to sublime out of the residue; at 200°, the residue, which may have become quite orange, has been entirely transformed into the white sublimate and colorless liquid. The two products, on mixing, reproduce the yellow colors observed in the mixture in the course of its thermal decomposition. From qualitative tests, each product contains chlorine, amine, and phosphorus or arsenic.

TABLE I
VAPOR PRESSURE OF TRIETHYLAMINE AS A FUNCTION
OF THE MOLE RATIO OF AMINE TO TRICHLORIDE

Chloride	Vapor pressure of triethylamine in mm. Hg					
	Mole ratio					
	6/1	5/1	4/1	3/1	2/1	1/1
PCl_3	48	47	30	0		
$AsCl_3$	48	48	31	8	0	
$SbCl_3$	48	48	47	47	46	0
$BiCl_3$	48	47	45	40	20	0
PCl_5 (*a*)	49	45	35	30	0	
PCl_5 (*b*)	48	48	40	35	36	0
$SbCl_5$	48	49	48	48	48	0

Temperature = 16°*C.*

(*a*) *After two hours.*
(*b*) *After two days.*

TABLE II

Composition and stability of addition compounds

Compound	Experimental data			
	Mole ratio $\frac{NR_3}{MX_a}$	Softening temperature, °C.	Transitions	Decomposition temperature, °C.
$PCl_3.Et_3N$	1.2	*ca.* 0	20°, −2 PCl_3 to triaminate	
$PCl_3.3Et_3N$	3.1			50
$AsCl_3.Et_3N$	0.85	30		
$AsCl_3.3Et_3N$	2.8			60
$SbCl_3.Et_3N$	0.96	50	40°, to black glass	
$BiCl_3.Et_3N$	1.1	210	140°, to gray glass	
$PCl_5.Et_3N$ (*b*)	1.1	200	170°, to black powder	115
$PCl_5.n\ Et_3N$ (*a*)	2.5	175	175°, to black liquid	125
$SbCl_5.Et_3N$	1.2	60		125
$SbCl_5.n\ Et_3N$	2.4	70		110

The addition of triethylamine to excess phosphorus trichloride at −78°C., or to arsenic trichloride at 0°C., produces oily liquids and transparent, colorless low melting glasses, as the mole ratio changes. One mole of amine in five moles of phosphorus trichloride is a transparent glass at −78°C., but shows the normal vapor pressure of phosphorus trichloride, and can be magnetically stirred, at 16°C. As phosphorus trichloride vapors are removed, the stirring becomes more difficult and at mole ratios of about 1:1 the vapor pressure begins to fall, rather abruptly, and continues to fall more slowly, as the gel transforms into a white powdery solid, with the experimental formula, $PCl_3.2.8\ Et_3N$. The latter compound, in its behavior at higher temperatures, is identical with the triaminate recovered from mixtures rich in amine.

Amine in excess arsenic trichloride produces mixtures that differ from those with phosphorus trichloride in that the softening temperatures of the glasses are higher, and the transformation to the triaminate is not complete. The experimental compositions and softening temperatures of what will be called the monaminates of phosphorus and arsenic trichlorides are shown in Table II.

The trichlorides of antimony and bismuth are solid compounds. No changes are observed in them when triethylamine is added at −78°. On warming to room temperature, the solids slowly expand to volumes many times the original one, but liquid amine remains visibly unassociated if the amine to trichloride ratio is greater than 6 : 1. On removing the amine from the mixture, although the solid shrinks, the vapor pressure very nearly remains normal until it drops to zero at about a 1 : 1 composition in the mixture (Table I). On warming, the white solids turn black and begin to melt, but no vapor pressure is developed. The aminate of arsenic trichloride turns black at 40° and begins to soften at about 50°, turning into a red-brown liquid at about 100°, without any signs of chemical decomposition. The monoaminate of bismuth trichloride transforms to a gray glassy solid at about 140° and begins to soften at about 210°. Once formed, the monoaminates remain glassy solids, even at low temperatures.

The Pentachlorides

Liquid triethylamine, condensed into solid phosphorus pentachloride at −78°C., disappeared in the formation of a new white solid that looked wet if the amine excess was greater than 6 to 1. The solids cracked and shrank, and the vapor pressure dropped slowly, as amine was removed (Table I). In two mixtures, one of which (PCl_5 *a*) had stood at room temperature for two hours, the other (PCl_5 *b*) for two days, the products remaining when all volatile amine had been removed had the experimental compositions, respectively, of $PCl_5.2.5\ Et_3N$ and $PCl_5.1.1\ Et_3N$. The former was white, the latter yellow. The thermal decompositions of the two aminates differed in the relative amounts of products, but were otherwise rather similar. Both compounds were unchanged at 115°C., but then began to decompose. The products were a gas volatile at −78°, a colorless nonvolatile liquid, and, from the monoaminate only, a solid sublimate. Both compounds were yellow at this temperature, turned black rather abruptly at 170–175°, and soon after began to soften (Table II).

Liquid antimony pentachloride also formed mixed products when mixed with triethylamine at 0°C. The addition of amine to pentachloride was accompanied by the immediate formation of colored compounds which, at about a 1 to 1 mole ratio, had become a glass-like, almost black solid. No further change occurred upon the addition of more amine, perhaps because stirring was not possible. Experimentally, the monoaminate had the composition, $SbCl_5.1.2\ Et_3N$. It began to soften at about 60° and to decompose (a gas volatile at −78°C.) above 100°C. (Table II). The addition of antimony pentachloride to excess triethylamine produced, in addition to the noncrystalline black solid, a white flocculent solid. The vacuum system technique did not permit the separate preparation of these compounds. The mole ratio of the mixture, $SbCl_5.2.4\ Et_3N$, has therefore no specific significance. It might be mentioned that the addition of a petroleum ether solution of antimony pentachloride to excess triethylamine produces only a white solid.

DISCUSSION

The Group V elements, like the Group IV elements, combine with halogens to form compounds in which all valence orbitals contain electron pairs. These molecular halides are nevertheless still able to form addition compounds with donor groups like triethylamine. The co-ordinate bonds presumably responsible for such intermolecular combinations require the presence of accepting orbitals on the molecular halide. However, only outer orbitals are vacant; it becomes necessary, therefore, to ascribe to them the property of reaction with donor electron pairs, if the addition compounds are to be explained.

Each atom in the molecular halide is expected to contribute to the molecular accepting orbitals to an extent dependent on the electronegativities and energy levels of its outer orbitals. The numerous atomic orbitals then combine with one another, through the geometry of the molecule, to provide the molecular accepting orbitals the molecular halide shows in its addition compounds. Perhaps the detailed problem involved in these combinations can be solved.

However, the geometry of the molecular halide depends only on the orbital configuration of the nonhalogen atom. It is also the point of highest symmetry in the molecule, which is a distinct consideration in the formation of the molecular accepting orbital. The nonhalogen atom may therefore itself largely determine the structures and valences shown in the addition compounds of these molecular halides. The simplification permits a specific discussion of the compounds, particularly in a series in which the halogen remains the same. In the trichlorides of phosphorus, arsenic, antimony, and bismuth, the outer orbitals are the $(n+1)s$, $(n+1)p$, nd, $(n-1)f$ orbitals of the Group V elements. As the outer s orbital is stabler than any others a 1 : 1 compound is a possibility for all the Group V chlorides. More extensive addition of donor groups, in which s, p, d hybrid orbitals are used, are also possible, particularly with the hybrid configurations that reflect the structure of the molecular halide (1). The increase in the stability of the orbitals, from phosphorus to bismuth, as the energy separation between the valence and the outer orbitals is diminished, is counterbalanced by a decrease in their accepting properties as the electronegativity of the Group V atoms becomes smaller.

The presence of an unshared electron pair on the Group V atom, if it occupies a directed orbital, would have definite effects on the addition compounds of the trihalides. The bond angles in the trichlorides of phosphorus, arsenic, and antimony are all greater than 100°, and indicate that the electron pair is in the fourth sp^3 orbital about those atoms. As long as this position is occupied a tetrahedral structure for the monoaminate is not possible, and looser, less distinctive 1 : 1 associations are implied. In contrast, the triaminates may have definite structures. Two related possibilities arise. In each, the same hybrid from the stabler outer orbitals, the $(n+1)s$ and the nd, is assigned to the coordinations. The hybrid most suited to the structure of the trichloride is the planar d^2s. It puts three amines in three identical positions around the molecular halide. Each amine is located between and above two chlorine atoms, in the plane perpendicular to the unshared sp^3 orbital. The alternative structure occurs if the lone-pair on the nonhalogen shifts from an sp^3 to an s orbital. The three bonds in the trichloride therefore become p^3. In combination with the d^2s co-ordinations, an octahedral type p^3d^2s structure for the triaminate is achieved. Either alternative implies a solid structure of perhaps chain or layer type, and therefore explains the valence and state of the triaminates.

Though the triaminates were definite compounds with PCl_3 and $AsCl_3$, only indirect and visual evidence for polyaminates were obtained with $SbCl_3$ and $BiCl_3$. That is, the triaminates were the more stable compounds with the liquid trichlorides, while the monoaminates were with the solid trichlorides. It is possible that this comparison is partly unreal, in the sense that it may reflect the experimental method, rather than a physical property; that is, the solid halides could not be added to the amine as isolated molecules. Nevertheless, the co-ordinations in a layer structure like $BiCl_3$ are always competitive with those involved in the addition of amine. For this reason the elimination of amine is an easier process from a solid chloride than from a liquid chloride, if the amine co-ordinations are similar in both cases. Apart from this, it seems likely that the bismuth monoaminate may have achieved extra stability through hybridization. Its lone-pair is most likely, of the Group V elements, to be undirected, physical evidence coming from its (6×2) layer structure and from its ionic valence. Then the monoaminate could have the more symmetrical p^3s structure, with the chlorines and the amine using equivalent bismuth orbitals. Transitions from white powders to dark glass-like compounds were observed in the monoaminates of antimony and bismuth at 40° and 140° respectively.

Oddly enough, perhaps, monoaminates and triaminates appear to be the best possibilities for the pentachlorides as well. The monoaminate uses the $(n + 1)s$ orbital to make the glass-like compounds, observed with antimony pentachloride, and at higher temperatures perhaps with phosphorus pentachloride. An alternative for the monoaminate is the combination of an *nd* orbital with the sp^3d pentachloride to make an octahedral sp^3d^2 monoaminate. One monoaminate of phosphorus pentachloride was a yellow powder, up to 115° (Table II).

The next definite addition compound, in the model, uses outer d^2s orbitals, and just fits three amines into the three equivalent hollows of the trigonal bipyramid pentachloride molecule. It was not, however, possible to prepare the polyaminates of these compounds in a pure state. The observed mole ratios of 2.5 in mixtures can only indicate that polyaminates occur, and do not imply that a real triaminate has been approximated. It is to be remembered that PCl_5 has a solid structure that combines PCl_4 with PCl_6 units in three dimensions. The nonintegral mole ratio may imply that these units add different numbers of amines, as the solid structure changes, and that further exchanges occur between them before aminated PCl_5 units are obtained.

It has not been possible from the data to draw any conclusions about the relative strengths of the amine co-ordinations with the series of Group V halides. This is partly because thermal decomposition precedes vaporization and dissociation for these compounds, and partly because the properties of the condensed phases depend in an important way on other structural factors. However, the occurrence of stable aminates with all of the chlorides does imply that at least two factors are involved in the additions, particularly as the triaminates were most marked with PCl_3, and the monoaminates with $BiCl_3$.

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THE ACETYL GROUP MIGRATIONS IN D-GLUCOSE DIETHYL THIOACETYL TETRAACETATE[1]

By R. U. Lemieux and H. F. Bauer

ABSTRACT

The D-glucose diethyl thioacetal tetraacetate prepared by Wolfrom and associates both by detritylation of 6-*O*-trityl-D-glucose diethyl thioacetal tetraacetate and mercaptalation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucose was obtained by direct acetylation of D-glucose diethyl thioacetal with acetic anhydride and sodium acetate. Methylation of the tetraacetate followed by deacetylation and demercaptalation gave only 2-*O*-methyl glucose and methyl β-D-glucopyranoside.

Acetylation of D-glucose diethyl thioacetal (I) with acetic anhydride and sodium acetate on the steam bath for a half hour results in the formation of a tetra-*O*-acetyl derivative (II) which can be readily isolated in 10–15% yield. The formation of II is analogous to the formation of the substance believed to be 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl thioacetal on reaction of D-glucose diethyl thioacetal with benzoyl chloride in aqueous alkali (1). We have found that the tetraacetate (II) behaves in a manner similar to the tetrabenzoate (2) in that it undergoes methylation at the C2-position on treatment with methyl iodide and silver oxide. Deacetylation of the product formed on the methylation of the tetraacetate (II) gave a 56% yield of 2-*O*-methyl-D-glucose diethyl thioacetal (III). The material in the mother liquor was deacetylated and demercaptalated. The only monomethyl derivative of glucose other than 2-*O*-methyl glucose which could be identified in the product by application of the method developed by the authors for identifying mono-*O*-methylglucoses (7) was methyl β-D-glucopyranoside. The formation of the glucoside is attributable to the ability of silver oxide to bring about the demercaptalation of thioacetals (4).

The tetraacetate (II) was found to be identical with the compound prepared by Wolfrom and associates (12) both by detritylation of 6-*O*-trityl-D-glucose diethyl thioacetal tetraacetate (IV) and by mercaptalation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (V) with ethanethiol containing zinc chloride. Our methylation experiments suggest that compound II is 3,4,5,6-tetra-*O*-acetyl-D-glucose diethyl thioacetal. However, Wolfrom and co-workers have shown (12) that partial demercaptalation of II yields ethyl tetra-*O*-acetyl-α-D-1-thioglucofuranoside (VI). Thus, the free hydroxyl group in II may be at positions 2 or 4. The tetraacetate (II) (and perhaps the tetrabenzoate of Brigl and Mühlschlegel (1)) may undergo preferential methylation at the C2-position for the same reason that D-glucose diethyl thioacetal undergoes preferential methylation at this position (8). Wolfrom and Anno (10) have shown that acetylation of D-glucosamine diethyl thioacetal with acetic anhydride in pyridine has yielded (11) a crystalline tetraacetate. Considering the ease with which amines can be acetylated, this substance, which is closely

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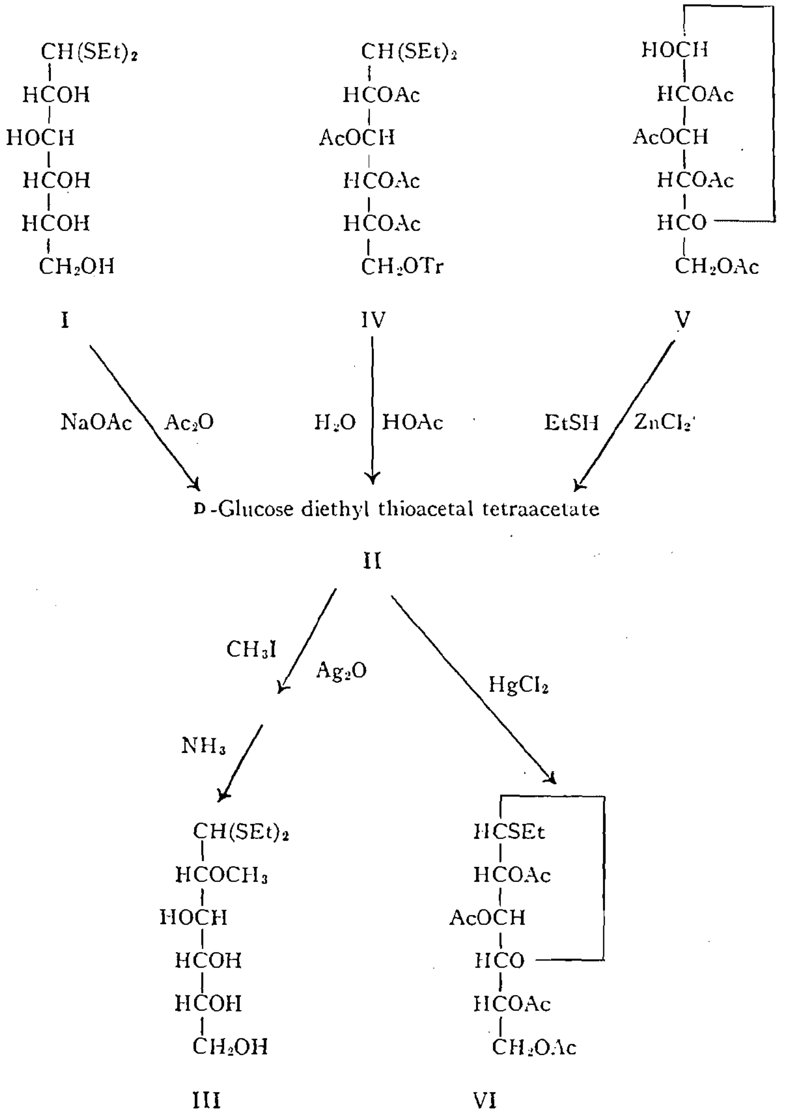

related to the tetraacetate (II) of D-glucose diethyl thioacetal, almost certainly possesses a 2-*N*-acetyl group. It is conceivable that the two tetraacetyl derivatives display resistance to acetylation for the same reason. It is of interest to note that an orthoacid structure could account for the resistance of these compounds toward acetylation. In this respect, it is noteworthy that Doerschuk (3) has confirmed the opinion of Fischer (5) that acyl group migrations are intramolecular and proceed by way of orthoacid intermediates.

In conclusion, the present data show that the tetraacetate (II) is a labile compound which can react as if either position 2 or position 4 were open. The position of the free hydroxyl group remains unknown.

EXPERIMENTAL

The rotations were measured at 22–25°C.

*Tetra-O-acetyl-*D*-glucose Diethyl Thioacetal* (II)

A mixture of D-glucose diethyl thioacetal (4), 5 gm., acetic anhydride, 50 ml., and sodium acetate, 5 gm., was heated on the steam bath for 30 min. The solution was stirred with ice water to decompose the anhydride and the mixture was extracted with chloroform. The chloroform solution was washed with aqueous sodium bicarbonate solution and water, dried, and evaporated to a sirup. The sirup readily yielded a crystalline product on being scratched in alcohol. Recrystallization from ethanol gave 1.22 gm. of material, m.p. 117–118°C., $[\alpha]_D$ −23° (*c*, 4 in chloroform), which did not depress the melting point of the tetra-*O*-acetyl-D-glucose diethyl thioacetal of same physical constants prepared by mercaptalation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucose as reported by Wolfrom and co-workers (12). Calc. for $C_{10}H_{18}O_5S_2(CH_3CO)_4$: acetyl, 37.8; S, 14.1%. Found: acetyl, 36.6; S, 13.9%. The substance possessed an absorption band at 3425 cm.$^{-1}$ which is characteristic of hydroxyl groups.

Methylation of the Tetraacetate (II)

The tetraacetate (II), 1 gm., was shaken at room temperature with 5 ml. of dry dioxane, 10 ml. of methyl iodide, 1 gm. of freshly prepared silver oxide, and 1 gm. of Drierite. After two hours, 1 gm. of silver oxide and 0.5 gm. of Drierite were added and the shaking was continued for four hours. The silver salts were collected and washed with methanol. The filtrate was evaporated to a sirup which was dissolved in 30 ml. of saturated methanolic ammonia solution. After standing overnight at 0°C., the solution was evaporated to a crystalline residue which was triturated with ether. Recrystallization from ethanol gave 0.34 gm., 56% yield, of a substance, m.p. 156–157°, $[\alpha]_D$ −25.5° (*c*, 2 in pyridine), which did not depress the melting point of an authentic sample of 2-*O*-methyl-D-glucose diethyl thioacetal (9) of same physical constants.

The mother liquors from the above isolation of 2-*O*-methyl-D-glucose diethyl thioacetal were evaporated to a sirup which was heated for 30 min. on a steam bath with 25 ml. of saturated aqueous mercuric chloride solution in 25 ml. of water. The clarified solution was deionized by using hydrogen sulphide to precipitate the mercuric ions and Amberlite IR4B to remove the hydrochloric acid. Evaporation gave 0.30 gm. of sirup which was found to contain monomethylglucoses as the main component and small amounts of glucose and di-*O*-methylglucoses. The mono-*O*-methylglucose fraction was isolated by preparative paper chromatography (7). The material crystallized after some time. Recrystallization from ethanol gave a substance which was identified as methyl β-D-glucopyranoside by its melting point (110–111°C. with a crystalline transformation at 104–105°C. (6)), specific rotation (−33.1° (*c*,1 in water)), mixed melting point (undepressed) and infrared spectrum (identical to that of the authentic sample). 2-*O*-methyl-D-glucose was the only mono-*O*-methyl-D-glucose which could be identified in the mother liquors by the procedure of Lemieux and Bauer (7).

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THE KINETICS OF THE PYROLYSIS OF ETHYL AND ISOPROPYL FORMATES AND ACETATES[1]

By Arthur T. Blades

ABSTRACT

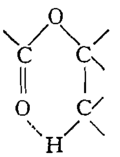
The pyrolysis of ethyl formate, isopropyl formate, ethyl acetate, and isopropyl acetate has been carried out under conditions which favor the decomposition of these esters into the corresponding acid and alkene to the exclusion of side reactions. The rate expressions found were: ethyl formate, $k = 2.13 \times 10^{11}\ e^{-44,140\pm200/RT}$ sec.$^{-1}$; isopropyl formate, $k = 3.8 \times 10^{12}\ e^{-44,000\pm100/RT}$ sec.$^{-1}$; ethyl acetate, $k = 3.06 \times 10^{12}\ e^{-47,750\pm100/RT}$ sec.$^{-1}$; isopropyl acetate, $k = 1.00 \times 10^{13}\ e^{-45,000\pm100/RT}$ sec^{-1}. The nature of the transition state is discussed and compared with that for similar decompositions.

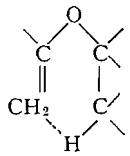
INTRODUCTION

The pyrolysis of esters has been the subject of extensive research (1, 3, 9, 10). In general, for those esters with a β-hydrogen in the alkyl group, the products are the corresponding acid and alkene. Methyl esters are comparatively stable, decomposing only at more elevated temperatures into a variety of products.

Kinetics studies have been made on the decompositions of ethyl (10), isopropyl, and *n*-propyl formates (1), the primary products being the alkene and formic acid. The interpretation of the data was, however, rendered difficult by the decomposition of the formic acid into hydrogen, carbon monoxide, carbon dioxide, water, and formaldehyde.

Hurd and Blunk (9) have proposed a mechanism involving a "cyclic hydrogen bridge" to explain the decomposition of esters into acid and alkene. Recent studies of the decomposition of vinyl alkyl ethers (6, 4) suggest that a similar type of activated complex is involved in the decomposition of these ethers.





The present pyrolyses have been carried out in a flow system with toluene as a carrier gas. Toluene has been used extensively to suppress chain reactions in thermal decompositions where free radicals are produced (11, 6, 7, 4). This research represents a successful attempt to apply this technique to a system in which heterogeneous reactions complicate the normal homogeneous decomposition.

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin, and the National Research Council of Canada, Ottawa, Canada. Issued as N.R.C. No. 3216.

[2] *National Research Laboratories Postdoctorate Fellow 1952–1954.*

EXPERIMENTAL

Similarly designed but different apparatuses were used for the decompositions of the ethyl and isopropyl esters; rate constants for the decomposition of ethyl acetate in the two, however, differed by no more than five per cent and consequently no distinction will be made in their description. Both have been described previously (7, 5).

Briefly, the technique involved the passage of the reactant through a long narrow reaction chamber in the presence of an excess of toluene vapor. The pressure of gas (about 1.5 cm. Hg) was maintained constant and the flow rate regulated by suitable capillaries chosen to give contact times between 0.15 and 0.8 sec. The products were condensed in liquid air traps and the alkenes isolated at the end of the experiment by being pumped off the traps at −120° C. with a Toepler pump. The quantity of acid produced was determined by shaking the liquid products with a few cubic centimeters of water and titrating with 0.1 *N* sodium hydroxide solution. With the formate esters it was necessary to carry out this titration at 5° C. to prevent the hydrolysis of the undecomposed ester.

The esters (Eastman) were purified by distillation on an efficient column.

Ethyl formate, b.p. 52.1° C. at 728 mm.

Isopropyl formate, b.p. 69.0° C. at 768 mm.

Ethyl acetate, b.p. 76.8° C. at 748 mm.

Isopropyl acetate, b.p. 88.7° C. at 764 mm.

RESULTS

The only products found in all of these pyrolyses were the corresponding acids and alkenes. No appreciable quantity of any of the normal decomposition products of the acids was detected even at the highest temperatures, i.e. 650° C. nor was there any evidence of the production of bibenzyl as would have been expected if the reaction had involved the production of free radicals.

The equivalence of acid and alkene was demonstrated in the products of the decomposition of each compound. By varying the flow rate of the gases in the reactor it was demonstrated that the rate of production of acid obeyed a first order rate expression up to 70 to 80% decomposition of these esters (see Table I, Expts. 6, 7, 8; 9, 10, 11; Table II, Expts. 8, 9, 10; 11, 12, 13, 14; Table III, Expts. 6, 7, 8; Table IV, Expts. 9, 10, 11; 14, 15, 16).

Fitting the data in Tables I, II, III, and IV to the Arrhenius equation by the method of least squares yields the following rate expressions.

Ethyl formate, $k = 2.13 \times 10^{11}\, e^{-44,140 \pm 200/RT}$ sec^{-1}.

Isopropyl formate, $k = 3.8 \times 10^{12}\, e^{-44,000 \pm 100/RT}$ sec^{-1}.

Ethyl acetate, $k = 3.06 \times 10^{12}\, e^{-47,750 \pm 100/RT}$ sec^{-1}.

Isopropyl acetate, $k = 1.00 \times 10^{13}\, e^{-45,000 \pm 100/RT}$ sec^{-1}.

Plots of these data are shown in Figs. 1 and 2.

By comparing these rate expressions with the absolute rate theory equation

$$k = \kappa \frac{k'T}{h}\, e^{\Delta S^{\ddagger}/R}\, e^{-\Delta H/RT} \text{ sec.}^{-1}$$

TABLE I
RATE STUDIES ON ETHYL FORMATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	*k*, sec.$^{-1}$
1	.0453	2.07	.710	17.1	810.6	0.264
2	.0451	2.06	.693	30.3	831.2	0.521
3	.0450	2.07	.685	43.3	845.4	0.827
4	.0770	1.47	.281	29.7	857.5	1.25
5	.0534	1.84	.504	52.3	864.0	1.47
6	.0869	1.66	.278	40.0	869.7	1.84
7	.0566	1.96	.503	58.6	869.8	1.75
8	.0452	2.11	.675	68.1	869.7	1.68
9	.0581	1.50	.278	48.2	880.1	2.36
10	.0431	2.03	.675	79.6	880.0	2.34
11	.0545	1.90	.499	68.6	880.0	2.31
12	.0535	1.85	.491	73.2	886.7	2.68
13	.0809	1.54	.261	83.7	920.0	6.92

TABLE II
RATE STUDIES ON ISOPROPYL FORMATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	*k*, sec.$^{-1}$
1	.0477	2.12	.813	14.3	721.3	0.189
2	.0563	2.15	.692	17.4	732.0	0.276
3	.0753	1.92	.459	12.5	733.0	0.290
4	.0590	1.82	.459	17.5	742.2	0.417
5	.0841	1.84	.384	21.3	752.4	0.622
6	.0832	1.82	.380	31.5	764.0	1.00
7	.0894	1.69	.375	44.9	776.4	1.59
8	.0804	1.75	.366	56.2	786.2	2.25
9	.0808	1.75	.364	57.3	786.8	2.34
10	.0706	1.83	.436	63.8	787.0	2.33
11	.0953	1.43	.248	59.8	800.0	3.66
12	.0774	1.71	.364	74.0	800.1	3.68
13	.1163	1.06	.150	42.4	800.2	3.68
14	.0665	1.76	.437	79.8	800.3	3.63
15	.0941	1.44	.250	74.5	810.6	5.44

TABLE III
RATE STUDIES ON ETHYL ACETATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	*k*, sec.$^{-1}$
1	.0475	1.88	.792	12.5	787.2	0.169
2	.0381	1.86	.767	20.5	802.0	0.299
3	.0499	1.63	.505	22.8	816.9	0.514
4	.0498	1.63	.502	27.6	822.8	0.642
5	.0505	1.65	.490	42.4	839.0	1.12
6	.0697	1.28	.286	36.0	848.3	1.56
7	.0385	1.91	.736	67.5	848.0	1.52
8	.0521	1.63	.489	52.5	848.5	1.51
9	.0606	1.19	.286	53.1	864.8	2.64
10	.0632	1.24	.280	73.0	883.4	4.67

TABLE IV
RATE STUDIES ON ISOPROPYL ACETATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	k, sec.$^{-1}$
1	.0690	2.28	.814	12.5	714.7	0.163
2	.0561	2.22	.808	16.6	722.2	0.225
3	.0519	2.27	.795	21.0	728.6	0.297
4	.0899	1.95	.459	12.7	729.3	0.296
5	.0773	1.97	.457	21.0	739.7	0.514
6	.0753	1.92	.457	19.6	739.7	0.477
7	.0755	1.92	.444	34.2	757.0	0.943
8	.0773	1.97	.441	45.4	766.5	1.37
9	.0678	1.78	.448	59.0	775.8	1.98
10	.0506	2.05	.677	74.0	775.8	1.99
11	.0978	1.47	.257	40.2	776.0	2.00
12	.1043	1.55	.249	52.7	787.8	3.01
13	.1001	1.45	.257	55.4	788.3	3.15
14	.1123	1.03	.152	52.6	800.7	4.92
15	.1147	1.05	.152	53.3	801.0	5.01
16	.0973	1.47	.250	70.9	801.0	4.95

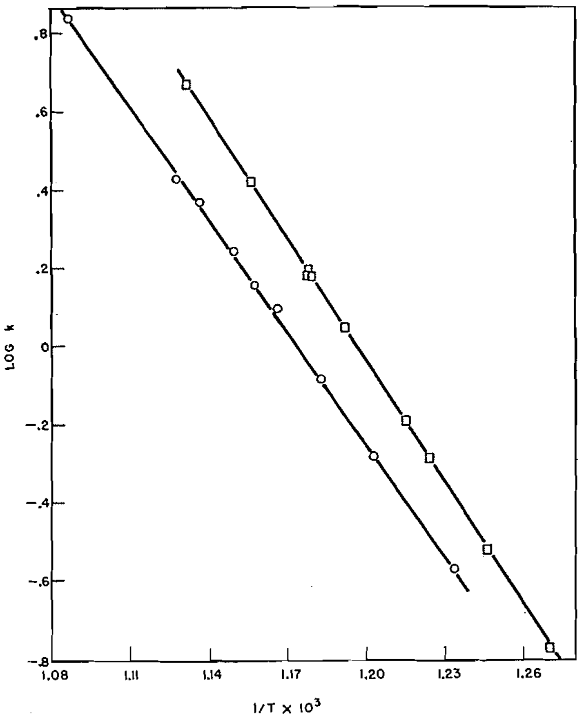

FIG. 1. The temperature coefficient of the rate.
○ Ethyl formate. □ Ethyl acetate.

and assuming that the transmission coefficient κ is unity, the following entropies of activation are obtained.

Ethyl formate $\Delta S^{\ddagger} = -10.7$ e.u. at 800° K.
Isopropyl formate $\Delta S^{\ddagger} = -4.9$ e.u. at 800° K.

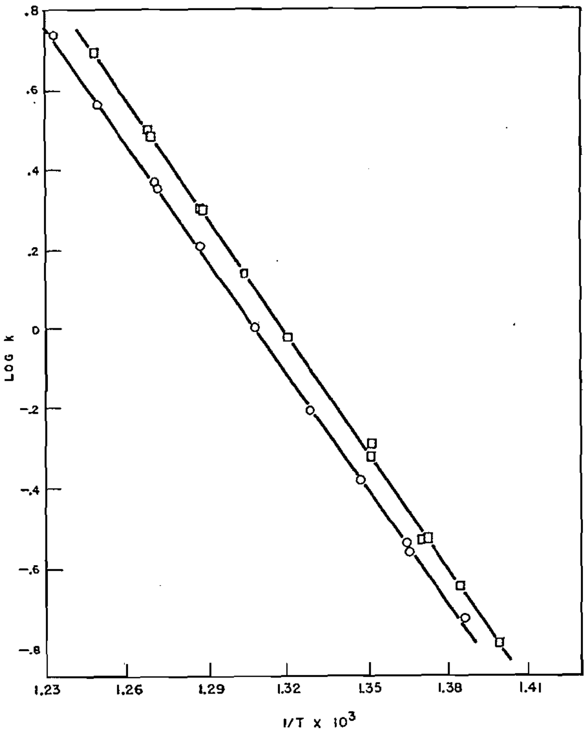

FIG. 2. The temperature coefficient of the rate.
○ Isopropyl formate. ☐ Isopropyl acetate.

Ethyl acetate	$\Delta S^{\ddagger}$ =	−5.4 e.u. at 800° K.
Isopropyl acetate	$\Delta S^{\ddagger}$ =	−3.0 e.u. at 800° K.

DISCUSSION

The molecular nature of the mechanism for the decomposition of esters with a β-hydrogen in the alkyl group is confirmed by the present research. If free radicals were produced they would be expected to react with the excess of toluene.

$$R^{\cdot} + C_6H_5CH_3 \rightarrow RH + C_6H_5CH_2^{\cdot}$$

The benzyl radicals would dimerize to bibenzyl. The lack of bibenzyl among the products is then good evidence against any free radical mechanism.

That the presence of the toluene prevented the normally heterogeneous decomposition of both the acids and esters suggests that these decompositions are free radical chain reactions initiated at the wall. Hinshelwood (8) has shown that the decomposition of methyl formate is sensitized by the photolysis of acetaldehyde, indicating that esters are, indeed, susceptible to radical chain decomposition.

The rate expression previously reported for the decomposition of ethyl formate (10) ($k = 2.52 \times 10^9\ e^{-40,010/RT}$ sec.$^{-1}$) compares unfavorably with that found in the present research. Rates calculated from the two expressions are sufficiently similar, however, to conclude that the same reaction is involved. For isopropyl formate, the rate expression found by Anderson and Rowley (1) ($k = 2.47 \times 10^{12} e^{-44,230/RT}$ sec.$^{-1}$) is very close to that recorded here.

The activation energies found for ethyl formate (44,140 cal./mole) and isopropyl formate (44,000 cal./mole) are identical within the experimental error. In this regard, these esters behave like ethyl vinyl ether (43,800 cal./mole) and isopropyl vinyl ether (43,560 cal./mole). The activation energies for the corresponding acetates (i.e. 47,750 and 45,000 cal./mole) are slightly higher and differ by considerably more than the experimental error. The difference between the activation energies for the formates and acetates is probably due to hyperconjugation in the normal acetate molecule which is absent in the transition state. No explanation can be given to account for the difference in activation energy between the ethyl and isopropyl acetates.

An interesting feature of this series of compounds is the negative value of the entropy of activation. Such a value is consistent with the formation of the cyclic transition state suggested by Hurd and Blunk (9) since three internal rotational degrees of freedom are converted to relatively inactive vibrations in the process of activation.

The regular trend in the entropy of activation as successive methyl groups are added to the molecule is predictable on the basis of the increased number of β-hydrogen atoms available for the formation of the activated complex, and of the increased restriction of internal rotation in the normal molecule. The effect of the increased moment of inertia, which would have the opposite effect, seems to be very small compared to the other two.

Remarkably similar entropies of activation were also observed in the decomposition of ethyl vinyl ether (6) ($\Delta S^{\ddagger} = -10.2$ e.u. at 800° K.) and isopropyl vinyl ether (4) ($\Delta S^{\ddagger} = -4.8$ e.u. at 760° K.), which differ from the ethyl and isopropyl formates only in the substitution of a methylene group for an oxygen atom. This similarity lends considerable support to the belief that similar activated complexes are involved in the decomposition of esters and vinyl ethers.

Finally, it is worthy of note that in this series of compounds which decompose via similar mechanisms, there is no suggestion of any relation between the logarithm of the frequency factor and the activation energy as has been found by Barton *et al.* (2) in the decomposition of alkyl chlorides. In fact, there is evidence for complete independence of the two variables.

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STUDIES IN THE POLYOXYPHENOL SERIES

VI. THE OXIDATION OF PYROGALLOL AND VANILLIN BY ALKALINE HYPOIODITE AND HYPOCHLORITE[1]

By G. Denis Thorn[2] and C. B. Purves

ABSTRACT

Approximately 0.003 M solutions of pyrogallol and of vanillin in boric acid – sodium hydroxide buffers were used at 25°C. to reduce hypoiodite and hypochlorite solutions made from sixfold molar amounts of the halogens. In all four cases the reduction reached a maximum in a narrow range near pH 9, and with hypoiodite the production of iodoform was restricted to this range. Slower secondary reductions were superimposed on very fast primary reactions. When oxidized with an equimolecular amount of halogen near pH 8.5, vanillin gave a 90% yield of 5-iodovanillin and 65% of the 5-chloro derivative. These yields decreased with increasing alkalinity as the halogenations became slower. A new, simple preparation of trichloropyrogallol in 72% yield consisted of carrying out the chlorination with 3 moles of hypochlorite at pH 12. An equilibrium between pyrogallol–hypoiodite and 3-hydroxy-1,2-benzoquinone–iodide appeared to exist at the same pH.

INTRODUCTION

Numerous researches have shown that a proper control of the hydrogen ion concentration and similar variables is of great importance in the removal of residual lignin from wood pulps by bleaching with alkaline hypochlorite. The results are difficult to interpret in a chemical sense because little is known about the structure of lignin beyond the fact that it is in great part based upon phenolic units related to vanillin and syringaldehyde. Soper and Smith (26), however, showed that simple monohydric phenols reacted with hypochlorous acid at a rate directly proportional to the concentration of the hydroxyl ion in the region of pH 7, but that the rate became inversely proportional near pH 12. Hypochlorous acid, unlike free chlorine, had no action on phenolic ethers, and the oxidation of phenols by hypoiodite was relatively slow. The last observation had its counterpart in the lignin field, because Hixon and his collaborators (5, 29) found that the consumption of alkaline hypoiodite by various lignins ceased at a rather low limit, whereas the consumption of hypochlorite proceeded almost indefinitely. The present research had the object of gaining information about the conditions necessary for the "limited" action of excess hypoiodite on simple phenols, and of discovering whether the action of hypochlorite could also be limited. Pyrogallol and vanillin were chosen for the study because the results might eventually prove relevant to lignin.

REACTIONS WITH ALKALINE HYPOIODITE

The initial experiments were carried out with dilute aqueous solutions of pyrogallol containing a sixfold molar amount of iodine, and buffered with

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Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from a Ph.D. Thesis submitted by G. D. T. in September, 1947.

[2] *Holder of a National Research Council of Canada Studentship in 1945-6, and of a Fellowship in 1946-7. Present address: Science Service Laboratory, Department of Agriculture, London, Ont.*

boric acid – sodium hydroxide (Table I). Since hypoiodite rapidly decomposed to iodate and iodide in solutions containing excess alkali (23), the estimation of unused hypoiodite at any time had to include the by-product iodate. This objective was attained by titrating the iodine liberated when aliquots were strongly acidified, and control experiments showed that the iodine consumed after the acidification was probably not more than 0.15 mole per mole of pyrogallol.

TABLE I

Reduction of hypoiodite by pyrogallol during 24 hr. at 25°C.[a]

Run	NaOH M	pH	Moles HIO reduced[b]	Run	NaOH M	pH	Moles HIO reduced[b]
Boric acid, 0.2 M; I_2, 0.0204 M				Unbuffered; I_2, 0.21 M			
1	0.04	8.0[c]	4.8	19	0.54	12.5	2.8
2	0.10	8.6	4.9	20	0.61	13	2.7
3	0.16	9.4	5.3	21	0.63	>13	2.65
4	0.21	9.7	4.1	Unbuffered; I_2, 0.0205 M			
5	0.26	12.0	1.25	22	0.05	11.7	2.4
6	0.31	12.5	1.7	Boric acid, 0.2M; I_2, 0.0205 M			
7	0.36	>13	1.7	23	0.26	11.9	0.71
8	0.42	>13	1.7	24[d]	0.26	11.9	0.74
9	0.47	>13	2.5	25[e]	0.26	11.9	0.72

[a] *All concentrations in moles per liter, the molar ratio of iodine to pyrogallol being 6 : 1.*
[b] *Per mole of pyrogallol.*
[c] *Final pH was 6.7 after 17.5 hr.*
[d] *Molar ratio of iodine to pyrogallol, 3 : 1.*
[e] *Molar ratio of iodine to pyrogallol, 2 : 1.*

Columns 4 and 8 of Table I record the molar amounts of iodine (or hypoiodite) reduced by 1 mole of pyrogallol after 24 hr., when the reaction had certainly ceased. These amounts passed through a maximum of 5.3 moles near pH 9.4 (run 3), and through a minimum of 1.25 moles near pH 12 (runs 5 to 9). Omission of the borate buffer and a 10-fold increase in the concentration both of iodine and pyrogallol gave solutions whose pH decreased seriously during the reaction unless the molarity of sodium hydroxide was at least 0.54 (run 19), but a greater concentration of alkali had little effect (runs 20, 21). Although the minimum of 1.25 moles near pH 12 was not maintained in the absence of the buffer (run 22), buffered solutions retained the minimum even when the molar ratio of iodine to pyrogallol was reduced from 6 : 1 to 3 : 1 and 2 : 1 (runs 23 to 25). The titrations in these particular runs could not be closely reproduced, and consumptions of iodine as high as 0.87 moles were observed at intermediate times.

The initial portions of the rate-plots for runs 1 to 6, and also for runs 9 and 25, (Fig. 1) clearly showed that the first stage in the reaction was always very rapid, and that the ultimate consumption of iodine by the pyrogallol (Table I) depended on the progress of secondary reactions. These secondary reactions were most extensive at pH 9.4 and decreased to zero, both in speed and in amount, near pH 12. The minimum at the latter pH was not caused by the prior conversion of all excess hypoiodite to iodate, because the consumption was about 2.5 times greater in stronger alkali (pH > 13) where competition with the conversion to iodate would be still more serious (23). The first four oxidations (Table I) resulted in pale orange solutions, of which the first and fourth deposited only traces of iodoform, whereas the second and third yielded 0.14 and 0.16 moles respectively, per mole of pyrogallol. Iodoform was therefore produced only in the range pH 8.6 to 9.4, when the secondary reaction was unusually extensive and prolonged.

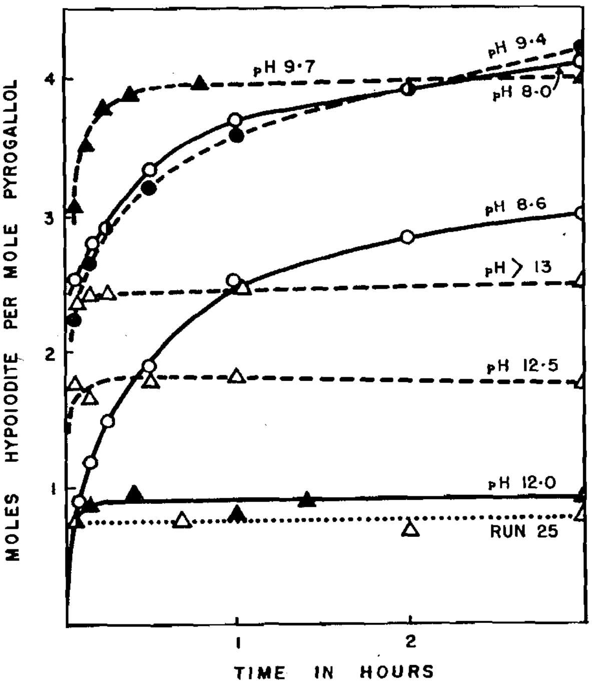
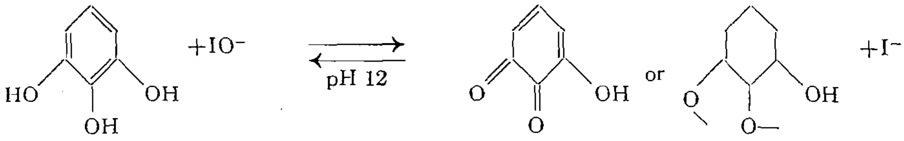


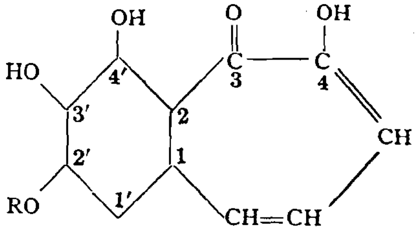
FIG. 1. Initial rate of reaction of 0.0033 *M* pyrogallol with 0.02 *M* iodine at 25°C. Moles of iodine reduced per mole of pyrogallol at the pH values shown. Run 25 with 0.01 *M* pyrogallol.

Since about one mole of iodine was reduced by pyrogallol (Structure I) at pH 12, the initial product could not be of a complicated nature, and the dark red color of the solution indicated the presence of a quinonoid rather than an aromatic structure. The most probable assumption (25, 33) for the initial product was the very labile 3-hydroxy-1,2-benzoquinone, (II*a*), or the corresponding radical (II*b*), (10) or other tautomer. Subsequent oxidations were carried out with equimolar amounts of iodine and pyrogallol in a borate buffer at pH 12, and, as the solutions were reproducible and stable for hours, they were designated "oxidized pyrogallol solutions." In accord with the above assumption, the red color of the "oxidized pyrogallol solution" lightened considerably when zinc dust was added as a reducing agent, and subsequent acetylation of the alkaline solution with acetic anhydride (3) recovered at least 52% of the pyrogallol as the crystalline triacetate. Sodium hydrosulphite also discharged the color of the solution to a light yellow, but pyrogallol triacetate could not be recovered, perhaps because sulphonation occurred (11). Although the addition of sodium thiosulphate failed to reduce the color of the solution noticeably, and presumably failed to reduce the supposed quinone, the subsequent acetylation gave an 89% yield of pyrogallol triacetate. The "oxidized pyrogallol solution" was then acetylated without prior reduction, and a control acetylation was made with a solution from which the iodine had been omitted. Pyrogallol triacetate was isolated in yields of 89% and 87%, respectively, from the two experiments. These observations suggested that the "oxidized pyrogallol solution" contained pyrogallol and hypoiodite in equilibrium with the hydroxyquinone and iodide, and that acetylation of the pyrogallol drove the equilibrium far to the left with the regeneration of hypoiodite. Aliquots of the solution, when acidified and titrated with standard sodium thiosulphate immediately before and after the acetylation, were found to contain 41% and 92%, respectively, of the original hypoiodite. An application of the law of mass action showed that the former figure corresponded to consumptions of 0.83 and 0.97 moles of iodine per mole of pyrogallol when the iodine was in twofold and sixfold molar amounts. The values found were of the same order (Fig. 1, run 25 and plot pH 12).



I IIa IIb

An attempt was then made to isolate the supposed 3-hydroxy-1,2-benzoquinone by acidifying the "oxidized pyrogallol solution" and extracting it with ether. Acidification with sulphuric acid, however, caused the prompt deposition of crystalline purpurogallin in 25% of the theoretical yield. Haworth and his collaborators (18) recently showed that purpurogallin had the structure (III, R = H). The ether extract from solutions acidified with acetic acid



III (R = H or CH_3)

contained dark red substances from which 17% to 46% yields of orange-red crystals were obtained after acetylation with an acidic catalyst. These crystals, melting at 162° to 163°C. were later identified (28) as a new triacetate of purpurogallin. In an endeavor to avoid the use of acid, the "oxidized pyrogallol solution" was methylated with dimethyl sulphate on the alkaline side of pH 10, and extraction of the methylated liquors with ethyl acetate recovered about 35% of the pyrogallol as an orange residue. The residue yielded the dark red needles of 2′-monomethyl purpurogallin (III; $R = CH_3$), which had been obtained by oxidizing a mixture of pyrogallol and its 1-methyl ether with hydrogen peroxide and peroxidase (33), or with potassium iodate (7). Since the production of purpurogallin from pyrogallol almost certainly required 3-hydroxy-1,2-benzoquinone (II) as an intermediate (6, 7, 33), the results supported the view that the quinone (or a tautomer) was present as such in the "oxidized pyrogallol solution". The experiments, however, failed to circumvent the great tendency of *o*-quinones to condense when in acid solution (12, 24, 27), and even the temporary local acidity accompanying the methylation apparently promoted condensation.

The oxidation of vanillin by a sixfold molar amount of iodine in sodium borate buffers, when continued to completion (Table II) revealed a maximum consumption of about 3.65 moles per mole near pH 10 (run 4). This maximum corresponded to a particularly rapid secondary oxidation during the first three hours, as shown in Fig. 2, in which the plots for the intermediate runs 2, 5, and 10 were not reproduced. Small, red, flocculent precipitates were

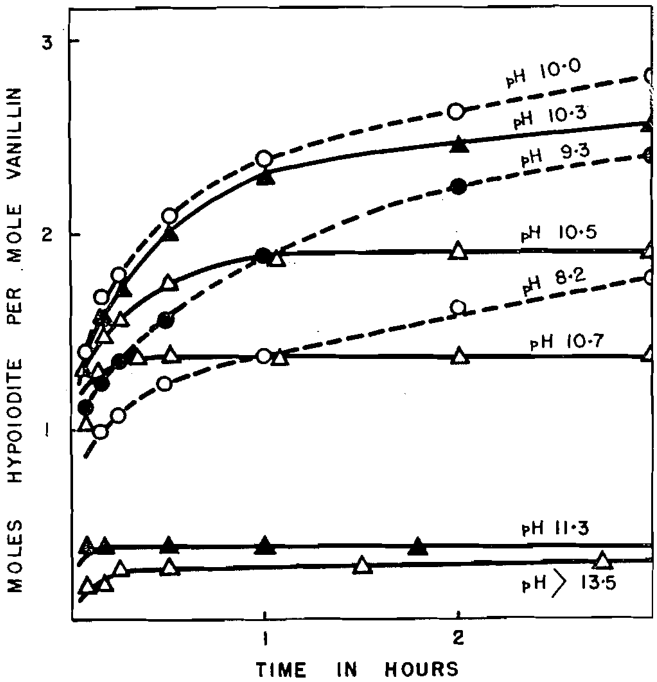


FIG. 2. Initial rate of reaction of 0.0033 *M* vanillin with 0.02 *M* iodine at 25°C. Moles of iodine reduced per mole of vanillin at the pH values shown.

formed in runs 1 to 5 (pH 8.2 to 10.2), and the mother liquors from these runs yielded 0.15, 0.16, 0.12, 0.06, and 0.0 moles of iodoform per mole of vanillin. As in the case of pyrogallol, therefore, the production of iodoform was at a maximum near pH 9, or when the secondary oxidation was approaching its greatest extent. Since vanillin very rapidly consumed about one mole of iodine in the pH range 8.2 to 10.7, equimolar amounts of vanillin and iodine were used in order to isolate the product of the initial reaction. Crystalline 5-iodovanillin was recovered in 90% yield from the reaction at pH 8.2, whereas the yield at pH 10 was only 62%, and 31% of hypoiodite remained at the end of the arbitrary period of 15 min. Although the oxidations at pH 11 or greater were not examined in detail, the lack of color in the solutions suggested the absence of quinones, and the small consumption of iodine put an upper limit of 35% on the production of 5-iodovanillin. The halogenating action of iodine on vanillin thus decreased abruptly on the alkaline side of pH 10. Erdtman's (9) similar preparation gave 73% of recrystallized 5-iodovanillin, and must therefore have been made in, or close to, the optimum pH range.

TABLE II
REDUCTION OF HYPOIODITE BY VANILLIN DURING 24 HR. AT 25°C.[a]

Run	NaOH M	pH	Moles HIO reduced[b]	Run	NaOH M	pH	Moles HIO reduced[b]
1	0.04	8.2	2.7	7	0.22	10.5	1.9
2	0.06	8.9	2.75	8	0.23	10.7	1.35
3	0.10	9.3	3.3	9	0.24	11.3	0.35[c]
4	0.16	10.0	3.65	10	0.28	12.6	0.3
5	0.20	10.2	3.2	11	0.32	13.5	0.3
6	0.21	10.3	2.6				

[a] *In 0.2 M boric acid, 0.02 molar in iodine and 0.0033 molar in vanillin (mole ratio 6 : 1).*
[b] *Per mole of vanillin.*
[c] *Constant from 1 hr. to 9 hr.*

REACTIONS WITH ALKALINE HYPOCHLORITE

The oxidation of pyrogallol with six times the molar amount of sodium hypochlorite in adequate borate buffers proceeded at all the pH values studied until the oxidant was almost entirely exhausted. Table III records the consumptions of oxidant after nine hours, when the oxidation at pH 8.8 (run 2) was practically complete; thereafter the necessary time increased to more than 24 hr. at pH 12.4 (run 8). The initial portions of the rate plots for runs 1, 3, 4, 5, 7, and 8 (Fig. 3) revealed a very rapid consumption of about three moles of hypochlorite per mole of pyrogallol, and a secondary consumption whose rate and extent went through a maximum near pH 11. These observations were supported by the plots at intermediate pH values (runs 2 and 6, not reproduced). The solutions remained colorless in the first three experiments (pH 8 to 9) but in the others initially ranged from light yellow to orange, becoming colorless only after 15 to 30 min. No precipitate was observed in any of the runs.

Pyrogallol, when mixed with a 3-molar proportion of chlorine dissolved in 10% sodium carbonate solution, within 10 min. gave a 72% yield of crystalline

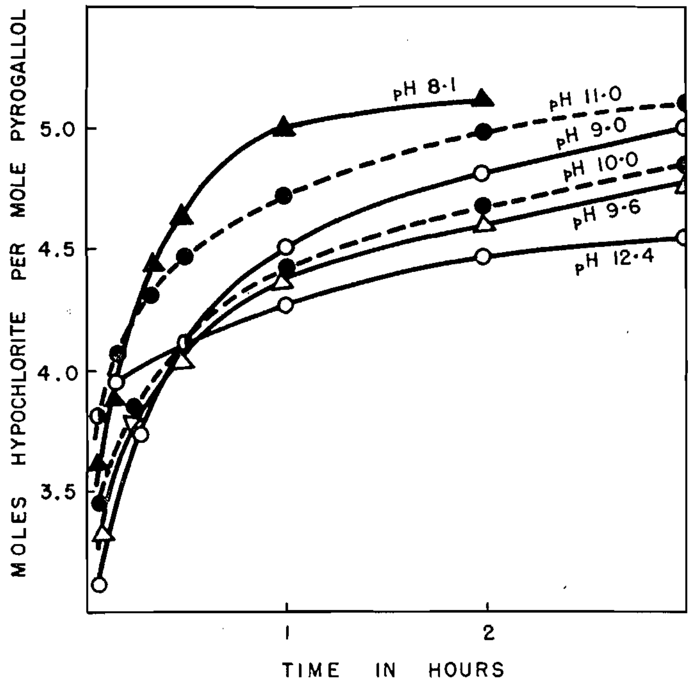


FIG. 3. Initial rate of reaction of 0.003 *M* to 0.004 *M* pyrogallol with a sixfold molar concentration of chlorine at 25°C. Moles of chlorine reduced per mole of pyrogallol at the pH values shown. Plot at pH 8.1 with 5.13 molar equivalents of chlorine.

trichloropyrogallol monohydrate. Even near pH 12, therefore, the initial action of hypochlorite was one of halogenation, and constituted a new and convenient method of preparing the trichloro derivative in good yield. The product was always contaminated with boric acid when a borate buffer was used in the preparation, and attempts to isolate the triacetate by adding acetic anhydride to the alkaline solution (3) failed. Webster (30) obtained

TABLE III

REDUCTION OF HYPOCHLORITE BY PYROGALLOL DURING NINE HOURS AT 25°C.[a]

Run	NaOH *M*	Cl_2 $M \times 10^2$	Pyrogallol $M \times 10^2$	pH	Moles HClO reduced[b]
1	0.03	1.54	0.299	8.1	5.1[c]
2	0.10	1.96	0.327	8.8	5.9
3	0.12	1.96	0.327	9.0	5.6
4	0.16	1.96	0.327	9.6	5.3
5	0.20	1.96	0.327	10.0	5.3
6	0.22	1.96	0.327	10.5	5.4
7	0.24	2.4	0.40	11.0	5.5[d]
8	0.28	2.4	0.40	12.4	5.0[e]

[a] *In 0.2 M boric acid with chlorine to pyrogallol in molar ratio 6 : 1.*
[b] *Per mole of pyrogallol.*
[c] *Chlorine to pyrogallol molar ratio 5.13 to 1. Oxidant exhausted after two hours.*
[d] *After nine hours pH was 10.6; after 24 hr. consumption was 5.94 moles.*
[e] *Consumption 5.4 moles after 24 hr.*

trichloropyrogallol in unstated yield by chlorinating pyrogallol in acetic acid, and Biétrix (1) in poor yield by chlorinating gallic acid suspended in chloroform. Biétrix also prepared the crystalline trichloro-triacetate.

The reduction of hypochlorite by vanillin was examined as in the case of pyrogallol and the details were therefore omitted from the experimental portion of this article. Vanillin consumed all of the oxidant much more rapidly than pyrogallol, but the minimum time required for complete reaction was at a pH near 10 (Table IV, run 5). The initial portions of the rate plots for runs 1, 3, 5, 7, and 8, together with the plots of the intermediate runs not shown in Fig. 4, showed, as expected, that the extent of the secondary reduction was greatest at pH 10. Run 1 at pH 8.1, however, was not closely comparable to the others because only 5 moles, instead of 6 moles, of hypochlorite per mole of vanillin was present. In all cases below pH 11 about three moles of chlorine was very rapidly consumed; all the solutions remained clear and colorless, but, when acidified after six to eight hours, deposited small amounts of a pink, flocculent substance.

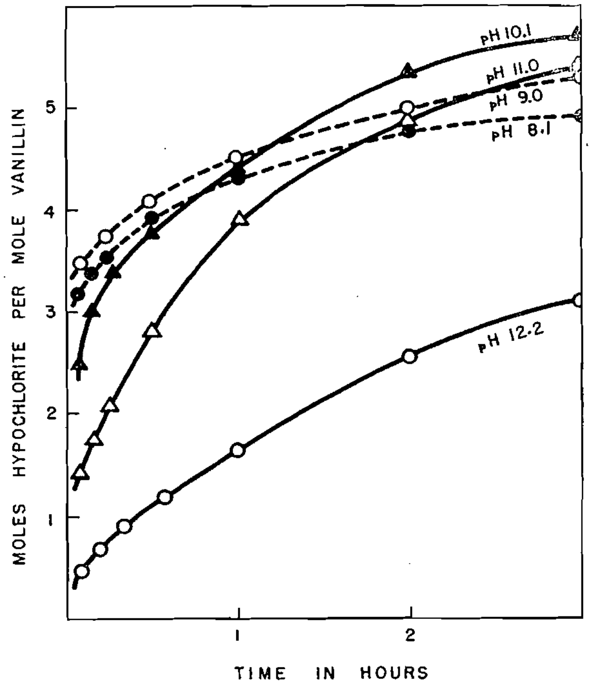


FIG. 4. Initial rate of reaction of 0.003 M to 0.004 M vanillin with a sixfold molar concentration of chlorine at 25°C. Moles of chlorine reduced per mole of vanillin at the pH values shown. Plot at pH 8.1 with 5.12 molar equivalents of chlorine.

Runs 2 and 8 (pH 8.7 and 12.2), when repeated with equimolecular amounts of vanillin and chlorine, required 10 min. and 60 min. respectively, for the oxidant to disappear. A 65% yield of 5-chlorovanillin resulted from the former experiment, but the latter gave only 43%, and 38% of the vanillin was recovered as the crystalline 2,4-dinitrophenylhydrazone. Since these figures failed to account for about 19% of the vanillin and 57% of the chlorine, another reaction probably occurred involving the two components in the 1 : 3 molar ratio. These observations, together with a consideration of Fig. 4, showed that the initial reaction, consuming 3 moles of chlorine almost instantly at lower pH values, became quite slow at pH 12.2, although its nature probably did not change. Hopkins and Chisholm (20) obtained a 90% yield of 5-chlorovanillin by permitting 1.5 moles of sodium hypochlorite to act on 1 mole of vanillin for one hour, apparently in a sodium carbonate buffer.

TABLE IV

REDUCTION OF HYPOCHLORITE BY VANILLIN AT 25°C.[a]

Run	NaOH M	Cl_2 $M \times 10^2$	Vanillin $M \times 10^2$	pH	Hours[b]
1	0.08	1.54	0.30	8.1	2.6[c]
2	0.10	2.4	0.40	8.7	5
3	0.12	2.4	0.40	9.0	5
4	0.16	2.4	0.40	9.5	5
5	0.20	2.3	0.38	10.1	3
6	0.22	2.3	0.38	10.5	4
7	0.24	2.3	0.38	11.0	5
8	0.28	2.3	0.38	12.2	9[d]

[a] *In 0.2 M boric acid with chlorine to vanillin in molar ratio 6 : 1.*
[b] *Approximate time when 93% to 95% of the hydrochlorite was reduced.*
[c] *Chlorine-vanillin molar ratio 5.1 : 1.*
[d] *Only 4.7 moles (52%) of chlorine reduced in nine hours.*

DISCUSSION

Since the reduction of hypoiodite by pyrogallol ranged from about one mole to 5.3 moles, and of vanillin from 1.9 mole to 3.65 moles, according to the hydrogen ion concentration (Tables I and II), this factor required very close control when phenols were estimated by iodometric methods. Failure to observe this requirement in the same way or to the same extent explained why Messinger and Vortman (21) found that 1 mole of various phenols reduced integral even numbers of iodine atoms, and why Orloff (22) thought that the molar consumption in 24 hr. to 48 hr. was fractional. Orloff decided that pyrogallol required approximately five moles, but later workers (15, 25) varied the technique of the estimation and claimed that exactly 3 moles was reduced in a short time. This figure was again revised to approximately five moles (4). Wilkie (31, 32) carefully compared several of the older methods.

As already mentioned, iodoform was produced both from pyrogallol and from vanillin only in a narrow range about pH 9. Booth and Saunders (2) presumably operated in this range when they obtained iodoform by adding sodium hydroxide to a solution of pyrogallol and iodine, but none was observed by Slotta and Neisser (25), who added iodine to a solution of pyrogallol in aqueous sodium carbonate (pH ~ 12). Since iodoform could also be derived on occasion from various *o*- and *p*-hydroquinones (2, 25), from gallic acid, resorcinol, and phloroglucinol (2), the standard iodoform test for the

$CH_3CO—C\equiv$ and related groupings (13, 14) became ambiguous when phenols were present. The production of iodoform (or chloroform) from lignins oxidized by alkaline hypohalites (17, 29) was therefore no decisive proof that lignin contained either methyl ketone or $CH_3CH(OH)—C\equiv$ units.

Green (16), who reviewed the inorganic chemistry of the hypohalites, quoted the dissociation constant of dilute aqueous hypochlorous acid as 6.5×10^{-8}, and of hypoiodous acid as of the order 5×10^{-13}. The former acid was therefore 79% dissociated to the hypochlorite ion at pH 8, and to practically 100% at pH 12; whereas the figures for the latter acid were about 0.005% and 49.5%, respectively. The species of oxidant present in alkaline solutions of iodine therefore varied greatly with pH, but change in the hypochlorite system was minor. With hypochlorite, the halogenating took precedence over the oxidizing action both for pyrogallol and for vanillin even at pH 12, when halogenation by hypoiodite was absent or slow.

If the standard potential of the redox system $H_2O + Cl^- = HClO + H^+ + 2e^-$ in acid solution was accepted as $E_0 = -1.49$ volts, and that of the corresponding iodide–hypoiodite couple as $E_0 = -0.99$ v. (16), calculation showed that these values corresponded to effective oxidation potentials of -1.14 v. and -0.64 v., respectively, at pH 12. When allowance was made for the approximate nature of the calculation, at pH 12 even hypochlorite might not oxidize vanillin, whose "critical oxidation potential" of $E_c = -1.08$ v. was among the highest found by Fieser (10) for the numerous phenols he examined. Since the "critical oxidation potential" of pyrogallol was $E_c = -0.609$ v., and the calculated normal potential of 3-hydroxy-1,2-benzoquinone was $E = 0.677$ v., the promotion of an equilibrium between these substances by hypoiodite at pH 12 might have been anticipated. These physical considerations supported the view that the action of the hypohalites on phenols became "limited", or less complex, on the alkaline side of pH 11 or 12.

EXPERIMENTAL

Rate of Oxidation of Pyrogallol with Hypoiodite (Table I, Fig. 1)

In a typical experiment, 150 cc. of 0.667 *M* aqueous boric acid and the desired volume of 1.0 *N* sodium hydroxide were mixed in a 500 cc. volumetric flask; the mixture was diluted to about 250 cc. with distilled water, and 200 cc. of 0.1 *N* iodine (0.02 equivalents) in aqueous potassium iodide was added. The pH of the solution was measured with a Coleman Model 3 pH Electrometer, with correction as described by Dole (8) for the salt error of the glass electrode. Control experiments with a high alkalinity glass electrode showed that this correction was valid. At zero time, a solution of about 0.21 gm. of pyrogallol (about 0.0017 mole or one-sixth the molar amount of iodine) in 25 cc. of water was added; the total volume was made up to 500 cc. with distilled water, and was promptly and thoroughly mixed. The iodine and pyrogallol solutions had been brought to 25°C. prior to mixing, and were subsequently maintained at 25° ± 0.05°C. in a constant temperature bath. The pH of the solution was measured at intervals, and runs in which the value decreased by more than 0.3 units in 24 hr. were rejected.

After various times, 10 cc. aliquots were discharged into a large excess, 100 cc., of 1% sulphuric acid, and the iodine liberated was promptly titrated with 0.025 *N* sodium thiosulphate. The starch indicator used was added before the titration was begun, since approach to the end point was masked by the color of the solution. It was necessary to accept the first end point reached, since traces of iodine continued to be liberated for some time in the acid solution.

To assess the error caused by acidifying the solution for titration, 0.047 millimoles of pyrogallol (5.78 mgm.) was added to 50 cc. of 2% sulphuric acid mixed with 50 cc. of 0.006 *N* iodine in potassium iodide. A prompt back-titration with 0.023 *N* sodium thiosulphate required 11.83 cc., when the first end point was accepted, whereas the value for a blank containing no pyrogallol was 12.30 cc. These data corresponded to a consumption of 0.12 mole of iodine per mole of pyrogallol; similar estimations with a 4 : 1 instead of a 6 : 1 molar ratio of iodine to pyrogallol were 0.11 and 0.14 moles.

Oxidations carried out at pH 8.6 and 9.4 (runs 2 and 3) deposited 0.095 gm. and 0.105 gm. of iodoform, or 0.14 and 0.16 moles, respectively, per mole of pyrogallol. The identification depended upon the characteristic odor of iodoform, and the proper melting point of 118° to 119°C. The only other precipitates observed were from oxidations carried out with 10-fold concentrations of iodine and pyrogallol at pH values drifting from 12 or 13 to 8 or less. These precipitates were jet black in color, did not melt below 300°C., and were not examined further.

"Oxidized Pyrogallol Solution"

Pyrogallol, 1.29 gm., or 0.01 mole, was added with stirring to 500 cc. of an aqueous solution containing 6.2 gm. of boric acid, 5.1 gm. of sodium hydroxide, and 2.59 gm. (0.01 mole) of iodine (added in potassium iodide solution). The mixture, whose pH was 12.0, immediately became red. This "oxidized pyrogallol solution" was kept at room temperature and under nitrogen for 30 min. to 2.5 hr. before use, and apparently did not change within the latter time.

Recovery of Pyrogallol Triacetate

An "oxidized solution" made 30 min. previously from 1.29 gm. of pyrogallol, was rapidly stirred with 5 cc. of acetic anhydride (3). A light cream-colored precipitate was obtained with a melting point of 163° to 164°C., undepressed by admixture with an authentic sample of pyrogallol triacetate, m.p. 164 to 165°C.; yield 2.29 gm. or 88.7%. A control experiment containing no iodine resulted in an 87% yield of the triacetate.

Aliquots, 10 cc., of a similar solution were removed before and after the addition of the acetic anhydride, and were discharged into 100 cc. of 1% sulphuric acid. The iodine in the mixtures was equivalent to 5.16 cc. and 11.6 cc., respectively, of 0.0324 *N* sodium thiosulphate. Since the blank containing neither acetic anhydride nor pyrogallol required 12.3 cc. of the thiosulphate, the recovery of iodine was 42% and 94%, respectively.

Recovery of Purpurogallin and Derivatives

(*a*) Pyrogallol, 1.89 gm. (0.015 mole) was dissolved in 400 cc. of water containing 1 gm. of sodium hydroxide, at room temperature and under nitrogen, and 150 cc. of 0.2 *N* iodine (0.015 mole) was added with stirring. The solution, pH 12.0, immediately became red-black in color, and after 10 min. gave a negative test for free iodine. Upon acidification with 10% sulphuric acid the color of the solution decreased considerably in intensity, and an orange, flocculent precipitate separated. After being washed and then dried *in vacuo*, the substance melted with decomposition at 264° to 268°C. Yield, 0.41 gm. or 25%. Recrystallization from toluene gave orange needles melting at 269° to 271°C., the value recorded for purpurogallin being 272° to 274°C. with decomposition (33).

A portion, 0.15 gm., was dissolved in 25 cc. of ethanol, and ether containing the diazomethane from 4 gm. of nitrosomethylurea was added. Next day the light yellow solution when evaporated to 50 cc. deposited 0.13 gm. (72%) of fine yellow needles, which when recrystallized from ether melted at 179° to 180°C. This melting point was 3°C. higher than the latest recorded value (18) and was not depressed by admixture with an authentic sample of 2′,3′, 4-trimethyl purpurogallin.

(*b*) An "oxidized solution", made 2.5 hr. previously from 1.3 gm. of pyrogallol, was acidified with acetic acid, and extracted continuously with ether for about five hours. After being concentrated, the dark-red extract was evaporated to dryness at room temperature and *in vacuo* over sodium hydroxide. Acetic anhydride, 15 ml., and five drops of concentrated sulphuric acid were added to the red-black mass. After 30 min. without external heating, the mixture was poured into 300 cc. of ice and water, and 0.3 to 0.8 gm. of a yellow precipitate formed. Repeated crystallization from ether yielded orange prisms with the composition of a purpurogallin triacetate and melting at 162° to 163°C. This melting point agreed with that of the isomer considered by Thorn and Barclay (28) to be the 4,2′,3′-triacetate, although Haworth, Moore, and Pauson (19) recorded a melting point of 138° to 140°C. for this compound.

(*c*) An "oxidized solution", made 30 min. previously from 1.3 gm. of pyrogallol, was continuously stirred under nitrogen while 5 cc. of dimethyl sulphate was slowly added during a 30 min. period. This addition caused the color of the solution to increase and after four hours the pH had decreased from 12 to about 10. After acidification with acetic acid, the mixture was extracted continuously with ethyl acetate and the extract was distilled in steam. The hot aqueous residue in the still was filtered to remove a small amount of dark amorphous material, and the filtrate on cooling deposited 0.3 to 0.4 gm. of an orange-red substance. About one-fifth of this substance was high-melting, red in color, and insoluble in ether. The remaining four-fifths when recrystallized from ether gave shining, dark-red rosettes of monoclinic needles in a yield of 25 to 32% based on the pyrogallol, and melting at 194.5° to 195°C. Their composition was that of a monomethyl ether of purpurogallin, and their melting point was close to the value of 193°C. reported by Critchlow, Haworth, and Pauson for the 2′ isomer (7).

On one occasion orange yellow crystals of m.p. 194° to 195°C. were obtained in place of the dark red needles, but there was no depression of melting point when the two forms were mixed.

Oxidations of Vanillin with Hypoiodite (Table II, Fig. 2)

Solutions of 3.09 gm. of boric acid in 75 cc. volumes of water were mixed with the proper volume of *N* sodium hydroxide (10 cc. to 80 cc.) to obtain the desired pH. After dilution to about 150 cc. with distilled water, 50 cc. of 0.2 *N* iodine in potassium iodide (0.005 mole) was added. Vanillin, 0.127 gm. or 0.00083 mole, was introduced at zero time as an aqueous suspension; the total volume was diluted to 250 cc. and the vanillin dissolved almost immediately. Solutions between pH 10 and 11 (runs 6 to 9) were orange to light yellow in color and remained clear, while those between pH 12 and 13.5 (runs 10 and 11) were both clear and colorless. The consumption of iodine at various times was followed as in the oxidations of pyrogallol, but the end point was definite and easy to observe. Iodoform was isolated after 24 hr. by making the solutions strongly alkaline and extracting with two 50 cc. volumes of ether. After being dried and evaporated, the extracts from runs 1, 2, 3, and 4 yielded 0.05, 0.052, 0.041, and 0.019 gm., respectively, of iodoform, which was identified by its melting point and odor.

5-Iodovanillin

The borate buffer – iodine solution was made up exactly as described, 10 cc. of the sodium hydroxide solution being included to give pH 8.2, and the amount of vanillin was increased to 0.76 gm. or 0.005 mole. Titration of an aliquot acidified after 15 min. indicated 2.9% of unused hypoiodite, and the equivalent amount of sodium thiosulphate was added to the remainder. The solution was then acidified with 10% sulphuric acid; the resulting cream colored precipitate was washed well with water and dried. Yield, 1.25 gm. (90%), and melting point 177° to 179°C. Two recrystallizations from glacial acetic acid yielded pale yellow needles with the analytical composition of an iodovanillin, and with a melting point, 181° to 182°C., in agreement with the recorded value of 180°C. (9) for 5-iodovanillin.

The above experiment, when repeated with a borate buffer including 50 cc. of *N* sodium hydroxide to keep the pH at 10, yielded a solution with the deep red color of iodine. This color required 15 min. to fade to a pale orange. An aliquot, when acidified at this time and titrated, contained 31% of "free" iodine, which presumably originated from by-product iodate. The remainder of the solution yielded 0.87 gm. (62.7%) of 5-iodovanillin, melting at 171° to 175°C., raised to the correct value of 181°C. by recrystallization.

Rate of Oxidation of Pyrogallol with Hypochlorite (Table III, Fig. 3)

The chlorine obtained from the action of excess hydrochloric acid on 4 gm. of potassium permanganate was swept with nitrogen into 250 cc. of *N* sodium hydroxide to yield a stock solution approximately 0.2 *M* in chlorine. Some of this stock solution, 25 cc. (0.005 mole) was transferred to a dark brown, glass bottle containing 75 cc. of 0.67 *M* boric acid and the amount of *N* sodium hydroxide to give the desired alkalinity. After the mixture had been diluted with distilled water to 225 cc. and had been brought to 25° ± 0.05°C., 0.11 gm. (0.00083 mole) of pyrogallol dissolved in 25 cc. of water at 25°C. was added.

The consumption of hypochlorite was followed by transferring 10 cc. aliquots into 100 cc. of water containing 0.1 to 0.2 gm. of potassium iodide; 10 cc. of 10% sulphuric acid and the starch indicator were added, and the liberated iodine was rapidly titrated with 0.025 N sodium thiosulphate solution. The end point was transitory.

Recovery of Trichloropyrogallol

A solution consisting of 200 cc. of 10% sodium carbonate and 25 cc. of 0.227 M chlorine (0.0058 mole) in N sodium hydroxide was added to 0.24 gm. (0.0019 mole) of pyrogallol dissolved in 25 cc. of water. Ten minutes later, when the hypochlorite was completely reduced, 1 gm. of zinc dust was added, the mixture (pH about 12) was acidified with 10% sulphuric acid, and was continuously extracted for 12 hr. with ether. Evaporation of the dried extract to 10 cc., followed by dilution with petroleum ether, caused the separation of 0.34 gm., (73%) of a white crystalline substance. When dried *in vacuo* over phosphorus pentoxide, this substance sintered markedly at 110°C. and melted at 179° to 180°C. with decomposition, as described for trichloropyrogallol monohydrate (1, 30). A sample was therefore dehydrated at 110°C. for 30 min. for analyses. Found: C, 30.9, 31.1; H, 1.51, 1.55; Cl, 45.7, 45.9%. Calc. for $C_6H_3O_3Cl_3$: C, 31.4; H, 1.3; Cl, 46.4%.

Recovery of 5-Chlorovanillin

(*a*) A suspension of 0.88 gm. of vanillin (0.0058 mole) in 100 cc. of water was mixed at room temperature with a solution composed of 75 cc. of 0.67 M boric acid, 25 cc. of N sodium hydroxide made 0.23 M (0.0058 mole) in chlorine, and 50 cc. of water. This mixture, pH 8.8, after 10 min. gave a negative test for hypochlorite. Acidification with 10% sulphuric acid then caused the deposition of 0.71 gm. of slightly yellow crystals, which sintered and darkened near 150°C. before melting to a red-black liquid at 158° to 162°C; yield, 65%. Solution in hot ethanol removed 70 mgm. of insoluble material, and the filtrate on cooling deposited pale yellow plates with the methoxyl and chlorine content of a chlorovanillin. The melting point of 163° to 164°C. was correct for the 5-chloro isomer (20), and admixture with an authentic sample of 5-chlorovanillin did not depress this value.

(*b*) The preparation in (*a*) was repeated with the exception that 45 cc. of N sodium hydroxide was substituted for the 50 cc. of water included in the mixture. This change altered the pH to 12.0, and one hour elapsed before the solution gave a negative test for hypochlorite. Acidification caused the precipitation of 0.46 gm. (41%) of 5-chlorovanillin melting at 158° to 162°C., undepressed by admixture with an authentic sample.

A red, flocculant precipitate immediately formed when the acidified mother liquor was mixed with 100 cc. of a saturated solution of 2,4-dinitrophenylhydrazine. After recovery, this precipitate weighed 0.92 gm. (39%), melted at 256° to 258°C., and contained no chlorine. Recrystallization from ethanol gave dark red crystals of vanillin 2,4-dinitrophenylhydrazone with the correct methoxyl content and the correct melting point of 264° to 265°C., not depressed by admixture with an authentic sample.

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THE SILVER CATALYZED OXIDATION OF ETHYLENE[1]

I. SLOW PROCESSES ON THE CATALYST SURFACE

BY A. ORZECHOWSKI[2] AND K. E. MACCORMACK

ABSTRACT

In the silver catalyzed oxidation of ethylene or ethylene oxide (EtO), the silver catalyst activity measured under constant standard conditions in a flow system was found to be dependent on the conditions of previous catalyst treatment such as reaction temperature and reactant composition. The results are explained on the basis of slow establishment of equilibrium respecting fixation of stably sorbed oxygen atoms and surface products of oxidation. It is emphasized that in view of the slow processes observed, the kinetic measurements must be punctuated by frequent stabilizing check runs in order to maintain the catalyst in the same reference state.

INTRODUCTION

This publication is the first of a series concerning the oxidation of ethylene on a silver catalyst. Part I presents the observations on slow processes which occur after changes of operating conditions during catalysis. Part II will deal with the kinetics of C_2H_4 oxidation and Part III with the kinetics of ethylene oxide (EtO), oxidation, and its isomerization to acetaldehyde. Part IV will be concerned with reaction mechanism.

A separate presentation of the slow processes which have been observed during the catalytic oxidation of C_2H_4 and which appear to be dependent on the conditions of pretreatment of the silver catalyst by the reacting gas mixture is considered useful from two main points of view. Kinetic measurements carried out under circumstances which fail to recognize the existence of slow processes cannot be deemed reliable for purposes of mechanism interpretation.

With the exception of the initial conditioning period, studied by Murray (5), very little has been reported in the literature concerning these effects. It is intended to emphasize the influence of catalyst "history" on its subsequent activity and the fact that true kinetics can only be observed on a silver surface soon after a standardized pretreatment which maintains the catalyst in the same reference state. This is opposed to observations made when true equilibrium is attained after very prolonged reaction with attendant changes in the nature of the catalyst.

EXPERIMENTAL

The flow apparatus and the single sample of catalyst, used throughout, will be described in Part II. Few experimental details will be mentioned here.

Having mounted the silver catalyst in the reactor, it was maintained in a N_2 atmosphere, when not in service. In beginning operations, it was heated in a N_2 stream to the desired temperature, then O_2, followed by C_2H_4 or EtO,

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[2] *National Research Council Postdoctorate Fellow, 1951–1953.*

was admitted at the desired flow rates. For close-down operations the reverse order was observed. When the flow rate or partial pressure was changed, it was always done quickly and in such a way as to keep the C_2H_4 concentration to a minimum during the change.

Except for the first conditioning period (Fig. 1), the catalyst remained in continuous operation over periods of weeks, with temperature control better than ±0.5° C., and flow rates constant to 1%.

The composition of the off-gas with respect to EtO and CO_2 was measured with an accuracy of ±2% of the absolute value. In the absence of catalyst, no products could be detected at 234° C.

The working pressure was atmospheric. Unit feed flow rate was arbitrarily set at 41.8 liters (N.T.P.)/hour of gas mixture. The following feed compositions were used, expressed by symbols which are described here and maintained throughout the forthcoming publications. The symbol pE_nO_m indicates a mixture flow rate of 41.8 p liters/hr., with C_2H_4 and O_2 contents, $2.35n\%$ and $9.90m\%$ respectively, the remainder being N_2. Thus, E_2O_2 corresponds approximately to a mixture of air–C_2H_4 of ratio 20: 1. X used instead of E refers to EtO.

A. Oxidation of C_2H_4

Feed $1E_2O_2$: 4.70% C_2H_4, 19.8% O_2, 75.5% N_2.

B. Oxidation of EtO

Feed $1X_2O_2$: 4.70% EtO, 19.8% O_2, 75.5% N_2.

C. Isomerization of EtO

Feed $1X_2O_0$: 4.70% EtO, 95.30% N_2.

The silver catalyst sample was estimated, on the basis of B.E.T. adsorption measurements using similar catalyst, to have a surface area of the order of 6 sq. meters and oxygen adsorption capacity in the order of 1 cc. (N.T.P.) at the working temperatures.

All the gases used were obtained from commercial cylinders. The EtO was manufactured by the Matheson Company with a specified purity of 99.5%. The authors are indebted to Dr. F. P. Lossing for mass spectrometric analysis of this gas which confirmed the absence of impurities other than possibly 3% of N_2. Ohio "Medical Grade" C_2H_4 with a specified purity of at least 99.5% and Dominion Oxygen Company nitrogen and oxygen, with a guaranteed purity of 99.7% in each case, were used.

RESULTS

A. Oxidation of Ethylene

1. *The Conditioning Period*

The conditioning period at reaction temperature 234° C., (feed $1E_2O_2$) is shown in Fig. 1. The conversion to EtO goes through a maximum; the conversion to CO_2 decreases, and the selectivity* increases. At least 150 hours are needed for approximate stabilization. The scattering of data is due to imperfections in the process control, which were eliminated at the end of this period.

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* *Selectivity = % C_2H_4 converted to EtO/total % C_2H_4 reacted.*

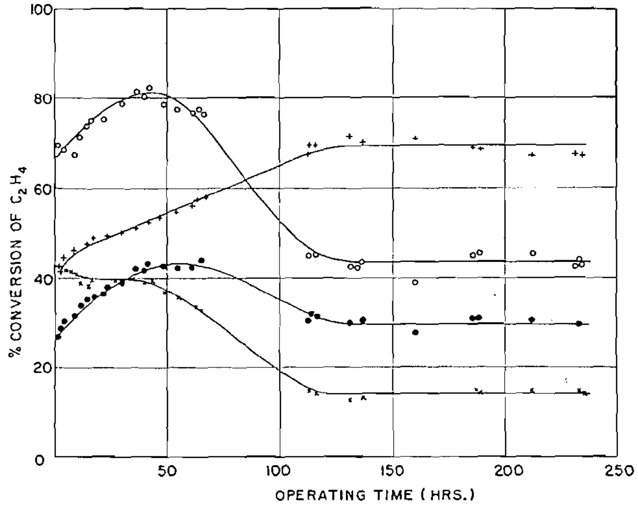

FIG. 1. Oxidation of C_2H_4. Conditioning period of new catalyst. 234° C. Feed $1E_2O_2$. ● Conversion to EtO; × conversion to CO_2 and H_2O; ○ total conversion; + selectivity.

2. *Slow Processes Due to Change of Temperature Level, (Feed $1E_2O_2$)*

If the operating temperature is changed upwards from 234 to 274° C. (see Fig. 2), the conversion slowly increases and selectivity decreases. The reverse occurs when the temperature level is reduced.

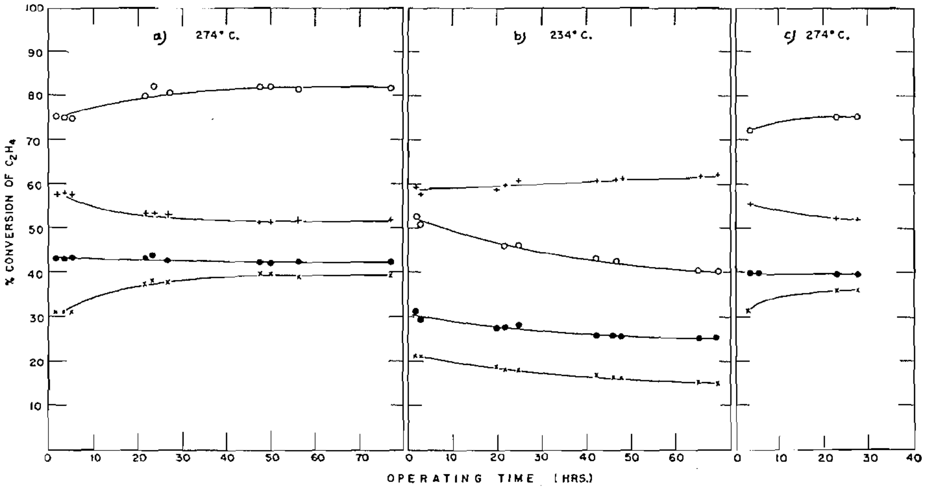

FIG. 2. Oxidation of C_2H_4. Slow processes due to changes of temperature level. Feed $1E_2O_2$. (*a*) After conditioning period at 234° C.; (*b*) after (*a*); (*c*) after (*b*). ● conversion to EtO; × conversion to CO_2 and H_2O; ○ total conversion; + selectivity.

3. *Slow Processes Due to Change of Flow Rate (at Constant Temperature 274° C.)*

Numerous observations were made after changes of flow rate extending between twofold and 16-fold. When the flow rate is increased, EtO and CO_2

formations decrease slowly, the latter decrease being of greater magnitude than the former with resulting increase in selectivity. The reverse is true when the change of flow rate is in the opposite direction. This drift in conversions becomes very slow after 24 hr. at the new flow value.

A typical case was as follows: after feeding $4E_4O_2$ the flow rate was decreased fourfold; three hours after the change the conversions were CO_2 23.5%; EtO 27%; selectivity 53.5%; 20 hr. later CO_2 26.5%; EtO 28.5%; selectivity 51.9%.

4. *Slow Processes Due to Change of Feed Composition (at Constant Temperature and Flow Rate)*

A striking change in catalyst behavior is caused by its pretreatment with an ethylene-rich feed (E_4O_1). The effect is the same at 234° C. and 274° C. and consists in substantially permanent lowering of EtO and increase of CO_2 production.

The conversions for the standard $1E_2O_2$ feed at 234° C. were: before runs E_4O_1: EtO 17.0%: CO_2, 10.5%: selectivity, 62%; after runs E_4O_1: EtO, 13.5%: CO_2, 12.0%: selectivity, 53%.

This effect lasted more than 200 hr. at 235° and is difficult to remove completely, although the passage of feeds enriched in O_2 is very helpful. It is easier to restore the surface activity when the same poisoning has occurred at 274° C.

With the knowledge of slow processes obtained at this stage, the kinetic runs for C_2H_4 oxidation were made at 274 and 234° C. Data will be presented in Part II.

5. *Slow Processes Due to Pretreatment of Catalyst by O_2 or by EtO and O_2*

Six runs with the standard $1E_2O_2$ feed at 274° C. are shown in Fig. 3. These data were obtained following a series of pretreatment variables listed in the table below. The numbers in brackets indicate the order in which they were

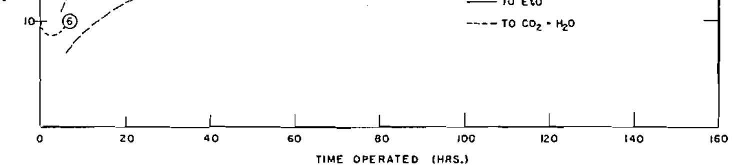

FIG. 3. Influence of catalyst pretreatment on oxidation of C_2H_4 at 274° C. Feed $1E_2O_2$. Runs 1–6 are explained in Table I.

performed for each experiment. The experiments numbered in column 1 are likewise in chronological order.

In each of the experiments 1–6 listed above involving final pretreatment by O_2 or by EtO + O_2, the standard ethylene oxidation runs resulted in abnormally low conversion and high selectivity. This effect diminished slowly during prolonged operation with the standard feed gas. The first experiment may include some influence of temperature change, but this was absent in the subsequent ones. It is noteworthy that pretreatment by oxygen alone (Curve 3) caused considerable poisoning, though this may be explained by the influence of EtO + O_2 employed in Experiment 2, which may not have been eliminated at that time. In support of this, further oxygen treatment in Experiment 4, where little influence could be attributed to previous treatment by EtO + O_2, produced a relatively minor effect on the standard ethylene oxidation. The break in continuity of Curve 6 was caused by cooling the reactor to room temperature in a stream of N_2 after five hours' operation.

6. *Slow Processes Due to Pretreatment of Catalyst by EtO + N_2 (X_2O_0)*

Fig. 4 shows the results of two experiments, 7 and 8, details for which are given in the table. The continuity of Curve 7 was interrupted at A by cooling to room temperature in a N_2 stream, and subsequently at B by accidental temperature drop to 250° C. for three hours.

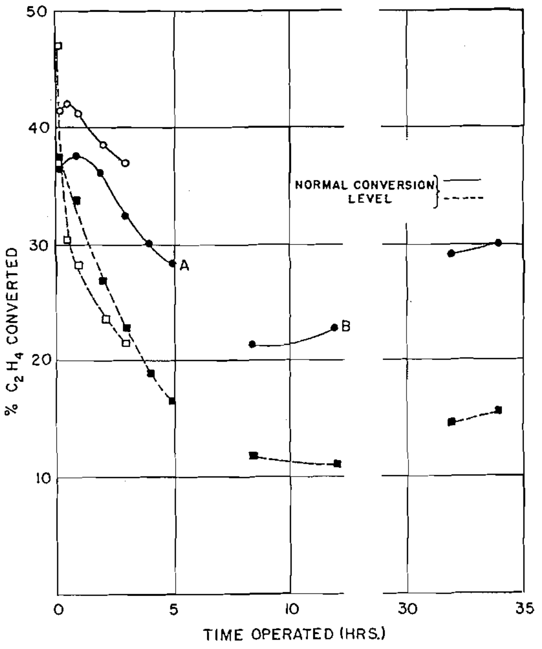

FIG. 4. Influence of catalyst pretreatment on oxidation of C_2H_4 at 274° C. Feed $1E_2O_2$, with pretreatment by EtO + N_2. ——— Conversion to EtO; – – – conversion to CO_2 and H_2O; ■ ● Expt. 7; □ O Expt. 8 (see Table I).

The feature of pretreatment by EtO + N_2 is an anomalous high level of conversion which decreases rapidly to the low poisoned level, followed by slow recovery.

B. Oxidation of Ethylene Oxide

1. Oxidation of EtO after pretreatment by C_2H_4 oxidation ($1E_2O_2$).

The results are shown in Fig. 5 for the feed, $1X_2O_2$, admitted after the following operations at 274° C.

Run I: pretreatment by Expt. 4 of Fig. 3
Run II: " " " 5 " Fig. 3
Run III: " " " 7 " Fig. 4

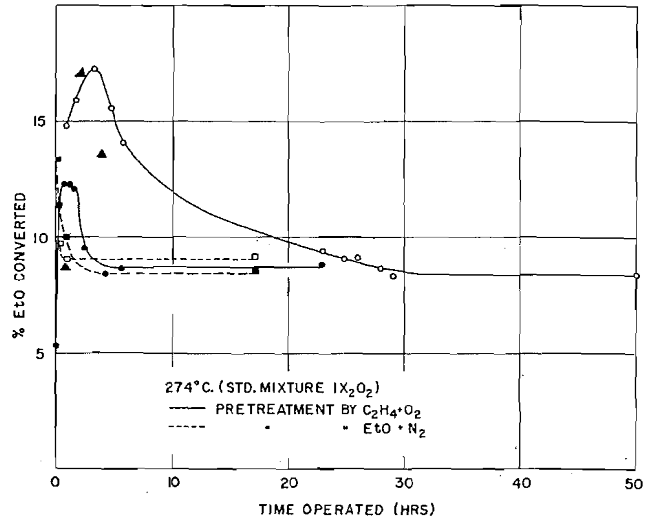

FIG. 5. Influence of catalyst pretreatment on oxidation of EtO at 274° C. Feed $1X_2O_2$. Pretreatment by C_2H_4 oxidation: runs I (▲), II (○), III (●). Pretreatment by EtO + N_2: runs A (□), B (■). (See Table I.)

The common feature of these results is that the conversion of EtO to CO_2 and H_2O goes through a maximum before a steady state is obtained.

2. Oxidation of EtO after pretreatment by EtO + N_2 (feed X_2O_0).

The results are shown in Fig. 5 for the feed $1X_2O_2$ admitted after the following operations at 274° C.

Run A: 1.5 hr. pretreatment by X_2O_0, which followed prolonged kinetic runs at EtO oxidation (see Table I, Expt. 6).

Run B: 28 hr. pretreatment by X_2O_0 which followed run A (see Table I, Expt. 6).

Characteristic of pretreatment by EtO + N_2 is the rapid decrease of the oxidation of EtO to a stable value.

DISCUSSION

The importance of these results lies in their influence on the correct establishment of the reaction kinetics. It became evident almost from the beginning

TABLE I
PRETREATMENT VARIABLES (ALL AT 274° C., EXCEPT WHERE OTHERWISE STATED)

Experiment No.	Pretreatment				Reference for standard $1E_2O_2$
	$C_2H_4 + O_2$	EtO + O_2	EtO + N_2	O_2	
1	(1) Kinetic series 234° C.	(2) 5 hr.		(4) 40% $O_2 + N_2$ 20 hr.	(3) 234°, poisoned (5) Curve 1, Fig. 3
2		(1) 1.5 hr.		(2) 18 hr.	(3) Curve 2, Fig. 3
3				(1) 67 hr.	(2) Curve 3, Fig. 3
4				(1) 35 hr.	(2) Curve 4, Fig. 3
5		(1) 5 hr. (Run I, Fig. 5)			(2) Curve 5, Fig. 3
6		(1) Run II, Fig. 5 and kinetic series	(2) 1.5 hr.		
		(3) 18 hr. (Run A, Fig. 5)	(4) 28 hr.		(6) Curve 6, Fig. 3
		(5) 46 hr. (Run B, Fig. 5)			
7			(1) 18 hr.		(2) Curve 7, Fig. 4
8		(1) 23 hr. (Run III, Fig. 5)	(2) 3 hr.		(3) Curve 8, Fig. 4

of this work that reliable data could not be obtained unless care were taken to maintain a standard state for the catalyst. Also, if the kinetics for EtO oxidation are to be correlated with those of the C_2H_4 oxidation, account must be taken of the fact that the catalyst conditioned for one reaction is certainly in an unsteady state with respect to the other.

It is suggested that the concept be introduced of separate rates of attainment of surface equilibrium to account for coverage (*a*) by reacting substances and (*b*) by substances which are nonreactive.

Nonreactive species behaving as poisons or moderators may be more stably sorbed either on the surface or within the silver lattice than reacting species. Oxygen atoms are known to diffuse and dissolve in silver (6). Surface substances could act as poisons simply by virtue of the space occupied whereas both lattice and surface substances may act as impurity centers with energetic effects which virtually alter the extent of the catalyst surface. Extremely small traces of bulk impurities are known to modify the electronic and catalytic properties of metals (3, 4).

On this basis the relations for the rate of establishment of equilibrium for reacting species on the free Ag surface may now be developed. The stoichiometry of the reactions is neglected for simplicity.

Let R = reaction rate
V = net adsorption rate for reactants (adsorption minus desorption rate)
Δq = change in quantity of reactants accumulated on surface which contribute to coverage during time, t.
q_0 = maximum possible amount of adsorbed reactants in the absence of poisoning effects.

Subscripts are used as follows:
e refers to reactant equilibrium coverage for a given poisoning level;
t refers to conditions at time, t;
av refers to average values over the time, t.

At equilibrium $V_e = R_e$.
Since $V_{av} > V_e$,
then
[1] $V_{av} > R_e$.
[2] $\Delta q = (V_{av} - R_{av})t$.
From [1] and [2] it follows
[3] $\Delta q > (R_e - R_{av})t$.
[4] Since $R_{av} < R_t < R_e$
[5] and $\Delta q < q_0$,
from [3], [4], and [5] we have
[6] $R_t < R_e < R_t + q_0/t$.

In the present case q_0 is in the order of 1 cc. (N.T.P.). At time $t = 0.1$ hr., R_t is already found to be in the order of 400 cc. (N.T.P.)/hr. and equation [6] may therefore be written,

$$R_t = 400 < R_e < 410 \text{ cc./hr.}$$

Hence the equilibrium coverage in question is certainly very closely approached within the first 0.1 hr.

Slow processes which continue for times in the order of 100 hr. or more cannot be identified with the establishment of equilibrium surface coverage by reacting species and must be attributed to establishment of equilibrium respecting poisons. In view of the large difference in the magnitude of these two rates, reaction kinetics may be studied on a poisoned catalyst surface, provided the same degree of poisoning is maintained throughout. This requirement was observed during all the measurements reported in Parts II and III, by preconditioning the catalyst at a given temperature with a gas mixture of average composition respecting the range employed. Frequent checks were made to verify the maintenance of the same reference state.

It is believed that stable poisons accumulate slowly during reaction and that for any given level of poisoning the remainder of the surface is available for rapid establishment of equilibrium respecting reacting species. A change in temperature or composition of the reactants will tend to affect the extent of poisoning in a direction dependent on the equilibrium position for the new system respecting poisons.

At first sight it may appear that where conversion of reactants exceeds the normal level, as for example, the case of C_2H_4 oxidation during the first few hours following treatment by EtO and N_2 (Fig. 4), it could be attributed to slow burning of carbonaceous deposit on the surface. However, calculation based on the estimated adsorption capacity of the catalyst sample shows that to account for the excessive CO_2 formation the carbon deposit would have to be several hundred atoms thick. Run 8, Fig. 4, shows during the first three hours an average conversion to EtO of 39% instead of the maximum of about 33% expected on the basis of curves for the preceding group of runs shown in Fig. 3. With feed flow equal to 41.8 liters (N.T.P.)/hr. containing 4.7% C_2H_4, at least 350 cc. of excess EtO are formed whereas the surface adsorption capacity is of the order of 1 cc. Hence the changes in conversion cannot be explained on the basis of massive desorption only.

It remains to deduce the nature of the inhibiting species which are responsible for observed slow processes.

(1) *Inhibition of Ethylene Oxidation by O_2 and by Residues Formed During Oxidation of EtO*

Pretreatment by O_2 or by EtO + O_2 (see Table I, Expts. 1–6 inclusive) results in the qualitatively similar observation that conversion both to CO_2 and EtO is abnormally low and selectivity high for standard conditions with a tendency to approach normal values with time. In addition to these, similar effects on the C_2H_4 oxidation are produced by pretreatment (*a*) at a higher flow rate and (*b*) at lower temperature with the same flow rate and composition of feed composed of C_2H_4 and O_2. The converse is also true.

The only common feature of all these pretreatments is that O_2 concentration in the off-gas is higher than in the case of standard run $1E_2O_2$, whose behavior they affect. However, according to Fig. 3, oxygen alone is a less active inhibitor than EtO + O_2 and the influence of O_2 decreases when the inhibition by EtO and O_2 is removed; on the other hand, EtO alone (with N_2) not only fails to poison, but enhances activity (Fig. 4). Hence it must be concluded that there are two inhibiting species:

(1) Oxygen atoms, slowly attaining stable positions.
(2) Slowly formed surface products of EtO oxidation.

Explanation (1) respecting oxygen action may be applicable to the observation of Benton and Elgin (1) that pretreatment of silver by O_2 always gave lower activity for H_2 oxidation than pretreatment by H_2.

Fig. 4 may now be explained. After the initial high conversion, which results from the removal of inhibiting oxygen by EtO + N_2 pretreatment, oxygen is slowly sorbed again with a drop in conversion to the former level probably determined by unremoved products of former EtO oxidation. The latter were not removed by runs prior to EtO + N_2. Then these also are slowly eliminated.

(2) *Influence of Pretreatment on EtO Oxidation*

In the case of pretreatment by EtO + N_2 the conversion of EtO to CO_2 is initially high and then decreases (Fig. 5, A, B). This conforms to the hypothesis that inhibiting particles are O atoms and EtO surface oxidation products.

If the pretreatment is C_2H_4 oxidation, the conversion of ethylene oxide to CO_2 goes through maximum (Fig. 5: I, II, III). Runs for C_2H_4 and for EtO oxidation differ largely in the absence of C_2H_4 and in higher concentration of EtO and O_2 in the latter runs. To explain the ascending portion before the maximum, it is therefore necessary to conclude that there is a third sort of stably sorbed particle formed during C_2H_4 oxidation. When EtO oxidation is started, these are at first removed, followed by the onset of oxygen inhibition and formation of EtO oxidation residues.

It may be noted here that Twigg (7) found the formation of residues on contact with oxygenated catalyst much greater in the case of EtO than in the case of C_2H_4.

(3) *Inhibiting Effect of Pretreatment by Feed Rich in C_2H_4 and Poor in O_2 Standard C_2H_4 Oxidation*

When the standard feed $1E_2O_2$ is passed after pretreatment by E_4O_1, initial measurement shows higher CO_2 and lower EtO conversions with lower selectivity than for normal conversion values. All these values tend to approach the normal level slowly with time.

The essential difference between E_4O_1 and $1E_2O_2$ is that the former has much lower O_2 and much higher C_2H_4 concentration in the outgas. The effect with respect to CO_2 conversion and to selectivity conforms well to the picture of inhibiting oxygen having been removed by an oxygen-deficient run. However, the decrease in conversion to EtO can only be understood if the formation of stable residues during C_2H_4 oxidation is assumed, as discussed in the previous section. The latter effect may be considered similar to that observed by Benton and Elgin (2); in the oxidation of H_2 the use of mixtures with large H_2 excess resulted in subsequent permanent decrease of catalytic activity. This could be due to fixation of H_2O or OH' in stable positions.

The slow processes which were found must therefore be attributed to the slow fixation and removal of three kinds of particles: oxygen atoms, surface products of C_2H_4 oxidation, and surface products of EtO oxidation.

These effects may be compared with known poisoning effects due to Cl_2 or SO_2. Both decrease the conversion*, the selectivity being higher than the normal selectivity extrapolated to zero contact time in the case of Cl_2, lower than normal in the case of SO_2. Obviously, this behavior cannot be due to the reduction of effective contact time by poisoning, as was suggested during discussion of Twigg's work (7). Rather, the conversion and selectivity changes are due to the formation of stably sorbed Cl_2 and SO_2 particles—impurity centers—which change the coverage and possibly the energetics of the catalyst system.

The investigation was not carried beyond this stage by virtue of large time consumption and the fact that a sound basis for kinetic measurements had been achieved.

SUMMARY

In the silver catalyzed oxidation of ethylene or ethylene oxide (EtO), the silver catalyst activity measured under constant standard conditions in a

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* *According to some preliminary work in this laboratory, this effect is reversible, the time needed for recovery being of the same order as in the case of slow processes discussed in this paper.*

flow system was found to be dependent on the conditions of previous catalyst treatment such as reaction temperature and reactant composition.

Oxidation of C_2H_4

Stabilization of new catalyst by an C_2H_4–O_2 mixture under standard conditions, referred to as (I) was found to occupy a period of about 150 hr. If this is followed by some other nonstandard conditions (II) a subsequent return to (I) will produce an abnormal activity (A), the effect being removed within a period of 50–200 hr., depending on II.

The following correlations were established between (II) and (A):

(*a*) (II) is the standard C_2H_4–O_2 mixture at lower (or higher) temperature than that used in (I).

(A) shows lower (or higher) conversions and higher (or lower) selectivity respecting EtO formation.

(*b*) (II) is an C_2H_4–O_2 mixture of high C_2H_4 and low O_2 concentration.

(A) shows increased CO_2 and decreased EtO formation; difficult to eliminate completely.

(*c*) (II) is O_2 or a mixture of O_2 and EtO.

(A) shows pronounced activity decrease with increased selectivity.

(*d*) (II) is EtO.

(A) shows high conversions rapidly declining.

Oxidation of EtO

The catalyst has to be stabilized under standard conditions by a mixture of EtO–O_2. Slow processes occur similar to those observed during C_2H_4 oxidation:

(*a*) (II) is EtO.

(A) shows abnormally high conversion to CO_2, rapidly decreasing.

(*b*) (II) is an C_2H_4–O_2 mixture.

(A) indicates that conversion to CO_2 passes through a maximum with time.

The results are explained on the basis of slow establishment of equilibrium respecting fixation of stably sorbed oxygen atoms and surface products of oxidation. It is emphasized that in view of the slow processes observed, the kinetic measurements must be punctuated by frequent stabilizing check runs in order to maintain the catalyst in the same reference state.

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EXCITED MOLECULES AS THE REACTIVE SPECIES IN ACTIVE NITROGEN[1]

By R. A. Back, Margaret Menzies,
and C. A. Winkler

ABSTRACT

No reaction has been detected between ethylene and nitrogen molecules obtained in the thermal decomposition of metallic azides. Since such decomposition reactions apparently produce nitrogen molecules excited to the same electronic level as those present in active nitrogen formed by a condensed discharge, it might be inferred that excited molecules are not the reactive species in active nitrogen.

INTRODUCTION

When nitrogen is passed through a condensed discharge under suitable conditions, its chemical reactivity is greatly enhanced. Strutt (7) attributed the reactivity to nitrogen atoms, but it has also been ascribed to N_2^* excited molecules, N_3 radicals, N_2^+ ions, and other species. Mitra has reviewed the various arguments and evidence (5); in a recent paper (6) he concludes that nitrogen atoms are probably the active species.

It is generally agreed that nitrogen atoms are formed in the discharge and recombine to form nitrogen molecules in the metastable $B^3\Pi_g$ state, mostly excited to the 11th or 12th vibrational level. These may redissociate, or may undergo transition to an $A^3\Sigma_u^+$ state with emission of the first positive band, corresponding to the persistent yellow afterglow associated with active nitrogen. Transition from the $A^3\Sigma_u^+$ state to the ground state results in emission of Vegard-Kaplan bands in the far ultraviolet. Both excited species are probably subject to radiationless transition to the ground state through a suitable third body collision.

A source of excited nitrogen molecules other than the electrical discharge would obviously be of assistance in identifying the reactive species in active nitrogen. The thermal decomposition of certain metallic azides seems to offer such a source. The results of kinetic studies by Thomas and Tompkins (8, 9) on the thermal decomposition of barium azide appear to be satisfactorily explained on the basis of recombination of N_3 excitons to form N_2 molecules, while the formation of atomic nitrogen appears to be excluded. Other studies by Audubert (1) and by Finkelstein (3) indicate that at least part of the nitrogen formed during decomposition of various metal azides is in an excited state. Strong excitation of the mercury resonance line in the presence of decomposing azides was observed, and interpreted in terms of a resonance transfer between nitrogen and mercury in the 1650 Å region, corresponding approximately to 173 kcal. per mole, and roughly to the $B^3\Pi_g$ state of the nitrogen molecule without vibrational excitation (4). It may be inferred, therefore, that the

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thermal decomposition of azides should provide a source of excited nitrogen molecules, unaccompanied by nitrogen atoms.

Since the reaction of ethylene with active nitrogen from a discharge tube has been found to occur rapidly, with production of hydrogen cyanide (10), it seemed of interest to decompose metallic azides in the presence of ethylene and examine the reaction products for hydrogen cyanide and other possible evidence for reaction between excited molecules of nitrogen and ethylene.

EXPERIMENTAL

Barium azide was prepared by distilling hydrazoic acid from a 3% solution into a suspension of barium hydroxide. The azide was precipitated with alcohol, filtered, and dried over concentrated sulphuric acid. Silver azide was precipitated by the addition of silver nitrate to sodium azide in aqueous solution, filtered, and dried in the same way. Both azides were used without further purification.

The azides were decomposed in a horizontal furnace made of 18 mm. Pyrex tubing. The azide was introduced in a boat, 12 cm. long, made of 14 mm. Pyrex tubing, open at both ends, and with a hole in the middle through which the azide was added.

Reaction rates were measured by rate of pressure increase, assumed to be due entirely to nitrogen evolved. Condensable products were analyzed for hydrogen cyanide by absorption in 1 N potassium hydroxide solution and titration with 0.01 M silver nitrate. A cupric acetate-benzidine acetate spot test was also used (2).

The decomposition of barium azide (50 to 175 mgm.) was studied in 17 experiments at 158° C. In 10 of these, ethylene was present at pressures ranging from 3 to 29 cm. The solid residue in the boat was dissolved in standard acid and spot tests were made for cyanide and ammonia, which would be formed if nitride were present in the residue. One aliquot portion of the solution was titrated with standard alkali to determine the amount of barium and ammonia present; a second aliquot was made alkaline, the ammonia boiled off, and the solution back titrated. The difference in titer value for the two aliquots allowed the amount of barium nitride formed during decomposition to be estimated.

Three experiments were made in which barium azide was dropped through a vertical furnace at 450° C. containing ethylene at a pressure of about 30 cm. Both gaseous products and solid residue were examined for the presence of hydrogen cyanide.

Three experiments were made with sodium azide and three experiments with silver azide in the presence of ethylene at temperatures of 360° C. and 300° C. with pressures ranging from 2 to 10 cm. and 8 to 20 cm. respectively. Analysis was made only for hydrogen cyanide in the condensable gaseous products and solid residue.

One experiment was made with each of ethylene, hydrogen, nitrogen, and helium to determine the effect on the rate of production and yield of nitrogen from barium azide at 158° C., with 13 cm. pressure of gas present.

RESULTS AND DISCUSSION

Hydrogen cyanide was not detected in either the condensable gaseous products or the solid residue from any of the experiments. For a 100 mgm. sample of azide, it should have been possible to detect conversion into cyanide of 0.1% of the nitrogen evolved.

The presence of ethylene during the decomposition of barium azide caused a decrease in both the rate of production and the yield of nitrogen, directly proportional to the pressure of ethylene. However, the recovery of ethylene and barium (2 to 4% as nitride) was complete. With hydrogen present, the decrease in rate of production and yield of nitrogen was much greater than with ethylene present, while nitrogen and helium had very little effect. The observed decrease in yield of nitrogen was much more than would correspond to complete conversion of the azide to nitride. A quantitative study of the behavior was not attempted but the results indicate that further studies of similar type might be interesting.

For a given preparation of azide the induction period was increased with increased ethylene pressure. Crystal size varied with each batch of azide prepared and the largest crystals had the shortest induction period. No measurable amounts of water were obtained following decomposition of the barium azide and the samples were assumed to be anhydrous. This was verified when the crystals were examined under a microscope and found to be monoclinic rather than triclinic.

With sodium and silver azides the yields of nitrogen corresponded to their complete decomposition and ethylene was totally recovered, although the rate of decomposition decreased with increased ethylene pressure. With none of the azides did an increase of temperature, after the reaction had stopped, cause further production of nitrogen.

The absence of hydrogen cyanide and other possible products of a reaction between active nitrogen and ethylene might be interpreted in several ways. It might, for example, be questioned that excited nitrogen molecules were produced in concentrations sufficient for chemical detection. While Finkelstein (3) has demonstrated the presence of excited nitrogen molecules in azide decompositions, through a study of energy transfers with mercury and other metallic vapors, a quantitative estimate of their concentration is rather difficult. However, for the consecutive processes of transfer and fluorescence,

$$\begin{aligned} N_2^{**} + \mathrm{Hg} &\longrightarrow \mathrm{Hg}^{**} + N_2 \\ \mathrm{Hg}^{**} &\longrightarrow \mathrm{Hg}^{*} + h\nu_1 \\ \mathrm{Hg}^{*} &\longrightarrow \mathrm{Hg} + h\nu_2\ (2537\ \text{Å})\ . \end{aligned}$$

Finkelstein calculated a lower limit of 3.5×10^{-8} for the over-all efficiency of conversion to 2537 Å radiation on the assumption that every molecule of nitrogen was excited. These calculations are rather crude, but they do suggest that an appreciable fraction of the nitrogen evolved must be in an excited state, probably sufficient for detection by the methods used if reaction between the excited nitrogen molecules and ethylene were possible.

It might also be suggested that, if the nitrogen is released mostly at the azide–metal interface (8, 9), it would have to diffuse through the lattice to reach the ethylene in the gas phase, and might suffer de-excitation in the process. However, the efficiency of transfer and fluorescence found by Finkelstein would seem to indicate that an appreciable quantity of excited nitrogen does reach the gas phase to effect energy transfer with mercury. Furthermore, in the present experiments in which barium azide was dropped through ethylene at 450° C., well above its detonation temperature, de-excitation of the nitrogen before contact with ethylene seems unlikely.

Interpretation of the present experiments must also recognize that excited molecules derived from recombination of atoms formed in a condensed discharge through nitrogen are generally believed to be in the 11th or 12th vibrational level of the $B^3\Pi_g$ state, while those obtained by thermal decomposition of azides are possibly in the same electronic state but vibrationally unexcited. The difference in energy would amount to about 52 kcal. per mole (4). Hence, the reactions of ethylene with excited molecules from the two sources could differ energetically to this extent.

It would seem, however, that reaction of excited molecules from azide need not be energetically improbable because of this difference. This may be illustrated by considering a reaction of the type that appears to be encountered in the reaction of ethylene with active nitrogen from a discharge tube (10),

$$C_2H_4 + N_2^* \longrightarrow HCN + CH_3 + N.$$

If the excited molecule involved in the reaction is one formed by recombination of atoms from a discharge through nitrogen, the energy required to break the $N{\equiv}N$ bond involved may be taken as zero. If the $C{=}C$ bond dissociation energy is taken as 120 kcal. per mole and that of the $C{\equiv}N$ bond as 175 kcal. per mole, the reaction indicated would be some 55 kcal. per mole exothermic. If, on the other hand, the excited nitrogen molecule involved were derived from azide the reaction would be about 52 kcal. per mole more endothermic, i.e., approximately thermoneutral. Hence, although a difference in rate of reaction of active nitrogen derived from the two sources might be expected, energetic considerations alone do not appear to rule out the possibility of reaction between ethylene and active nitrogen obtained from azides, particularly in the experiments at higher temperatures.

Possible reactions other than that suggested above might well be more favorable energetically, as for example,

$$C_2H_4 + N_2^* \longrightarrow 2HCN + H_2$$

or

$$C_2H_4 + N_2^* \longrightarrow (CN)_2 + 2H_2\,.$$

The various observations and arguments outlined above indicate, although they do not prove, that excited molecules of nitrogen are incapable of reactions of the type observed with active nitrogen from a discharge tube, and that the chemically reactive species in active nitrogen is not the excited nitrogen molecule.

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PREPARATION OF SOME NEW BRANCHED-CHAIN CARBOHYDRATES FROM D-α-FRUCTOHEPTONIC LACTONE[1]

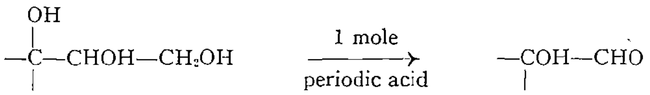
By R. J. Woods[2] and A. C. Neish

ABSTRACT

D-α-Fructoheptonic lactone (I) was oxidized with an equimolar amount of periodic acid to give formaldehyde and a hexuronic lactone (II) which was hydrolyzed to crystalline 4-*C*-hydroxymethyl-L-xyluronic acid (III), (68% yield). Hydrogenation of III gave an aldonic acid which was isolated as crystalline 2-*C*-hydroxymethyl-L-xylonic lactone (V). Reduction of V by sodium amalgam gave 2-*C*-hydroxymethyl-D-xylose (VI), which crystallized after purification as the 2,5-dichlorophenylhydrazone. Hydrogenation of VI gave 1,1-di(*C*-hydroxymethyl)-D-threitol (VII) which was purified as the crystalline hexaacetate. Treatment of III with methanolic hydrogen chloride gave a glassy material which was reduced by sodium borohydride and hydrolyzed by hydrochloric acid to give 4,4-di(*C*-hydroxymethyl)-D-threose (IX), which was isolated and characterized as the crystalline 2,5-dichlorophenylhydrazone. Oxidation of III by either bromine or nitric acid gave 2-*C*-hydroxymethyl-D-xylaric acid (IV), which was characterized as the crystalline ammonium salt.

INTRODUCTION

The structure of D-α-fructoheptonic lactone (I) may be written as a γ-lactone since it gives aqueous solutions with a constant optical rotation. This molecule has three diol bonds that one would expect to be split by periodic acid. These are the primary–secondary, the primary–tertiary, and the secondary–tertiary carbon bonds. Cleavage of the secondary–tertiary carbon bond would be expected to proceed at a slower rate than cleavage of the other bonds. For example Prins and Reichstein (18) have oxidized sterols of type A to sterols of type B in good yields.



$$-\overset{\overset{\displaystyle OH}{|}}{\underset{|}{C}}-CHOH-CH_2OH \xrightarrow[\text{periodic acid}]{\text{1 mole}} -\underset{|}{C}OH-CHO$$

Sterol A Sterol B

Furthermore it has been the experience of carbohydrate chemists that carbon-to-carbon bonds in rings (as in glycosides) are split more slowly than bonds in open chains (as in sugar alcohols).

The yield of formaldehyde obtained on treating D-α-fructoheptonic lactone (I) with excess periodic acid shows that both primary alcohol groups can be split off (see Table I). If only one mole of periodic acid is used per mole of I the high yield of formaldehyde (0.93 moles) indicates that this type of splitting is faster than ring cleavage. This may not be generally true for all lactones judging from the results obtained with galactonic and mannonic γ-lactones (Table I) where the rather low yield of formaldehyde suggests that either the ring and

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[2] *National Research Council of Canada Post-doctorate Fellow, 1952–53.*

terminal diol bonds are attacked at about the same rate or else the lactone ring is opened rapidly in about half the molecules prior to oxidation.

We have found that the most rapid reaction during the oxidation of fructoheptonic lactone (I) is the cleavage of the terminal diol bond between the secondary and primary carbons. When an aqueous solution of this lactone was treated with an equimolar amount of periodic acid, 0.93 moles of formaldehyde were liberated (Table I). The acids were removed by an acid absorbing resin to give a solution of the lactone (II). This lactone was a sirup but on forming the sodium salt and replacing the sodium by hydrogen, with an ion exchange resin, the crystalline 4-*C*-hydroxymethyl-L-xyluronic acid (III) was obtained in good yield (68%). The structure of this uronic acid was proved (see Fig. 1) by oxidation to 2-*C*-hydroxymethyl-D-xylaric acid (IV), which was characterized as a crystalline diammonium salt, and also by hydrogenation to 2-*C*-hydroxymethyl-D-xylonic acid, which was isolated as the crystalline lactone (V). A tricarboxylic acid was not obtained on prolonged oxidation of III with nitric acid. This is not surprising since Freudenberg and Blummel (5) had difficulty in obtaining one by nitric acid oxidation of hamamelose.

TABLE I
YIELD OF FORMALDEHYDE ON OXIDATION OF LACTONES BY PERIODIC ACID

	Periodic acid (moles/mole of lactone)	Reaction time (hours)	Formaldehyde (moles/mole of lactone)
D-α-Fructoheptonic lactone	1	15	0.93, 0.93
	8	0.25	1.07
	10	15	1.83
D-Mannonic γ-lactone	1	0.25	0.42
	1	1	0.45, 0.34
	10	1	0.80
D-Galactonic γ-lactone	1	1	0.49, 0.52
	10	1	0.98
2-*C*-Hydroxymethyl-D-xylonic lactone	10	3	1.95
	10	15	1.98

The uronic acid (III) is shown as an open chain in Fig. 1, since it is not known whether it forms a furanose ring with the tertiary hydroxyl or a pyranose ring with the primary hydroxyl. There are two reasons for believing that a ring is formed; firstly, because the compound shows mutarotation and, secondly, because crystals of the uronic acid are deposited from the sirupy lactone (II), on long standing, thus indicating the acid to be the stable modification. The acid would not be expected to be the stable form unless formation of a glycosidic ring has so changed the shape of the molecule that formation of a lactone ring is no longer possible.

The uronic acid (III) was used as a starting material for the preparation of some other new branched-chain carbohydrates, as shown in Fig. 1. Reduction of the aldehyde group followed by reduction of the acid group gave 2-*C*-hydroxymethyl-D-xylose (VI), a crystalline aldose which gave the alcohol (VII) on further reduction. This aldose formed crystalline hydrazones but not osazones.

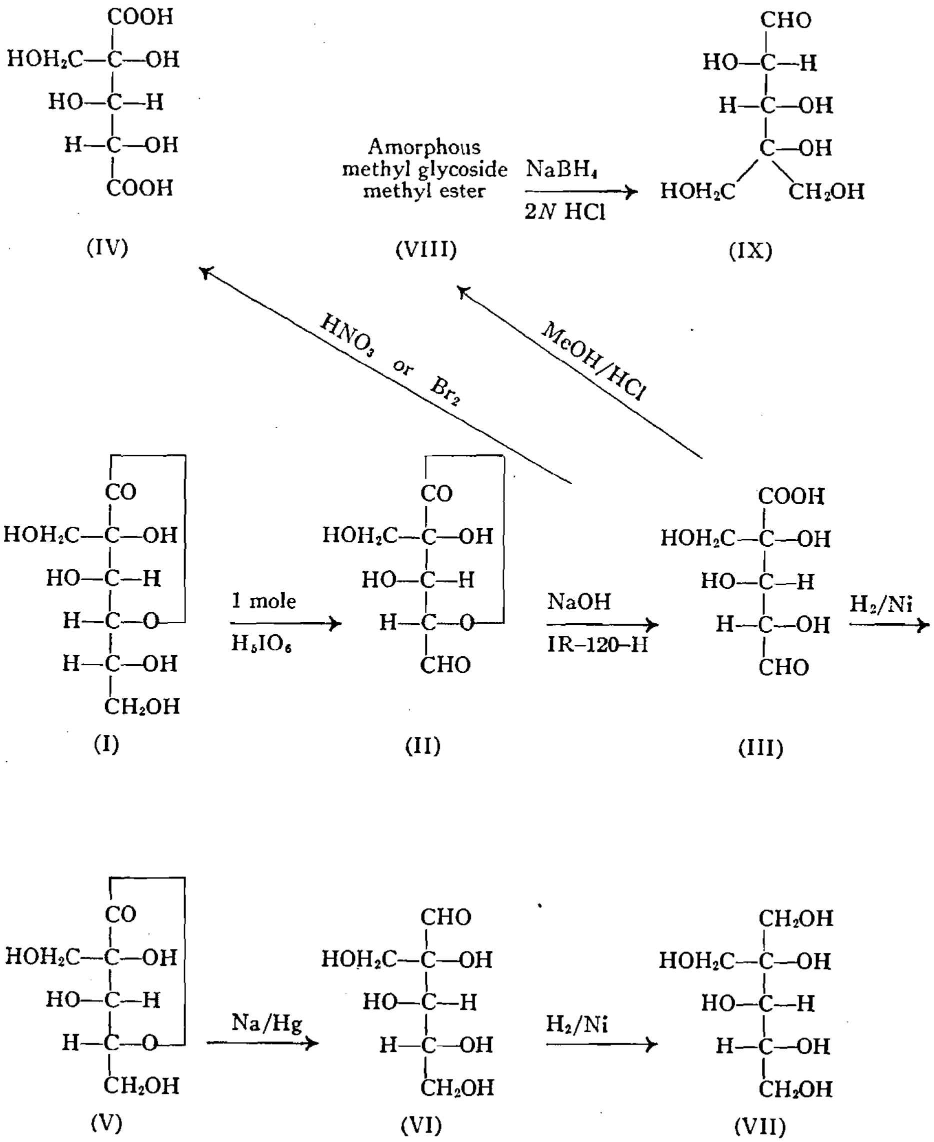

FIG. 1. Branched-chain carbohydrates from D-α-fructoheptonic lactone (I).

Reduction of the carboxyl group (21) of III without reduction of the aldehyde group gave the sirupy 4,4-di(*C*-hydroxymethyl)-D-threose (IX). This aldose was characterized as a crystalline 2,5-dichloro-phenylhydrazone. It also formed an osazone.

The alcohol (VII) was a sirup even after purification as a crystalline hexaacetate. Its optical rotation, as well as that of fructoheptitol (23), is higher than is usual for unsubstituted pentitols or hexitols. This may be occasioned by distortion of the usual intramolecular arrangement by the side chain (13).

It is difficult to establish the configuration of the asymmetric tertiary carbon in branched-chain carbohydrates since there are no compounds of established configuration to which they can be directly related. The configurations of the branched-chain sugars, apiose (19) and cordycepose (2), were established by applying the empirical acid–salt (15, 16), amide (11, 12), or phenylhydrazide (10, 17) rules to the corresponding aldonic acids and their derivatives. Since the tertiary carbon is not asymmetric in these sugars there is no reason to question the validity of this procedure. Streptose has an asymmetric tertiary carbon but its structure has been fully determined, largely by degradation to compounds of known configuration (3, 8, 22). It was found that dihydrostreptosonic acid obeyed the hydrazide and amide rules (14) thus suggesting that the empirical rules of rotation can be applied to carbohydrates having an asymmetric tertiary carbon atom. Freudenberg *et al.* (6, 7) have concluded that the acid–salt, amide, and phenylhydrazide rules are applicable to α-methyl-α-hydroxy fatty acids.

The rules of rotation have been used by Schmidt and Weber-Molster (20) to assign configurations to three different 2-*C*-hydroxymethyl aldonic acids. They found that hamamelonic acid resembled ribonic acid, D-α-fructoheptonic acid resembled gluconic acid, and D-β-fructoheptonic acid resembled mannonic acid. These acids were thus taken to be the 2-*C*-hydroxymethyl-D-ribonic, 2-*C*-hydroxymethyl-D-gluconic, and 2-*C*-hydroxymethyl-D-mannonic acid, respectively. The configuration assigned to the compounds in this paper is based on Schmidt's formulation of D-α-fructoheptonic acid as 2-*C*-hydroxymethyl-D-gluconic acid. The data on which the assigned configurations are based are collected together in Table II.

TABLE II
SPECIFIC ROTATIONS*

	Free acid	Na salt	Amide	Phenylhydrazide
D-Gluconic acid	−13	+22.5	+61	+35
D-α-Fructoheptonic acid	−45.7	−28.7	−21	+30.5
D-β-Fructoheptonic acid	+ 3.2	+ 5.2	—	−97
D-Mannonic acid	− 2	−19.2	−33.6	−30
D-Ribonic acid	−29.2	+ 4.3	+27.1	+53.8
Hamamelonic acid	−35.6	− 9	—	+97
D-Arabonic acid	+15.8	−11.8 (Calcium salt)	−63.4	−35.6
D-Xylonic acid	− 5	+30.6 (Strontium salt)	+73.5	+50.4
2-*C*-Hydroxymethyl-D-xylonic acid	−57	−34.9	—	—
D-Lyxonic acid	+11	−19	—	−33

* *The rotations tabulated are as given by Schmidt and Weber-Molster (20) except the values for* D-*xylonic and* D-*lyxonic acid which are taken from the current literature and the values for 2-hydroxymethyl-*D-*xylonic acid which are from this paper.*

Schmidt and Weber-Molster were led to the conclusion that the amide and phenylhydrazide rules were applicable to the 2-substituted acids though the acid–salt rule could not be used. We now have the opportunity of applying the latter rule to 2-*C*-hydroxymethyl-D-xylonic acid with the knowledge that the branched-chain acid has the same configuration at carbon-2 as D-α-fructoheptonic acid. These acids and their derivatives are listed in Table II. The corresponding derivatives of xylose and lyxose are included for comparison. It can be seen that the branched-chain acid derivatives listed obey the empirical rules if the emphasis is altered from the absolute sign of the rotation of the derivatives to the rotations of the derivatives relative to those of the free acids. Thus, if the rules are stated in the form, "the hydroxyl group will be on the right (D) in the normal vertical formula if the salt, amide, and phenylhydrazide are more dextrorotatory, or less levorotatory, than the acid," then the accepted carbon-2 configurations of the acids can be predicted by this generalization. The acid–salt relationship of D-β-fructoheptonic acid is anomalous though the difference between the two rotations is probably not sufficiently great for the rule to be applied with any confidence in this case.

EXPERIMENTAL

General Methods

The micromelting points were determined on a Kofler block and are corrected. Anions and cations were removed from solutions by the weakly basic and strongly acidic Amberlite IR-4B and IR-120 resins respectively, and the filtrates, and other aqueous solutions, were evaporated under reduced pressure in a Craig evaporator (4) (bath temperature about 50–60° C.; 10 mm. pressure). The brucine salts all crystallized with solvent of crystallization, which could not be easily removed. Unless the conditions of drying are specified the physical properties given for these salts are for material dried overnight in a vacuum desiccator containing phosphorus pentoxide and evacuated to about 0.1 mm. The pure salts were crystallized to constant rotation, taken after a standard drying period. Aldose equivalents were determined by oxidation with alkaline iodine as has been used with glucose (9).

Yield of Formaldehyde on Periodic Acid Oxidation of Lactones

Samples of the lactones (1 millimole) were dissolved in water (10 ml.), the solution was cooled in an ice-bath, and the appropriate quantity of 0.1 *M* or 0.5 *M* periodic acid solution added. Excess periodic acid and iodic acid were decomposed with arsenite solution and the formaldehyde was weighed as the dimedone derivative (1). All samples of the formaldehyde-dimedone had m.p. 196 to 198° (uncorr.), undepressed upon admixture with an authentic sample of formaldehyde-dimedone prepared in a similar manner, m.p. 196–197.5° (uncorr.). The results are collected in Table I.

Preparation of 4-C-Hydroxymethyl-L-xyluronic Acid (III)

A solution of periodic acid (54.8 gm.; H_5IO_6) in water (200 ml.) was added dropwise to a solution of 50 gm. of crystalline D-α-fructoheptonic lactone (23) in 400 ml. of water, the reaction vessel being cooled in an ice–salt bath. After the addition was complete (about 30 min.) the reaction mixture was allowed to stand at 4° overnight and then, while still cold, was passed through a column of Amberlite IR-4B resin sufficient to remove the inorganic acids present (about 350 ml. of resin). The usual precipitation methods of removing the iodic acid were unsatisfactory as traces of this oxidizing acid remained and the hexuronic acid could only be isolated with difficulty and in small yield. Sodium hydroxide solution (N) was added to the filtrate and washings (about 2500 ml.; pH 3.5) from a Beckman automatic titrator set to maintain the pH at 8.0. About 200 ml. was required over a period of four hours. Cations were removed from the solution by passage through a column of cation-exchange resin and the filtrate evaporated to a sirup which crystallized when diluted with ethanol and seeded with the solid acid prepared as described below. The crystals were filtered off, washed with ethanol, and dried (32 gm.; 68%), $[\alpha]_{\mathrm{D}}^{23.3^\circ}$ -63.9° after two hours (c, 4 in water). Recrystallization from aqueous ethanol gave *4-C-hydroxymethyl-L-xyluronic acid* as short needles, m.p. about 180° (decomp.), $[\alpha]_{\mathrm{D}}^{25.2^\circ}$ -39.45° changing rapidly to -64.21° (c, 1.75 in water). (Found: C, 35.7; H, 5.15; neutralization equivalent, 198.5; aldose equivalent, 189. $C_6H_{10}O_7$ requires C, 37.1; H, 5.2; equivalent weight, 194.)

The mother liquors from which the crystalline acid had separated were neutralized with sodium hydroxide solution, the cations removed, and the theoretical amount of brucine was added. The crude brucine salt (37 gm.; $[\alpha]_{\mathrm{D}}$ -28.6) was recrystallized from aqueous ethanol and dried over calcium chloride in a vacuum desiccator; (21 gm.), m.p. 167–168°, $[\alpha]_{\mathrm{D}}^{26.5^\circ}$ -25.15° (c, 4.7 in water), unchanged by further recrystallization from the same solvent. (Observed constants for the brucine salt of D-α-fructoheptonic acid, m.p. 170°, $[\alpha]_{\mathrm{D}}^{23^\circ}$ -26.65°.) Regeneration of the acid from a small portion of the brucine salt gave a sirup which crystallized slowly. The solid crystallized from ethanol as needles, m.p. 130–130.5°, $[\alpha]_{\mathrm{D}}^{22.1^\circ}$ 77.2° (c, 2.0 in water). A specimen of D-α-fructoheptonic lactone had $[\alpha]_{\mathrm{D}}^{23.6^\circ}$ 77.8° and m.p. 130°, unchanged upon admixture with the material just described. The weight of pure brucine salt corresponds to a recovery of 6 gm. of starting lactone, giving an over-all conversion from D-α-fructoheptonic lactone to the crystalline acid of 77%.

Seeds of the crystalline hexuronic acid were first obtained as follows. The calculated amount of brucine was added to a solution of hexuronic acid, free from iodic acid, obtained from 50 gm. D-α-fructoheptonic lactone, and the solution evaporated to a viscous sirup. The brucine salt crystallized when the sirup was diluted with an equal volume of ethanol and cooled. Fractional crystallization of the brucine salt from aqueous ethanol gave three fractions showing constant optical rotation; (a) a brucine salt, probably that of D-α-fructoheptonic acid, (5.5 gm.) $[\alpha]_{\mathrm{D}}^{25^\circ}$ -27.65° (c, 4.2 in water), (b) a salt (20.2 gm.) m.p., after drying over phosphorus pentoxide for seven days, 166–168° (decomp.), $[\alpha]_{\mathrm{D}}^{24.4^\circ}$ -32.15° (c, 4 in water). (Found: C, 57.0; H, 6.35; N, 5.0%), and (c) a salt (73.0 gm.) m.p., after drying over phosphorus pentoxide for five days, 178° (decomp.), $[\alpha]_{\mathrm{D}}^{24.4^\circ}$ -40.55° (c, 4.2 in water). (Found: C, 59.45; H, 5.9; N, 5.05%.) A mixture of equal parts of the salts (b) and (c) melted at 161–165° (decomp.).

Both unidentified brucine salts (m.p. 166–168° and m.p. 178°) yielded crystalline 4-*C*-hydroxymethyl-L-xyluronic acid, which was obtained in 16% and 34% yield (w/w) respectively. The acid from the lower melting salt had m.p. about 180° (decomp.), $[\alpha]_{\mathrm{D}}^{25.2^\circ}$ -41.2° changing to -64.2° (c, 1.7 in water), and the acid from the higher melting salt m.p. 177–180° (decomp.), $[\alpha]_{\mathrm{D}}^{24.4^\circ}$ -40.2° changing to -65.4° (c, 4.2 in water). Both samples of acid gave a brucine salt m.p. 174° (decomp.), $[\alpha]_D^{24.4°}$ $-40.45°$ (*c*, 4.2 in water.) It seems probable that the lower melting of the two brucine salts was a double salt containing the salt of the hexuronic acid and the salt of D-α-fructoheptonic acid, although this was not verified and only one acid could be isolated from it.

If the crude reaction product, free of inorganic acid, was evaporated, and the neutralization and deionization stages were omitted, a sirup (46.3 gm.; $[\alpha]_D^{24.8°}$ 36.1) was obtained which could not be crystallized, though a sample of the sirup deposited the hexuronic acid described above when left at room temperature for eight weeks. Subsequent neutralization and deionization of the uncrystallizable sirup enabled the crystalline acid to be isolated in the usual yield. Only a single phenylhydrazine condensation product could be isolated from either the sirupy lactone or the crystalline acid. From either material this was obtained from ethanol as yellow, unstable needles, m.p. 160° (decomp.). (Found: C, 57.26; H, 5.85. $C_{18}H_{22}N_4O_5$ requires C, 57.74; H, 5.92.) The product separated in a gelatinous condition and could not be purified satisfactorily.

*Bromine Oxidation of 4-C-Hydroxymethyl-*L*-xyluronic Acid*

The acid (5.0 gm.) was dissolved in water (50 ml.) containing suspended calcium carbonate (30 gm.), the solution cooled to 5°, and bromine (3 ml.) was slowly added with stirring. After standing overnight at 25°, the mixture was filtered and the filtrate concentrated under reduced pressure until free of bromine. The sirup was diluted and filtered through a column of cation exchange resin and again concentrated under reduced pressure, and the sirup was kept at about 40° at 10 mm. for one hour to remove hydrogen bromide in so far as possible. A solution of brucine (30 gm.) in ethanol (100 ml.) was added to the sirup and the solution kept at 4° overnight. The crude salt (37.4 gm.; m.p. 200–205° uncorr.) was dissolved in a minimum of water and the excess brucine removed by extraction with chloroform. The salt crystallized as transparent rectangular plates after the addition of ethanol, (22.1 gm.) m.p. 210° (decomp.). Further recrystallization of a sample gave the pure brucine salt, m.p. 208° (decomp.), $[\alpha]_D^{24.2°}$ $-41.2°$ (*c*, 4.3 in water). Regeneration from the brucine salt (6.5 gm.; m.p. 208° decomp.) gave an acid sirup (1.1 gm.), $[\alpha]_D^{23°}$ $-27.7°$ (*c*, 1.2 in water), which upon treatment with ammonium hydroxide solution gave the crystalline diammonium salt of 2-hydroxymethyl-D-xylaric acid as needles from water and aqueous ethanol, m.p. 146–149° (decomp.), $[\alpha]_D^{23°}$ $-36.1°$ (*c*, 2.1 in water). (Found: C, 29.78; H, 6.63; N, 11.39. $C_6H_{16}O_8N_2$ requires C, 29.51; H, 6.60; N, 11.47%.)

Regeneration from the diammonium salt (1.9 gm.) gave 2-*C-hydroxymethyl-*D-*xylaric acid* as a colorless sirup (1.58 gm.), $[\alpha]_D^{25.0}$ -24.88 after five minutes changing to $[\alpha]_D^{23.0}$ $-27.70°$ after 75 hr. (*c*, 2.75 in water). (Found: C, 34.79; H, 4.77; neut. equiv., 106. $C_6H_{10}O_8$ requires C, 34.30; H, 4.80%; neut. equiv., 105.)

*Nitric Acid Oxidation of 4-C-Hydroxymethyl-*L*-xyluronic Acid*

A solution of the uronic acid (7.0 gm.) in water (10 ml.) and nitric acid (10 ml.; specific gravity, 1.4) was kept at 25° for 48 hr. The solution was evaporated under reduced pressure to a thick sirup and the bulk of the nitric acid removed by repeating the concentration three times after the addition of successive portions of water (100 ml.). Oxalic acid was removed by continuous extraction with ether and the aqueous solution was treated with an excess of brucine; the excess was then removed by extraction with chloroform. The crude brucine salt crystallized when the solution was diluted with ethanol and was recrystallized from aqueous ethanol to give the pure salt as transparent plates (7.75 gm.), m.p. 208° (decomp.), $[\alpha]_D^{23.2}$ $-40.7°$ (*c*, 4.1 in water). Regeneration from a portion of the brucine salt gave a sirup, $[\alpha]_D$ $-28.6°$ (*c*, 7.2 in water) which gave a diammonium salt $[\alpha]_D^{23°}$ $-36.65°$ (*c*, 2.3 in water), m.p. 147–149° (decomp.), which was unchanged upon admixture with the salt obtained from the bromine oxidation described above.

In a subsequent experiment, carried out under identical conditions, the brucine salt obtained had m.p. 170–172°, $[\alpha]_D^{26°}$ $-30.6°$ (*c*, 2.1 in water), and yielded an acid sirup $[\alpha]_D^{23°}$ $-8.8°$ (*c*, 4 in water) which formed an ammonium salt identical with that described above. Oxidation at 60° for 15 hr. gave an acid sirup and diammonium salt identical with those just described.

*2-C-Hydroxymethyl-*D*-xylonic Lactone* (V)

A solution of the crystalline hexuronic acid (15 gm.) in water (50 ml.) was shaken in an atmosphere of hydrogen, in the presence of a Raney nickel catalyst (10 gm. moist solid), at 3700 lb./sq. in., and 100° C. for 12 hr., when it was found to contain less than 5% of the original aldose content. After cooling, the solution was filtered, titrated at pH 7.8 with sodium hydroxide (*N*) solution using a Beckman automatic titrator, and passed through a column of cation exchange resin. The calculated amount of brucine was added and the solution concentrated to a thin sirup which crystallized when diluted with ethanol (2–3 volumes). The crude salt (28.4 gm.) had m.p. 173–174.5°, $[\alpha]_D^{26}$ $-27.4°$ (*c*, 4.2 in water), and was recrystallized once from aqueous ethanol to give the pure salt, m.p. 175°, $[\alpha]_D^{28}$ $-28.35°$ (*c*, 4.2 in water). The acid was regenerated from a solution of the pure brucine salt (25 gm.) in water (75 ml.) by adding sodium hydroxide solution (25 ml.: 2 *N*), filtering off the precipitated brucine, and passing the filtrate through a column of cation exchange resin. After evaporation of the acid solution the crude sirup (9.2 gm.) was heated on the steam bath for two and one half hours, triturated with acetone, and allowed to crystallize. The crude solid (4.75 gm.; m.p. 120–121.2°) was recrystallized from a mixture of ethanol and acetone to give the pure *lactone* as rectangular prisms, m.p. 121°, $[\alpha]_D^{25.5°}$ 107.4° (*c*, 2.2 in water). (Found: C, 40.37; H, 5.95; neutralization equivalent, 179. $C_6H_{10}O_6$ requires C, 40.45; H, 5.66%; neut. equiv., 178.) The product did not reduce alkaline iodine solution. With excess periodic acid 1 mole of the lactone gave 1.95 and 1.98 moles of formaldehyde, determined as the dimedone derivative (see Table I).

The pure lactone gave a brucine salt crystallizing from aqueous ethanol as flat colorless needles, m.p. 175°, $[\alpha]_D^{25}$ $-28.41°$ (*c*, 4.2 in water). (Found: C, 57.6; H, 7.35%.) Addition of the equivalent quantity of standard sodium hydroxide solution to a portion of the lactone gave a solution of sodium 2-*C*-hydroxymethyl-D-xylonate, $[\alpha]_D^{23.5°}$ $-16.0°$ (4.2 in water). Further addition of the equivalent quantity of standard hydrochloric acid gave a solution containing the free acid, $[\alpha]_{\mathrm{D}}^{23.5°}$ −29.1° changing to −47.4° in 30 days (*c*, 1.8 in water). A sirupy ammonium salt, prepared by adding excess ammonium hydroxide solution to the pure lactone and allowing the solution to evaporate had, after drying over phosphorus pentoxide for 48 hr., $[\alpha]_{\mathrm{D}}^{22.6°}$ −13.85° changing rapidly to −14.25° (*c*, 13 in water). (Found: C, 33.33; H, 7.09. $C_6H_{13}O_6N$ requires C, 33.80, H, 7.09%.)

When the hydrogenation was carried out under milder conditions (2000 lb./sq. in. and 100° C. for two hours) no appreciable reduction occurred and 75% of the starting material could be recovered in the crystalline condition.

*2-C-Hydroxymethyl-*D*-xylose* (VI)

Mother liquors from which crystalline 2-*C*-hydroxymethyl-D-xylonic lactone had been obtained were evaporated and the residue was heated for two hours on the steam bath. The viscous sirup (4.9 gm.) was assumed to be a mixture of the γ and δ lactones since the parent acid had been regenerated from a homogeneous brucine salt. A solution of the sirup in an oxalate buffer solution (4.0 gm. oxalic acid dihydrate in 35 ml. warm water diluted with 16 ml. 2 *N* sodium hydroxide solution) was cooled in an ice-salt bath. Sodium amalgam (89 gm.; 3%) was added portionwise, while the temperature was kept below 10°, and the pH was maintained below 4 by the addition of powdered oxalic acid. After being stirred for a further 45 min., the cold solution was filtered, passed through cation- and anion-ion-exchange resins, and evaporated to a thin sirup. 2,5-Dichlorophenylhydrazine (5.5 gm.) in methanol (30 ml.) was added and the mixture evaporated on the steam bath. The residue set solid on cooling. After washing with ether and water, the crude solid (5.35 gm.; 57%; m.p. 160°) was recrystallized from aqueous ethanol and ethanol to give the pure *2,5-dichlorophenylhydrazone* as colorless plates, m.p. 162–162.5°, $[\alpha]_{\mathrm{D}}^{22.7}$ −9.75° (*c*, 4.1 in pyridine). The magnitude of the rotation fell on standing but the change was accompanied by darkening of the solution so that an equilibrium value could not be obtained. (Found: C, 42.70; H, 4.76; Cl, 20.59. $C_{12}H_{16}O_5N_2Cl_2$ requires C, 42.49; H, 4.76; Cl, 20.91%.)

The sugar did not form an osazone under the usual conditions of osazone formation. A colorless, waxy solid, presumably a phenylhydrazone (cf. Woods and Neish (23)), was obtained from the reaction mixture at one stage, however in the crude state the solid was very unstable and we were not able to isolate any pure material.

The sugar was recovered from the 2,5-dichlorophenylhydrazone (3.0 gm.) after a solution of the derivative in ethanol (25 ml.) and water (37.5 ml.) was refluxed with benzaldehyde (7.5 ml.) and benzoic acid (0.75 gm.), as previously described (23). The resulting sirupy sugar crystallized from an ethanolic solution upon standing for several weeks (1.50 gm.; 94%), m.p. 107–109° (uncorr.), and was recrystallized from ethanol and acetic acid to give the pure sugar as small, colorless needles, m.p. 106–107°, $[\alpha]_{\mathrm{D}}^{24.5°}$ 30.65° after four minutes changing rapidly to 17.45° (*c*, 2.2 in water). (Found: C, 39.93; H, 6.71. $C_6H_{12}O_6$ requires C, 40.0; H, 6.71%.) Aldose equivalent, 182; equivalent wt., 180.

Crystalline 2-*C*-hydroxymethyl-D-xylonic lactone (1.5 gm.; m.p. 120.5–121°) was reduced with sodium amalgam (27 gm.; 3%) as previously described. The sirupy sugar crystallized when triturated with ethanol and seeded with the solid sugar obtained above (0.71 gm.), m.p. 105–106°, unaltered upon admixture with the above sugar (m.p. 106–107°).

*1,1-Di(C-hydroxymethyl)-*D*-threitol Hexaacetate*

A solution of crystalline 2-*C*-hydroxymethyl-D-xylose (5.0 gm.) in water (15 ml.) was shaken in an atmosphere of hydrogen, in the presence of a Raney nickel catalyst (1 gm.) until the uptake of hydrogen ceased (four hours), at 2600 lb./sq. in. and 100° C. The catalyst was filtered off and the filtrate concentrated to a sirup (5 gm.) containing 2.4% of unreduced sugar (estimated by hypoidite oxidation).

The bulk of the sirup (4.8 gm.) was acetylated by refluxing with anhydrous sodium acetate (4.7 gm.) and acetic anhydride (60 ml.) for four hours. Isolation of the product in the usual manner gave a gummy acetate which was dissolved in benzene (10 ml.) and filtered through a column of alumina (200 gm.; Merck, washed with 10% acetic acid and then water and dried at 180°). Evaporation of the eluate and washings (1 liter of benzene), which had been collected portionwise, gave fractions all of which crystallized rapidly. The crude fractions (m.p. from 70° to 75° uncorr.) were combined and gave the pure *hexaacetate* (7.4 gm.) as prisms after a single recrystallization from ethanol, m.p. 73°, $[\alpha]_D^{23.0°}$ 27.78° (*c*, 5.3 in chloroform). (Found: C, 49.85; H, 5.97; $CH_3.CO.$, 59.0. $C_{18}H_{26}O_{12}$ requires C, 49.77; H, 6.03; $CH_3CO.$, 59.44%.)

The hexaacetate is only weakly adsorbed by the alumina used for removing impurities which hinder the crystallization of the crude acetate. These impurities appear to be strongly adsorbed and to be present in only small amounts so the amount of alumina used above is excessive. Once seeds had been obtained the crude acetate could be crystallized directly.

*1,1-Di(C-hydroxymethyl)-*D*-threitol* (VII)

A solution of the pure hexaacetate (3.6 gm.) in anhydrous methanol (15 ml.) and methanolic sodium methoxide solution (0.2 ml.; 2 *N*) was allowed to stand at room temperature for 24 hr. and then evaporated. The sirup was taken up in a little water and extracted with chloroform, then evaporated to give a viscous sirup which was dried over phosphorus pentoxide for 48 hr. (1.8 gm.), $[\alpha]_D^{21.8°}$ $-10.2°$ (*c*, 17.7 in water).

*4,4-Di(C-hydroxymethyl)-*D*-threose 2,5-Dichlorophenylhydrazone*

A solution of the 4-*C*-hydroxymethyl-L-xyluronic acid (4.7 gm.) in anhydrous methanol (200 ml.) containing hydrogen chloride (1% w/w) was kept at room temperature for 12 hr., concentrated and the sirup stored in a vacuum desiccator over potassium hydroxide until free of hydrogen chloride (5.1 gm.), $[\alpha]_D^{25.8°}$ -96.5 (*c*, 4.73 in water). The glassy residue (VIII) was dissolved in water (15 ml.) and added dropwise and with stirring to a solution of sodium borohydride (1.0 gm.) in water (20 ml.) during 25 min. The temperature was kept below 40° by the occasional addition of a piece of ice. The stirring was continued for a further 15 min. and 2 *N* sulphuric acid was added until the evolution of hydrogen ceased. After standing at 4° for three hours the solution was passed through columns of IR-120 and IR-4B resins and the filtrate evaporated to give a brittle, fluffy solid (3.6 gm.). The solid was heated on the steam bath with dilute hydrochloric acid (36 ml.; 2 *N*) for two hours and the solution cooled and filtered through a column of IR-4B resin. It was then concentrated to a thin sirup, evaporated on the steam bath with a solution of 2,5-dichlorophenylhydrazine (4 gm.) in methanol (40 ml.), and set aside overnight. The solid which separated was washed with ether and water and crystallized from aqueous ethanol to give the pure *hydrazone* as colorless plates (1.4 gm.), m.p. 137–138°. (Found: C, 42.49; H, 4.76; Cl, 20.60. $C_{12}H_{16}O_5N_2Cl_2$ requires C, 42.49; H, 4.76; Cl, 20.91%.)

4,4-Di(C-hydroxymethyl)-D-*threose* (IX)

A portion of the 2,5-dichlorophenylhydrazone (0.9 gm.; m.p. 137–138°) was treated with benzaldehyde as described above to give the free sugar as a colorless, viscous sirup (0.47 gm.) $[\alpha]_D^{22.6°}$ −60.12° (*c*, 4.7 in water). Found: aldose equivalent, 204, required 180. From this the rotation of the anhydrous sugar is $[\alpha]_D^{22.6}$ −68.2°. The sugar gave a gelatinous yellow osazone when it was warmed with phenylhydrazine acetate for 15 min. and the resulting solution was cooled; m.p. of the dried material 109–111° (uncorr.).

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THE SILVER CATALYZED OXIDATION OF ETHYLENE

II. KINETICS OF C_2H_4 OXIDATION[1]

By A. Orzechowski[2] and K. E. MacCormack

ABSTRACT

A flow-type apparatus is described and results given for the investigation of the kinetics of the silver catalyzed oxidation of C_2H_4 by oxygen. Using N_2 as diluent, the concentrations of both O_2 and C_2H_4 were varied independently from 9.9 to 79.0% and 2.35 to 9.40% respectively, whilst maintaining a total pressure of 1 atmosphere. Flow rates were varied to give a range of contact times varying from 0.05 to 1 sec. Measurements were made at 234° C. and 274° C. and the data used to estimate initial reaction velocities for both EtO and CO_2 formation as a function of O_2 and C_2H_4 partial pressures. These rates were fitted successfully to equations deduced theoretically in Part IV of the present series.

INTRODUCTION

The development of a catalytic process for the direct oxidation of C_2H_4 to ethylene oxide (EtO) was undertaken in these laboratories several years ago. In spite of the extensive work of Twigg (12) and others it was thus considered important to verify and extend the investigation of the kinetics and proposed mechanism of the reactions concerned. Comprehensive surveys of the work in this field have been presented recently by Pokrovskii (8) and Schultze and Theile (10).

The catalyst developed by Cambron and McKim (3) was used coupled with their principles of reactor design (5) whereby excellent temperature control could be maintained, especially where the highly exothermic CO_2 formation is involved. This catalyst was sufficiently active to permit its convenient adaptation to a flow system with contact times less than one second. Burgoyne and Kapur (2) have reported that EtO undergoes about 30% homogeneous oxidation in one hour at 300° C. It is questionable, therefore, whether static systems involving long contact times can give reliable information for the study of the kinetics of heterogeneous C_2H_4 oxidation.

This paper presents the results of investigations employing wide variations of O_2 and C_2H_4 partial pressures with N_2 as diluent in a flow system maintained throughout at 1 atmosphere. Procedure was adopted according to the findings in Part I of this series, whereby all measurements were made for the catalyst maintained in the same reference state of activity.

APPARATUS

Cylinder gases, O_2, N_2, and C_2H_4 were used throughout with purities specified in Part I. Two-stage reducing valves followed by series needle valves ensured very constant flow rates measured by capillary flow meters carefully calibrated and having an accuracy of ±1%. These could be adjusted and left without attention for periods up to 24 hr.

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The catalyst (3) was prepared by grinding a Ag–Ca alloy containing 8.5 wt. % Ca and pressing the granules (−20 + 100 mesh) on to pure Ag sheets of 1 mm. thickness. The compacted sheets were then steamed for five hours at 350° C. and subsequently boiled for two hours in 20 vol. % aqueous acetic acid.

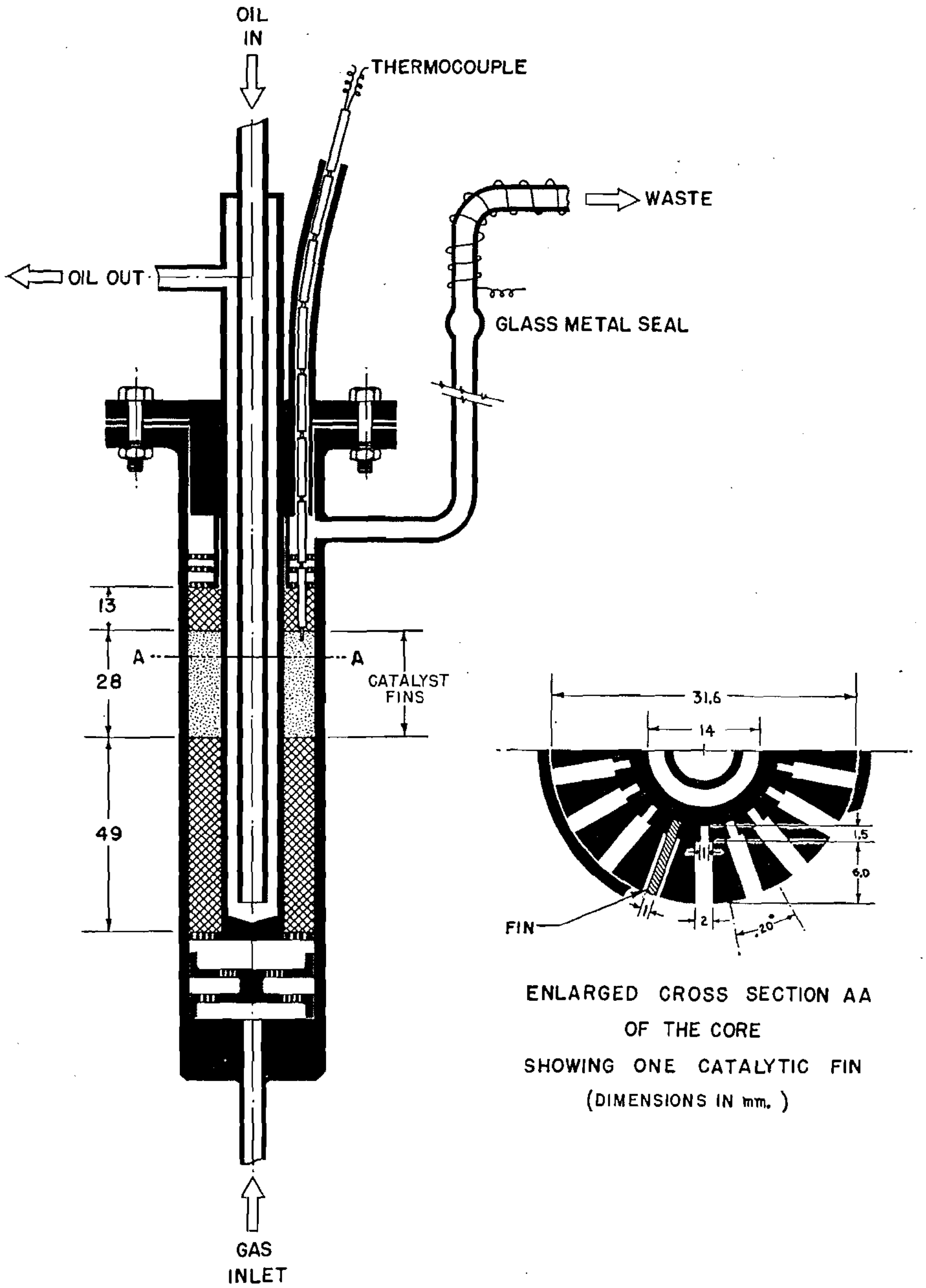

FIG. 1. Diagram of reactor.

By this treatment the Ca content was reduced to 0.48 wt. % to give a highly porous and active catalyst.

The reactor, made of brass and silver plated inside, shown in Fig. 1, consisted essentially of a central core carrying circulating oil as the heat transfer medium and of a shell machined to fit very closely. Catalyst strips or fins are mounted radially in 18 longitudinal grooves cut 0.15 cm. deep in the core surface. Each fin shown as the shaded area in the cross section A–A was 2.8 cm. long × 0.75 cm. wide. The free space between each fin was reduced by fillers on the core, shown as the black areas in the cross section A–A. The lower and extreme upper portion of the core carried similarly mounted pure Ag fins (cross-shaded area in the side elevation) which served respectively to preheat the reaction mixture and preserve flow symmetry at the end of the catalyst zone. The free cross-sectional area for gas flow comprised 36 rectangular elements each 6.0 × 0.5 mm., equivalent to a total area of 1.1 cm^2. The reaction zone free volume was 3.1 cm^3. Pressure drop through the reactor was negligible at the maximum flow rate of 170 liters/hr., amounting to approximately 8 mm. H_2O. The geometric area of the exposed catalyst surface was 60.5 cm.^{2}, whereas on the basis of B.E.T. area measurements on a similar catalyst sample, the actual area would be approximately six square meters, assuming a total of 12 gm. of granular catalyst compacted on the fins.

One fin was cut near the end, normal to the core axis and the short fin thereby produced was firmly peened into the groove. A chromel–alumel thermocouple was previously silver-soldered to this isolated fin. In this way only a small fraction of the total catalyst was damaged by the heat necessary during soldering. Though the catalyst surface temperature was not measurable, the location of the couple was adequate for the determination of a reference temperature level.

The thermocouple insulated by ceramic sections passed through a long narrow copper tube to a seal of neoprene tubing made leakproof by a strong clamp on the bare thermocouple wires. The reactor and oil lines were grounded and well insulated by a thick layer of magnesia cement.

The rapidly circulating heat transfer oil (total vol. 500 cc.) was pumped and heated externally, partially by intermittent heat input supplied through a Bristol controller, activated by a thermocouple immersed in the oil. The temperature of the catalyst was measured using a Wheelco model 311 potentiometer and recorded continuously. It was maintained constant within ±0.5° C. over periods of 24 hr. without attention.

In the absence of catalyst no reaction products could be found under operating conditions.

The variations of feed flow rate from 10 to 200 liters N.T.P./hour, which were used, corresponded approximately to contact times of 1 to 0.05 sec.; linear velocities, 2.5 to 50 cm./sec.; Reynolds numbers, 1 to 20. The flow was thus always laminar.

Gas Analysis

Fig. 2 shows the assembly used for gas analysis. Samples varying from 70 to 1000 cm.^{3} were drawn, at a rate slower than the feed flow rate, into the

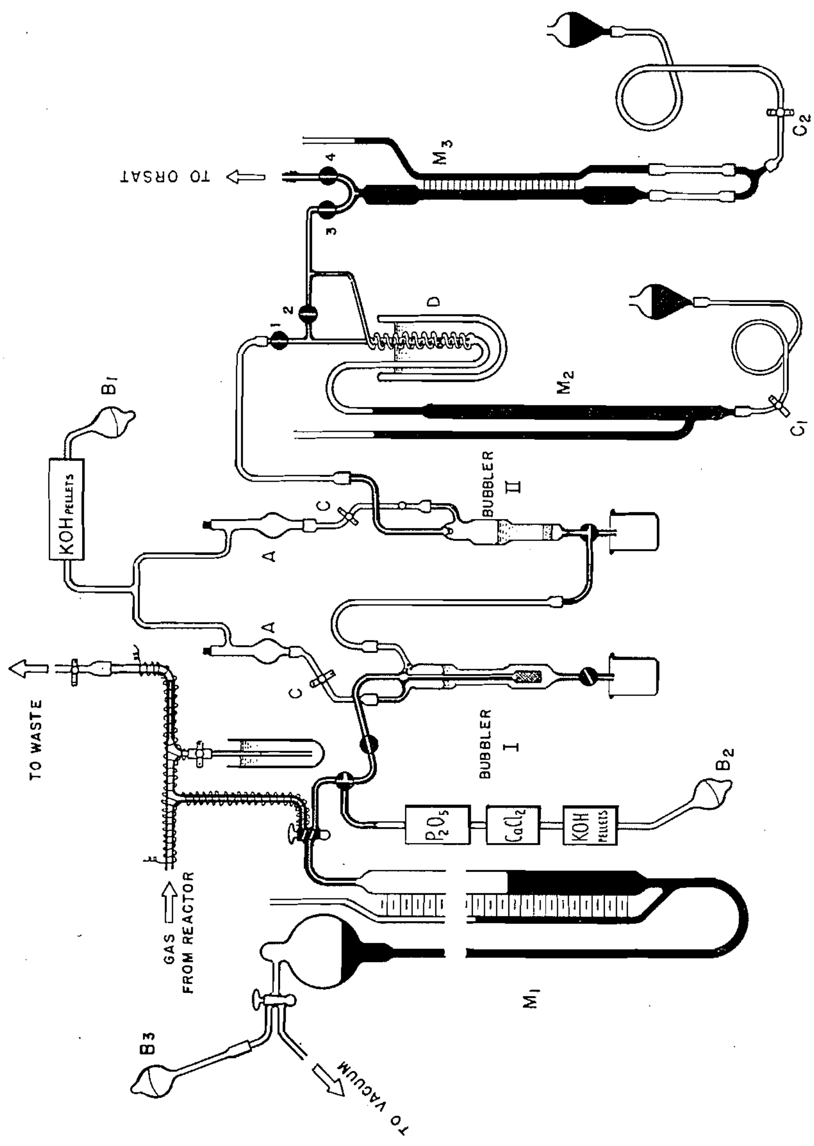

FIG. 2. Gas analysis apparatus.

gas burette, M_1, and, after measuring pressure and temperature the volume was read within 0.5 cm^3. The gas was then forced through the sintered glass bubblers I and II connected in series. Sintered glass was of coarse grade giving very numerous and fine bubbles. Bubbler I contained 10 cc. of 0.05 *N* $HCl–MgCl_2$ solution (1, 4, 6) for EtO absorption, while II contained 5 cc. of 0.1 *N* NaOH for CO_2 absorption. These solutions were pipetted into *A* and forced in by air from rubber bulb B_1.

After gas absorption the excess reagent was back-titrated with reagents of appropriate normality contained in microburettes.

It was shown during blank tests on mixtures of known composition within the experimental range that the II bubbler was efficient for complete absorption of CO_2, that no acid vapors were carried on from I to II, but approximately 2% of EtO could escape absorption in 0.05 *N* $HCl–MgCl_2$ reagent, with a maximum 3% of CO_2 being lost by solution in I, especially with this low concentration of reagent used. In spite of this systematic error, it was essential to the maintenance of accuracy at low conversions to employ this low reagent concentration. No correction was applied for this systematic error.

Gas lines were purged by means of air from the rubber bulb B_2 and thorough rinsing was carried out via *A–A* aided by an air stream from B_1 and B_2. In the case of simultaneous C_2H_4 determination following the bubblers the remaining gas passed through a trap, *D*, immersed in liquid O_2 where C_2H_4 was retained in a small volume of about 10 cc. The content of this trap was subsequently quantitatively transferred by mercury from M_2 (returned by siphoning) to the gas burette M_3 and thence to a Burwell-Orsat type apparatus for C_2H_4 determination. The efficiency of this procedure was tested using samples containing 1–4% C_2H_4 in N_2 which showed that at least 96% of the C_2H_4 could be determined.

The outgas from the reactor was mildly heated to avoid condensation prior to sampling.

In the case of gas samples containing H_2O in excess of the saturation value at room temperature, a correction was applied to the measured volume to

TABLE I

MATERIAL BALANCE BY ANALYSIS

% C_2H_4 converted		% C_2H_4 unconverted	Total %	Deviation from 100%
To EtO	To CO_2			
26.5_5	16.4_5	51.6	94.5	−5.5
40.2	32.1	26.6	98.9	−1.1
11.5_6	13.6_5	68.8	94.0	−6.0
11.5_5	13.5	71.0	96.0	−4.0
16.3	20.3	62.2	98.8	−1.2
16.3_5	19.2	63.1	98.6_5	-1.3_5
17.7	19.3_5	57.8	94.8_5	-5.1_5
17.7_5	22.9	55.7	96.3_5	-3.6_5
17.7	22.8	56.2	96.7	−3.3
15.2_5	27.1	55.0	97.3_5	-2.6_5
32.1	35.9	32.6	100.6	+0.6
			Mean deviation	−3.0

allow for the water condensed in the sampling burette. Dry air was added after volumetric measurements were complete, to vaporize the condensate which could retain some ethylene oxide. Since the amount of H_2O is equivalent to the CO_2 produced, the former is accurately known for correction purposes.

Table I indicates the accuracy with which complete determination of the reaction products could be achieved. The mean deviation of -3% from the ideal 100% appears to indicate a systematic error very likely attributable to the incomplete absorption of EtO and C_2H_4 in the reagents used and the probable loss of some CO_2 in bubbler I.

Gas flow rates and titration procedure are each accurate within $\pm 1\%$. Accordingly, the expected accidental error in the final C_2H_4 conversion values is approximately $\pm 2\%$ of the absolute values.

RESULTS

C_2H_4 oxidation was investigated at 274° C. and 234° C., two or three measurements being made after a period of constant operating conditions lasting approximately 24 hr. Reproducibility was within the limits of the foregoing estimated accuracy as is illustrated in Figs. 1 and 2, Part I. The rapid equilibria referred to in Part I were well established in this time with no significant onset of interference by slow processes within the range of composition studied. The latter processes are less significant with decreasing temperature, but may become appreciable when oxygen deficient mixtures are used.

The composition of the gas mixture entering the reactor and its flow rate are expressed by symbols pE_nO_m, where p refers to the flow rate, n to C_2H_4 partial pressure, m to oxygen partial pressure.

Chosen purely for convenience, the unit of total flow rate p is 41.8 liters N.T.P./hour, the unit of ethylene partial pressure n is 17.9 mm. Hg, the unit of oxygen partial pressure m is 75 mm. Hg.

The catalyst quantity, constant throughout, is taken as unity.

The reaction time co-ordinate is defined as: catalyst quantity/gas mixture feed flow rate. For example, $0.5E_2O_2$ refers to a feed flow rate of 20.9 liters N.T.P./hour, the partial pressures in the feed, at total pressure of 1 atm. being C_2H_4, 35.8 mm. Hg; O_2, 150 mm. Hg; the remainder, N_2 and the reaction time co-ordinate is 2.0.

1. Runs at 274° C.

Preliminary conditioning had been carried out at 234° C. along with an investigation of the slow processes described in Part I. At 274° C. treatment involving the standard check run ($1E_2O_2$) approximating a 20:1 air–C_2H_4 mixture, was followed by the kinetic series lasting about 900 hr. The dependence of C_2H_4 conversion on flow rate and partial pressures of C_2H_4 and O_2 are shown in Table II.

All the data are corrected to the reference state finally established at the end of the series (run 49) by the procedure described later. Experimental values measured for the check run conditions at various times through the series are given at the end of this table and indicate a slight decline in total catalyst activity up to run 26.

TABLE II
CONVERSION OF C_2H_4 AT 274° C.
(TOTAL PRESSURE = 1 ATM.)

Run No.	Feed composition symbol	Reaction time co-ordinate	% C_2H_4 converted to:		Selectivity, %	% O_2 converted Total
			C_2H_4O	CO_2		
5	E_2O_2	0.25	17.0	15.2	52.8	12.78
3	"	0.50	26.4	24.3	52.0	20.47
1	"	*1.00*	35.6	33.9	51.3	28.36
2	"	2.00	40.5	41.0	49.1	34.21
4	"	4.00	39.0	49.0	44.3	39.76
11	E_2O_4	0.167	15.4	14.4	51.7	6.07
13	"	0.25	20.0	19.0	51.3	7.99
9	"	0.50	29.0	28.2	50.6	11.81
7, 10	"	*1.00*	38.5	37.5	50.6	15.70
8	"	2.00	41.0	46.6	46.8	19.10
12	"	4.00	38.0	52.5	42.0	21.05
17	E_4O_2	0.25	11.4	10.5	52.0	17.7
15	"	0.50	18.6	17.0	52.2	28.7
14, 18	"	1.00	27.6	26.0	51.5	43.8
16	"	2.00	35.0	33.5	51.0	56.2
19	"	4.00	35.0	39.0	47.2	64.0
24	E_4O_4	0.25	16.0	14.5	52.5	12.29
21	"	0.50	23.6	22.2	51.5	18.72
23	"	*1.00*	32.2	31.0	50.9	26.05
22	"	2.00	38.0	38.5	49.7	32.14
25	"	4.00	38.4	46.4	45.3	37.79
29	E_1O_1	0.20	16.8	15.7	51.7	13.26
27	"	0.50	28.5	27.1	51.1	22.89
28	"	*1.00*	35.6	35.8	49.7	29.91
30	E_1O_1	2.00	37.7	42.1	47.1	34.70
31	"	4.00	31.5	48.4	39.4	38.47
37	E_1O_4	0.125	14.0	14.0	50.0	2.92
36	"	0.250	23.0	23.0	50.0	4.80
32	"	0.50	31.0	32.5	48.8	6.74
33	"	*1.00*	37.2	42.5	46.7	8.71
34	"	2.00	35.0	51.[illegible]	40.4	10.26
35	"	4.00	28.5	58.0	32.9	11.23
38	E_4O_1	0.167	5.8	5.9	49.6	19.66
39	"	0.250	7.8	8.0	49.3	26.60
40	"	0.50	12.5	12.8	49.4	42.61
41	"	*1.00*	16.6	18.8	46.8	61.71
42	"	2.00	17.2	22.3	43.5	72.00
43	"	4.00	14.0	25.8	35.2	80.47
Checks of standard run—E_2O_2						
6	E_2O_2	1.00	38.0	35.0	52.0	After E_2O_2
20	"	1.00	36.8	36.0	50.5	After E_4O_2
26	"	1.00	36.7	33.0	52.6	After E_4O_4
44	"	1.00	32.8	35.9	47.8	After E_4O_1
47	"	1.00	33.5	35.0	49.0	After E_4O_1
48	"	1.00	35.3	34.4	50.7	After E_4O_1
49	"	1.00	35.6	33.9	51.3	After E_4O_1

The final kinetic runs 38–43, using the composition E_4O_1, resulted in almost permanent decrease of selectivity* indicated by check run 44. (Twofold and

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* *Selectivity = % C_2H_4 converted to EtO/total % C_2H_4 converted.*

sixfold increase in flow rate using standard E_2O_2 feed gave similarly abnormal selectivity at this moment: runs 45 and 46 (not shown).)

Attempts were made to restore the original standard selectivity following E_4O_1 runs. Fifty hours operation at $1E_2O_2$ (274° C.) showed slight improvement (run 47) but equally effective was a six hour pretreatment by air (274° C.)—run 48, and further 50 hr. of operation at $1E_2O_2$ (run 49).

For the purpose of studying the kinetics, some reference state for the surface had to be chosen. It should be recalled that the initial and final check runs (run 6 and 49) do not differ much respecting selectivity; on the other hand the total activity declines up to check run 26 and then remains constant; this is most likely attributable to slight over-all sintering of the surface during the first kinetic runs, with subsequent stabilization of the catalyst. Therefore the apparently more stable final state (run 49) was chosen as the reference state for the surface and all experimental values were then corrected on the basis of the relation between this final standard run and the check runs made immediately following each composition group.

Figs. 3 and 4 show C_2H_4 conversions to EtO and CO_2 respectively as a function of the reaction time co-ordinate defined above.

Several analyses for acetaldehyde in the products were made, especially during the runs for E_4O_1, which are likely to constitute the most favorable conditions for its formation; none was ever detected though the method (see Part III) was checked for its sensitivity to quantities which would account for 0.1% conversion of C_2H_4 to acetaldehyde.

2. Runs at 234° C.

A further conditioning period at 234° C. with the standard flow rate and composition ($1E_2O_2$) followed the kinetic series at 274° C. Measurements were made over a period of 100 hr. to ensure that a steady state had been

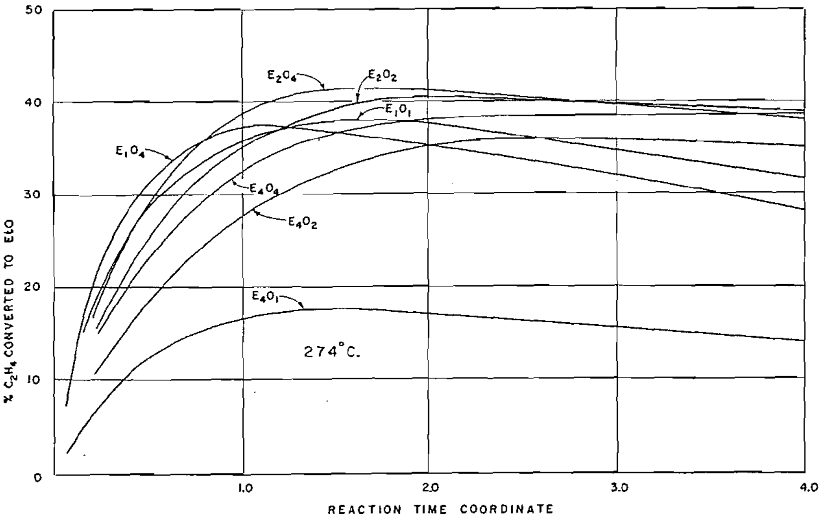

FIG. 3. Conversion of C_2H_4 to EtO at 274° C. vs. reaction time for different feed compositions.

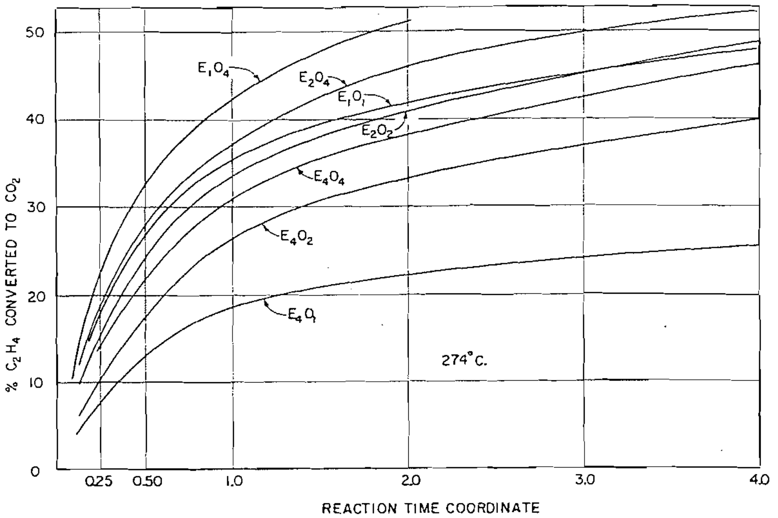

FIG. 4. Conversion of C_2H_4 to CO_2 and H_2O at 274° C. vs. reaction time for different feed compositions.

achieved. The experimental results measured at 234° C. over a total period of approximately 1200 hr. are presented in Table III and plotted in Figs. 5 and 6.

Frequent checks of the reference conditions are included in this table and indicate no departure from the standard state until the oxygen-deficient runs E_4O_1 were made. All subsequent check runs were indicative in general of higher conversion to CO_2 and lower conversion to EtO than were the previous standards. This behavior is similar to that observed at 274° C. and again responded slightly to oxygen treatment (cf. runs 19 and 18). Further recovery was effected by operating with composition E_1O_8 (check run 23). Prolonged operation under standard conditions following E_4O_8 runs effected some restoration of selectivity (cf. runs 27 and 28). The standard reference state of the catalyst adopted here is that of run No. 13.

3. *Corrections of Results for Changed Reference State*

(*a*) *Corrections at 274° C.*

The experimental conversions E_2O_2 established during runs 1–5 were plotted against reaction time co-ordinate. The conversions of $1E_2O_2$ chosen as reference state (run 49) corresponded on this plot to a reaction time co-ordinate only about 0.8 instead of 1. Therefore it was assumed that about 20% of the surface was lost by sintering during the kinetic series, and the reference plot E_2O_2 for the final state of the surface, corresponding to run 49 was established by increasing the reaction time co-ordinate of the experimental conversions in runs 1–5 by a factor of 1/0.8.

In this way the corrected conversions of E_2O_2 (runs 1–5 in Table II) were obtained and were considered to be the reference plot for the other check runs.

Subsequently the other results were corrected by comparing the conversions of check runs made after each composition group with this reference plot

TABLE III

CONVERSION OF C_2H_4 AT 234° C.
(TOTAL PRESSURE = 1 ATM.)

Run No.	Feed composition symbol	Reaction time co-ordinate	% C_2H_4 converted to:		Selectivity, %	Checks *
			C_2H_4O	CO_2		
A. Experimental values						
1	E_4O_4	0.25	5.02	3.36	60.0	
2	"	0.50	8.35	5.26	61.2	
3	"	1.00	14.35	8.35	63.2	
4	"	0.25	5.29	3.36	61.2	
5	E_2O_2	1.00	17.60	10.52	62.6	*
6	E_1O_1	1.00	17.60	11.05	61.5	
7	"	0.50	12.20	8.15	60.0	
8	"	1.00	17.70	11.00	61.6	
9	E_2O_2	1.00	17.05	10.52	61.9	*
10	E_1O_4	1.00	27.80	16.85	62.2	
11	"	0.50	18.62	11.20	62.5	
12	"	0.25	10.70	6.33	62.9	
13	E_2O_2	1.00	16.95	10.50	61.7	*
14	"	0.50	10.80	7.10	60.2	
15	"	0.25	6.73	4.92	57.8	
16	E_4O_1	1.00	6.32	5.29	54.5	
17	"	0.50	3.70	3.50	51.4	
18	E_2O_2	1.00	14.00	12.20	53.5	*
19	E_2O_2	1.00	16.70	12.80	56.6	*
20	E_1O_8	0.50	20.10	13.65	59.6	
21	"	0.25	11.80	8.90	57.0	
22	E_1O_8	1.00	28.63	17.70	61.90	
23	E_2O_2	1.00	16.90	11.80	58.9	*
24	E_4O_8	1.00	16.50	11.30	59.4	
25	"	0.25	6.50	4.70	58.1	
26	"	0.50	11.05	7.76	58.9	
27	E_2O_2	1.00	17.20	13.15	56.7	*
28	"	1.00	16.10	11.50	58.4	*
B. Experimental values corrected						
16	E_4O_1	0.50	4.9	3.0	62	
17	"	0.25	2.7	1.8	60	
20	E_1O_8	0.50	20.10	11.7	63	
21	"	0.25	11.80	7.2	62	
25	E_4O_8	0.25	6.50	3.6	64	
26	"	0.50	11.05	6.1	64	

above. For instance the check run 44 following the composition group E_4O_1 shows a change in conversions relative to the reference plot of E_2O_2 corre-

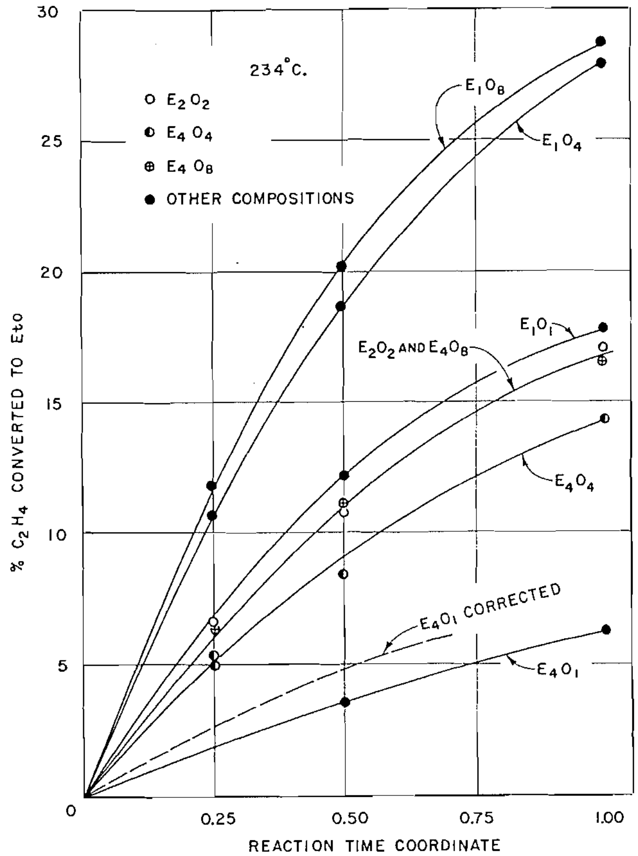

FIG. 5. Conversion of C_2H_4 to EtO at 234° C. vs. reaction time for different feed compositions.

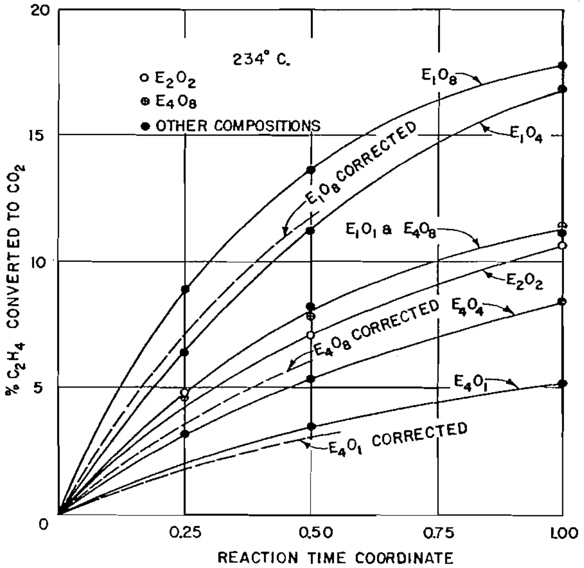

FIG. 6. Conversion of C_2H_4 to CO_2 and H_2O at 234° C. vs. reaction time for different feed compositions.

sponding approximately to a 10% increase in reaction time respecting CO_2 and a 10% decrease in reaction time respecting EtO. The catalyst behaves as if its surface had been increased for CO_2 production and decreased for EtO production.

The correction procedure applied to the E_4O_1 group therefore involved correction of the reaction time co-ordinate by a factor which increased it respecting CO_2 production and decreased it respecting EtO production, the magnitude of the factor being determined by the relative increase and decrease of the time co-ordinates for the standard check conversions immediately following these runs.

(*b*) *Corrections at 234° C.*

Since no sintering was observed, the reference plot for the standard E_2O_2 composition versus reaction time co-ordinate was chosen using the experimentally observed conversions (runs 13–15). Corrections similar to those explained for run E_4O_1 at 274° C. were applied here to the data on compositions: E_4O_1, E_1O_8, and E_4O_8, since these were investigated during or after the irreparable inhibition caused by composition E_4O_1.

4. Initial Reaction Rates

The rate of reaction may be calculated at a given contact time from the plots of C_2H_4 conversion versus reaction time co-ordinate. This rate, r, is expressed by the relation,

$$r = dx/d\frac{M}{F_E} = V_E\, dx/d\frac{M}{F} \tag{1}$$

where

x = fractional C_2H_4 conversion to a given product,

M = catalyst amount (constant throughout; assumed unity as described earlier),

F_E = C_2H_4 feed flow rate (arbitrary units described previously),

F = mixture feed flow rate in the same units,

V_E = vol. or mole fraction of C_2H_4 in feed mixture.

TABLE IV
INITIAL RATE (r_0) OF ETHYLENE OXIDE FORMATION

Feed composition symbol	Feed gas volume fraction		$\left[dx/d\frac{M}{F}\right]_0^*$		$r_0 = \left[dx/d\frac{M}{F}\right]_0 V_E$ *			
	V_E	V_O	234° C.	274° C.	234° C.		274° C.	
					Exp.	Calc.	Exp.	Calc.
E_1O_1	0.0235	0.0988	0.30	0.95	0.00706	0.0072	0.0223	0.0229
E_1O_4	0.0235	0.395	0.46	1.25	0.0108	0.0112	0.0294	0.0307
E_1O_8	0.0235	0.790	0.54	—	0.0127	0.0124	—	0.0326
E_2O_2	0.0471	0.198	0.26	0.87	0.0122	0.0125	0.0410	0.0411
E_2O_4	0.0471	0.395	—	1.02	—	0.0158	0.0476	0.0486
E_4O_1	0.0942	0.0988	0.11	0.40	0.0103	0.0100	0.0377	0.0387
E_4O_2	0.0942	0.198	—	0.55	—	0.0150	0.0518	0.0543
E_4O_4	0.0942	0.395	0.21	0.74	0.0198	0.0199	0.0697	0.0682
E_4O_8	0.0942	0.790	0.26	—	0.0245	0.0238	—	0.0784

* *The arbitrary unit used is: 41.8 liters (N.T.P.)/hour for the constant amount of catalyst used.*

The rate, r, is thus expressed in the arbitrary units of 41.8 liters (N.T.P.) of product per hour for the constant amount of catalyst employed. The initial reaction rates, r_0, have been obtained by extrapolation of the data to zero conversion and time; for EtO formation these are presented in Table IV. Initial rates of reaction may be simply expressed in terms of the partial pressures of C_2H_4 and O_2 only, since reaction products may be assumed absent at this stage. The results could not be fitted to an equation of the type,

$$r_0 = kp_E^a \, p_O^b$$

nor in general to the equation,

$$r_0 = k.f(p_E).f'(p_O)$$

where f is a function only of p_E, and f' a function only of p_O.

In Part IV which deals with the proposed reaction mechanism, reasons will be given which led, on the basis of the known adsorption behavior of O_2 and

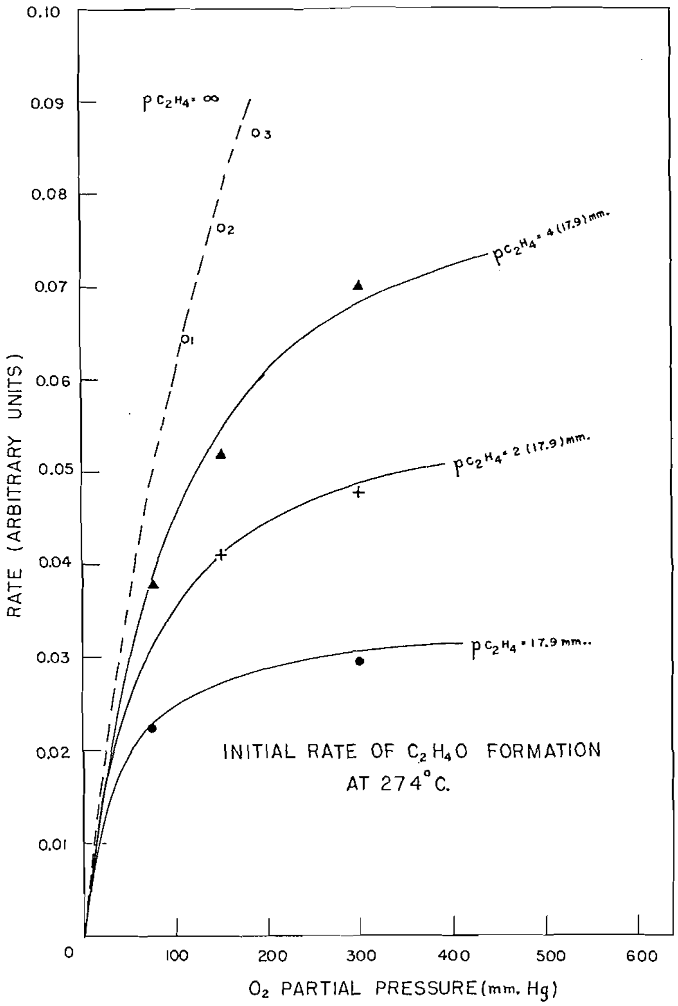

FIG. 7. Initial rate of EtO formation at 274° C. as a function of reactant partial pressures. Points 1, 2, 3; rates calculated for the gas compositions used by Shen-Wu Wan.

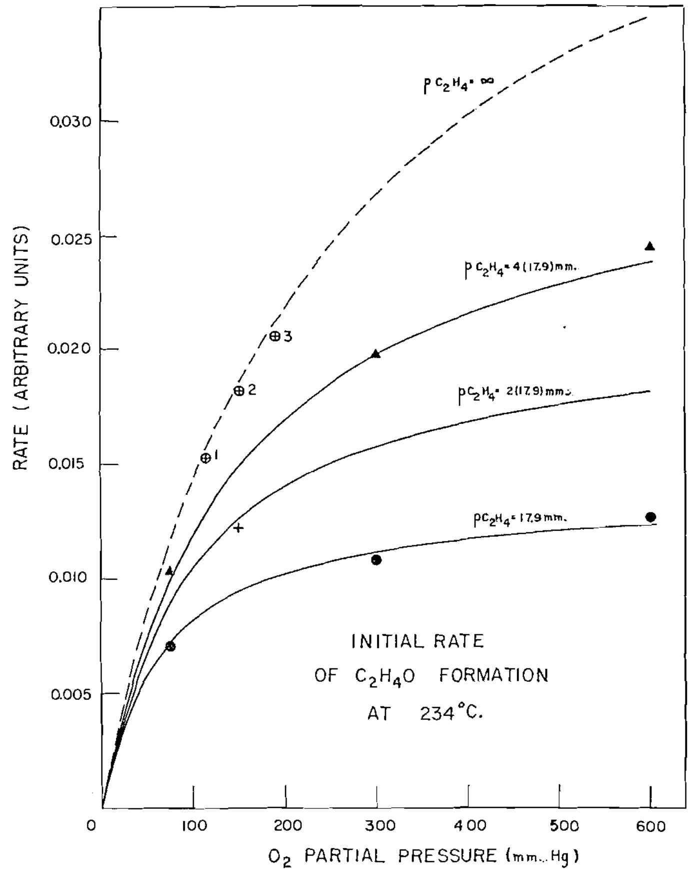

FIG. 8. Initial rate of EtO formation at 234° C. as a function of reactant partial pressures. Points 1, 2, 3; rates calculated for the gas compositions used by Shen-Wu Wan.

C_2H_4 to the development of a rate equation of the type,

$$r_0 = \frac{k}{1 + \dfrac{a}{p_E} + \dfrac{b}{p_O}}. \tag{2}$$

The constants were calculated from the experimental data for EtO formation by the method of least mean squares. With r_0 expressed in the above units and partial pressures in mm. of Hg, these are as follows:

Temperature	k	a	b
274° C.	0.200	86	225
234° C.	0.048	45	240

The applicability of these equations over the whole range of pressures employed may be judged by the close agreement between experimental and calculated values of the rate shown in Table IV, and in Figs. 7 and 8. The solid lines of the latter are calculated according to these equations.

TABLE V

COMPARISON OF SHEN-WU WAN EXPERIMENTAL DATA WITH VALUES OBTAINED USING THE PROPOSED EQUATION FOR THE REACTION VELOCITY

Temp.	Feed composition, vol. %		Partial pressures feed gas, mm. Hg		Shen-Wu Wan: Initial rate (R) EtO formation (gm. mol./hr. gm. catalyst)	Rate (r) calc. for N.R.C. reactor (units of this paper*)		r/R
	C_2H_4	O_2	C_2H_4	O_2				
230° C.	85	15	645	114	0.00127	0.0152	(*a*)	11.95
	80	20	607	152	0.00151	0.0182		12.03
	75	25	570	190	0.00171	0.0206		12.03
260° C.	85	15	645	114	0.00386	0.0646	(*b*)	16.75
	80	20	607	152	0.00457	0.0765		16.75
	75	25	570	190	0.00518	0.0865		16.70

* *The unit is: 41.8 liters (N.T.P.)/hour for the constant amount of catalyst used in N.R.C. reactor.*

(*a*) *Calculated for 234° C.*

(*b*) *Calculated for 274° C.*

Substantial confirmation of the form of the equation is provided by the data of Shen-Wu Wan (9). These data include C_2H_4 concentrations higher than those employed in this work by a factor of about ten. Table V presents a comparison of the rate of EtO formation calculated on the basis of the above equation with the rates measured by Shen-Wu Wan. Since it would be unlikely that similar activity per unit mass of Ag exists in each work, no attempt to convert to similar rate units is made. However, the ratio of the rates should be constant, as was found to be the case. The numerical difference between the two sets of ratio values given in Table V arises because ratio (*a*) involves Shen-Wu Wan's data at 230° C. and present data at 234° C., and ratio (*b*) involves comparison of the respective data at 260° C. and 274° C.

The constant k is very temperature sensitive but the form of the dependence is not definitely known. It can be shown, however, assuming that $\ln k$ is proportional to reciprocal absolute temperature, that isothermal rate ratios are constant and independent of temperature. Since the constants a and b are not very dependent on temperature this procedure is justified.

Figs. 7 and 8 include the rates calculated for the present reactor for feed compositions employed by Shen-Wu Wan (points 1, 2, and 3) and the limiting curve (broken line) for infinite C_2H_4 partial pressure. Similar qualitative curves are obviously obtained for rates plotted as a function of C_2H_4 partial pressure with O_2 pressure constant.

DISCUSSION

In general it may be concluded that the present work confirms the observations made by Twigg (12) that there are two main simultaneous reactions, namely, C_2H_4 oxidation to EtO and also to CO_2 and H_2O and, in addition, a consecutive reaction for EtO oxidation. The maximum occurring in the conversion to EtO arises when the rate of EtO formation becomes equal to its rate of oxidation. The data do not support the belief expressed recently (11), and kindly drawn to our attention by Dr. N. Thon, that all CO_2 is formed by consecutive oxidation of EtO. Selectivity at zero conversion appears to approach values appreciably different from 100%, the latter being of necessity expected if the initial rate of CO_2 formation approached zero. Observed values lie between 50–52% at 274° C. and 60–64% at 234° C. Furthermore, the rate of EtO oxidation, reported in Part III, was found too low to account for all the CO_2 produced during C_2H_4 oxidation. It is also noteworthy that the data of Shen-Wu Wan (9) at extremely low C_2H_4 conversion (0.2 to 2%) indicates a constant selectivity of about 60%.

In contrast to the data reported by Twigg (12) C_2H_4 conversion to CO_2 was not approximately linear with time. In consequence, selectivity did not vary greatly with reaction time up to the maximum in conversion to EtO. As mentioned earlier declining selectivity could be due to homogeneous EtO oxidation (2) likely to occur under static conditions where reaction times of several minutes rather than fractions of a second are used. It will be noted also that selectivity at zero conversion or time appears to be independent of the reactant composition. This leads to the conclusion that each of the parallel reactions is initiated by the same kind of reaction step with similar rate dependence on reactant concentrations. The initial rates of formation of CO_2 can be shown to be about 95% and 60% of the rates of EtO formation at 274° C. and 234° C., respectively.

No attempt has been made at this stage to interpret the rapidly declining rate with increasing time on a basis such as inhibition by reaction products. The primary object of this work has been to provide information concerning the reaction mechanism which will be described in Part IV.

The present results are consistent with those of Murray (7) respecting the influence of reactant partial pressures. With respect to the influence of total pressure, reference to Fig. 7 of that publication shows similar qualitative trends to those observed at reaction time co-ordinate 2 for runs E_1O_1, E_2O_2, and E_4O_4 where the total pressure of the reactants varies as 1:2:4.

The present investigation may also be of value in determining optimum operating conditions for the production of EtO by direct oxidation of C_2H_4. The following summary shows the influence of conditions on reaction behavior at 274° C.

I. Influence of p_{O_2}, at constant $p_{C_2H_4}$

(a) Low $p_{C_2H_4}$

High rate of conversion, increasing with p_{O_2}. The maximum conversion to EtO is obtained more rapidly with increasing p_{O_2}. However, large O_2 excess can possibly result in a slight decrease of the maximum EtO value, by virtue of increased EtO combustion.

(b) High $p_{C_2H_4}$

Low rate of conversion and low maximum conversion to EtO both increasing at first largely, then more slowly, with increasing p_{O_2}. However, the maximum is attained at shorter contact time with decreasing p_{O_2}.

II. Influence of $p_{C_2H_4}$ at constant p_{O_2}

(*a*) Low p_{O_2}

Large decrease of conversion rate and of the value of the EtO maximum with increasing $p_{C_2H_4}$. The time required to attain maximum conversion to EtO does not seem to vary.

(*b*) High p_{O_2}

Decrease of conversion rate and increase of the time required to attain maximum conversion to EtO with increasing $p_{C_2H_4}$. The value of the EtO maximum increases with $p_{C_2H_4}$, at least within a certain range.

III. Influence of total pressure; $p_{O_2}/p_{C_2H_4}$ = const.

The conversion rate decreases and the time required to attain maximum conversion to EtO increases slightly with total pressure. However, the value of the EtO maximum increases with pressure at least within a certain range.

By virtue of this complex behavior it cannot be said definitely that high p_{O_2} and low $p_{C_2H_4}$ are to be chosen for optimum EtO production. For instance, a high EtO maximum can be obtained relatively quickly with the feed E_2O_4, where C_2H_4 content was average respecting the range investigated.

The proposed reaction mechanism will be presented in a later publication (Part IV) where the present results will be compared with those on EtO oxidation.

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THE SILVER CATALYZED OXIDATION OF ETHYLENE

III. KINETICS OF ETHYLENE OXIDE OXIDATION[1]

By A. Orzechowski[2] and K. E. MacCormack

ABSTRACT

A flow type apparatus was used for kinetic studies of the silver catalyzed oxidation of ethylene oxide (EtO) by oxygen at 274°C. Using N_2 as diluent the concentrations of O_2 and ethylene oxide were varied independently from 9.9 to 79% and 2.35 to 9.4% respectively while a total pressure of 1 atmosphere was maintained. Flow rates were varied to give a range of contact times varying from 0.06 to 0.25 sec. It was shown that EtO is oxidized without previous dissociation into C_2H_4 and O_2. The dependence of the initial rate of oxidation of EtO on reactant concentrations excludes isomerization of EtO (to acetaldehyde) as a main step in its oxidation, and a direct oxidation mechanism is suggested. The results of a few experiments to determine the extent of isomerization of EtO to acetaldehyde in the absence of oxygen are presented. No steady state could be achieved but the results may be used semiquantitatively to support the belief that isomerization is not the rate determining step in the oxidation of ethylene oxide.

INTRODUCTION

In order to further the establishment of a reaction mechanism for the oxidation of C_2H_4 on a silver catalyst, Parts I and II of this series are here supplemented by a study of the oxidation of ethylene oxide (EtO) and its isomerization on the same catalyst sample.

EXPERIMENTAL

The apparatus, catalyst sample, and determination of reaction products have been described in Part II. The source of the gases used and their purity was specified in Part I.

Flow rates of EtO were controlled by a two-stage reducing valve followed by three needle valves in series. Mild infrared heating of the cylinder head and reducer ensured constancy of flow with downstream pressure of about 7 P.S.I.G. A dual range orifice meter was used (1–5 and 5–20 liters/hr.) filled with Apiezon-B oil, and having a scale graduation accurate to 0.5%. This was calibrated by mixing the EtO with a N_2 stream of known flow rate to cover a range of composition from 1.5 to 10% EtO. Samples were drawn into a gas burette and the EtO content determined within 1% of the true value employing previously described techniques.

To determine acetaldehyde samples were measured into a mercury burette and then forced through a sintered glass bubbler containing a solution of hydroxylamine hydrochloride.* The HCl liberated by the equivalent amount of aldehyde was titrated with NaOH from microburettes. Checks on the efficiency of this method were made by vaporizing pure liquid acetaldehyde

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**Seven grams of $NH_2OH.HCl$ was dissolved in 100 cc. of water. For each determination 0.1 cc. of this reagent was diluted with 10 cc. H_2O, a drop of bromophenol blue solution added, and titrated with 0.005 N NaOH to the first blue color, before absorption of aldehyde.*

into a mercury burette. After measuring the pressure, volume, and temperature of the sample, N_2 was added to give 0.1% CH_3CHO by volume. The estimation of hydroxylamine hydrochloride accounted for at least 75% of the aldehyde present.

Polarographic measurements, kindly made by Dr. R. J. Cvetanović, showed that the aldehyde found in the products of EtO isomerization was acetaldehyde.

As described in Parts I and II, the catalyst was conditioned with respect to C_2H_4 oxidation at the working temperatures, and kinetic runs at 274° and 234°C. were made. Subsequently the investigation on EtO was started. It was realized (Part I) that the catalyst conditioned by ethylene oxidation was in a very unsteady state with respect to EtO oxidation. On the other hand, as soon as runs of the latter reaction were made, the catalyst tended to be conditioned by them and behaved, then, inhibited with respect to ethylene oxidation. An explanation of these phenomena is offered in Part I.

As was the case during the study of ethylene oxidation, the obtaining of reproducible results would therefore appear to necessitate catalyst conditioning at the given reaction temperature with a standard gas mixture having average composition respecting the range employed. Runs of short duration were made, followed by the standard mixture. In this way frequent checks of the catalyst's activity and the maintenance of its reference state were achieved.

The symbols for feed composition are similar to those used previously except that instead of E (ethylene) symbol X (ethylene oxide) is used. The arbitrary unit of gas mixture flow rate is 41.8 liters (N.T.P.)/hour. The symbol $[pX_nO_m]$ means 41.8 p liters (N.T.P.)/hour of feed gas mixture having composition 2.35 n% C_2H_4O; 9.90 m% O_2, the remainder being N_2 at a total pressure of 1 atmosphere.

The standard feed for the purpose of conditioning and checking was $1.X_2O_2$.

In the preliminary stages of the work, seven measurements were made to check the material balance of reactants and products (EtO and CO_2). Three of them included C_2H_4 determination. At a later stage analyses for acetaldehyde were made frequently, particularly for the composition X_4O_1, but always with negative result.

Ethylene was determined as described in Part II. The method did not allow detection of less than 0.1–0.2 cc. (N.T.P.) as was shown by blank runs. The results with $1X_2O_2$ and $4X_2O_2$, using gas samples of 250–500 cc. showed that the conversion of EtO to C_2H_4, if any, was below 1%.

The over-all balance was found to be between 97 and 101%* (without counting the possibility of slight C_2H_4 formation).

Therefore all conversions were determined directly by CO_2 analysis instead of indirect determination by EtO analysis.

There is some indication that during the first 40 min. after admission of $1X_2O_2$ to the catalyst preconditioned by C_2H_4 oxidation, the balance of EtO, CO_2, and possibly C_2H_4 is only about 90%. The data are not sufficient to explain or confirm this behavior.

TABLE I

OXIDATION OF ETHYLENE OXIDE AT 274°C.

Kinetic run No.	Feed composition symbol	Time operated (hr.)	% EtO to CO_2	Standard check No.
1*a*	$1X_1O_1$	0.65	10.7	—
1*b*	$1X_1O_1$	1.65	10.3	—
1*c*	$1X_1O_1$	2.80	10.2	—
2*a*	$2X_1O_1$	0.65	6.27	—
2*b*	$2X_1O_1$	1.40	6.35	—
—	$1X_2O_2$	0.60	9.00	1*a*
—	$1X_2O_2$	1.20	9.30	1*b**
—	$1X_2O_2$	1.25	8.86	2*a*
—	$1X_2O_2$	3.35	8.65	2*b*
3*a*	$1X_1O_4$	0.65	12.85	—
3*b*	$1X_1O_4$	2.00	12.85	—
—	$1X_2O_2$	0.65	9.46	3*a*
—	$1X_2O_2$	17.00	9.00	3*b*
4*a*	$2X_1O_4$	0.65	8.12	—
4*b*	$2X_1O_4$	2.00	8.30	—
5*a*	$1X_1O_8$	1.00	13.30	—
5*b*	$1X_1O_8$	1.75	13.05	—
6*a*	$2X_1O_8$	0.65	7.22	—
6*b*	$2X_1O_8$	1.35	7.40	—
—	$1X_2O_2$	0.65	9.50	4*a*
—	$1X_2O_2$	17.00	8.95	4*b*
7*a*	$1X_4O_4$	0.65	7.92	—
7*b*	$1X_4O_4$	1.35	8.25	—
7*c*	$1X_4O_4$	2.00	8.39	—
8*a*	$2X_4O_4$	0.65	4.51	—
8*b*	$2X_4O_4$	1.35	4.42	—
9*a*	$4X_4O_4$	0.65	2.84	—
9*b*	$4X_4O_4$	2.00	2.74	—
—	$1X_2O_2$	0.65	8.95	5*a*
—	$1X_2O_2$	18.00	9.46	5*b*
—	$1X_2O_2$	18.75	8.70	5*c*
—	$1X_2O_2$	19.25	8.86	5*d*
—	$1X_2O_2$	20.00	8.66	5*e*
—	$1X_2O_2$	20.75	8.92	5*f*
—	$1X_2O_2$	22.00	8.86	5*g**
—	$1X_2O_2$	1.50	9.70	6*a*
—	$1X_2O_2$	3.65	8.41	6*b*
—	$1X_2O_2$	20.50	8.70	6*c*
11*a*	$2X_2O_2$	0.65	5.30	—
11*b*	$2X_2O_2$	1.35	5.34	—
12	$4X_2O_2$	0.65	3.04	—

**The apparatus was closed down (cooling to room temp. in N_2 stream) after check 1b, 5g, and 10b.*

TABLE I (*Concluded*)

Kinetic run No.	Feed composition symbol	Time operated (hr.)	% EtO to CO_2	Standard check No.
13	$4X_1O_4$	0.65	4.25	—
14	$2X_1O_4$	0.65	7.90	—
15	$1X_1O_4$	0.65	13.45	—
—	$1X_2O_2$	0.65	9.20	7*a*
—	$1X_2O_2$	18.00	9.20	7*b*
16	$4X_1O_8$	0.65	4.20	—
17*a*	$1X_1O_8$	0.65	12.85	—
17*b*	$1X_1O_8$	1.35	12.75	—
—	$1X_2O_2$	0.65	8.82	8*a*
—	$1X_2O_2$	1.50	8.63	8*b*
18*a*	$1X_4O_8$	1.00	8.94	—
18*b*	$1X_4O_8$	1.50	8.65	—
18*c*	$1X_4O_8$	2.75	8.60	—
19*a*	$2X_4O_8$	1.50	5.31	—
19*b*	$2X_4O_8$	2.20	5.52	—
—	$1X_2O_2$	0.65	8.75	9*a*
—	$1X_2O_2$	17.50	9.09	9*b*
20	$4X_4O_8$	0.65	3.09	—
21	$4X_4O_4$	0.65	2.80	—
22	$4X_4O_1$	0.65	1.60	—
23	$2X_4O_1$	1.00	2.62	—
24	$1X_4O_1$	0.65	4.60	—
—	$1X_2O_2$	0.65	11.70	10*a*
—	$1X_2O_2$	1.20	11.30	10*b**
—	$1X_2O_2$	0.65	9.55	11*a*
—	$1X_2O_2$	1.35	9.16	11*b*

**The apparatus was closed down (cooling to room temp. in N_2 stream) after check 1b, 5g, and 10b.*

RESULTS

1. *Oxidation Kinetics at Constant Temperature*

The influence of feed composition and flow rate was studied after overnight stabilization of the catalyst using mixture $1X_2O_2$ in all cases.

Table I shows the results of kinetic runs and of the frequent checks for the standard $1X_2O_2$ feed. Operation times are included in this table.

All checks for $1X_2O_2$ indicated 8.5–9.5% conversion to CO_2 and hence the surface was assumed to be in the same reference state. One exception was the check run $1X_2O_2$ made after studying the composition X_4O_1, where CO_2 conversion of $1X_2O_2$ was found as high as 11.5% during the first few hours.

Hence the values for X_4O_1 are corrected to the normal reference state. This behavior of oxygen deficient feed is very similar to the behavior observed with similar ethylene-oxygen compositions. (Compare feed E_4O_1 in Parts I and II.)

Conversions versus reaction time co-ordinate for different feed compositions are plotted in Fig. 1.

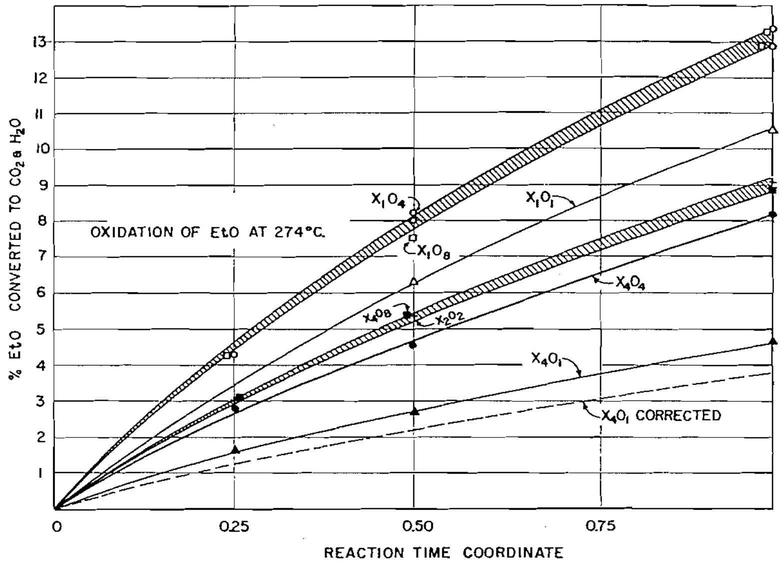

FIG. 1. Conversion of EtO to CO_2 and H_2O at 274°C. vs. reaction time for different feed compositions.

The initial rate of reaction is given by

$$r_0 = V_x\left(dx/d\frac{M}{F}\right)_0 \qquad [1]$$

where V_x = volume fraction of EtO in the feed,
x = fraction of EtO converted to CO_2 and H_2O,
M = catalyst quantity (assigned unity and constant throughout),
F = flow rate of feed gas mixture in previously defined arbitrary units,
r = rate of reaction in the same units with $M = 1$.

Suffix $_0$ means conditions at zero reaction time when $M/F = 0$.

The initial rates are shown by the points on Fig. 2.

In Part IV, which deals with reaction mechanism, the reasons will be presented which led to a rate equation of the form

$$r_0 = \frac{A}{1+\frac{B}{p_x}+\frac{C}{p_o}} \qquad [2]$$

where p_X = EtO partial pressure

p_O = O_2 partial pressure

A, B, C are constants.

The constants were found by the method of least mean squares to give

$$r_0 = \frac{0.032}{1 + \dfrac{90}{p_X} + \dfrac{270}{p_O}} \qquad \text{at } 274^\circ\text{C.}$$

(Partial pressures are expressed in mm. Hg.)

Fig. 2 includes as solid lines the values of rates calculated according to the above equation showing good agreement between experimental and calculated data.

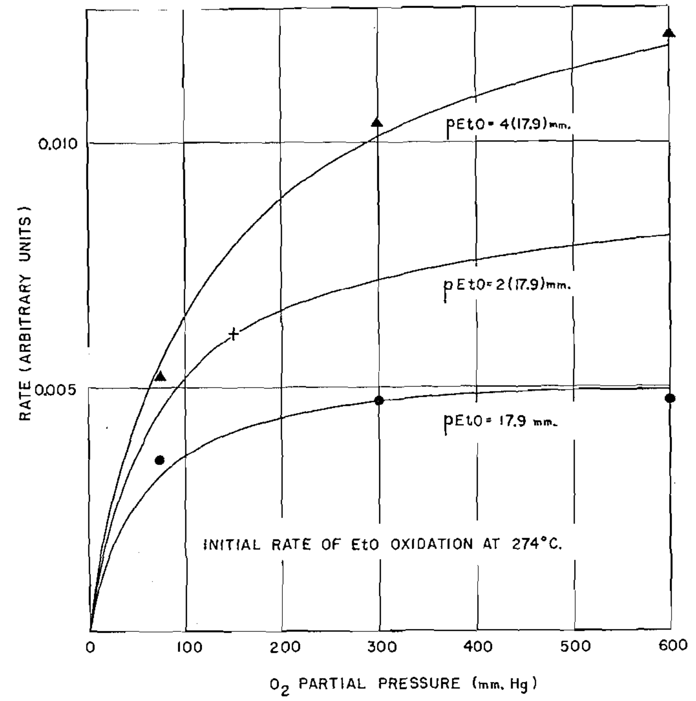

FIG. 2. Initial rate of CO_2–H_2O formation from EtO at 274°C. as a function of reactant partial pressures.

It is noteworthy that the equation obtained is very similar to the one derived for C_2H_4 oxidation (Part II), except for the constant A.

2. *Oxidation Temperature Dependence*

A few measurements were made shortly after the temperature was changed, and are presented in Table II. (Times necessary for heating or cooling to the required temperature were usually in the order of half an hour.) These are not the steady values which would have been obtained after very prolonged opera-

TABLE II
TEMPERATURE DEPENDENCE
OXIDATION OF ETHYLENE OXIDE (FEED $1X_2O_2$)

T, °C.	Time operated at T°C. (hr.)	Sample No.	% EtO to CO_2
274	17.70	4	8.55
254	0.25	1	5.6
254	0.75	2	4.9
254	1.50	3	4.9
294	0.16	1	14.3
294	0.66	2	12.5
274	0.16	1	8.5
274	0.83	2	8.4
274	1.83	3	8.7
274	19.50	4	8.9

tion where slow processes have changed the nature of the catalyst (compare Part I). Therefore they indicate more correctly the dependence of kinetics on temperature. Checks at 274°C. after operating at other temperatures included in Table II prove indeed that the reference state of the surface has been maintained throughout.

3. *Isomerization to Acetaldehyde*

Immediately following the kinetic runs for EtO oxidation, the investigation of EtO isomerization at 274°C. was begun by feeding only EtO and N_2. All data are presented in Table III.

In Expt. 3, after 2.25 hr. operation, a check was made for the presence of C_2H_4 in the outgas. This, if any, corresponded to less than 0.6% conversion of EtO. The over-all balance of EtO was also within the limits of experimental error.

In view of the absence of C_2H_4, the formation of CO_2 seems surprising. If the oxygen were supplied by decomposition of EtO, according to:

$$5\ C_2H_4O \rightarrow 5\ C_2H_4 + 2.5\ O_2$$
$$C_2H_4O + 2.5\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

then for each mole of EtO converted to CO_2, there would be 5 moles of EtO converted to C_2H_4. The conversion to CO_2 being of the order of 2%, this would result in conversion to C_2H_4 of the order of 10%, which is not the case. Also, the adsorption capacity of the catalyst is far too small to account for the missing C_2H_4.

It is therefore concluded that the N_2 employed contained small amounts of oxygen which are responsible for CO_2 formation; 0.2–0.5% of O_2 in nitrogen might be sufficient quantitatively, based on the kinetics of EtO oxidation. The conversion to CO_2 increases with decreasing EtO pressure (compare Expts. 6 and 8 in Table III) which also conforms to the kinetics of EtO oxidation but is not paralleled by the behavior of isomerization in the same experiments.

TABLE III
ISOMERIZATION OF ETHYLENE OXIDE TO ACETALDEHYDE

Flow composition symbol	Time operated (hr.)	% EtO converted			Expt. No.
		To CH_3CHO	To CO_2	Total	
$1X_2O_0$	0.40	2	—	—	1
$1X_2O_0$	0.85	2	—	—	1
$1X_2O_0$	1.50	2	—	—	1
$1X_2O_2$	0.33	—	9.78	—	2 Oxidation
$1X_2O_2$	0.85	—	9.10	—	2
$1X_2O_2$	17.50	—	9.16	—	2
$1X_2O_0$	0.16	2.1	—	—	3
$1X_2O_0$	0.55	1.6	—	—	3
$1X_2O_0$	1.50	1.5	—	3.2	3
$1X_2O_0$	2.25	—	1.7		3
$1X_2O_0$	4.00	—	1.6	2.9	3
$1X_2O_0$	4.67	1.25	—		3
$1X_1O_0$	0.33	0.85	—	—	4
$1X_1O_0$	0.66	0.85	—	—	4
$1X_1O_0$	0.90	0.85	—	—	4
$1X_2O_0$	0.33	1.35	—	—	5
$1X_2O_0$	18.00	0.67	—	—	5
$1X_4O_0$	0.40	—	1.3	2.2	6
$1X_4O_0$	0.75	0.87	—		6
$1X_4O_0$	1.00	0.87	—	2.1	6
$1X_4O_0$	1.25	—	1.2		6
$0.25X_4O_0$	0.40	—	1.85	4.9	7
$0.25X_4O_0$	0.90	3.0	—	5.0	7
$0.25X_4O_0$	1.25	—	2.0		7
$1X_1O_0$	0.40	—	3.6	3.9	8
$1X_1O_0$	0.75	0.28	3.6		8
$1X_2O_0$	0.50	0.56	—	—	9
$1X_2O_2$	0.16	—	13.4	—	10 Oxidation
$1X_2O_2$	0.33	—	11.4	—	10
$1X_2O_2$	0.90	—	10.1	—	10
$1X_2O_2$	17.65	—	8.55	—	10
After 58 hr. ($1E_2O_2$)					
X_2O_0	0.25	2.4	—	3.6	11
X_2O_0	0.58	—	1.2	3.2	11
X_2O_0	0.83	1.95	—	3.1	11
X_2O_0	1.25	—	1.2	2.7	11
X_2O_0	1.80	1.50	—	2.7	11
X_2O_0	2.75	—	1.2	2.5	11
X_2O_0	3.00	1.30	—		11
X_2O_0	18.00	0.80	—	2.0	11
X_2O_0	18.25	—	1.2		11

DISCUSSION

1. *Oxidation*

Twigg (1) reported that EtO is oxidized on silver catalyst, but there is little information concerning the kinetics of this reaction. Also there are insufficient data relating to rate of C_2H_4 formation, especially at small reaction times.

There were, a priori, three possibilities:

1. EtO is oxidized without previous dissociation into C_2H_4 and O_2.
2. EtO is decomposed into C_2H_4 and O_2* followed by oxidation of C_2H_4, with no EtO being oxidized directly.
3. EtO undergoes simultaneous direct oxidation and dissociation to O_2 and C_2H_4, the latter being subject to further oxidation.

The present data substantiate statement (1) for the main reaction step, since C_2H_4 did not occur in detectable quantities in the products.

The dependence of oxidation rate on the reactant partial pressures excludes isomerization of EtO on the Ag surface as a main step in its oxidation, because there is no reason for isomerization to increase with oxygen pressure. Instead, it is suggested that one of the following mechanisms is responsible for the formation of intermediates, which are then capable of undergoing rapid oxidation.

(*a*) Reaction between EtO and an oxygen adatom, adsorbed side by side.

(*b*) Collision of a gaseous EtO molecule with an oxygen adatom.

In accordance with this (see discussion below) the rate of EtO isomerization to acetaldehyde is shown to be substantially lower than the rate of EtO oxidation.

A private communication from industrial sources claimed that the rate of EtO oxidation passes through maximum at 260°C. This would imply that mechanism (*a*) may be valid where EtO desorption rates become comparable with oxidation rates at approximately 260°C.

We were unable to observe such an effect (Table II) and therefore believe that the mechanism (*b*) cannot be excluded.

The present data may be compared with those for C_2H_4 oxidation (Part II). It transpires that the same factors favorable to high conversions of ethylene to EtO in the initial stages of the reaction are also operative for the conversion of EtO to CO_2. Those factors are: large oxygen partial pressure and low oxygen acceptor pressure. Therefore a high $p_{O_2}/p_{C_2H_4}$ ratio does not necessarily represent the best operating conditions for EtO production as was pointed out previously (Part II).

The present data may be helpful in attempting to correlate the reaction rate data for the over-all C_2H_4 oxidation as a function of contact time.

Before this can be done, however, more data are needed for the influence of CO_2 and H_2O. Also the effect of the initial composition ratio $p_{C_2H_4}/p_{C_2H_4O}$ should be investigated, which could be followed experimentally by using carbon-labelled EtO. This method would provide further evidence for the formulation of a reaction mechanism.

2. *Isomerization*

The quantitative interpretation of the isomerization process is unfortunately obscured by the presence of oxygen traces in the diluent N_2 and influenced

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**This was actually found to occur by Twigg (1) when EtO is admitted to oxygen free silver in a static system.*

adversely by the difficulty of estimating low concentrations of acetaldehyde in the products. Furthermore, the conversion level is not steady. Higher conversions to acetaldehyde (about 2%) are obtained immediately after pretreatment by EtO oxidation (Expts. 1 and 3, Table III) or by C_2H_4 oxidation (Expt. 11). Further, the isomerization decreases with operating time. This confuses the interpretation of data but might indicate the formation of a surface deposit. It will be noted that the standard oxidation of ethylene oxide (Expt. 10) gives higher than normal values: 13.4% instead of 9%, when made immediately after the series of isomerization runs. The same is true if C_2H_4 oxidation is run after isomerization: initially, abnormally high conversions both to CO_2 and to EtO are obtained as described in Part I. The adsorption capacity of the catalyst used (about 1 cc. N.T.P.) seems too small to explain this excess conversion only on the basis of a deposit which burns on contact with O_2.

This behavior could be explained if we assume that feeding EtO with practically no oxygen is effective as follows:

(*a*) stably sorbed oxygen, inhibiting the reaction (see Part I) is removed;

(*b*) the surface is slowly covered by acetaldehyde residues.

When oxygen is admitted later, together with C_2H_4 or EtO, the acetaldehyde residues are burned off immediately. The fixation of oxygen in stable positions and the formation of oxidation residues (see Part I) being slow, the rate of oxidation during the first few hours will be greater than normal on this cleaned surface.

Notwithstanding the complications due to the unsteady level of isomerization and to the presence of oxygen, it appears that isomerization increases with increasing EtO pressure (comparing Expts. 3, 4, and 5; 6 and 8; 8 and 9). This is expected since the rate of isomerization will be proportional to the fraction of Ag surface covered by adsorbed EtO, and this must increase with its pressure.

As was pointed out in the discussion of EtO oxidation, the kinetics of this reaction do not conform to the hypothesis that isomerization to acetaldehyde is the rate determining stage during oxidation. To support the independent direct oxidation of EtO as the main path of CO_2 formation it should be possible to show that isomerization of EtO to acetaldehyde is slower than the oxidation of EtO under comparable conditions.

Experiments 2 and 3 in Table III show that initial conversion to acetaldehyde is 2.1% against about 9% conversion to CO_2, when oxygen is present. Thus, less than 25% of EtO oxidized undergoes isomerization. Moreover the conditions of Expts. 2 and 3 are not strictly comparable because in the latter case, the available free Ag surface is increased in the absence of oxygen, and consequently measured values for isomerization could be actually higher than those which occur during oxidation.

The CO_2 conversions shown in Table III can be attributed without difficulty to the direct oxidation of EtO by traces of oxygen. On the other hand, if it is assumed that all CO_2 shown in Table III arises by prior isomerization followed by oxidation due to traces of oxygen, the highest isomerization values would be

3.6% (Expt. 11). This would still account for only 40% of the EtO which is oxidized under comparable conditions.

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THE SILVER CATALYZED OXIDATION OF ETHYLENE

IV. REACTION MECHANISM[1]

By A. Orzechowski and K. E. MacCormack[2]

ABSTRACT

A reaction mechanism for the silver catalyzed oxidation of C_2H_4 by oxygen has been formulated which is consistent with kinetic data for this system. It is suggested that both ethylene oxide and CO_2 formation involve interaction of single gaseous C_2H_4 molecules with single oxygen adatoms. This may be a system of two parallel reactions of different activation energy requirements or a common initiation step to form adsorbed ethylene oxide which may then desorb immediately or isomerize to acetaldehyde followed by rapid oxidation to CO_2 and H_2O. Account is taken of the known adsorption characteristics of O_2 on silver to deduce expressions for initial rates of ethylene oxide and CO_2 formation as a function of reactant partial pressures. The generalized form of the equation is $r = k(1 + a/p_E + b/p_O)^{-1}$, where k, a, and b are temperature dependent constants and p_E and p_O are partial pressures of ethylene and of oxygen respectively.

A mechanism is also suggested for the heterogeneous oxidation of ethylene oxide which involves interaction between a gas phase ethylene oxide molecule and a single oxygen adatom to form an intermediate (probably formaldehyde) which is rapidly oxidized to CO_2 and H_2O. A similar expression to that above for the initial oxidation rate is deduced. These expressions have been fitted successfully to experimental data.

The experimental data presented in the previous parts (I–III) of this series of publications have been used to formulate a consistent reaction mechanism for ethylene oxidation on silver. It was shown in Part II that only two parallel reactions can account for the production of ethylene oxide (EtO) on the one hand (rate, r_1), and CO_2 and H_2O on the other (rate, r_2) from C_2H_4 and oxygen. Initially these exist alone but are accompanied during the course of the reaction by a slow consecutive oxidation of EtO. Though the major part of CO_2 formation arises from C_2H_4, this does not exclude the possibility that adsorbed EtO (as opposed to desorbed EtO) formed by C_2H_4 adsorption on an oxygen adatom, is the intermediate in the so-called direct oxidation of C_2H_4 to CO_2 and H_2O. This point will be expanded later.

Further, the initial selectivity given by the expression $r_1/(r_1 + r_2)$ appears to be dependent only on temperature and not on reactant composition provided the same catalyst reference state is carefully maintained as described in the earlier parts of this series. Consequently, the two primary reactions show the same initial rate dependence on reactant concentrations and may well proceed through the same type of, if not a common reaction step. This is in contrast to the opinion expressed by Twigg (5) who proposed two dissimilar steps,

$$C_2H_4 \text{ (gas)} + 0 \text{ (ads.)} \rightarrow C_2H_4O,$$

$$C_2H_4 \text{ (gas)} + 20 \text{ (ads.)} \rightarrow CO_2 + H_2O \text{ (via short-lived intermediates)}.$$

In considering data for the initial stages of the reactions the influence of products may be neglected. The known adsorption characteristics of the

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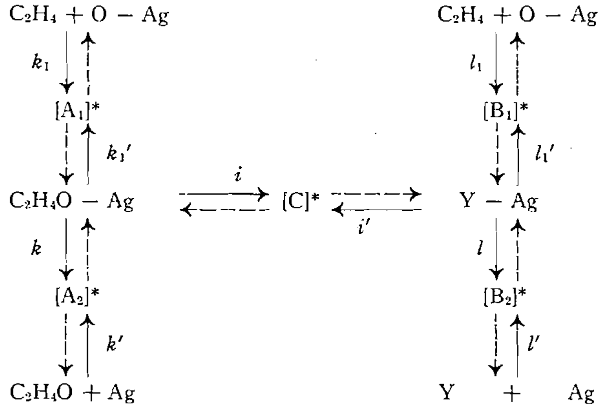
[2] *National Research Council Postdoctorate Fellow, 1951–53.*

reactants suggest that the initial reaction step involves impact of gaseous C_2H_4 with adsorbed oxygen. It is proposed that only single adatoms of the latter are involved, according to the reaction scheme presented below.



A*, B*, and C* are activated complexes with k, l, and i, the velocity constants of the various rate determining steps. Y is isomeric with EtO and is very rapidly oxidized to CO_2 and H_2O. In several respects, this scheme is similar to that proposed by Twigg. The direct oxidation to EtO follows the path k_1k with his observed reverse reaction $k'k_1'$. In agreement with the present work (Part III) EtO was found to isomerize to $CH_3.CHO$ in the absence of O_2 which is represented by the path $k'il$ and Y would thus be identified as $CH_3.CHO$.

It follows then that one possible path for the direct production of CO_2 from C_2H_4 is through adsorbed EtO (k_1il) in contrast with any postulation concerning separate deep oxidation of C_2H_4 by its reaction with either single or paired O_2 adatoms. However, since the present evidence does not allow differentiation between identical and similar primary steps for the formation of both EtO and CO_2, it is also necessary to introduce the other possible step (l_1l) by which the same isomer Y can be formed with different activation energy requirements. In both cases, however, only single oxygen adatoms are proposed.

Although some acetaldehyde is formed via $k'il$ when EtO is placed in contact with Ag, it was shown in Part III that this reaction cannot be considered the rate determining step in the oxidation of EtO. Another independent reaction was proposed which involved either (*a*) surface reaction between adsorbed EtO and an oxygen adatom, or (*b*) reaction between gaseous EtO and an oxygen adatom. If the latter mechanism be correct, its influence on the kinetics of C_2H_4 oxidation need not be considered under conditions where the gas phase concentration of EtO may be neglected. If, however, mechanism (*a*) were valid, its bearing on the interpretation of the kinetics of C_2H_4 oxidation becomes important depending on the fraction of surface (ϵ) covered by adsorbed EtO, (1) during C_2H_4 oxidation (ϵ_1) and (2) during EtO oxidation (ϵ_2).

This may now be considered in relation to the path by which the major part of CO_2 is produced during C_2H_4 oxidation. It will be recalled that under comparable conditions the conversion of C_2H_4 to CO_2 is greater* than the conversion of EtO to CO_2. Allowing $\epsilon_1 \ll \epsilon_2$ which would occur for $k_1 \ll k'$, the C_2H_4 oxidation mechanism by isomerization of adsorbed EtO (path *i*) would not account for the greater CO_2 production. Therefore the independent path l_1 has to be introduced to account for the major CO_2 producing reaction. This would be equally necessary if mechanism (*a*) above were valid in the oxidation of EtO.

Assuming the alternative case of $\epsilon_1 \gg \epsilon_2$ where $k_1 \gg k'$, deep oxidation of C_2H_4 to CO_2 via the isomerization path *i* could account for the major part of the CO_2 produced and step l_1 would be unnecessary. In this case EtO oxidation by mechanism (*a*) must be excluded for otherwise the initial selectivity during C_2H_4 oxidation would show a dependence on reactant concentration.

The above may be summarized as follows:

$\epsilon_1 \ll \epsilon_2$; oxidation of C_2H_4, step l_1 necessary; oxidation of EtO, mechanism (*a*) or (*b*) valid.

$\epsilon_1 \gg \epsilon_2$; oxidation of C_2H_4, step l_1 unnecessary; oxidation of EtO, mechanism (*a*) excluded.

Oxygen Adsorption

One of the chief difficulties in the mathematical interpretation of the mechanism of C_2H_4 oxidation lies in assessing the part played by oxygen adsorption.

At temperatures within the range studied during the present work it is known (1) that the adsorption is extremely rapid, decreasing very quickly with extent of surface coverage. Desorption is extremely slow and may thus be neglected in estimating the surface coverage during the oxidation of C_2H_4. Since C_2H_4 adsorption on Ag can be neglected (5), oxygen adsorption is obviously prerequisite to reactions with C_2H_4.

Information concerning the adsorption of O_2 on a similar silver catalyst has been communicated privately by Drs. E. L. Tollefson and W. Smeltzer. Rates were measured between 200 and 300°C. at constant pressures ranging from 200 to 700 mm. Hg. In every case the surface attains at least 50% of its equilibrium coverage corresponding to given values of pressure and temperature in less than 0.1 min. and over this region the rate of adsorption appears to be directly proportional to the pressure. The maximum amount of O_2 sorbed by a 50 gm. sample was 5.4 cc. (N.T.P.) at 200°C. and 700 mm. Hg. After deduction of 0.7 cc. which according to the data of Steacie and Johnson (3) could dissolve in Ag under these conditions, there remains a minimum value of 4.7 cc. for O_2 adsorption when θ, the fractional surface coverage, becomes

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**In Part I, dealing with slow processes, it was shown that quantitative replacement of C_2H_4 undergoing oxidation (35% conversion to CO_2) by EtO involved an initial decline to about 5–10% conversion to CO_2, then passage through a maximum of 17% and finally a stable level of 9% (Fig. 5). The immediate return to C_2H_4 oxidation showed an initial conversion to CO_2 of only 10% (Fig. 3) slowly increasing to the previous level of 35%. Thus a change from C_2H_4 to EtO oxidation indicates higher rates of CO_2 production for the former, whereas a change in the opposite direction shows similar rates at least initially. In no case is the rate of CO_2 formation greater for EtO than for C_2H_4 oxidation. The possible explanation of these effects is that EtO admitted after C_2H_4 undergoes oxidation mainly via the isomerization step. The slow development of surface residues causes a decline in the part played by this mechanism relative to that of the direct oxidation step described. Consequently, the return to C_2H_4 oxidation on the poisoned surface shows a correspondingly low conversion to CO_2, slowly increasing with the removal of surface residues.*

unity. In all cases, during the first 0.1 min., the derived values of θ are less than 0.65. At 0.2 min. the rate falls to less than 0.03 of the average rate during the first 0.1 min., followed by further rapid decline. It is reasonable to infer that initial rates at very low coverage will be very fast.

Comparing the above adsorption sample with the catalyst sample used in the present work (12 gm.) and assuming the same surface properties, calculation shows that the O_2 adsorption rate during the catalyzed C_2H_4 oxidation is rather greater than the average rate estimated from the Tollefson–Smeltzer data up to $\theta = 0.65$. For example, by interpolation and extrapolation of the latter results at 75 mm. Hg and 234°C. the average O_2 adsorption rate during the first 0.1 min. is 3.5 cc./min. (for 12 gm.). The O_2 adsorption rate deduced from C_2H_4 oxidation data at the same temperature and O_2 pressure and with C_2H_4 partial pressure = 72 mm. Hg, is 7 to 25 cc./min. (for 12 gm.) depending on the selectivity and mechanism of the direct oxidation to CO_2. Therefore, during the catalyzed oxidation of C_2H_4 it can be inferred that the Ag surface is quite sparsely covered by O_2.

Although the dependence of adsorption rate on coverage below $\theta = 0.3$ is too fast to be measured accurately at temperatures in the order of 250°C., the data of Tollefson and Smeltzer as well as an extrapolation of Benton and Drake's data (1) indicate the possibility of large decrease of adsorption rate with increasing θ even for $\theta < 0.3$.

Taylor and Thon (4) have recently shown that in many cases adsorption rates obey the equation $dq/dt = ae^{-bq}$, where q is the amount adsorbed in time, t, with b constant and a, a function of the pressure. This is substantiated by recent measurements of Porter and Tompkins (2). In addition it is also possible to fit the data of Benton and Drake (1) to an equation of this type, one valid for the approximate range $0.3 < \theta < 0.5$, another for the range $0.5 < \theta < 0.7$. In each range a is directly proportional to the oxygen pressure.

A series expansion of the Taylor–Thon equation, using θ in place of q and retaining only the first two terms gives

$$d\theta/dt = jp_O(1 - m\theta) \qquad [1]$$

where $a = jp_O$ (j = const.) and $b = m$.

SURFACE COVERAGE BY REACTING SPECIES

Considering C_2H_4 oxidation under initial conditions of reaction, let

p_O, p_E = the partial pressures of O_2 and C_2H_4 respectively,
θ = fraction of catalyst surface covered by O_2 atoms,
α = fraction of this O_2 layer covered by C_2H_4 adsorbed in any form,
β = fraction of C_2H_4 adsorbed on the O_2 layer which can be identified as EtO adsorbed on Ag.

The velocity constants are used according to the foregoing reaction scheme.

I. Steady State Balance of EtO in the Adsorbed Phase

At the steady state the formation rate of adsorbed EtO by reaction between C_2H_4 and O_2 adatoms and by reverse isomerization of Y will be balanced by its removal by desorption, by decomposition into C_2H_4 and O_2 adatoms, and by isomerization to Y. This may be expressed

$$k_1p_E(1-\alpha)\theta + i'\alpha\theta(1-\beta) = k\alpha\theta\beta + k_1'\alpha\theta\beta + i\alpha\theta\beta$$

or,

$$[2] \qquad k_1p_E(1-\alpha) = \alpha[\beta(k + k_1' + i + i') - i'].$$

II. Steady State Balance of Y in the Adsorbed Phase

By argument similar to that above,

$$l_1p_E(1-\alpha)\theta + i\alpha\theta\beta = l\alpha\theta(1-\beta) + l_1'\alpha\theta(1-\beta) + i'\alpha\theta(1-\beta)$$

or,

$$[3] \qquad l_1p_E(1-\alpha) = \alpha[(1-\beta)(l + l_1' + i + i') - i].$$

Dividing equation [1] by equation [2]

$$\beta = \text{a function only of the velocity constants,}$$
$$= \text{constant at constant temperature.}$$

Therefore each of the expressions contained by square brackets in equations [2] and [3] is constant.

$$[4] \qquad \therefore\ \alpha/(1-\alpha) = Ap_E \quad \text{or} \quad \alpha = Ap_E/(1 + Ap_E)$$

where A is a constant at constant temperature.

III. Steady State Balance of O_2 Atoms in the Adsorbed Phase

At the steady state, the rate of formation of oxygen adatoms both by O_2 adsorption and by decomposition of adsorbed isomers of EtO with reconstitution of ethylene will be balanced by removal of O_2 adatoms as a result of C_2H_4 adsorption on these atoms and the possible heterogeneous oxidation of gaseous Y. Consecutive oxidation of Y is known to be very much more rapid than that of gaseous EtO as no Y can be detected in the gas phase.

Neglecting the rate of desorption of O_2 and writing the adsorption rate according to equation [1], we have,

$$[5] \quad jp_O(1 - m\theta) + [k_1'\beta + l_1'(1-\beta)]\alpha\theta = (k_1 + l_1)p_E(1-\alpha)\theta + nl\alpha\theta(1-\beta)$$

where n is the number of O_2 adatoms used in the heterogeneous oxidation of one molecule of Y. With $0 < n < 5$, equation [5] gives,

$$[6] \quad \theta = \frac{jp_O}{jp_Om + (k_1 + l_1)(1-\alpha)\,p_E + [nl(1-\beta) - k_1'\beta - l_1'(1-\beta)]\alpha}.$$

Now, the rate of formation of EtO (r_1) is given by,

$$[7] \qquad r_1 = k\alpha\theta\beta$$

and the rate of formation of CO_2, (r_2) is given by,

$$[8] \qquad r_2 = l\alpha\theta(1-\beta).$$

Combining equations [4], [6], and [7], we have,

$$[9] \qquad r_1 = \frac{k\beta/m}{1 + (1/Ap_E) + (B/jmp_O)}$$

where $B = (k_1 + l_1)/A + nl(1-\beta) - [k_1'\beta + l_1'(1-\beta)]$
$= \text{constant at constant temperature.}$

Inspection of equations [7] and [8] indicates that r_2 may be represented by an expression similar to equation [9] except that the numerator will be $l(1 - \beta)/m$ instead of $k\beta/m$.

As was demonstrated in Part II of this series, the dependence of initial reaction rates on reactant partial pressures obeyed the relationship derived in equation [9], which lends support to the over-all reaction mechanism proposed.

It is now possible to discuss further the consistency of equation [1] with respect to the experimental data and the adsorption concepts offered. Equation [6] may be written in the form,

$$m\theta = \frac{1}{1 + \alpha B/jmp_{\mathrm{O}}} \qquad [10]$$

from which values of $m\theta$ may be computed knowing α by equation [4], the over-all constants A and B/jm being given by fitting equation [9] to the experimental rate data. The following table shows the calculated range of values of $m\theta$.

Temp., °C.	p_{O}, mm. Hg	p_{E}, mm. Hg	$m\theta$
234	600	18	0.88 max.
	75	72	0.34 min.
274	300	18	0.88 max.
	75	72	0.43 min.

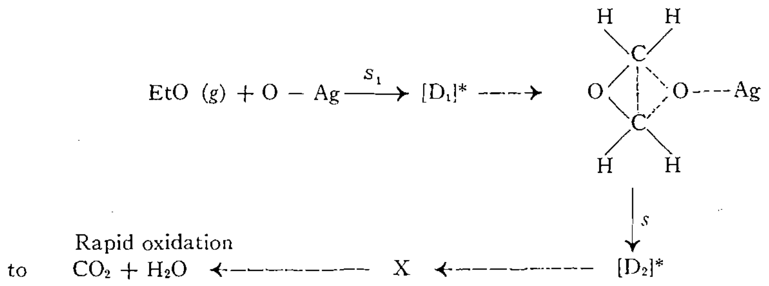
The range of variation of $m\theta = 0.34$ to 0.88 so that m should be at least in the order of 3. In this case θ would vary from about 0.1 to 0.3. Lower values of m would broaden the range of θ too greatly to permit use of the approximate equation [1]. These values of θ are also consistent with values inferred and discussed earlier respecting the extent of O_2 adsorption.

The proposed mechanism may apply equally well to homogeneous and heterogeneous catalyst surface. In the latter case one of the several crystal planes could be preponderantly active for one type of reaction (e.g., k_1k or l_1l). Selective poisoning, referred to in Part I, may be attributed to preferential poisoning of one or other of these planes or to the establishment of impurity centers with consequent influence on the activation energies of the several reaction paths. The latter would be the only possible explanation of these effects in the case of a homogeneous surface.

APPENDIX

Suggested Mechanism for the Heterogeneous Oxidation of EtO

With reference to the previously written reaction scheme, it is assumed that $k' \ll k$ implying that the fraction of catalyst surface covered by adsorbed EtO may be neglected during EtO oxidation. It is suggested that the reaction occurs by impact of gaseous EtO with an adsorbed oxygen atom, according to the following scheme.



Heavy arrows indicate the relatively slow rate determining steps with rate constant s_1 and s for the formation of intermediate activated complexes $[D_1]^*$ and $[D_2]^*$ respectively. The resulting intermediate X (which could be formaldehyde) is rapidly oxidized by either heterogeneous or homogeneous steps.

Let θ = fraction of catalyst surface covered by adsorbed oxygen,
ϕ = fraction of θ covered by EtO adsorbed on oxygen,
p_O, p_X = the partial pressures of O_2 and EtO respectively.

1. Steady State Balance of EtO Adsorbed on Oxygen

The rate of adsorption of EtO on the oxygen layer is balanced by the rate of its reaction. The rate of evaporation is omitted for simplicity as its inclusion will not change the form at any of the subsequent mathematical expressions.

$$s_1 p_X \theta(1 - \phi) = s\theta\phi$$

Hence,

[11] $$\phi = s_1 p_X/(s + s_1 p_X).$$

2. Steady State Balance of O_2 in the Adsorbed Phase

The rate of adsorption of oxygen adatoms is balanced by their rate of removal due to EtO adsorption on the oxygen layer and to heterogeneous oxidation of X. If n is the number of oxygen adatoms required for the oxidation of X, the following relation exists,

[12] $$jp_O(1 - m\theta) = s_1 p_X \theta(1 - \phi) + ns\theta\phi.$$

The rate of removal by reaction of EtO is given by,

$$R = s\theta\phi$$

which in conjunction with equations [11] and [12] becomes

[13] $$R = \frac{s/m}{1 + s/s_1 p_X + s(n+1)/jmp_O}.$$

This type of equation has been found to account satisfactorily for experimental values of the initial rate of EtO oxidation (see Part III), which is support for the proposed mechanism. Nevertheless, as was indicated earlier, the mechanism involving surface reaction between adsorbed EtO and oxygen adatoms cannot be regarded as impossible. However, mathematical treatment of this system becomes exceedingly complex.

It is interesting to compare the values of θ for C_2H_4 and EtO oxidation. Values of $m\theta$ can be calculated as for C_2H_4 oxidation, using equations [11], [12], and [13]. Equations [9] and [13] can be seen to have the same form. The overall constants (see equation [2], Part II, and equation [2], Part III) of the denominators were found to have very similar numerical values at 274°C. This means that for

$$[14] \qquad p_E = p_X, \text{ and } (p_O)_1 = (p_O)_2, \quad (m\theta)_1 = (m\theta)_2$$

where subscripts $_1$ and $_2$ refer to C_2H_4 and EtO oxidation respectively.

Hence either

$$[15] \qquad m_1 = m_2 \text{ and } \theta_1 = \theta_2$$

or,

$$[16] \qquad m_1/m_2 = \theta_2/\theta_1 \text{ with } m_1 \neq m_2.$$

In developing an equation for the rate of O_2 adsorption it will be recalled that a large decrease of the rate with increasing θ was assumed, and m = constant was an approximation valid to account for the rate dependence on θ only over narrow ranges of θ. If θ_1 is very different from θ_2 equation [16] will apply.

The rate of reaction and therefore the rate of oxygen adsorption was found to be several times greater for C_2H_4 than for EtO oxidation. Hence, for $p_E = p_X$ and for $(p_O)_1 = (p_O)_2$ we have,

$$[17] \qquad [jp_O(1 - m\theta)]_1 > [jp_O(1 - m\theta)]_2.$$

From equations [14] and [17] we get,

$$(j)_1 > (j)_2.$$

This result can be explained on the basis of different states of catalyst activity during kinetic runs for each of the reactions. It was found that following EtO oxidation runs, the catalyst was appreciably poisoned for C_2H_4 oxidation (see Part I).

Calculation of Integral Conversions

A final test of any rate equation which may be developed theoretically is its successful comparison with experimental conversion data by substitution and integration of the differential reaction rate equations (e.g. Equation 1, Parts II and III).

Thus

$$\frac{M}{F_E} = \int_0^x \frac{dx}{r}.$$

Knowing the activities of the various components of the system as a function of M/F_E, the constants of the r function may then be tested by integration. The values of x thus obtained should be comparable with experimental values.

The theoretical development of the rate equations for both EtO production and its heterogeneous oxidation are based on zero time or initial reaction conditions where the inhibiting effects of reaction products may be neglected.

This has been stressed in the Discussion of Parts II and III. For this reason it is not justifiable to apply these equations in the type of calculation described above. Numerical tests show that graphically measured differential reaction rates for EtO production at various values of the reaction time co-ordinate are very much lower than those calculated on the basis of the initial rate equation; the similarly calculated rate of EtO oxidation is too small to account for this difference. The maxima in conversion/time curves for EtO, occur when the rate of production of EtO is balanced by its oxidation rate. It must be assumed then that there is a functional dependence of EtO production rate on product concentration whose exact nature remains to be determined by further experimental work where products are included in the feed gas.

ACKNOWLEDGMENTS

The authors are particularly indebted to Drs. I. E. Puddington, S. Chu Liang, and J. S. Dugdale for their continued interest and suggestions during the course of this work and to the late Dr. A. Cambron under whose direction and advice it was begun. It is also desired to express appreciation of the assistance of Messrs. F. Liuzzo and J. K. Waterman in the construction and maintenance of the apparatus.

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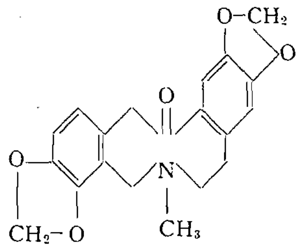
NOTE

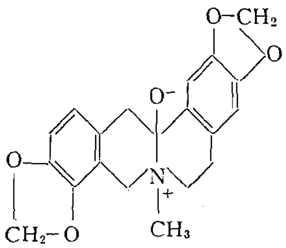
THE STRUCTURE OF PROTOPINE METHIODIDE: A CORRECTION[1]

By F. A. L. Anet[2] and Léo Marion

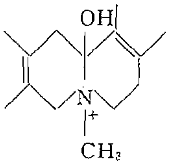
The recent work of Anet, Bailey, and Robinson (1) and of Mottus, Schwarz, and Marion (3) has shown that interaction between a tertiary nitrogen atom and a suitably placed carbonyl group in a large ring can take place. One of the examples chosen by the latter authors was protopine (I) which was shown to give salts with mineral acids by the addition of a proton to the carbonyl oxygen as in (II). In agreement with this it was mentioned that the metho-salts contained no carbonyl band in their infrared spectra and had the new methyl group on the oxygen atom as in (III) (at least in the solid state). The base itself was considered as a resonance hybrid between (I*a* and I*b*).



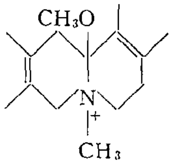
Ia



Ib

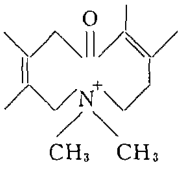


II



III

The former authors (1) working with cryptopine (the dimethoxy analogue of protopine) obtained similar results as far as the structures of the base and ordinary salts were concerned, but found that cryptopine methiodide had an infrared spectrum containing a carbonyl absorption band and so must have structure IV.



IV

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[1] *Issued as N.R.C. No. 3222.*

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

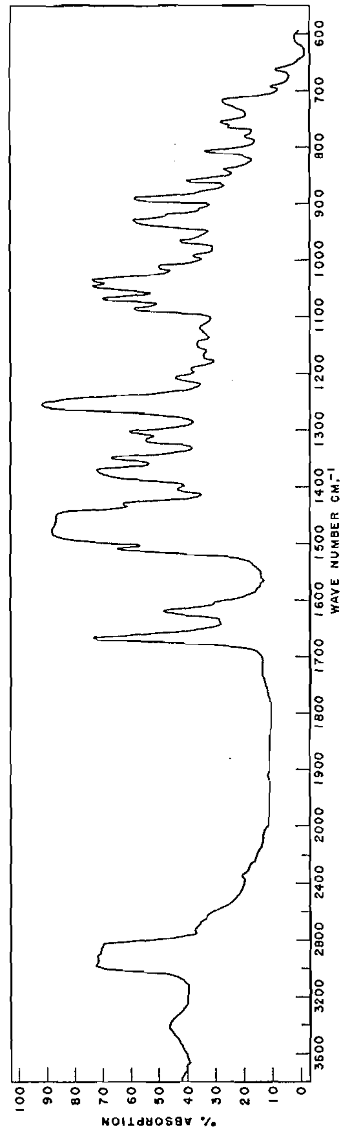

FIG. 1. Infrared spectrum in a nujol mull of protopine methiodide taken on a Perkin-Elmer double beam spectrophotometer model 21.

In view of the close relationship of the two alkaloids this difference in structure of the metho-salts was contrary to what might have been expected. A reinvestigation of the problem has shown that the "protopine methiodide" of Mottus, Schwarz, and Marion (3) was actually protopine hydriodide whose infrared spectrum (which contains a strong bonded hydroxyl band) was identical with that published for the supposed protopine methiodide. Authentic protopine methiodide has now been examined and its infrared spectrum did indeed show a carbonyl absorption band (Fig. 1). It, like cryptopine methiodide but unlike the two parent alkaloids, also gave an immediate color with *m*-dinitrobenzene and alkali in the cold showing the presence of a reactive methylene group.

The above findings remove the necessity for postulating equilibria of various forms of protopine methiodide in solution. The structure of protopine methiodide is then (IV), which is the only form consistent with the chemical evidence of Perkin (4). It might be stated that the negative result in the Zeisel determination of protopine methiodide (3) is not in itself evidence against the methoxy structure, as the proximity of the quaternary nitrogen atom would hinder the addition of a proton to the oxygen atom of the methoxyl group, thus making hydrolysis more difficult than usual. This situation indeed occurs in the metho-salts of *N*-methyl *sec.pseudo*-strychnine (and almost certainly of those of vomicine), which were found by Anet, Bailey, and Robinson (1) to have a methoxy structure, but which are reported by Leuchs (2) to give no methyl iodide in the Zeisel determination.

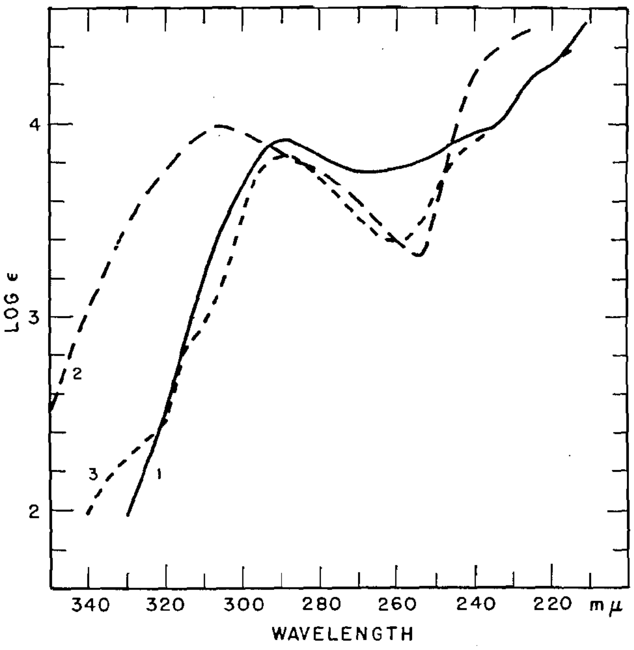

FIG. 2. Ultraviolet spectra in alcohol, curve 1, protopine; curve 2, protopine methiodide; curve 3, protopine hydriodide.

Models of protopine methiodide indicate that the carbonyl group can conjugate to some extent with the adjacent benzene ring, and this is confirmed by the ultraviolet spectrum (Fig. 2) as well as by the position of the carbonyl band in the infrared spectrum. This band (1667 cm.$^{-1}$) is at appreciably lower wave numbers than that of acetophenone (1690 cm.$^{-1}$) but it is close to the more comparable acetoveratrone (1670 cm.$^{-1}$). The photographs of models of protopine given by Mottus *et al.* (3) show that the carbonyl group is very much out of the plane of the benzene ring when in position for favorable interaction with the nitrogen atom. As the carbonyl band in protopine is at 1658 cm.$^{-1}$ it appears that the "nitrogen bonding" can more than annul the shift towards higher wave numbers which would be caused by the loss of conjugation due to noncoplanarity of the carbonyl group and benzene ring.

EXPERIMENTAL

Protopine Hydriodide

The salt was obtained by adding potassium iodide to a solution of protopine in dilute hydrochloric acid. After recrystallization from water it was obtained as small colorless needles which gradually became discolored on heating, were black at 270°, but did not melt up to 300°. Calc. for $C_{20}H_{20}O_5NI$: C, 49.91; H, 4.19; one N–CH_3, 3.12%. Found: C, 50.11; H, 4.09; N–CH_3, 3.46%.

Protopine Methiodide

To protopine dissolved in chloroform was added a large excess of methyl iodide. After two days, colorless needles had separated which, after recrystallization from methanol, melted at 213–215° (dec.). Calc. for $C_{21}H_{22}O_5NI$: C, 50.93; H, 4.48; two N–CH_3, 6.07%. Found: C, 51.16; H, 4.60; N–CH_3, 5.07%.

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THE PHOTOLYSIS OF DIMETHYL MERCURY IN HEXANE SOLUTION AT LOW TEMPERATURES[1]

BY D. H. DERBYSHIRE[2] AND E. W. R. STEACIE

ABSTRACT

The photolysis of dimethyl mercury in solution in *n*-hexane has been studied over the temperature range +25° C. to −80° C. The results indicate that methane is produced by an abstraction reaction involving the solvent, and ethane is produced by dimerization of methyl radicals. The mechanism of the reaction is discussed, and it is concluded that the abstraction reaction involves radicals possessing considerable energy carried over from the photodissociation.

INTRODUCTION

A considerable number of investigations of the photolysis of mercury dimethyl have been made. The indications are that at higher temperatures "hot" radical effects are of no importance (2, 11). At room temperature, however, there are indications that such effects are becoming noticeable (7). There are also indications of such effects in other systems at low temperatures (7, 8, 13, 14, 15, 17) and in the liquid state. It therefore seemed of interest to investigate the mercury dimethyl photolysis at low temperatures in solution. *n*-Hexane was used as a solvent because of its ready availability in a pure state, its low melting point, and its ease of manipulation in a vacuum apparatus.

EXPERIMENTAL

Materials

Dimethyl mercury as supplied by Messrs. H. K. Lights Ltd. was dried over anhydrous calcium chloride and purified by a bulb to bulb distillation; only the middle fraction was collected. The compound was thoroughly degassed and was stored in the dark in a glass bulb isolated by a mercury cutoff. The vapor pressures agreed with the values recorded by Linnett and Thompson (6). The compound was degassed further before each experiment.

The *n*-hexane was a "Phillips Pure Hydrocarbon" stated to be 99 mole % pure. It was found, however, that in 1 cm. depths the material absorbed *ca.*

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70% of incident light in the region of 2300 Å; a region where pure hexane is transparent. It was purified by passing through a column of silica gel (3) which removed practically all of the light absorbing impurities. The product obtained transmitted 99% of incident light at 2300 Å in 1 cm. depths. The hexane was dried over anhydrous calcium chloride and purified by a bulb to bulb distillation, the middle fraction being collected. Since relatively large quantities of hexane were used (*ca.* 1 ml. of liquid in each experiment), about 100 ml. were stored in a reservoir containing a "cold finger" isolated by a mercury cutoff. The hydrocarbon was degassed by filling the cold finger with a freezing mixture at −80° C. and pumping continuously for several hours while allowing the hexane to reflux.

Light Source

Preliminary experiments using the unfiltered radiation from a low pressure mercury lamp showed that mercury dimethyl in hexane solution was photolyzed at a convenient rate at room temperature and that metallic mercury was deposited.

Reichardt and Bonhoeffer (12) have shown that hexane is capable of dissolving a significant amount of mercury and that the saturated solutions so obtained absorb a considerable fraction of incident light in the region 2530–2650 Å. Phibbs and Darwent (9) have also shown that such solutions undergo a photosensitized decomposition when irradiated with mercury resonance radiation. In order to avoid complicating factors due to a concomitant mercury photosensitized reaction, a light source was therefore used having a negligible intensity in the region of 2537 Å. Owing to the broadening of the mercury resonance line in solution, a high pressure mercury arc emitting a reversed line at 2537 Å is obviously unsuitable.

The light source finally adopted was a cadmium–neon discharge lamp, which had strong lines at 2288 Å and 3261 Å with only weak lines in between (10). The lamp was enclosed in a furnace with a small additional heater situated near the center of the lamp. With this arrangement the central part of the lamp could be maintained about 15° higher than the two electrodes, thus preventing the distillation of cadmium to the center of the tube and so the obscuring of the window. The lamp was operated at about 280° C. with a current of 80 ma. from a Jefferson sign transformer. The radiation from the lamp was roughly collimated by passing through a 5 cm. quartz cell containing distilled water which also served to absorb infrared radiation. Spectrographic investigation showed that the cadmium line at 2288 Å was almost completely absorbed by the solutions of dimethyl mercury in hexane, but the 3261 Å line was relatively unaffected; the unfiltered cadmium radiation was therefore used as a light source. The light intensity was varied by means of neutral density filters consisting of chromel deposited on quartz.

Apparatus

The analytical method was designed to handle samples of liquid of about 1 ml. and so the photolyses were carried out in a quartz cell of approximately 5 cm. diameter and 0.05 cm. in depth. The cell was provided with two outlets so that after filling, it could be sealed off and removed to carry out the photolysis, after which it was resealed into the apparatus and the products liberated into the analytical apparatus by breaking a thin glass internal seal with a plunger. The solutions used contained about 1 mole % of dimethyl mercury and never more than 5% of the dimethyl mercury was decomposed during the photolysis.

Solutions were prepared by taking known volumes of dimethyl mercury vapor at a given temperature and pressure and mixing them with a fixed quantity of liquid hexane (measured at −78° C.), after which the reagents were condensed into the cell and the apparatus sealed off at a constriction. Mercury cutoffs were used at all points in the apparatus which came into more than fleeting contact with the vapor of hexane and dimethyl mercury.

The gaseous products of the reaction were found to be methane and ethane in a ratio of about 4: 1 in the experiments at 25° C. The quantities of these gases produced were, however, quite small, e.g. about 0.1 ml. of methane and 0.025 ml. of ethane measured at N.T.P., and an analytical method had to be devised for separating these small quantities of methane and ethane from the large liquid residue. It was found convenient to divide the analytical procedure into two stages, the first being the separation of methane and ethane from the liquid residue, and the second the resolution of the mixture of methane and ethane.

After an experiment the contents of the cell were distilled into a column at the top of which was a "cold finger" maintained at −78° C. with a freezing mixture. The liquid was refluxed continuously in this vessel while the degassing was carried out. The combined pressure of methane and ethane above the solution was measured by a McLeod gauge, but since hexane has a vapor pressure of *ca.* 0.1 mm. at −78° C., it was necessary to insert a trap maintained at −160° C. between the refluxing liquid and the McLeod gauge in order to remove the hexane vapor from the methane and ethane. The two gases were then pumped away by a Toepler pump until the total pressure above the liquid residue was reduced to 10^{-3} mm. and remained stationary at this value. Experiments in which known quantities of methane and ethane were taken and mixed with hexane showed that by this procedure these gases could be removed from hexane solution practically completely. With quantities of gases of the order found in the photolysis experiments the reproducibility was of the order 3–4%.

The mixtures of methane and ethane were separated by low temperature fractionation using a modified type of Ward still (5). Mass spectrometer analyses of the products showed no traces of hexane.

Liquid Residue

In a number of experiments the infrared spectra of the liquid contents of the cell were determined before and after irradiation, using a Perkin-Elmer double-beam spectrometer. These were identical in the region of 900 cm.$^{-1}$ showing that detectable amounts of unsaturated hydrocarbons were not produced in the reaction. However, it would appear from the values of the extinction coefficients for ethylenic hydrocarbons quoted in the literature (1) that this method may be insufficiently sensitive to detect the amounts of unsaturated hydrocarbon expected.

Low Temperature Photolysis

For the irradiations at low temperatures, several types of apparatus were constructed and used with varying degrees of success.

The first type of apparatus constructed was similar in principle to apparatus used in low-temperature calorimetric work. The thermostat consisted of an aluminum block suspended in a steel cylinder from a cup which also formed part of the lid. The apparatus was evacuated and light entered the apparatus through quartz windows sealed into the sides of the cylinder. The aluminum block was cooled by placing a refrigerant, e.g., liquid nitrogen or carbon dioxide – acetone, in the steel cup, and the temperature brought to a constant value by balancing the loss of heat from the block by a heater in good thermal contact with the aluminum block. By varying the current in the heater and the thermal contact between the block and the cup containing the refrigerant, the temperature of the block could be varied over a wide range. The cell was placed in a slot cut into the side of the aluminum block and light entered the cell through a circular aperture cut into the face of the thermostat. Thermal contact with the block was made at the back and sides of the cell. This type of apparatus was convenient to use and experiments were conducted with the thermostat at temperatures down to −70° C. It was found, however, that the thermal contact between cell and thermostat was not sufficient and considerable temperature gradients existed between the cell and the aluminum block. In view of this fact, extensive experiments with this type of system were not carried out at low temperatures but the apparatus was used for experiments in the vicinity of room temperature.

The apparatus finally adopted for the low temperature experiments was of a more conventional type and consisted essentially of an unsilvered glass dewar filled with ethyl alcohol. Light was conducted into the cell through quartz windows of approximately 3 cm. diameter sealed into the sides of the dewar. The alcohol used as a bath liquid was purified by the method of Leighton (4) and had a transmission of 80% at 2288 Å in 1 cm. depths. The cell was placed 1 mm. or less behind the quartz window and so absorption of light by the alcohol was negligible. The cooling of the bath liquid was carried out by placing a "cold finger" into the alcohol. The "cold finger" consisted of a glass cylinder closed at one end, with numerous indentations to increase the surface area and containing a refrigerant such as carbon dioxide – acetone. The glass cylinder was sealed into the bottom of a long silvered glass dewar which formed a reservoir which could be filled with solid carbon dioxide. With a carbon dioxide – acetone mixture in the "cold finger", the bath could be maintained at −60° ± 0.5° C. For temperatures between −60° C. and 0° C. heat was supplied to the thermostat by a heater of chromel wire wound around the "cold finger". This type of thermostat was found to be extremely convenient for the low temperature experiments.

RESULTS

Mixtures of hexane and dimethyl mercury were found to be quite stable when kept in the dark at 25° C. Irradiation of liquid hexane in the presence of mercury produced no gaseous products.

TABLE I
Temperature = 25° C.; $Hg(CH_3)_2$ = *ca.* 10^{-4} mole; C_6H_{14} = *ca.* 10^{-2} mole

Duration of run in hours	6	12	12	12	18	24
CH_4 produced, ml. (N.T.P.)/hr. × 10^{-3}	7.0	7.0	6.9	6.9	6.8	6.9
C_2H_6 produced, " " "	1.6	1.6	1.5	1.6	1.6	1.6

The results given in Table I show that the rate of production of methane and ethane at 25° C. is independent of time, and that there is no induction period associated with the reaction. Variation of the concentration of dimethyl mercury had no effect on the rate of reaction. The rate of formation of methane and ethane remained constant at constant intensity when the concentration of dimethyl mercury was increased by a factor of four, as shown by the data in Table II.

TABLE II
EFFECT OF $Hg(CH_3)_2$ CONCENTRATION
Temperature = 25° C.; C_6H_{14} = *ca.* 10^{-2} mole

Expt.	$Hg(CH_3)_2$ (mole)	CH_4 (ml. (N.T.P.)/hr.)	C_2H_6 (ml. (N.T.P.)/hr.)	Time (hr.)
1	4×10^{-5}	6.7×10^{-3}	1.5×10^{-3}	12
2	8×10^{-5}	6.8×10^{-3}	1.4×10^{-3}	12
3	2×10^{-4}	6.8×10^{-3}	1.5×10^{-3}	12
4*	2×10^{-4}	6.9×10^{-3}	1.4×10^{-3}	17
5	2×10^{-4}	6.6×10^{-3}	1.6×10^{-3}	12

* *Experiment using liquid thermostat. Volume of light in cell approximately half that in other experiments.*

The effect of a 50-fold variation in light intensity on the rate of production of methane and ethane is given in Table III. Relative intensities are not explicitly stated for most runs but may be inferred from the values of R_{CH_4}. At the lower light intensities the amount of ethane produced was quite small and its determination was therefore less accurate than in the other experiments. Values of the ratios $R_{CH_4}/R_{C_2H_6}$ and $R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}$ are given in the table and it is seen that the data point clearly to the conclusion that the former ratio is more nearly independent of light intensity than the latter. In a few runs, Nos. 5–12, the optical system and lamp were unchanged and the intensity was varied by interposing filters. While the results are rather scattered, they indicate that within the experimental error both R_{CH_4} and $R_{C_2H_6}$ are directly proportional to I.

Table IV summarizes the effect of temperature on the reaction. Between 25° C. and −80° C. the rate of production of ethane remains approximately constant whilst the rate of production of methane varies by a factor of three.

TABLE III
EFFECT OF INTENSITY
Temperature = 25° C.; $Hg(CH_3)_2$ = *ca.* 10^{-4} mole; C_6H_{14} = *ca.* 10^{-2} mole

Expt.	R_{CH_4} (ml. (N.T.P.)/hr.)	I, relative	$R_{C_2H_6}$ (ml. (N.T.P.)/hr.)	$R_{CH_4}/R_{C_2H_6}$	$R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}$	Time (hr.)
1	2.50×10^{-2}	—	5.59×10^{-3}	4.5	0.34	21
2*	2.51×10^{-2}	—	5.71×10^{-3}	4.4	0.33	5
3	1.80×10^{-2}	—	4.29×10^{-3}	4.2	0.28	12
4	1.90×10^{-2}	—	4.42×10^{-3}	4.3	0.28	12
5	6.90×10^{-3}	100	1.50×10^{-3}	4.6	0.18	12
6	6.76×10^{-3}	100	1.62×10^{-3}	4.2	0.17	18
7	4.60×10^{-3}	58	6.94×10^{-4}	6.6	0.17	24
8	4.10×10^{-3}	58	7.70×10^{-4}	5.3	0.15	22
9	1.35×10^{-3}	25	2.91×10^{-4}	4.6	0.080	48
10	1.19×10^{-3}	25	3.28×10^{-4}	3.6	0.066	41
11	1.01×10^{-3}	10	1.10×10^{-4}	9.1	0.096	93
12	5.53×10^{-4}	10	1.08×10^{-4}	5.1	0.053	96
13**	3.13×10^{-3}	—	7.13×10^{-4}	4.4	0.12	14
14**	6.87×10^{-3}	—	1.43×10^{-3}	4.8	0.18	17
15	4.99×10^{-3}	—	1.16×10^{-3}	4.3	0.15	11

* *Experiments 1 and 2 carried out by R. G. Partington.*
** *Experiments 13 and 14 using a liquid thermostat.*

TABLE IV
EFFECT OF TEMPERATURE
$Hg(CH_3)_2$ = *ca.* 2×10^{-4} mole; C_6H_{14} = *ca.* 10^{-2} mole

Expt.	Time (hr.)	Temp. (° C.)	R_{CH_4} (ml. (N.T.P.)/hr.)	$R_{C_2H_6}$ (ml. (N.T.P.)/hr.)	$R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}$	ϕ
1*a*	14	25	3.13×10^{-3}	7.13×10^{-4}	4.4	4.5
2*a*	14	−30	2.54×10^{-3}	6.95×10^{-4}	3.6	3.9
3*a*	12	−60	1.78×10^{-3}	7.50×10^{-4}	2.4	3.3
4*a*	20	−80	1.05×10^{-3}	7.50×10^{-4}	1.4	2.5
5*b*	22	22	3.72×10^{-3}	8.11×10^{-4}	4.6	—
6*b*	22	−60	2.01×10^{-3}	8.28×10^{-4}	2.4	—
7*c*	17	25	6.87×10^{-3}	1.43×10^{-3}	4.8	—
8*c*	20	−60	2.78×10^{-3}	1.34×10^{-3}	2.1	—
9*d*	12	25	7.03×10^{-3}	1.50×10^{-3}	4.7	—
10*d*	12	−43	4.78×10^{-3}	1.74×10^{-3}	2.8	—

(*a*), (*b*), (*c*), (*d*) *refer to sets of experiments with different lamps.*
In experiments (*d*) *the aluminum thermostat was used.*

The relative over-all quantum yield of production of hydrocarbon (ϕ), i.e., $CH_4 + 2C_2H_6$, falls with temperature in one set of experiments from 4.5 at 25° C. to 2.5 at −80° C. All the experiments with the exception of experiments 9 and 10 were carried out using the liquid thermostat; in experiments 9 and 10 the aluminum thermostat was used.

DISCUSSION

The main steps in the mechanism of the gas-phase photolysis of mercury dimethyl are (2, 11)

$$Hg(CH_3)_2 + h\nu \rightarrow Hg + 2CH_3, \qquad [1]$$

$$CH_3 + Hg(CH_3)_2 \rightarrow CH_4 + Hg(CH_3)CH_2, \qquad [2]$$

$$2CH_3 \rightarrow C_2H_6, \qquad [3]$$

$$CH_3 + Hg(CH_3)CH_2 \rightarrow Hg(CH_3)C_2H_5. \qquad [4]$$

In the presence of hexane, the reaction

$$CH_3 + C_6H_{14} \rightarrow CH_4 + C_6H_{13} \qquad [5]$$

would also be expected (16). There are also certain complications in the mechanism whereby some additional ethane may be formed by a reaction of methyl radicals with mercury dimethyl (2). In the present case, however, $R_{C_2H_6}$ is independent of the concentration of mercury dimethyl and such reactions cannot be important. Also, since the concentration of hexane is so much greater than that of mercury dimethyl, reaction [2] may be ignored relative to [5] as a source of methane. The mechanism in solution can therefore be considered to consist of reactions [1], [3], [5] and reactions whereby C_6H_{13} disappears by dimerization, disproportionation, or by reaction with methyl. Under these conditions

$$\frac{R_{CH_4}}{R^{\frac{1}{2}}_{C_2H_6}} = \frac{k_5}{k_3^{\frac{1}{2}}}[C_6H_{14}] = \text{const.}\,\frac{k_5}{k_3^{\frac{1}{2}}}.$$

This relation is not obeyed, since $R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6}$ is not constant. Also if this were fulfilled the temperature coefficient of the ratio would be equal to $E_5 - \frac{1}{2}E_3 \approx E_5 \approx 8$ kcal. Actually the temperature coefficient of methane production is very small, and corresponds to about 1 kcal. Also, in view of the magnitudes of E_5 and E_2 methane production would be expected to be negligible at low temperatures, instead of which it exceeds that of ethane at all temperatures.

It seems almost certain that these results are to be explained on the basis of "hot radicals." In reaction [1] excess energy of about 60 kcal. is available. We may therefore write the essential steps of the mechanism as:

$$Hg(CH_3)_2 + h\nu \rightarrow Hg + 2CH_3^*, \qquad [6]$$

$$CH_3^* + C_6H_{14} \rightarrow CH_3 + C_6H_{14}, \qquad [7]$$

$$CH_3^* + C_6H_{14} \rightarrow CH_4 + C_6H_{13}, \qquad [8]$$

$$2CH_3 \rightarrow C_2H_6, \qquad [4]$$

together with steps involving the disappearance of C_6H_{13}. On this basis

$$\frac{R_{CH_4}}{R_{C_2H_6}} = \text{constant},$$

independent of $[Hg(CH_3)_2]$, and of intensity. Table III shows that this relationship is fulfilled. On such a basis also, an apparent activation energy of *ca.* 1 kcal. appears reasonable. (The positive temperature coefficient might, however, also be due to the diminished stability of $HgCH_3$ at higher temperatures.)

It may therefore be concluded that hot radical reactions become predominant at very low temperatures in the present system, in spite of their relative unimportance in the gas-phase at higher temperatures.

ACKNOWLEDGMENT

The authors are indebted to Dr. R. G. Partington for the development of the analytical methods used, and for carrying out preliminary experiments. Thanks are also due to Miss F. Gauthier and Dr. F. P. Lossing for mass-spectrometer analyses.

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ATISINE: THE HETEROCYCLIC RING AND FUNCTIONAL GROUPS[1]

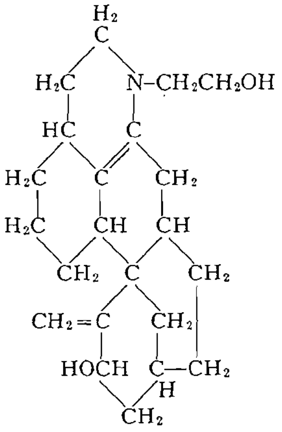
By O. E. Edwards and Tara Singh[2]

ABSTRACT

Evidence is presented which confirms the presence in atisine and isoatisine of vinylamine double bonds, an N-(β-hydroxyethyl) group, an exocyclic methylene group, and a secondary hydroxyl in an allylic relation to the latter. The size and substitution of the heterocyclic ring is discussed. The pyrolysis of atisine and isoatisine hydrochlorides to give a $C_{20}H_{29}ON$ base is described.

INTRODUCTION

The alkaloid atisine is of interest as a representative of the less oxygenated aconite group (kobusine, talatisine, napelline, and hetisine are others). It is a dihydroxy pentacyclic base of empirical formula $C_{22}H_{33}O_2N$ containing two double bonds (10). The nitrogen is tertiary, and is substituted by a group which can give ethyl iodide in the Herzig-Meyer N-alkyl determination (7). On the basis of information obtained by oxidative degradation and selenium dehydrogenation Jacobs put forward a tentative structure (Formula 1) for the base (9). In work preliminary to systematic degradation of the alkaloid we have provided proof of the presence of some of the structural features postulated by Jacobs.[3]



Formula 1

Jacobs and co-workers demonstrated that atisine was a very strong base (7), that it was isomerized by alkali to a weaker base, isoatisine (7,11), and that both bases could be converted by prolonged heating with sodium hydroxide in methanol to dihydroatisine (11). They interpreted the isomerization as migration of a vinylamine double bond from one side of the nitrogen to the

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[2] National Research Council Postdoctorate Fellow.

[3] A preliminary report of some of this work was published earlier (6).

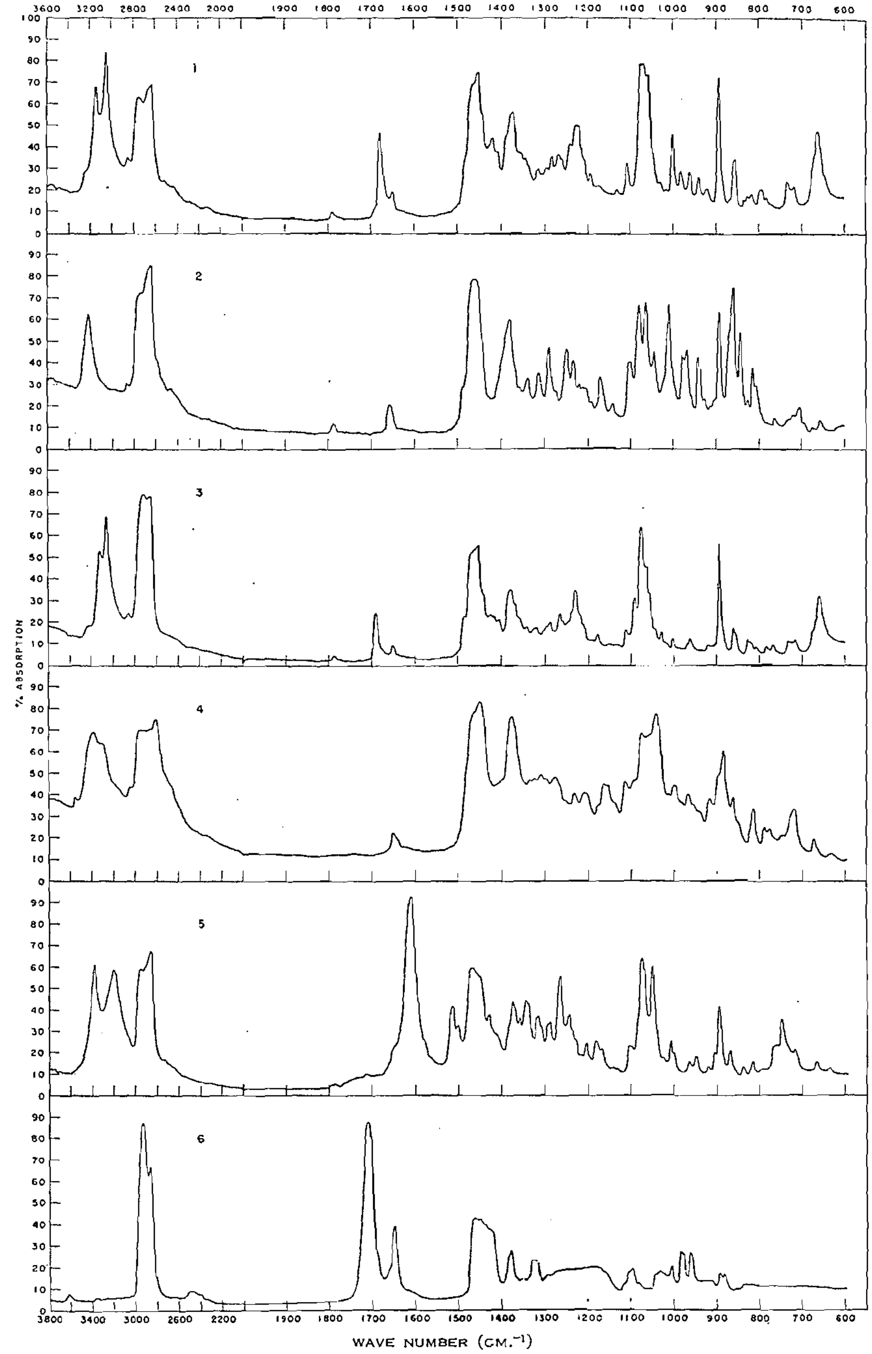

FIG. 1. Infrared spectra.
1. Atisine hydrochloride (nujol mull). 2. Isoatisine (nujol mull). 3. Isoatisine hydrochloride (nujol mull). 4. Dihydroatisine (nujol mull). 5. Oxoatisine (nujol mull). 6. The $C_{20}H_{29}ON$ base in chloroform (6.4 mgm. per ml., 1 mm. cell).

NOTE ADDED IN PROOF: *The wave numbers at the top of the figure, between 2000 and 3600 cm.$^{-1}$ are displayed one division to the left.*

other, and the formation of the dihydroatisine as reduction of the vinylamine double bond.[4]

Adams and Mahan showed that simple tertiary vinylamines are stronger by several pK units than the corresponding saturated amines. They suggested that this was due to the formation of salts with quaternary ammonium character (1).

$$\rangle C=C-N\langle \xrightarrow{H^+} \rangle CH-C=\overset{+}{N}\langle$$

We have demonstrated that atisine (pK 12.2)[5] and isoatisine (pK 10.0) are stronger bases than dihydroatisine (pK 8.2) as would be expected if Jacobs' postulate were correct. The infrared spectra (mulls) of atisine and isoatisine hydrochlorides contain bands at 1680 cm.$^{-1}$ and 1692 cm.$^{-1}$ respectively, which are absent in the parent bases (Fig. 1). Such bands are characteristic of salts containing the $\rangle C=\overset{+}{N}\langle$ group (4, 13).

Saturated tertiary bases show more intense absorption in the ultraviolet above 220 mμ than the corresponding hydrochlorides or perchlorates (4, 5). The converse seems to be true for aliphatic bases whose salts contain the $\rangle C=\overset{+}{N}\langle$ chromophore (4). Both atisine and isoatisine fall into the latter category (Fig. 2).

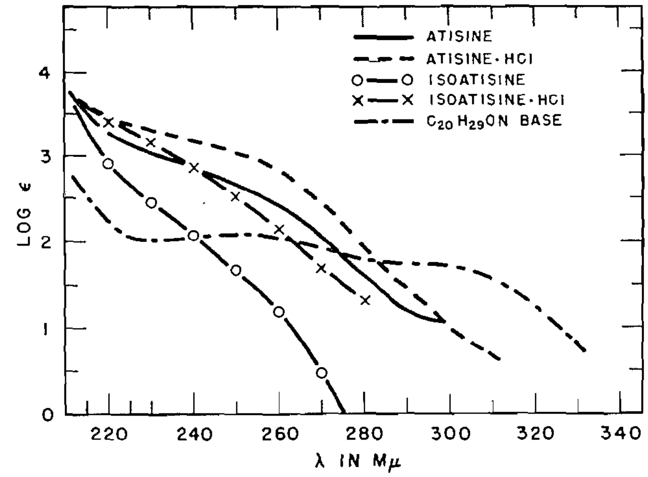

FIG. 2.

Finally, evidence for the vinylamine character of the isomeric bases comes from the fact that both could readily be reduced by sodium borohydride to the same dihydroatisine obtained on drastic alkali treatment of the bases (11). This can be considered as reduction of a small percentage of the carbinol-

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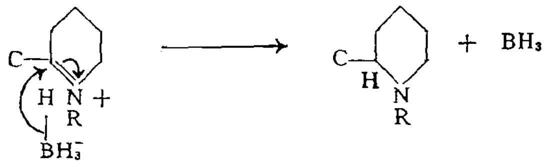
[4] *This is not a simple analogue of the Cannizzaro reaction, since the yield of reduced product is 75%. Hence oxidation of methanol probably accompanies the reduction of the alkaloid.*

[5] *The pK values were determined in 50% aqueous methanol solution.*

amine form present in aqueous methanol solution, or as reduction of the salt form (always present in polar solvents) as shown:



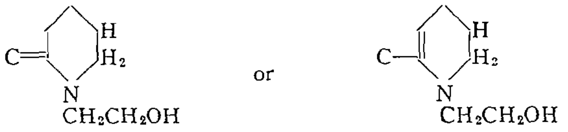
Huebner and Jacobs (7) showed that a two carbon fragment and one oxygen were rather readily eliminated from atisine by heating with nickel on alumina. They also found that the lactam tricarboxylic acid from isoatisine lost a $C_2H_2O_2$ fragment when treated with thionyl chloride (8, 9). Jacobs concluded that a $>NCH_2CH_2OH$ group was present in atisine. It seems reasonable that such a group could give ethyl iodide in the Herzig-Meyer determination (7).

Wiesner and co-workers (3) heated atisine at 300° with selenium and obtained the same $C_{20}H_{29}ON$ base obtained by Huebner and Jacobs with nickel on alumina. They found it to contain an imino and a carbonyl group. When this base was reduced to the secondary amine and the product condensed with ethylene chlorohydrin a base isomeric with tetrahydroatisine was obtained. Thus supporting evidence, but not decisive proof of the presence of the ethanolamine structure had been presented.

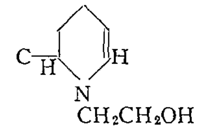
Leonard and Rebenstorf have shown (12) that simple β-(dialkylamino)-ethanols are cleaved by lead tetraacetate at 60° to a glycolic aldehyde derivative. This reaction has now been applied to tetrahydroatisine, and glyoxal bis-*p*-nitrophenylhydrazone obtained in 31% yield from the products. This provides decisive confirmation of the presence of the ethanolamine system in the alkaloid.

Since isoatisine could be oxidized to a lactam with disappearance of the vinylamine double bond, while atisine gave a lactam retaining its vinylamine bond, Jacobs concluded (9) that in atisine there are two hydrogens on one ring carbon α to the nitrogen but none on the other. An examination of the infrared spectrum of oxoisatisine has shown the lactam carbonyl band to be at 1610 cm^{-1}. This suggests that the heterocyclic ring is six membered[6] with hydrogen bonding to the carbonyl lowering the frequency from the usual position near 1640 cm^{-1}. An active hydrogen determination on isoatisine confirmed that there are two hydroxyls in this base, as in atisine.

Thus the heterocyclic ring in the bases can be written as:



Atisine



Isoatisine

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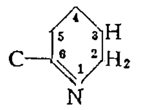
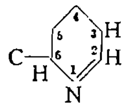
[6] *Unpublished results in this laboratory indicate that saturated five membered lactams absorb near 1690 cm^{-1}.*

The fact (3) that atisine when heated with selenium at 300° gives considerable material containing the system



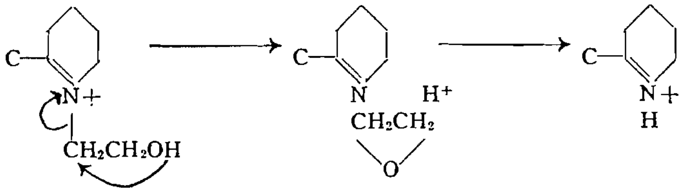
or



must mean that the heterocyclic ring cannot aromatize without carbon migration. There cannot be meta bridging from carbons 4 to 6, or 3 to 5 in this ring since then either atisine or isoatisine would have a bridgehead double bond (Bredt's rule violated). Thus the most likely explanation of the failure to aromatize is that carbon 4 or 5 is quaternary. The formula for atisine postulated by Jacobs does not contain this feature, hence doubt is cast on its validity.

The infrared spectra of atisine, isoatisine, and dihydroatisine contain bands characteristic of an exocyclic methylene group (2) at 894 cm.$^{-1}$, 1650 cm.$^{-1}$, and 3060 cm.$^{-1}$, thus confirming Jacobs' interpretation of his oxidation studies.

It seemed probable that the pyrolysis of atisine or isoatisine salts would proceed smoothly with elimination of the N-(β-hydroxyethyl) side chain:



Actually, when either salt was heated at 310° a mixture was obtained. When the base liberated from this was chromatographed on alumina, the fraction rapidly eluted by benzene crystallized readily. When recrystallized from petroleum ether it melted at 82–84° and analyzed correctly for $C_{20}H_{29}ON$. On repeated recrystallization from the same solvent a small amount of material melting at 142° was obtained. The 84° base gave a picrate melting at 252°, from which base melting at 84° could be recovered. The infrared spectra of the 84° and 142° samples were nearly identical, containing a carbonyl band at 1707 cm.$^{-1}$ and what is probably an imino band at 1646 cm.$^{-1}$ (Fig. 1). Thus in the light of the above evidence, and of the fact that the 84° base has an ultraviolet spectrum (Fig. 2) very similar to that published by Huebner and Jacobs for the $C_{20}H_{29}ON$ compound, it is most likely that it is a stereoisomer of the base described by the previous workers (3, 7).

The $C_{20}H_{29}ON$ base could be reduced in acid solution in the presence of platinum to a dihydro derivative. This was still a ketone (band at 1710 cm.$^{-1}$) but the band at 1646 cm.$^{-1}$ in the infrared and the ultraviolet maximum at 250 mμ (Fig. 2) were no longer present. This is consistent with reduction of a $>C=N-$ group in the base.

The bands which can be assigned to an exocyclic methylene group in atisine and isoatisine are absent in the $C_{20}H_{29}ON$ base and a clear band due to a methyl group (1376 cm.$^{-1}$) is present in the infrared spectrum of chloroform solutions of the $C_{26}H_{29}ON$ and the dihydro bases. Thus it appears that Jacobs' suggested relation of the exocyclic methylene to the secondary hydroxyl is correct, and that the allylic system is readily isomerized by heat and probably by acid (7) to the corresponding ketone. The position of the carbonyl band in the infrared makes it probable that it is on a six membered or larger ring.

The reactions in the heterocyclic ring are very stereospecific. Only one isomer is formed when the vinylamine double bond in atisine is reduced chemically and when it is isomerized to give isoatisine. Thus the mixture of stereoisomers formed on catalytic reduction of atisine, isoatisine, and dihydroatisine is most probably due to the two orientations of the new methyl group.

Systematic degradation of the alkaloid, using the various functional groups, is projected.

EXPERIMENTAL

Ultraviolet spectra were determined on a Beckman DU spectrophotometer. Infrared spectra were obtained using a Perkin-Elmer model 21 double beam spectrophotometer. The pK's were determined by titration of the bases with 0.05 *N* hydrochloric acid in 50% aqueous methanol, using the same mixture as solvent.

Atisine

The alkaloid was isolated from the roots of *Aconitum heterophyllum* obtained from the S. B. Penick Co. The finely ground root was percolated at room temperature with methanol. Removal of the solvent from the extract was carried out under reduced pressure. Crystalline sugar which separated from a concentrated methanol solution of the residue was removed by filtration, the filtrate reduced to a sirup, and the alkaloids separated by the method of Jacobs and Craig (10). Fifty pounds of root yielded approximately 63 gm. of atisine hydrochloride.

The recrystallized hydrochloride had the form of needles, m.p. 303° dec. (immersed at 190°), $[\alpha]_D^{29}$ 28 ± 1° (c = 1.6 in water). The infrared spectrum (Fig. 1) contained bands at 3060, 1652, and 895 cm.$^{-1}$ ($>C{=}CH_2$) and at 1680 cm.$^{-1}$ ($>C{=}\overset{+}{N}<$).

The base liberated from the salt with aqueous sodium hydroxide and extracted into ether was a colorless glass. Its infrared spectrum (film) had bands at 3060, 1652, and 895 cm.$^{-1}$ ($>C{=}CH_2$). It had a pK of 12.2 ± 0.2. A sample of the base distilled at 110° under 5×10^{-4} mm. had $[\alpha]_D$ $-21 \pm 2°$ (c = 2.4 in carbonate-free ethanol). Its infrared spectrum (film) contained bands at 1020 and at 865 cm.$^{-1}$ not present in the base as described above, hence changes appear to have taken place on distillation. Found: active hydrogen, 0.567, 0.541. Calc. for $C_{22}H_{33}O_2N$: two active hydrogens, 0.587.

Isoatisine

This was prepared by the methods of Jacobs and Craig (11) and recrystallized from aqueous methanol. It melted at 152° after softening at 148°, and had a pK of 10.0. Its infrared spectrum had bands at 3070, 1656, and 894 cm.$^{-1}$ ($>C=CH_2$) (Fig. 1). Found: active hydrogen, 0.530, 0.592. Calc. for $C_{22}H_{33}O_2N$: two active hydrogens 0.587. The hydrochloride had the form of needles, m.p. 296° dec. (immersed at 260°), $[\alpha]_D$ $-1 \pm 1°$ (c = 1.0 in ethanol). It showed no mixed melting point depression with atisine hydrochloride. Its infrared spectrum (mull) had bands at 3060, 1650, and 894 cm.$^{-1}$ ($>C=CH_2$) and at 1692 cm.$^{-1}$ ($>C=\overset{+}{N}<$).

Dihydroatisine

(*a*) To a solution of 50 mgm. of atisine hydrochloride in 5 cc. of 80% methanol–water was added 30 mgm. of sodium borohydride. There was brisk evolution of hydrogen. The solution stood at room temperature for 1.5 hr. after which the solvent was removed under reduced pressure. The residue was extracted with ether. The dried concentrated ether solution deposited rhombic plates (45 mgm.) m.p. 157–159°. This did not depress the melting point of the products from (*b*) and (*c*).

(*b*) Isoatisine (108 mgm.) in 10 cc. of 80% methanol–water containing 63 mgm. of sodium borohydride was left at room temperature for 1.5 hr. The product was isolated as in (*a*). Yield, 100 mgm. in three crops. The first crop of crystals melted at 157–159°, $[\alpha]_D$ $-45.4 \pm 0.5°$ (c = 2.72 in ethanol), pK, 8.2. Found: C, 76.32; H, 9.95. Calc. for $C_{22}H_{35}O_2N$: C, 76.47; H, 10.22. Infrared bands (mull) at 3050, 1650, and 886 cm.$^{-1}$ ($>C=CH_2$) (Fig. 1).

(*c*) Atisine hydrochloride (100 mgm.) was added to 5 cc. of a hot saturated solution of sodium hydroxide in methanol in a pressure tube. The tube was sealed and heated at 100° for 90 hr. with occasional shaking. The mixture was then diluted with 15 cc. of water and the base extracted with ether. From the dried concentrated ether solution 40 mgm. of rhombic plates were obtained, m.p. 152–154° with previous sintering. This gave no mixed melting point depression with the products from (*a*) and (*b*).

The three samples had identical infrared spectra.

Dihydroatisine Hydrochloride

This crystallized from methanol as prisms, m.p. 261–263°. Its infrared spectrum (mull) had no $>C=\overset{+}{N}<$ band between 1660 and 1700 cm.$^{-1}$.

Tetrahydroatisine

Two hundred and fifty milligrams of atisine hydrochloride in 50 cc. of methanol in the presence of platinum from 50 mgm. of platinum oxide (Adams) absorbed 31.6 cc. of hydrogen in seven minutes (27.5°C., 1 atm.). The catalyst was removed by filtration and the solvent evaporated. The residue was taken up in sodium hydroxide solution and extracted with ether. The dried and concentrated ether solution deposited 150 mgm. of small needles, m.p. 155–160°. When recrystallized from ethanol this gave 40 mgm., m.p. 170–172° after preliminary softening. Jacobs and Craig record a melting point of 173° (11). Its infrared spectrum (mull) contained no band in the 1600–1700 cm.$^{-1}$ region and no band near the 890 cm^{-1}.

Glyoxal from Tetrahydroatisine

A solution of 250 mgm. of tetrahydroatisine (m.p. 150°) and 650 mgm. (2 molar equivalent) of lead tetraacetate in 25 cc. of glacial acetic acid was heated at 62 ± 4° for 24 hr. All the lead tetraacetate was consumed. The mixture was diluted with 25 ml. of water and 500 mgm. of *p*-nitrophenylhydrazine added. The resulting solution was filtered and then heated on the steam bath for four hours. The red crystalline precipitate (25 mgm.) melted at 310° dec. This was sparingly soluble in glacial acetic acid but was recrystallized from the boiling solvent, m.p. 311–312° dec. Found: C, 51.25; H, 3.65. Calc. for $C_{14}H_{12}N_6O_4$: C, 51.21; H, 3.66. This compound did not depress the melting point of authentic glyoxal bis(*p*-nitrophenyl)-hydrazone, and the two specimens had identical infrared spectra.

On further heating (15 hr.) the filtrate from the first crop of osazone gave 50 mgm. more of the osazone (total, 31% of theory).

Pyrolysis of Atisine Hydrochloride

Atisine hydrochloride (400 mgm.) was immersed in a metal bath at 310–320°C. and held at that temperature for 1.5 min. The dark brown product was extracted with dilute hydrochloric acid and filtered after the addition of charcoal. The filtrate was made alkaline with sodium hydroxide and extracted with benzene. The benzene solution on evaporation yielded 230 mgm. of base, which was again dissolved in benzene, then adsorbed on 3 gm. of alkaline alumina (activity 1). The first 20 cc. of benzene eluted 133 mgm., and the following four 20 cc. portions eluted 40 mgm. more. This material slowly solidified. When crystallized from petroleum ether the compound melted at 82–84° with previous shrinking. Found: C, 80.61; H, 9.77. Calc. for $C_{20}H_{29}ON$: C, 80.22; H, 9.76. Ultraviolet spectrum (Fig. 2): $\lambda_{\max}$ 250 mμ, log ϵ 2.09; shoulder at 295 mμ, log ϵ 1.74. Its infrared spectrum (chloroform) had bands at 1646 and 1707 cm.$^{-1}$ (Fig. 1).

Pyrolysis of Isoatisine Hydrochloride

When 380 mgm. of isoatisine hydrochloride was treated as above, 190 mgm. of base was recovered. This gave 139 mgm. of the readily eluted base. After one recrystallization from petroleum ether this melted at 83–85°. It proved identical with the product from atisine hydrochloride (mixed melting point and comparison of infrared spectra).

The samples melting at 84° or 85° from both salts on repeated recrystallisation from petroleum ether gave small quantities of base melting at 142° after previous sintering. The infrared spectrum of this material showed only minor differences in the fingerprint region from that of the 85° base.

The combined 85° base prepared from both salts was converted to the picrate. This crystallized from ethanol as long needles, m.p. 250–252°. Found: C, 59.20; H, 6.16. Calc. for $C_{26}H_{32}O_8N_4$: C, 59.08; H, 6.10. Base recovered from the pure picrate and crystallized from petroleum ether melted at 80–84°.

Dihydro-keto Base

$C_{20}H_{29}ON$ base (25 mgm.) in 3 cc. of ethanol containing three drops of concentrated hydrochloric acid in the presence of platinum from 10 mgm. of platinum oxide (Adams) absorbed 2.08 cc. of hydrogen in eight hours at 26°C. and 761.5 mm. pressure (mole ratio 1.0). The product crystallized as prisms from petroleum ether, m.p. 135°. Found: C, 79.22; H, 9.99. Calc. for $C_{20}H_{31}ON$: C, 79.67; H, 10.37. Ultraviolet spectrum: λ_{min} 266 mμ, log ϵ 1.74; λ_{max} 291 mμ; log ϵ 1.91. Infrared spectrum (chloroform) had bands at 1710 cm.$^{-1}$ and at 1376 cm^{-1}.

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ADDITION OF METHYL RADICALS TO UNSATURATED HYDROCARBONS[1]

By L. Mandelcorn[2] and E. W. R. Steacie

ABSTRACT

The rates of addition of methyl radicals, produced by the photolysis of acetone between 140° C. and 240° C., to unsaturated hydrocarbons were determined by two independent methods. From the kinetics of the addition and the methyl radical combination reactions, addition of methyl radicals to ethylene, propylene, acetylene, and butadiene was found to proceed with activation energies of 7.0, 6.0, 5.5, and ~2.5 kcal. respectively and steric factors of the order of 10^{-4}.

INTRODUCTION

The kinetics of a simple free radical addition reaction such as

$$CH_3 + C_2H_4 \rightarrow C_3H_7 \quad k_A$$

are generally difficult to investigate because of complications arising from the various other reactions in which the reactants also participate, and from the nature of the product, which is a free radical. The main difficulty obviously lies in the tendency for the unsaturated hydrocarbon to polymerize, which may obscure the fate of the free radicals in the system, and often prevents quantitative study of any single process.

In this investigation the unsaturated hydrocarbons were kept at as low concentrations as possible to prevent them from participating in reactions other than addition by methyl radicals.

Methods of Determining the Rate of Addition

In a previous paper (5) it was shown that almost all the methyl radicals in the photolysis of acetone between 100° C. and 284° C. are accounted for by the following reactions:

$$CH_3COCH_3 + h\nu \rightarrow CO + 2CH_3 \qquad [1]$$

$$2CH_3 \rightarrow C_2H_6 \qquad [2]$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2 \qquad [3]$$

$$CH_3 + CH_3COCH_2 \rightarrow CH_3COC_2H_5 \qquad [4]$$

This conclusion was based on the fact that, within 3%,

$$(2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5})/R_{CO} = 1.90,$$

where R_X is the rate of formation of the product X. It follows that, if in the presence of an unsaturated hydrocarbon the only other reaction of methyl radicals is addition, and R_{CO} is unaffected, the rate of addition, designated as R'_A for this method, may be obtained from

$$(2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5} + R'_A)/R_{CO}$$

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[2] *National Research Council of Canada Postdoctorate Fellow 1951–53.*

equated to the ratio obtained in the absence of unsaturated hydrocarbon. However, methyl radicals may combine with the product of addition, i.e.

$$CH_3 + C_3H_7 \rightarrow C_4H_{10},$$

thereby making R'_A higher than the true rate of addition. But unless the methyl radical concentration is controlled only by the addition reaction, which is not so here, this reaction will decrease and diminish in effect on R'_A with increasing temperature, and will lead to too low a value for E_A.

Since ethane and methane account for most of the methyl radicals produced, it would be expected that the greatest effect on the material balance of the addition reaction is on the $2R_{C_2H_6} + R_{CH_4}$ portion. Therefore it would appear possible to evaluate the rate of addition from

$$(2R_{C_2H_6} + R_{CH_4} + R''_A)/R_{CO}$$

equated to $(2R_{C_2H_6} + R_{CH_4})/R_{CO}$ in the absence of unsaturated hydrocarbon. By comparing R''_A with R'_A it can be seen that the former will be lower, the difference between the two depending on the magnitude of $R_{CH_3COC_2H_5}/R_{CO}$ and the extent to which it is decreased by the addition reaction. R''_A may therefore be lower than R'_A, especially when the amount of addition is large, i.e., at high temperatures.

The other method used is based on the assumption that the rate of addition of methyl radicals is equal to the rate of disappearance of unsaturated hydrocarbon. Because of polymerization and, possibly, addition by acetonyl radicals, R'''_A, the rate obtained by this method, should be higher than the true rate of addition of methyl radicals, these effects being accentuated with increasing temperature. Although the unsaturated hydrocarbon may also disappear by methyl radical abstraction of hydrogen atoms, the rate of abstraction can be calculated from the ratio $R_{CH_4}/R^{1/2}_{C_2H_6}$ in the presence and absence of the olefin. It is obvious that if hydrogen abstraction occurs to any large extent the rates of addition obtained by the material balance method lose much of their significance.

The limitations of the two methods are such that activation energies based on R'_A and R''_A will be low while those obtained from R'''_A will be high. Since these methods are also essentially independent, the extent to which the results agree will be an indication of their validity.

EXPERIMENTAL

The apparatus was essentially the same as that reported previously (5). Most experiments were done with the reaction cell separated from the rest of the apparatus by a stopcock situated very close to the furnace, the volumes of the cell and connecting tubing being 195 cc. and 10 cc. respectively. Some experiments, as indicated in the tables, were done with the cell isolated by a mercury cutoff, the volume of the connecting tubing being 37 cc.

The following unsaturated hydrocarbons were used: ethylene, propylene, butadiene (Philips Research Grade), and acetylene (Ohio Chemical and Mfg. Co.). Ethylene, propylene, and acetylene were degassed by bulb to bulb distillation at −196° C. and the second of three fractions coming over at −80° C. was retained. Butadiene was degassed at −196° C. and −116° C. and fractionated at −30° C. Some experiments were done with deuterated acetylene (C_2D_2), primarily to see if there was hydrogen abstraction from acetylene. The deuterated acetylene was prepared by the action of D_2O on calcium carbide.

Because acetylene absorbs wave lengths below 2200 Å, the light from the Hanovia S-100 lamp was filtered with a Corning No. 7910 filter for that series of experiments. Since it was found that this filter had no significant effect on the material balances, the data for acetone alone, which were obtained with this filter, were used as reference in determining R''_A for ethylene and propylene where no filter was used. In the series of experiments with butadiene a Corning No. 9863 filter was used throughout to avoid any photopolymerization of butadiene, which absorbs light at 2300 Å and below. It should be noted that the light intensities, or R_{CO}, in the reference experiments and in those with unsaturated hydrocarbon were within 10% of each other. The precaution of keeping the light intensity constant for both experiments was taken since it was found that the material balance $(2R_{C_2H_6} + R_{CH_4})/R_{CO}$ varies slightly with light intensity (5). Irradiation time was invariably one hour.

The analytical procedure was also similar to that reported previously (5) except that it was extended to determine a larger range of components, notably the amount of unsaturated hydrocarbon remaining at the end of an experiment. It was noted that by removing the products condensable at −116° C. in a trap situated before the analytical system, separation of the components that are volatile at lower temperatures was more rapid.

In the experiments with ethylene, methane and carbon monoxide were separated at the temperature of solid nitrogen since ethylene distills slowly at −196° C., the temperature of liquid nitrogen. The C_2, C_3, and C_4 fractions were separated at −180° C., −160° C., and −130° C. respectively and analyzed with a mass spectrometer. It was found in the experiments with propylene that ethane and propylene could be separated effectively at −180° C. and −160° C. With acetylene present, fractions were removed at −180° C., −150° C., and occasionally at −130° C. and analyzed for C_2, carbon monoxide, C_3, and C_4 with the mass spectrometer. Acetylene appeared to retain some of the carbon monoxide at the temperature of liquid nitrogen. This observation was confirmed by photolyzing two separate samples of acetone, adding some acetylene at the end of the photolysis of one to the acetone and its products while they were still in the reaction cell, and analyzing both as in a typical experiment with acetylene. No analyses were made for butadiene remaining at the end of an experiment.

RESULTS

The rate constants appearing in the tables were calculated on the basis of the addition reaction and reaction [2], e.g.

$$\frac{k''_A}{k_2^{\frac{1}{2}}} = \frac{R''_A}{R^{1/2}_{C_2H_6}[C_2H_4]},$$

and are expressed as cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$. The concentration of unsaturate is the average during the photolysis. Arrhenius plots gave $E_A - \frac{1}{2}E_2$ and from these the $P_A/P_2^{\frac{1}{2}}$ ratios, or relative steric factors, were obtained. Since it has been shown that for methyl radical combination, i.e. reaction [2], $E_2 \sim 0$ and $P_2 \sim 1$ (4), the activation energies and steric factors correspond to the addition reaction.

In Table I are shown the material balances for the photolysis of acetone alone.

TABLE I
MATERIAL BALANCES IN THE PHOTOLYSIS OF ACETONE

Temp., °C.	$R_{C_2H_6}$	R_{CH_4}	$R_{CH_3COC_2H_5}$	R_{CO}	$\frac{2R_{C_2H_6} + R_{CH_4}}{R_{CO}}$	$\frac{2R_{C_2H_6} + R_{CH_4} + R_{CH_3COC_2H_5}}{R_{CO}}$
	× 10^5 cc. N.T.P./sec.					
(*a*)						
Acetone conc. = 1.76 × 10^{-6} M./cc.						
144	6.55	1.81	—	8.39	1.78	
177	4.99	3.73	—	8.59	1.60	
189	5.51	5.34	—	10.19	1.61	
204	4.25	6.55	—	10.05	1.50	
205	4.89	7.03	—	11.02	1.53	
241	2.69	11.18	—	11.57	1.43	
286	1.56	16.66	—	13.62	1.45	
Acetone conc. = 0.9 × 10^{-6} M./cc.						
159	3.21	.98	—	4.36	1.70	
175	3.36	1.54	—	4.94	1.67	
199	2.78	2.51	—	5.09	1.58	
219	2.18	3.29	—	5.21	1.47	
(*b*) (*No. 9863 filter*)						
Acetone conc. = 1.76 × 10^{-6} M./cc.						
164.5	7.08	2.98	—	10.24	1.67	
180	7.10	4.39	—	11.49	1.62	
200	4.63	6.40	—	10.41	1.50	
236	2.55	10.36	—	10.37	1.49	
(*c*) (*No. 9863 filter*)						
Acetone conc. = 1.76 × 10^{-6} M./cc.						
144	6.06	1.70	1.2	7.72	1.79	1.95
183	3.29	2.90	1.9	5.98	1.59	1.89
240	1.34	6.41	2.3	6.11	1.48	1.86

Since the rates of addition are based on differences between relatively large quantities, small analytical errors could cause large deviations in the calculated rates of addition. The analytical accuracy was, however, better than ± 0.10 × 10^{-5} cc. N.T.P. per sec. and reproducibility of $k''_A/k_2^{\frac{1}{2}}$ and $k'''_A/k_2^{\frac{1}{2}}$ was accordingly ±20% at the lower temperatures and ±5% at the higher temperatures. These deviations correspond to ±1 kcal. in the activation energies, which is consistent with the accuracy of the Arrhenius plots.

In each series of experiments at least one reference photolysis of acetone was done in the same period of time as the corresponding photolysis of acetone with

TABLE II
PHOTOLYSIS OF ACETONE AND ETHYLENE (REF. TABLE I, *c*)

Temp., ° C.	$[C_2H_4]$ init.	$[C_2H_4]$ fin.	$R_{C_2H_6}$	R_{CH_4}	$R_{CH_3COC_2H_5}$	R_{CO}	R_{C_3}	R'_A	R''_A	R'''_A	$\frac{k'_A}{k_2^{\frac{1}{2}}}$	$\frac{k''_A}{k_2^{\frac{1}{2}}}$	$\frac{k'''_A}{k_2^{\frac{1}{2}}}$
	$\times 10^6$ M./cc.		$\times 10^5$ cc. N.T.P./sec.								$\times 10^{12}$ cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$		
144*	0.072	0.068	4.76	1.58	1.2	6.68	0.0	0.8	0.9	0.8	10	11	10
184	0.082	0.066	2.89	2.81	1.5	6.23	0.2	1.7	1.3	2.0	25	20	30
240	0.082	0.056	1.02	5.70	1.9	6.48	1.1	2.4	1.8	3.4	53	41	74

* *Used mercury cutoff for cell.*

unsaturated hydrocarbon. No significant change in R_{CO} was observed with the addition of unsaturated hydrocarbon, thereby indicating the absence of addition of acetyl radicals. This was probably due to the low concentrations of unsaturated hydrocarbon, since Volman and Graven (10) found that larger concentrations of butadiene decreased R_{CO} in the photolysis of acetone.

Because each of the hydrocarbons manifested certain particular characteristics, their results will be given separately.

Ethylene

Because of its importance, ethylene was studied more thoroughly than the other hydrocarbons. Emphasis was placed on ascertaining the validity of the methods used in determining the rate of addition and on the analysis of products.

The C_3 fraction (Table II) consisted of propane and propylene, possibly formed by,

$$CH_3 + C_3H_7 \rightarrow CH_4 + C_3H_6,$$

$$C_3H_7 + RH \rightarrow C_3H_8 + R.$$

Small C_4 fractions, at rates not exceeding 0.5×10^{-3} cc. N.T.P./sec., were found by mass spectrometric analysis to contain at least 50% acetone while the rest could not be identified positively as butane. Higher hydrocarbons, i.e., C_5 and C_6, were not detected at all by the mass spectrometer.

From Table II it is evident that the $k'_A/k_2^{\frac{1}{2}}$ and $k''_A/k_2^{\frac{1}{2}}$ values agree reasonably well. A comparison of the k'_A and k''_A values with k'''_A (Table III and Fig. 1) also shows reasonable agreement, viz. 7.5, 5.5, and 8.5 kcal. respectively.

TABLE III
PHOTOLYSIS OF ACETONE AND ETHYLENE (REF. TABLE I, *a*)

Temp., ° C.	$[(CH_3)_2CO]$	$[C_2H_4]$ init.	$[C_2H_4]$ fin.	$R_{C_2H_6}$	R_{CH_4}	R_{CO}	R''_A	R'''_A	$\frac{k''_A}{k_2^{\frac{1}{2}}}$	$\frac{k'''_A}{k_2^{\frac{1}{2}}}$
	$\times 10^6$ M./cc.			$\times 10^5$ cc. N.T.P./sec.					$\times 10^{12}$ cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$	
144	1.76	0.083	0.074	6.01	1.79	8.46	1.3	1.4	12	13
159	0.90	0.042	0.038	3.34	1.01	4.97	0.8		20	
177	1.76	0.083	0.068	4.70	3.59	9.49	2.2	1.8	25	20
204*	1.76	0.084	0.058	3.32	5.60	9.70	2.3	3.3	35	47
219	0.90	0.042	0.031	1.90	3.28	5.48	1.0	1.4	35	51
240	1.76	0.085	0.057	1.98	9.05	10.93	2.7	3.5	50	64
241	1.76	0.043	0.025	2.28	9.88	10.97	1.2	2.3	45	83
286	1.76	0.084	0.044	.94	13.15	12.40	3.0	5.1	88	153

**Irradiation time = 3840 sec.*

We may therefore state the value of E_A as $E_A = 7.0 \pm 1.5$ kcal. It is noteworthy that changes in concentration of acetone and ethylene have no significant effect on the $k''_A/k_2^{\frac{1}{2}}$ values. Furthermore, it can be seen that the addition of such small quantities of ethylene has no significant effect on the $R_{\mathrm{CH}_4}/R^{1/2}_{\mathrm{C}_2\mathrm{H}_6}$ ratios, thereby indicating that there are no complications due to abstraction of hydrogen atoms from ethylene.

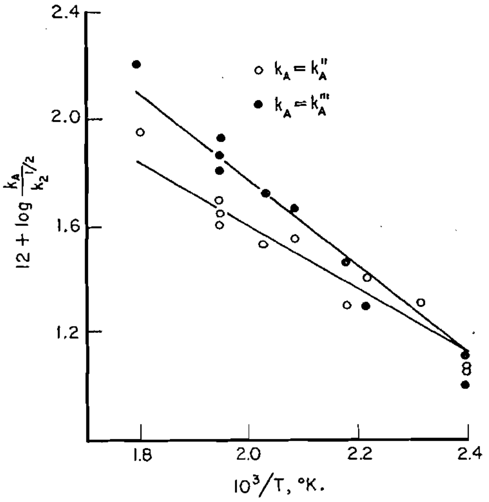

FIG. 1. Arrhenius plot for the addition of methyl radicals to ethylene.

Propylene

The presence of propylene (Table IV) caused a small increase in the $R_{CH_4}/R^{1/2}_{C_2H_6}$ ratios for the acetone photolysis which necessitated a correction for hydrogen abstraction in determining R'''_A. This correction was only about 10% of the rate of addition.

From Table IV and Fig. 2 it can be seen that up to 200° C. the $k''_A/k_2^{\frac{1}{2}}$ and $k'''_A/k_2^{\frac{1}{2}}$ values agree quite well, with the latter continuing the linear Arrhenius relationship while the former values fall off at higher temperatures. It may be concluded, therefore, that the activation energy for addition of methyl radicals to propylene is reasonably well established by the two methods to be approximately 6 kcal.

TABLE IV

PHOTOLYSIS OF ACETONE AND PROPYLENE (REF. TABLE I, *a*)

Temp., ° C.	$[(CH_3)_2CO]$	$[(C_3H_6)]$ init.	$[C_3H_6]$ fin.	$R_{C_2H_6}$	R_{CH_4}	R_{CO}	R''_A	R'''_A	$\frac{k''_A}{k_2^{\frac{1}{2}}}$	$\frac{k'''_A}{k_2^{\frac{1}{2}}}$
	$\times 10^6$ M./cc.			$\times 10^5$ cc. N.T.P./sec.					$\times 10^{12}$ cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$	
144	1.76	0.166	0.150	6.32	1.90	9.58	2.5	1.9	12	9
160	0.9	0.166	0.148	2.68	1.17	5.15	2.2	2.0	16	15
177	1.76	0.085	0.069	6.00	4.34	11.36	1.8	1.8	18	18
189	1.76	0.083	0.067	4.75	5.09	10.30	2.0	1.9	23	22
189*	1.76	0.180	0.143	3.72	4.78	10.04	4.0	5.2	24	32
205	1.76	0.084	0.062	3.64	6.37	10.63	2.3	2.5	30	33
219	0.9	0.083	0.065	1.94	3.30	6.32	2.1	2.1	37	37
242	1.76	0.083	0.051	2.22	10.18	11.67	2.1	3.8	37	68
286	1.8	0.083	0.058	1.28	14.28	12.93	1.4	3.7	33	79

* *Used mercury cutoff for cell.*

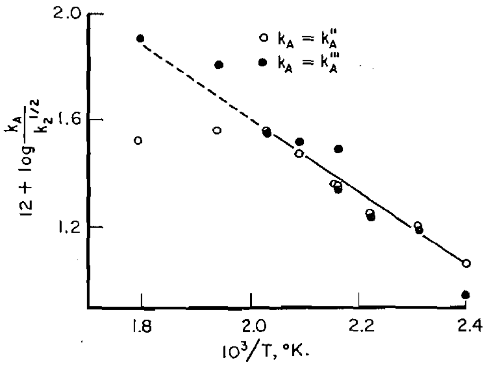

FIG. 2. Arrhenius plot for the addition of methyl radicals to propylene.

Acetylene

The products that were found in the various low temperature fractions were propylene, ethylene, and butene. Propylene, which was produced at about one third of the rate of addition (Table V), may be accounted for by abstraction of hydrogen atoms from acetone by propenyl radicals ($CH_3CH=CH$) formed by addition of methyl radicals to acetylene. Butene was produced at a much smaller rate, less than 5% of the rate of addition, and therefore contributed very little to the loss of methyl radicals. The presence of ethylene in the C_2 fraction was unexpected and is not readily explicable.

Two experiments were done at 270° C. with deuterated acetylene at concentrations of 0.08×10^{-6} mole/cc. and 0.28×10^{-6} mole/cc. acetylene in the presence of 1.7×10^{-6} mole/cc. acetone. Mass spectrometric analyses showed that both CH_3D, about 2% of the methane, and C_2H_5D were formed, thereby indicating an insignificant amount of abstraction of deuterium atoms by methyl radicals. Furthermore the absence of abstraction can be seen, as for ethylene, from the $R_{CH_4}/R_{C_2H_6}^{1/2}$ ratios, which were hardly altered by the addition of acetylene to acetone.

From Table V and Fig. 3 it is evident that the $k''_A/k_2^{\frac{1}{2}}$ and $k'''_A/k_2^{\frac{1}{2}}$ values agree reasonably well. The Arrhenius plot is based on an average of the two

TABLE V
PHOTOLYSIS OF ACETONE AND ACETYLENE (REF. TABLE I, *a*)

Temp., ° C.	$[(CH_3)_2CO]$	$[C_2H_2]$ init.	$[C_2H_2]$ fin.	$R_{C_2H_6}$	R_{CH_4}	R_{CO}	R''_A	R'''_A	$\frac{k''_A}{k_2^{\frac{1}{2}}}$	$\frac{k'''_A}{k_2^{\frac{1}{2}}}$
	$\times 10^6$ M./cc.			$\times 10^5$ cc. N.T.P./sec.					$\times 10^{12}$ cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$	
144	1.76	0.085	0.061	6.04	1.74	9.39	2.9	3.1	28	31
175	0.9	0.042	0.037	3.09	1.45	5.40	1.4	1.4	40	40
177	1.76	0.085	0.059	4.10	3.56	10.07	4.3	3.3	52	40
199	0.9	0.083	0.059	2.06	2.02	5.97	3.3	3.1	63	57
205	1.76	0.085	0.057	3.44	6.50	11.16	3.7	3.6	52	51
219	0.9	0.042	0.029	1.82	3.14	5.76	1.7	1.7	73	72
241	1.76	0.085	0.039	1.81	9.84	12.91	5.0	5.9	113	131

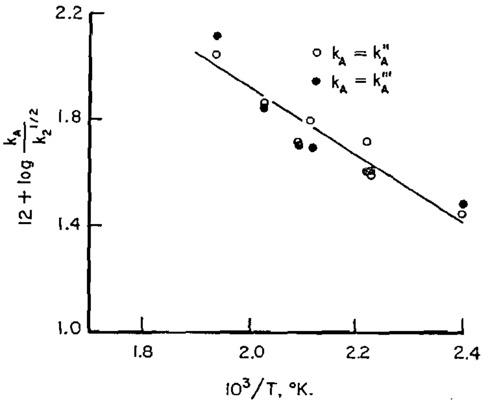

FIG. 3. Arrhenius plot for the addition of methyl radicals to acetylene.

values at each temperature, but if they are considered separately the difference in activation energies by the two methods is 1 kcal.

Butadiene

The experimental results for butadiene are shown in Table VI but the rate constants, which contain a term for the average concentration of unsaturated hydrocarbon, could not be calculated directly since analyses for butadiene were not made at the end of the experiments. From the $R_{CH_4}/R_{C_2H_6}^{1/2}$ ratios it can be seen that there was some hydrogen abstraction at the lower temperatures and none at the higher temperatures indicating that, at the higher temperatures, butadiene disappeared rapidly and almost completely. Therefore if the $k''_A/k_2^{\frac{1}{2}}$ values are calculated on the assumption that no butadiene remained at the end of the experiments at the higher temperatures and that its rate of consumption was equal to R''_A at the lower temperatures, an activation energy of ~2.5 kcal. is obtained for the addition reaction.

TABLE VI
PHOTOLYSIS OF ACETONE AND BUTADIENE (REF. TABLE I, *b*)

Temp., ° C.	C_4H_6 init. × 10^6 M./cc.	$R_{C_2H_6}$	R_{CH_4}	R_{CO}	R''_A
		× 10^5 cc. N.T.P./sec.			
164	0.018	6.18	2.88	10.12	1.7
164	0.019	6.08	2.94	9.98	1.6
164	0.039	4.78	2.61	9.92	4.4
180	0.019	5.37	4.04	10.39	2.1
180	0.038	4.99	3.87	10.97	3.9
200	0.018	3.72	5.67	9.61	1.4
200	0.035	3.04	5.17	9.41	2.9
236	0.019	2.18	9.45	10.17	1.3
236	0.036	1.82	8.61	9.95	2.6

Used mercury cutoff for cell.

DISCUSSION

The activation energies and steric factors obtained for the addition of methyl radicals to the various hydrocarbons investigated are summarized in Table VII.

TABLE VII

ADDITION OF METHYL RADICALS TO UNSATURATED HYDROCARBONS

Hydrocarbon	$k_A/k_2^{\frac{1}{2}}$ at 200° C. $\times 10^{12}$ cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$	$E_A - \frac{1}{2}E_2$, kcal.	$\frac{P_A}{P_2^{\frac{1}{2}}} \times 10^4$
C_2H_4	29	7.0	5
C_3H_6	28	6.0	3
C_2H_2	60	5.5	5
C_4H_6	$\sim$110	$\sim$2.5	0.3

One striking feature of these results is the similarity of the values obtained for addition to ethylene, propylene, and acetylene.

Raal, Danby, and Hinshelwood (2, 7, 8) studied the addition of methyl radicals to unsaturated hydrocarbons, the methyl radicals being produced by the photolysis of acetaldehyde. According to their kinetic scheme they found that the ratios of the rate constants of addition to that of abstraction of hydrogen, by methyl radicals from acetaldehyde were essentially similar for the series of hydrocarbons investigated, that for ethylene being lower than the others. For ethylene, they also determined the difference in activation energies of the two reactions, from which 6.8 kcal. was obtained for the addition reaction by assuming 9.7 kcal. for the abstraction reaction. However, if the values of 7.5 kcal. and $\sim 10^{-3}$ for the activation energy and steric factor for the latter reaction (9) are applied to their data on ethylene an activation energy of 4.6 kcal. and steric factor of $\sim 10^{-5}$ are obtained which are at least of the same order as the results of the present investigation.

The activation energy of chain propagation in the polymerization of butadiene induced by methyl radicals has been found to be 5.4 kcal. by Volman and Graven (10), who considered it as the activation energy for the addition of methyl radicals to butadiene. This value is in poor agreement with the value of 2.5 kcal. obtained here for this reaction, but it may not correspond to the addition reaction.

The difference between the activation energies of the addition reaction and its back reaction, or decomposition of the free radical product, should be equal to the heat of the reaction. Three independent investigations (1, 3, 6) agree on an activation energy of $\sim$20 kcal. for the decomposition of propyl radicals to methyl radicals and ethylene. This activation energy is, however, about 3 kcal. lower than the lower limit of the heat of the reaction, a discrepancy which has been pointed out. With the present value of the activation energy of the addition reaction, the discrepancy is about 10 kcal. The values for the decomposition of the propyl radical should, therefore, be regarded with some suspicion.

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THE VISCOSITY OF GASES AND THE THEORY OF CORRESPONDING STATES[1]

BY E. WHALLEY

ABSTRACT

The viscosity of gases is examined using the theory of corresponding states. The curve of reduced viscosity plotted against reduced temperature is compared with the theoretical curves obtained for several intermolecular potentials. The approximate Sutherland equation gives the best fit and it is suggested that this be used to extrapolate viscosities to high temperatures where experimental data are not available. The reduced viscosity – reduced temperature plot can be used for estimating the viscosities of simple gases from critical data, or critical data from the viscosities.

INTRODUCTION

Several authors have shown (6, 17) that if one makes certain assumptions the reduced low pressure transport properties of monatomic gases obeying classical statistics should be universal functions of the reduced temperature. The arguments were based on the principle of corresponding states discussed by Pitzer (16) and Guggenheim (3, 4) and on the kinetic theory of gases, and need not be detailed again. The validity of the arguments depends on several assumptions, the most restrictive of which is that the potential $\phi(r)$ of two molecules separated by a distance r is given by an equation of the form

$$\phi(r) = \epsilon f(r_0/r), \tag{1}$$

where ϵ is an energy, r_0 a distance, and f a universal function. Some authors have preferred to use the molecular quantities ϵ and r_0, where ϵ is the depth of the minimum of the potential energy curve and r_0 is the value of r for either $\phi = 0$ or $\phi = \epsilon$, to reduce the properties considered. However, to apply the reduced equations, ϵ and r_0 have to be evaluated using an assumed form of f, and the Lennard-Jones 12 : 6 potential is frequently used. It is more general practice to assume that ϵ is proportional to the critical temperature T_c and that r_0^3 is proportional to the critical volume V_c and to use T_c and V_c as reducing quantities. The advantage of this procedure is that it is independent of the form of f and uses macroscopic quantities only. In this paper I use the latter assumption.

The reduced transport coefficients are (6, 17) $\eta V_c^{2/3}/\sqrt{MT}$, $\lambda V_c^{2/3}\sqrt{M/T}$, $D_{12}V_c^{2/3}P/T^{3/2}[(M_1+M_2)/M_1M_2]^{1/2}$, and R_T, where η is the viscosity, λ the thermal conductivity, D_{12} the coefficient of mutual diffusion of molecules 1 and 2, R_T the thermal diffusion ratio for isotopic mixtures, M the molecular weight, T the temperature, and P the pressure. Each of these quantities should be a universal function of the reduced temperature $T_r = T/T_c$ for gases which obey the principle of corresponding states.

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There are insufficient data on monatomic gases to test the reduced thermal conductivity. The conductivity of other gases is complicated by exchange between translational and internal energy. Rowlinson and Townley (17) have shown that the reduced diffusion coefficients plotted against reduced temperature do not fall on a good line, possibly because of fairly large errors in the experimental measurements. A graph of R_T vs. T_r was prepared, but showed a similar scatter to the one for concentration diffusion. The discussion is therefore confined to the viscosity.

REDUCED VISCOSITY CURVE

It appears to have been first suggested by Onnes (15) that $\eta V_c^{2/3}/\sqrt{MT}$ should be a universal function of T_r. Several authors (2, 17, 18, 21) have verified this by plotting the above form of the reduced viscosity or a related one and obtained good curves. The published graphs have, however, been

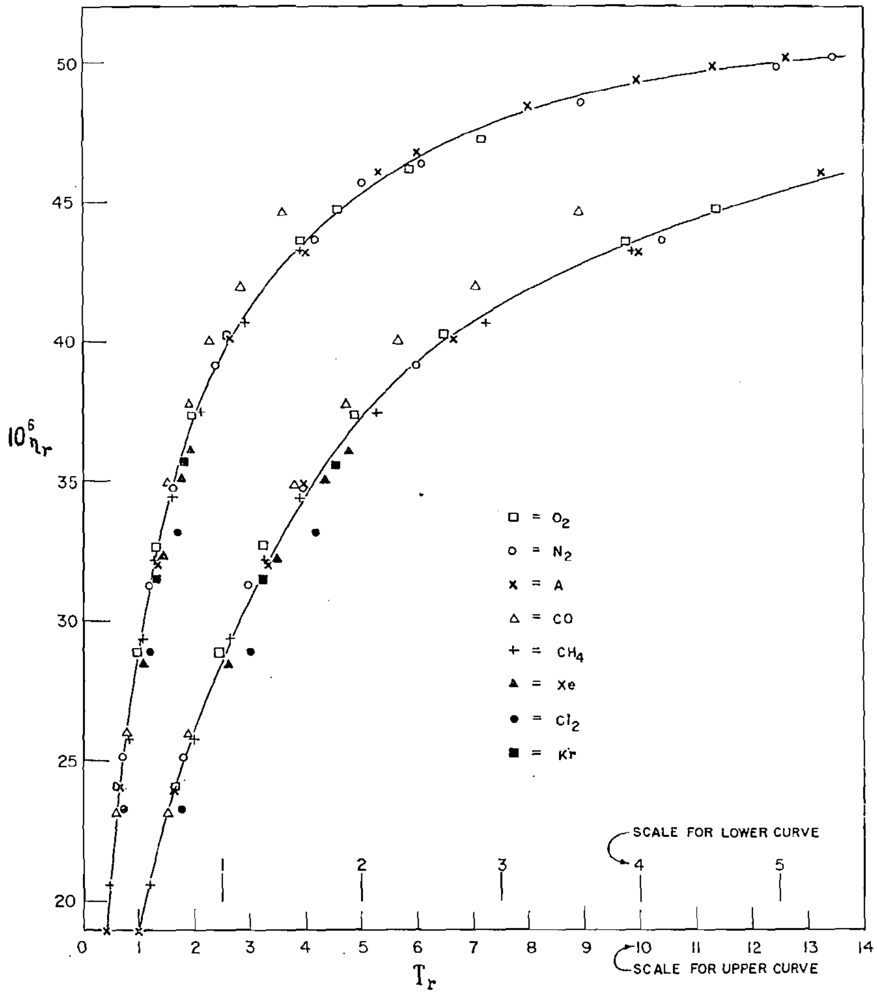

FIG. 1. Reduced viscosity against reduced temperature for several gases.

confined to comparatively low temperatures. Fig. 1 is a graph of this function over a fairly wide range of T_r using the smoothed viscosity data obtained for another paper (24) and the critical constants collected by Guggenheim (3, 4), except that for xenon the data of Weinberger and Schneider (22) were used. The viscosity data for methane (7, 20), carbon monoxide (19), krypton and xenon (11) were obtained by smoothing the data in the literature.

Neon does not fit the normal curve and hydrogen and helium deviate much further. These deviations are due at least partly to quantum effects. The use of "corrected" critical constants, i.e. those which would be obtained if there were no quantum effects, as suggested by Guggenheim and McGlashlan (4), did not bring hydrogen, helium, and neon into line with the other gases, nor was it found possible to choose empirical values of the "critical constants" which would bring them into line. Carbon monoxide falls a little above the curve for the remaining gases, probably owing to its small dipole moment.

COMPARISON WITH THEORY

Since the reduced viscosities of many gases fall quite close to one curve, it seems likely that the true potential of these gases approximates closely to the form of Equation [1], and by comparing the experimental and theoretical reduced viscosity curves one can examine the degree of fit with the viscosity obtained with various forms of f.

The general theory of viscosity (1) gives the equation

$$10^6\eta = 26.693\sqrt{MT}\,r_0^{-2}f_\eta/\Omega(2,2), \tag{2}$$

where f_η and $\Omega(2,2)$ are functions of kT/ϵ to be worked out for each potential, and r_0 is in angstroms.

(1) *The Sutherland Potential*

For this potential

$$\begin{aligned} &\text{when } r < r_0, \quad f = \infty, \\ &\text{when } r > r_0, \quad f = (r_0/r)^n, \end{aligned} \tag{3}$$

and ϵ is the depth of the potential energy minimum. The values of f_η and $\Omega(2,2)$ have been worked out for values of n of 4 (5) and 6 (10) only. To a first approximation, neglecting second and higher powers of ϵ/kT, Equation [2] reduces to the Sutherland equation

$$10^6\eta = 26.693(MT)^{1/2}r_0^{-2}(1+S/T)^{-1}, \tag{4}$$

where S is Sutherland's constant and is proportional to ϵ. Equation [4] is not a good approximation to Equation [2] except at high temperatures when S/T is small, but it is simple and easy to apply and has been very frequently used in correlating viscosity data. We shall see later that Equation [4] provides the best representation of the reduced viscosity curve of any of those considered.

We first consider Equation [2]. We assume

$$\begin{aligned} V_c &= \beta N r_0^3\,10^{-24}, \\ T_c &= \gamma\epsilon/k, \end{aligned} \tag{5}$$

where N is the Avogadro number, and obtain by substituting into Equation [2]

[6]
$$10^6\eta_r = 10^6\eta V_c^{2/3}/\sqrt{MT} = 18.759\beta^{2/3}f_\eta/\Omega(2,2).$$

It is generally accepted that $n = 6$ is the best simple representation of the attractive potential. I have therefore not discussed the potential $n = 4$. Using the tables of f_η and $\Omega(2,2)$ given by Kotani for $n = 6$ and solving the two simultaneous equations obtained from the values of η_r at $T_r = 1$ and 10, i.e. forcing Equation [6] to fit the experimental curve at $T_r = 1$ and 10, we solve for β and γ. The theoretical curve can then be calculated. It is not plotted in Fig. 2 since it is of little practical or theoretical importance and would confuse the graph. Up to $T_r = 3$ it follows roughly curve 5 and above about $T_r = 10$ it is indistinguishable from curve 2.

Equation [4] is of more practical value. We assume (12) that the reduced Sutherland constant

$$S_r = S/T_c$$

is constant for all gases; since $S \propto \epsilon$, this is equivalent to assuming that $T_c \propto \epsilon$. Also we assume that r_0 is related to the critical volume by the equation

$$V_c = \beta N r_0^3\, 10^{-24}.$$

Inserting these in Equation [4] and rearranging, we obtain

[7]
$$10^6\eta_r = 18.759\ \beta^{2/3}/(1 + S_r/T_r).$$

By fitting Equation [7] to the curve of Fig. 1 at $T_r = 1$ and 10, we obtain

[8]
$$\beta = 2.006,$$
$$S_r = 0.8385.$$

This value of S_r is close to the value of 0.8 used by Light and Stechert (12). The curve obtained using Equations [7] and [8] is compared with the experimental curve in Fig. 2.

(2) 12 : 6 Potential

For this potential

$$f = 4\{(r_0/r)^{12} - (r_0/r)^6\},$$

where r_0 is the low velocity collision diameter and ϵ is the depth of the potential energy minimum. f_η and $\Omega(2,2)$ are tabulated by Hirschfelder *et al.* (6). We assume Equations [5] and obtain

[9]
$$10^6\eta_r = 18.759\beta^{2/3}f_\eta/\Omega(2,2).$$

By solving graphically the simultaneous equations [9] at $T_r = 1$ and 10, we obtain

[10]
$$\beta = 2.784,$$
$$\gamma = 1.540.$$

By fitting viscosity data of a number of gases to the 12 : 6 potential, usually at moderate temperatures only, Hirschfelder *et al.* obtained $\beta = 3.1$, $\gamma = 1.28$.

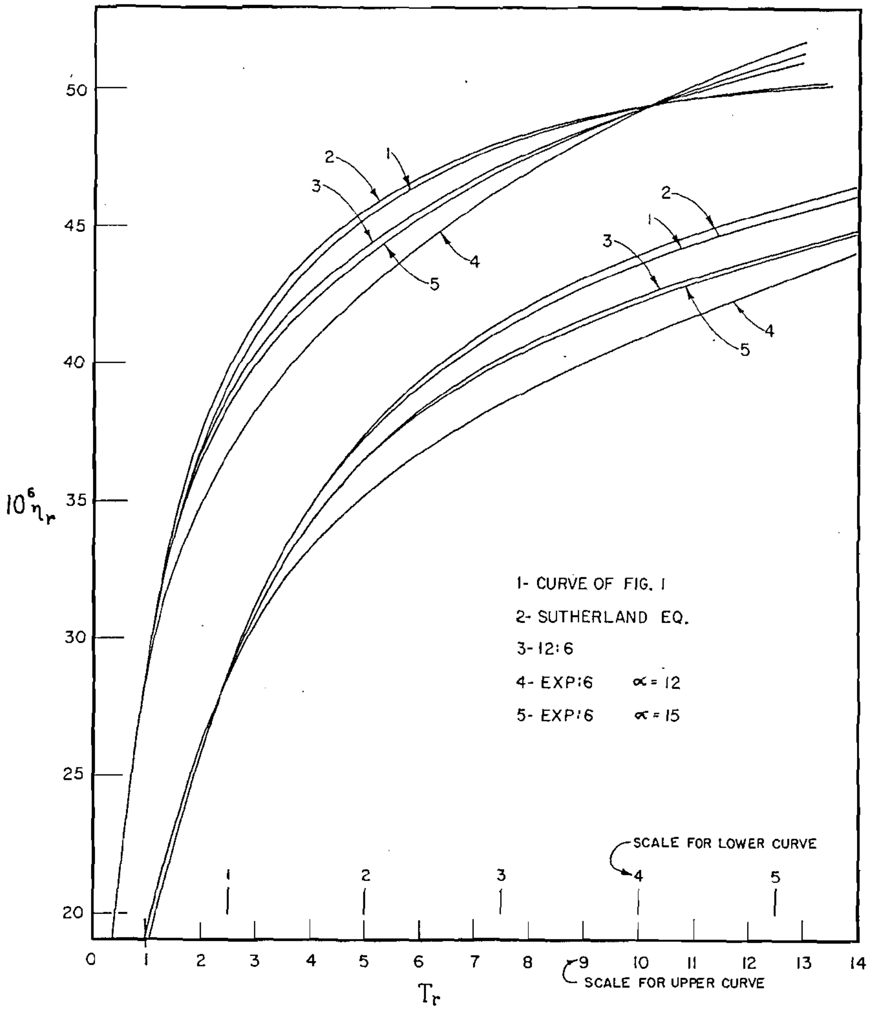

FIG. 2. Comparison of experimental and theoretical reduced viscosity curves.

Guggenheim and McGlashan fitted the reduced second virial coefficient curve and obtained $\beta = 2.836$, $\gamma = 1.28$. The calculated η_r curve is compared with the experimental curve in Fig. 2.

(3) *Exponential : 6 Potential*

Very recently Mason (13) has given a table of the transport integrals for a potential of the form

$$f = \frac{1}{1 - 6/\alpha} \left\{ \frac{6}{\alpha} \exp\left(1 - r/r_m\right) - \left(\frac{r_m}{r}\right)^6 \right\},$$

where r_m is the position of the potential energy minimum, α is a measure of the steepness of the repulsive potential, and ϵ is the depth of the potential energy minimum. For this potential

$$10^6\eta_r = 26.693\sqrt{MT}\, r_m^{-2} f_\eta/\Omega(2,2), \tag{11}$$

where r_m is in angstroms and f_η and $\Omega(2,2)$ are functions of kT/ϵ and α only. They are tabulated for values of α of 12, 13, 14, and 15. We assume the relations [5] and fit the reduced viscosity as before for $\alpha = 12$ and for $\alpha = 15$. The curves are compared with the experimental curve in Fig. 2. For $\alpha = 12$ we find

$$\beta = 1.510,$$
$$\gamma = 2.409.$$

For $\alpha = 15$ we find

$$\beta = 1.858,$$
$$\gamma = 1.536.$$

DISCUSSION

For the gases considered the approximate Sutherland equation provides a better fit over a wide temperature range than the "exact" Sutherland, 12 : 6 or exp : 6 potentials. It has been pointed out several times (8, 9, 23, 24) that a 12 : 6 potential is not good for the viscosity of many gases at higher temperatures. Kihara and Kotani showed that for nitrogen and methane the accurate Sutherland potential is better than the 12 : 6. The approximate Sutherland equation is better still. It was shown recently (23, 24) that the 12 : 6 potential does not give a good representation of the viscosity of most gases at high temperatures, e.g. for nitrogen it was impossible to obtain any 12 : 6 parameters to fit the viscosity above about 570°K., whereas the Sutherland equation could be used over the whole range of 80–1800°K. with only a few per cent change in S. It should be remarked however that this conclusion does not hold for all the simple gases. The viscosity of neon (24) is quite well represented by a 12 : 6 potential over the temperature range 80–1100°K. for which data are available. The viscosity of helium and hydrogen (14) is well described by an exp : 6 potential.

If any conclusions about the shape of the potential energy curve which will give the best fit to the viscosity data can be drawn from this comparison it is that the repulsive energy should be steeper than that of the exp : 6, $\alpha = 15$. This does not necessarily indicate that the true repulsive energy should be steeper. Undoubtedly a better fit to the observed data could be obtained with a modified Sutherland equation. Keyes (8) used the equation

$$10^6\eta = \frac{a_0\sqrt{T}}{1 + a\tau/10^{a_1\tau}}$$

where $\tau = T^{-1}$, a_0, a, and a_1 are constants to correlate successfully the viscosities of a number of simple gases over a wide temperature range. At higher temperatures this reduces to the Sutherland equation. Simple modifications involving the substitution of $1 + S_r/T_r + S_r^2/T_r^2$ or $\exp(1 + S_r/T_r) - 1$ for $1 + S_r/T_r$ gave a worse fit than Equation [7].

The curve of Fig. 1 is very useful in providing a means of estimating the viscosity of a simple gas when only critical data or scanty viscosity data are available. Alternatively it is possible to obtain values of the critical volume and temperature from viscosity data, to enable one to make use of other reduced curves for estimating rough values of gas properties.

One should be able to make a similar plot for the viscosity of simple liquids, but a few graphs showed fairly considerable deviations and the subject was not pursued further.

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MICROCALORIMETRIC STUDIES OF POLYVINYL ACETATE SOLUTIONS[1]

BY HUBERT DAOUST[2] AND MARCEL RINFRET

ABSTRACT

A relation between intrinsic viscosity and the sign of heat of mixing of a linear polymer in different solvents has been predicted by Alfrey, Bartovics, and Mark. To verify this, the intrinsic viscosities and heats of mixing at one concentration for two samples of polyvinyl acetate in six solvents were determined. The heats of mixing have been measured with a Tian–Calvet microcalorimeter especially designed for slow processes and having a sensitivity of one thousandth of a calorie per hour. The results generally agree with the above prediction. Furthermore, the heats of mixing of two fractions of polyvinyl acetate in three solvents have been measured over a range of low concentrations to study the behavior of the quantity B from the theory of van Laar, Scatchard, and Hildebrand on energy of mixing of nonelectrolytes. It was found that B goes through a minimum at low concentrations when the mixing process is exothermic. This effect may be explained by the existence of a critical concentration below which entanglement between macromolecules ceases. For a poor solvent, B seems to be constant at high dilution.

INTRODUCTION

When a linear polymer such as polyvinyl acetate has a high molecular weight, it usually assumes a solid form of an amorphous or slightly crystalline structure. Thus, a solid high polymer is far from being a perfect solid and is often considered as a very viscous liquid (10). A solution of linear and nonelectrolytic macromolecules in an organic solvent is the limiting case of solutions of nonelectrolytes of different molecular dimensions. These solutions deviate strongly from ideal behavior and the mixing process is often accompanied by a thermal effect.

Van Laar, Scatchard, and Hildebrand have worked out a general theory on total energy of mixing ΔE_M for two nonpolar nonelectrolytic liquids (9). Since the volume change on mixing ΔV_M is negligible for very dilute polymer solutions, then, according to this theory,

$$\Delta H_M \simeq \Delta E_M = V_M B \Phi(1 - \Phi), \tag{1}$$

V_M being the total volume of mixture, and Φ the volume fraction of the solute.

The quantity B is a parameter characterizing the net heat of interaction for a given pair of nonelectrolytes (8) which theoretically is independent of concentration and varies with temperature. If only dispersion forces are present it may be given as (9)

$$B = (\delta_1 - \delta_2)^2 \tag{2}$$

where δ_1 and δ_2 are solubility parameters. Therefore according to [2], ΔH_M is

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always positive or zero, i.e. the mixing is an endothermic or an athermic process.

However when there is specific interaction between two species in solution the value of B is not given by [2] but becomes more complex and often negative. Equation [1] is still applicable but ΔH_M can be negative.

Based on theoretical considerations of the shape of polymers in solution and intrinsic viscosity, Alfrey, Bartovics, and Mark (2) have predicted that in an energetically unfavorable solvent, the polymer segments will attract each other and will reduce the polymer–solvent contacts. The intrinsic viscosity should then be low and the mixing process should be endothermic, i.e. $\Delta H_M > 0$. However if a solvent is energetically more favorable, the intrinsic viscosity should be higher and the mixing process, exothermic. According to their investigations and those of others (1,7) on the viscosity, at various temperatures, of linear polymers in different solvents, these predictions were essentially correct. Here the values of B along with the intrinsic viscosities were determined at one low concentration for two samples of polyvinyl acetate in six solvents to verify previous work on viscosity behavior of the same polymer in the same solvents (6) and the predictions of Alfrey, Bartovics, and Mark. Furthermore, the variation of B was studied in the low concentration range for one poor and for two good solvents of polyvinyl acetate.

EXPERIMENTAL

An unfractionated sample of polyvinyl acetate of average molecular weight 145,000 was provided by Bakelite Corp. Fractions of the same polymer were obtained through the kindness of Dr. Sheffer of the Defence Research Board of Canada. The samples of polymer were kept under vacuum over phosphoric anhydride. The solvents used were rectified through a high efficiency distilling column (13) and stored over "Drierite".

Intrinsic viscosities were measured by a method described in a previous paper (6). Flow time for benzene at 25°C. was 128.7 sec. and the concentration range studied extended from 0.2 to 1.0 gm. per 100 ml.

The heats of mixing were measured with a conduction microcalorimetric system which was originally designed by Tian (16) for measuring very small quantities of heat evolved in very slow phenomena. This apparatus was further modified by Calvet (4) by the introduction of a differential system which gave higher sensitivity and a greatly lengthened period of operation (one week or more).

The microcalorimeter used here was of the Calvet modification type and comprised two cells, each having 144 iron–constantan thermocouples, connected differentially through a high sensitivity galvanometer and a switching arrangement providing three sensitivities.

As shown by the Tian equation (16) the measurement of heat evolved is made by integrating the area under the curve of galvanometer deflections versus time. These deflections were recorded by a photographic drum or by a Beckman "Photopen" photoelectric light spot follower described by Pompeo and Penther (12). The areas were measured with a planimeter. Calibration was effected by passing a known current through a manganin resistor immersed in a liquid in the calorimeter cell. Results of calibrations for a paper speed of 10.16 cm. per hour are given in Table I. The accuracy was limited to ±0.5% by the reproducibility of galvanometer deflections in the range of relatively high heat exchanges, i.e. 0.1, 0.8, and 2.0 calories per hour at the high, medium, and low sensitivities respectively. For still smaller evolutions of heat the limiting factor lies in the determination of the area under the deflection–time curve which can be measured to ±0.02 cm². Thus it can be seen from Table IV that for the smallest value of ΔH_M of -0.020 cal., which corresponds at high sensitivity to 4.5 cm.², 0.02 cm.² contributes an error of ±0.5%. This coupled with the possible galvanometer error gives a maximum error of 1%. For higher ΔH's the error would tend towards 0.5%.

TABLE I

Sensitivity in use	Calibration factor in cal. per cm.²
Low	$0.0870 \mp .0004$
Medium	$0.0324 \mp .00015$
High	$0.00446 \mp .00002$

The method used for mixing solvent and solid polymer has been described by Calvet (3) and a new method has been developed when the polymer is not a compact solid (5). The volume of solvent varied between 6 and 8 ml. and the mass of polymer used was from 8 to 224 mgm.

RESULTS

Table II shows the intrinsic viscosities along with the quantities B calculated from equation [1] for a fractionated sample of polyvinyl acetate (M.W. 135,000) at 25°C. in six solvents. The values of B are given for one concentration only (1 gram of polymer in 1 mole of solvent). The densities of the solvents have been calculated from the International Critical Tables and the density of polyvinyl acetate has been taken as 1.17 (11). The relation between B and $[\eta]$ is illustrated by the curve in Fig. 1.

TABLE II
HEAT OF MIXING AND INTRINSIC VISCOSITY OF POLYVINYL ACETATE IN VARIOUS SOLVENTS

Solvents	ΔH_M	B, cal. per ml.	$[\eta]$
Chloroform	-0.885	-12.5	1.06
Ethylene chloride	-0.252	-3.7_4	0.91_7
Chlorobenzene	-0.092	-1.5_0	0.76_7
Benzene	0.046	0.642	0.71_3
Toluene	0.119	1.53	0.50_9
Methanol	1.04_6	7.9_4	0.44_8

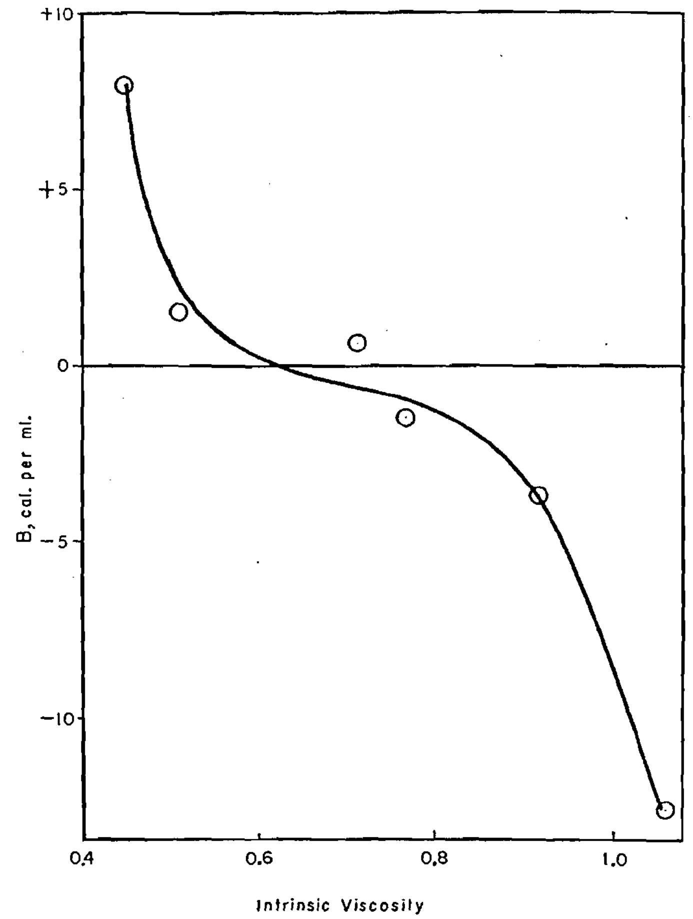


FIG. 1. Variation of parameter B with the intrinsic viscosity for polyvinyl acetate in different solvents.

The results of the study of the parameter B in the low concentration range are given in Tables III, IV, and V for a fraction of polyvinyl acetate (M.W. 85,000) in methanol and ethylene chloride and for another fraction (M.W. 58,000) in *s*-tetrachloroethane. Figs. 2–7 show the curves obtained from these

TABLE III

HEATS OF MIXING POLYVINYL ACETATE IN METHANOL AT 25.2°C.
(M.W. 85,000, FRACTIONATED)

Φ	ΔH_M, cal.	V_M, ml.	$\Delta H_M/V_M$	B, cal. per ml.
.002	0.123	7.343	.017	8.4_0
.004	0.213	6.480	.033	8.2_3
.009	0.54_1	7.127	.076	8.5_3
.012	0.74_9	7.469	.100	8.4_3
.019	0.92_9	6.356	.146	7.8_6
.021	1.18	7.311	.162	7.8_5
.030	1.38	6.271	.220	7.5_6

TABLE IV
HEATS OF MIXING POLYVINYL ACETATE IN ETHYLENE CHLORIDE AT 25.2°C.
(M.W. 85,000, FRACTIONATED)

Φ	ΔH_M, cal.	V_M, ml.	$\Delta H_M/V_M$	B, cal. per ml.
.001	−.020	6.436	$-.003_1$	-3.1_0
.002	−.044	6.920	$-.006_4$	-3.2_0
.003	−.079	7.565	$-.010_4$	-3.4_7
.004	−.115	7.194	$-.016_0$	-4.0_0
.006	−.167	7.215	$-.023_1$	-3.8_5
.009	−.192	6.664	$-.029_0$	-3.2_4
.011	−.220	6.482	$-.034_0$	-3.1_1
.013	−.252	6.391	$-.039_4$	-3.0_9
.016	−.240	6.430	$-.037_3$	-3.0_8

TABLE V
HEATS OF MIXING OF POLYVINYL ACETATE IN *s*-TETRACHLOROETHANE AT 25.2°C.
(M.W. 58,000, FRACTIONATED)

Φ	ΔH_M, cal.	V_M, ml.	$\Delta H_M/V_M$	B, cal. per ml.
.0009	−0.110	7.920	$-.013_9$	−15.3
.0013	−0.149	6.973	$-.021_4$	−16.5
.0016	−0.264	6.869	$-.038_4$	−24.0
.0048	−0.682	7.492	$-.091_0$	−19.0
.0065	−0.852	6.783	−.126	−19.6
.0081	−1.07	7.339	−.146	−18.3

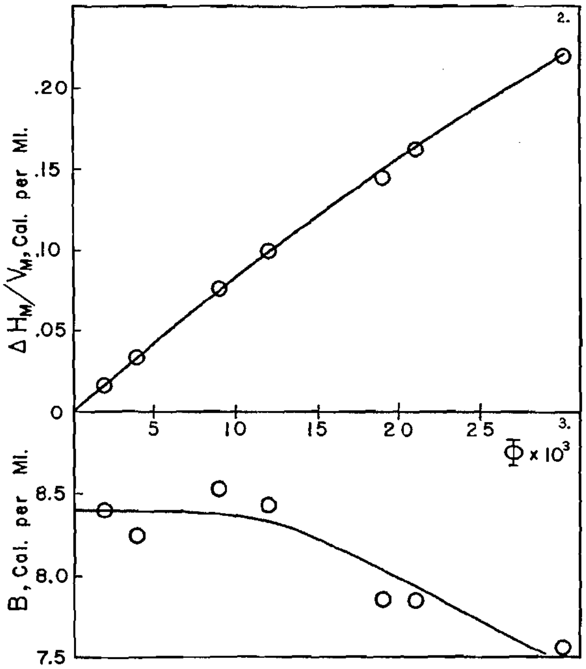
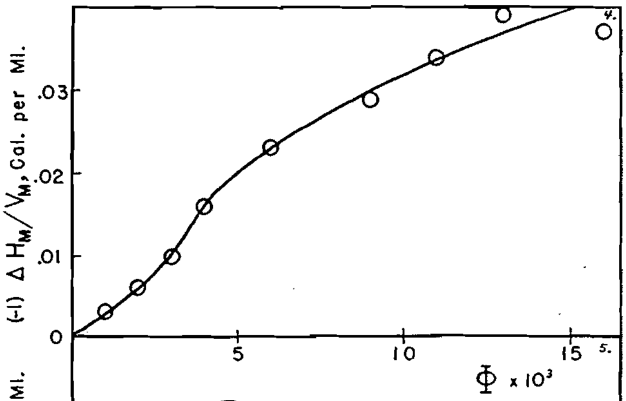


FIG. 2. Heats of mixing of polyvinyl acetate (M.W. 85,000, fractionated) in methanol at 25.2°C.

FIG. 3. Variation of B with Φ for polyvinyl acetate (M.W. 85,000, fractionated) in methanol at 25.2°C.

results. In Figs. 2, 4, and 6 we have used Φ instead of $\Phi(1 - \Phi)$ because in this range of concentration $\Phi \simeq \Phi(1 - \Phi)$.



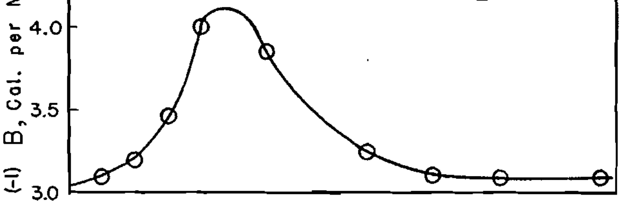
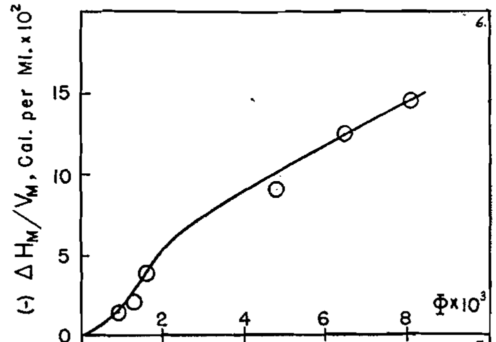


FIG. 4. Heats of mixing of polyvinyl acetate (M.W. 85,000, fractionated) in ethylene chloride at 25.2°C.

FIG. 5. Variation of B with Φ for polyvinyl acetate (M.W. 85,000, fractionated) in ethylene chloride at 25.2°C.



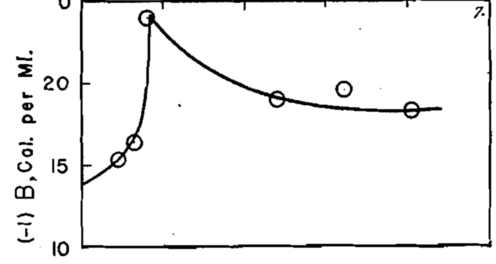


FIG. 6. Heats of mixing of polyvinyl acetate (M.W. 58,000, fractionated) in *s*-tetrachloroethane at 25.2°C.

FIG. 7. Variation of B with Φ for polyvinyl acetate (M.W. 58,000, fractionated) in *s*-tetrachloroethane at 25.2°C.

DISCUSSION

It has been shown here experimentally that the relation between the heat of mixing and the intrinsic viscosity predicted by Alfrey, Bartovics, and Mark is correct. Referring to Table II, it can be seen that for "acidic" solvents (in the sense of Lewis' theory), such as chloroform, ethylene chloride, and chlorobenzene, the mixing process is exothermic. A negative heat of mixing is usually explained by solvation, i.e. there is a strong attraction between solvent and solute. Molecules of acidic solvent are fixed to the polymeric chain by the "basic" carbonyl groups in polyvinyl acetate; thus the contacts between segments in the chain are hindered and the macromolecule assumes a less compact form causing high values of the intrinsic viscosity. In a neutral solvent such as benzene, ΔH_M is very small, indicating that the values of the solubility parameters of the two substances are very close (6). In toluene and in methanol, which is a "basic" solvent, ΔH_M is positive and the values for $[\eta]$ are lower. This is explained by the more compact form of the polymer molecules in solution in these solvents. Results very similar to those in Table II were obtained for the unfractionated sample of polyvinyl acetate of average molecular weight 145,000 both at 25 and 35°C.

The results obtained on the heats of mixing of polyvinyl acetate in methanol at different concentrations (Table III, Figs. 2 and 3) show that when ΔH_M is positive the theory of Van Laar, Scatchard, and Hildebrand holds at high dilutions, i.e. parameter B is constant. However, as the concentration increases, B decreases. When the mixing is exothermic the results are rather surprising as the curves (Figs. 4 and 6) possess an inflection point in the low concentration region. This particular behavior was established by repeating the experiments several times with utmost care to avoid any fortuitous error. For ethylene chloride, Table IV and Fig. 5 show that the absolute value of B increases to a maximum at $\Phi = 0.45 \times 10^{-2}$. This phenomenon is also illustrated by the inflection point in the curve of the heats of mixing per ml. vs. Φ (Fig. 4). Similar results were obtained with *s*-tetrachloroethane (Table V, Figs. 6 and 7), but the maximum absolute value for B occurs here at $\Phi = 0.17 \times 10^{-2}$. Apparently there is a critical concentration (14) in a given polymer–solvent system for exothermic mixing at which B goes through a minimum value.

Streeter and Boyer (15) also observed a critical effect on the viscosity of very dilute solutions of polystyrene in toluene. They found that reduced viscosity decreases linearly as concentration is lowered from 1.0 to 0.1 gm. per 100 ml. and then increases with further dilution. They have accounted for the phenomenon by the fact that at medium and high concentration, polymer molecules are closely packed together and the solution is continuous. But if the mixture is diluted a critical concentration is reached at which the macromolecules do not touch each other and the solution becomes discontinuous. In other words at very low concentration, the polymer molecules are free in their movements and at high concentration they are entangled. The concentration region through which B varies rapidly apparently corresponds to the change in structure of the polymer in solution.

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ORGANIC DEUTERIUM COMPOUNDS

XI. SYNTHESIS OF 1-CHLORO-1-ALKYNES AND 1-CHLORO-1-PROPYNE-d_3[1]

BY A. T. MORSE AND L. C. LEITCH

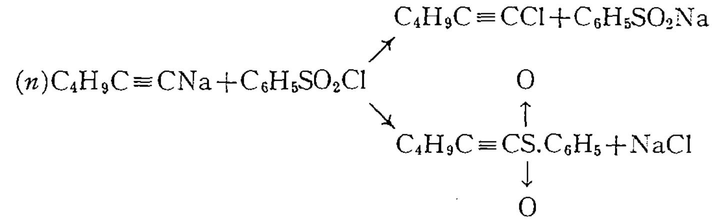
ABSTRACT

Dehydrohalogenation of *cis*-1,2-dichloro-1-alkenes, RCCl=CHCl, with potassium hydroxide in butanol has been used to prepare a number of new 1-chloro-1-alkynes, viz. 1-chloro-1-propyne-d_3, 1-chloro-1-propyne, 1-chloro-1-butyne, and 1-chloro-1-pentyne in good yields. The last three compounds were also prepared by chlorination of 1-propyne, 1-butyne, and 1-pentyne with sodium hypochlorite.

INTRODUCTION

The synthesis of several deuterated organic compounds of potential use in molecular spectroscopy has been reported in previous papers of this series (9, 10, 11). We have now synthesized normal and deuterated 1-chloro-1-propyne for further investigations in this field, which will be reported in this journal in a separate paper by Bernstein and Davidson (1).

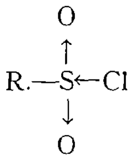
As a class, the 1-chloro-1-alkynes have not been studied as extensively as other chlorinated hydrocarbons. In 1931, Truchet (18) obtained 1-chloro-1-hexyne (I) from benzenesulphonyl chloride and the sodium derivative of hexyne-1 instead of the expected sulphone (II).



$$(n)C_4H_9C\equiv CNa + C_6H_5SO_2Cl \nearrow C_4H_9C\equiv CCl + C_6H_5SO_2Na \quad (I)$$

$$\searrow C_4H_9C\equiv C\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}.C_6H_5 + NaCl \quad (II)$$

This result is not surprising in view of the charge distribution between the sulphur and chlorine atoms in sulphonyl chlorides (III).



$$R.\!-\!\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\!\leftarrow\!Cl$$

(III)

1-Hexyne, 1-octyne, and 1-nonyne reacted similarly. These chloroalkynes were later prepared by the same method by Pflaum and Wenzke (15) for dipole moment measurements. Cleveland, Taufen, and Murray (3) failed to obtain

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1-chloro-1-propyne from sodium methyl acetylide but an impure product, b.p. 37 to 41°C. was isolated in low yield using the magnesium derivative. In the present work, 1-chloro-1-propyne was actually obtained by Truchet's method but only in 10% yield; no improvement was observed using *p*-toluenesulphonyl chloride.

Another synthesis of 1-chloro-1-alkynes was reported by McCusker and Vogt (13). These authors prepared the potassium derivative of 1-heptyne in the usual manner and chlorinated a suspension of the solid in ether at −70°C. The yield of 1-chloro-1-heptyne was good, but the rate of adding the chlorine was an important factor affecting the yield. This method appeared unpromising to us and was not tried. Chlorination of the lithium derivative, however, might be advantageous.

According to Strauss, Kollek, and Hauptmann (17), the methine or acetylenic hydrogen is replaced by bromine when heptyne-1 is shaken with alkali hypobromite; the reaction with hypochlorite was reported to be too slow to make this method a useful preparative route to 1-chloro-1-alkynes. However, vinylacetylene is reported to give 60 to 65% yields of 1-chloro-3-butene-1-yne when shaken at 0°C. with aqueous sodium hypochlorite for 16 hr. (8). There is also a reference to the chlorination of the methine hydrogen in propargyl alcohol by aqueous sodium hypochlorite by Copenhaver and Bigelow (4). In the present work, it was found that propyne, butyne-1, and pentyne-1 were converted into the corresponding 1-chloroalkynes at approximately the same rate when stirred for 80 hr. with 10% sodium hypochlorite. While slow, the reaction is satisfactory, particularly for the preparation of 1-chloro-1-pentyne.

Theoretically, this reaction may proceed by a carbanion, a carbonium ion, or even a free radical mechanism. Of these alternatives, we believe the carbonium ion mechanism shown below is the most probable.

$$\underset{\text{(IV)}}{\mathrm{RC{\equiv}CH \leftrightarrow R\overset{+}{C}{=}\overset{-}{C}H}} \xrightarrow{\mathrm{Cl^+}} \underset{\text{(V)}}{\mathrm{R\overset{+}{C}{=}CHCl}} \rightarrow \mathrm{RC{\equiv}CCl} + \mathrm{H^+}$$

Electrophilic attack of the positive chlorine ion on the resonance hybrid (IV) gives the carbonium ion (V) which is converted into the 1-chloroalkyne by loss of a proton. A free radical mechanism appears to us ruled out by the failure to isolate any product other than the chloroalkyne. A carbanion mechanism, though improbable, cannot be excluded on the basis of the present experiments. In this connection, it is proposed to investigate the behavior of other 1-alkynes with sodium hypochlorite at some future date, as syntheses of suitable alkynes will first have to be devised.

Although dehydrohalogenation has been widely used in the preparation of acetylenic hydrocarbons (6), there are few references to its application to the synthesis of chloroalkynes (2, 5). 1-Bromo-1-propyne was prepared in 25% yield (12) by dehydrohalogenation of 1,1,2-tribromopropane. No doubt, one of the reasons this method has not been exploited in the past has been the inaccessibility of the required 1,2-dichloro-1-alkenes, $RCCl{=}CHCl$. In a previous paper of this series (9), the preparation of *cis*- and *trans*-1,2-dichloro-1-propene and their deuterated analogues was described. It was felt that these compounds might serve as starting materials for the synthesis of 1-chloro-1-propyne, depending upon the manner in which hydrogen chloride is split off by alcoholic alkali.

When *cis*-1,2-dichloro-1-propene was added to a boiling solution of potassium hydroxide in butanol, a liquid (b.p. approx. 32°C.) distilled over which was

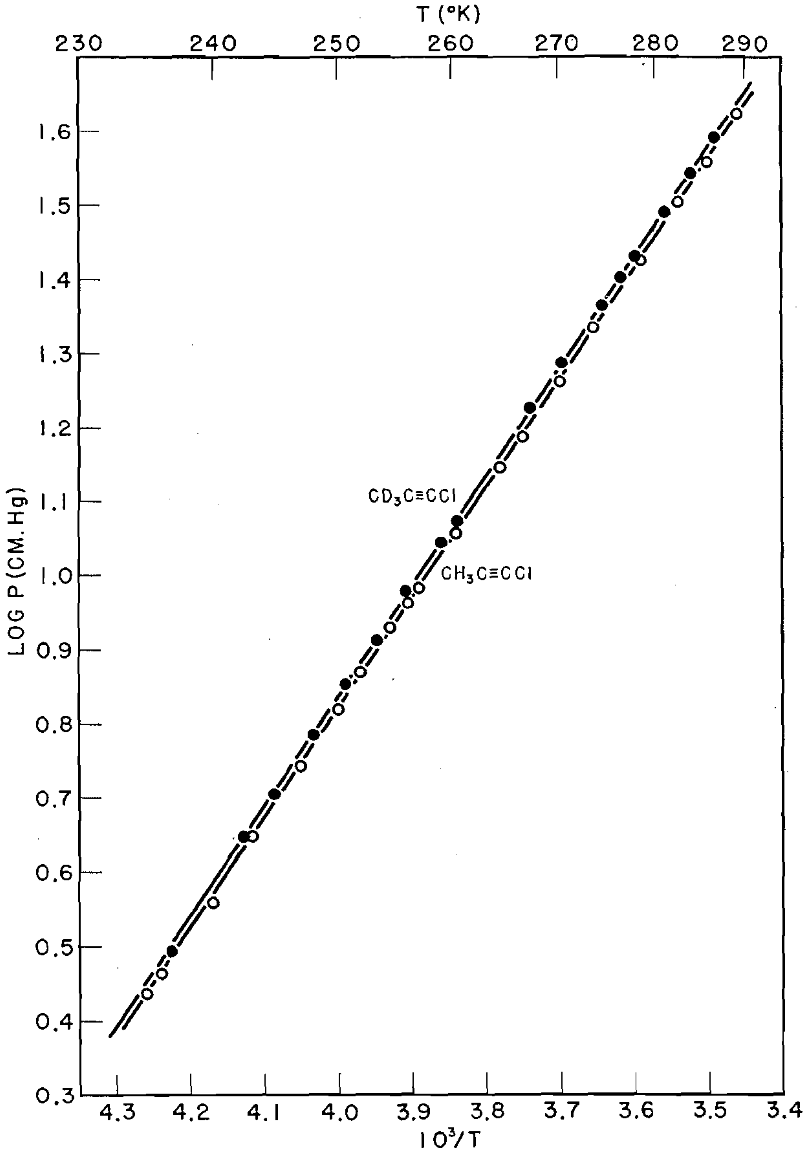

FIG. 1. Vapor pressure of 1-chloro-1-propyne and of 1-chloro-1-propyne-d_3.

identified by its mass spectrum as 1-chloro-1-propyne. The alternative product, 1-chloropropadiene ($CH=C=CHCl$), was recently reported by Jacobs and Brill (7) and boils at 44°C. The product, b.p. 32°C., was identical with that obtained by chlorination of propyne with sodium hypochlorite. By treating *cis*-1,2-dichloro-1-propene-d_4 in the same manner, the corresponding deuterated chloropropyne was obtained.

The vapor pressures of 1-chloro-1-propyne and its deuterated analogue were measured by the method described in earlier papers of this series (9, 10, 11). The values obtained at various temperatures were then plotted logarithmically to give the curves shown on Fig. 1. For temperatures below 16°C., the results were expressed by the equations

$$\log_{10} p \text{ (mm.)} = -(1.480 \times 10^3)/T + 7.740$$

and

$$\log_{10} p \text{ (mm.)} = -(1.487 \times 10^3)/T + 7.782$$

for $CH_3C\equiv CCl$ and $CD_3C\equiv CCl$ respectively.

The structure of 1-chloro-1-propyne was proved by chlorination at 0°C. to 1,1,1,2,2-pentachloropropane identical with the product recently reported by Nesmayanow, Friedlina, and Firstov (14). Furthermore, dehalogenation of the pentachloropropane with zinc dust gave 1,1,2-trichloro-1-propene.

trans-1,2-Dichloro-1-propene reacted much more sluggishly than the *cis*-isomer and was largely recovered after refluxing for a long period. This observation is in agreement with those of other workers who have investigated the dehydrohalogenation of 1,2-dichloroethylene (2) and of 1-ethoxy-1-chloro-1-propene (5). In each case, the *cis* form showed a considerably greater rate of reaction due also to *trans* elimination.

Dehydrohalogenation of *cis*-1,2-dichloro-1-butene and of *cis*-1,2-dichloro-1-pentene likewise gave 1-chloro-1-butyne and 1-chloro-1-pentyne respectively. These products were also identical with those obtained from the chlorination of 1-butyne and 1-pentyne by sodium hypochlorite.

The synthesis of these new chloro alkynes now completes the series to C_9.

EXPERIMENTAL

1-Chloro-1-propyne

cis-1,2-Dichloro-1-propene (36.0 gm.) prepared as in (9) was dissolved in 20 ml. of *n*-butanol and added dropwise to a refluxing solution of 25 gm. of potassium hydroxide in 300 ml. of *n*-butanol during stirring with a magnetic bar. Water entering the reflux condenser was precooled to 5°C. by circulation through a copper spiral immersed in ice water in a Dewar flask. By this means loss of the volatile 1-chloro-1-propyne was avoided. After addition of the halide, the reaction mixture was cooled to 0°C. and the reflux condenser was replaced by a 12 in. Stedman column and a still-head. The 1-chloro-1-propyne distilled as an azeotrope, b.p. 31 to 32°C. It was dried by distillation through a U-tube containing phosphorus pentoxide on a vacuum line. Redistillation through the Stedman column gave a product, b.p. 32.8 to 33°C., n_D^{20} 1.4131 in 68% yield. The mass spectrum showed two strong peaks at 74 and 76.

1-Chloro-1-propyne-d_3

This compound was prepared from 36.4 gm. of *cis*-1,2-dichloro-1-propene-d_4 in exactly the same manner. The yield was 19.4 gm. (78.5%) of product b.p. 31.7°C. at 750 mm., n_D^{20} 1.4105. Mass spectrometric analysis: 98.17 atom % D.

1-Chloro-1-butyne

(*a*) *Dehydrochlorination method.*—*cis*-1,2-Dichloro-1-butene (20 gm.) (preparation to be described in a forthcoming paper) gave 13.2 gm. (93.5%) of 1-chloro-1-butyne, b.p. 63–64.5°C., n_D^{20} 1.4221. The mass spectrum showed two strong peaks at 88 and 90 corresponding to the two chlorine isotopes.

(*b*) *Hypochlorite method.*—A solution of sodium hypochlorite prepared on one tenth the scale reported by Smith and McLeod (16) was attached to a vacuum line which was then evacuated. 1-Butyne was introduced from a gasholder into the apparatus. After four days' stirring, all the butyne had been absorbed and there was a layer of oily liquid above the hypochlorite solution. This upper layer was separated, dried over phosphorus pentoxide on the vacuum line, and fractionated. Four liters of unreacted 1-butyne were recovered. The 1-chloro-1-butyne had b.p. 63.5–64.5°C., n_D^{20} 1.4210. Yield: 76%.

1-Chloro-1-pentyne

(*a*) *Dehydrochlorination method.*—*cis*-1,2-Dichloro-1-pentene (8.5 gm.) which was prepared by a method to be reported in a forthcoming paper was treated as described for the lower homologues. It gave 6.0 gm. (96%) of 1-chloro-1-pentyne, b.p. 91.5–92.0°C., n_D^{20} 1.4302. Calc. for C_5H_7Cl: Cl, 34.56%. Found: Cl, 33.58%.

(*b*) *Hypochlorite method.*—A mixture of 34.0 gm. of pentyne-1 and 800 ml. of sodium hypochlorite was stirred with a magnetic bar for 180 hr. The upper layer was then separated, dried, and fractionated. It gave 29.2 gm. (76.5%) of 1-chloro-1-pentyne, b.p. 91.5–92.0°C., n_D^{20} 1.4302.

1,1,1,2,2-Pentachloropropane

A solution of 14.0 gm. of 1-chloro-1-propyne in 50 ml. of methylene chloride was placed in a 100 ml. flask equipped with a cold finger condenser cooled with dry ice. Chlorine was introduced through a side-arm while the reaction mixture was kept at 0° in the dark. Five liters of chlorine were introduced in three hours. The mixture was allowed to stand at room temperature overnight, the volatile material was then removed under vacuum, and a white residue remained. Sublimation on a vacuum line gave 34.8 gm. (85% yield) of white solid, which after recrystallization from 15 ml. of petroleum ether gave 25.0 gm. of product m.p. 179–180°C., identical with the value reported in (14) for 1,1,1,2,2-pentachloropropane. Dehalogenation with zinc dust in ethanol gave a liquid b.p. 114–5°C., n_D^{20} 1.4827, identical with the values reported for 1,1,2-trichloro-2-propene obtained by the dehydrohalogenation of 1,1,2,2-tetrachloropropane (9).

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SOME OBSERVATIONS ON DETERMINING DENSITY OF FLUIDS BY THE FALLING DROP METHOD[1]

By R. P. A. Sims

ABSTRACT

The shape of the calibration curve obtained with a commercial Falling Drop apparatus has been investigated for drops varying in viscosity and surface tension and in media of varying solvent power. Drop velocity affects drop shape when the viscosity of the drop substance is low, and drop volume when the medium exerts solvent action on the drop. "End effect" appears to be significant even when "wall effect" is large.

INTRODUCTION

The falling drop method has been used frequently to determine the density of fluids (3, 6, 8, 13). With most materials, nonlinear calibration curves were obtained. In a previous study (13), the parabolic calibration curve for methyl esters falling through aqueous ethanol was found to be steeper than that for glycerides and appeared to cross the curve for glycerides at high drop velocities. Drops of glycerides fell at constant rates through different portions of the tube. In contrast, the rate of fall of drops of methyl esters was observed to decrease with depth. This effect was reduced by saturating the medium with drop substance and increased by using acetonitrile instead of ethanol in the medium. Possible causes of these effects are being reported here. Although some of the characteristics are peculiar to the systems studied, others are of general interest.

The application of Stokes' law to solid and liquid spheres falling through a finite medium and factors affecting their rates of fall have been well summarized by Merrington (11). Two factors which have not been considered previously and which may also affect rate of fall are the shape of the drop and the solvent power of the medium. The shape of a drop is a function of its viscosity, surface tension, and velocity. At high rates of fall, the drop would be expected to assume a prolate spheroid shape and at low rates of fall, or at rest, to become oblate, the surface tension and viscosity of the drop substance opposing the changes in shape. In addition, when the medium exerts solvent action on the drop, diffusion into and out of the drop occurs.

PROCEDURE

A commercial "Falling Drop Apparatus" (Fisher Scientific Co.) was used in the investigation. The media in the tubes were kept at 25 ± 0.003° C. by pumping distilled water through the jacket from a constant temperature bath. Auxiliary sighting marks were inscribed on the tubes, 5 cm. above and below the regular marks, to permit measurement of rate of fall over a variety of distances.

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The materials used in this study were samples of linseed oil that had been thermally polymerized to various extents and methyl esters of C_{18} fatty acids. The media were aqueous solutions of either acetonitrile or ethanol, selected to produce desired rates of fall. Details of the technique have been published elsewhere (13).

Photographs of falling drops of triglyceride oils and methyl esters were taken through plane glass surfaces set parallel to the camera lens and film. To permit comparison of a drop at the beginning and end of its fall, both images were recorded on the same negative. Shape and area of the images were measured on 12-fold enlargements and the volumes of the corresponding solids of revolution were calculated from the axes of each drop.

Interfacial tensions were measured at 25 ± 0.5° C. using a Cenco-du Nuoy tensiometer.

EXPERIMENTAL AND RESULTS

Behavior of the Drop

Deceleration of a drop during its fall could be caused by one or all of the following factors: reduction in radius due to diffusion of drop substance into the medium, decrease in density difference caused by diffusion of fat solvent from the medium into the drop, change in shape of the drop. Since falling drops of methyl ester decelerated even when the medium was saturated with drop substance and the difference in rate of fall in the saturated and unsaturated medium was insufficient to change the shape, it can be inferred that diffusion into and out of a drop takes place.

The effect of drop velocity on the shape of the drop was investigated for glycerides and esters using drops of constant size falling through media of different densities. Photographs of drops falling at slow and fast rates taken at the start and end of the timing zones were compared. They showed that drops of glycerides were spherical on release and retained their shape at velocities as high as 3 cm. per sec. Drops of ester were oblate on release but approached spherical shape on gaining speed, and at velocities greater than 1 cm. per sec. were spherical. However, even a velocity of 1.5 cm. per sec. did not cause a drop of ester to become prolate. Representative photographs of drops are shown in Fig. 1.

Volumes were calculated from the axes of the drops with an accuracy of ±1% in each case. A glyceride drop, falling at 0.6 cm. per sec., did not change in volume. However, when the velocity was 3.0 cm. per sec., its volume increased by 7%. With esters falling through unsaturated media, the volume increased 4% at a speed of 0.6 cm. per sec. and 9% at 1.5 cm. per sec. When the medium was saturated with ester, the drop fell at a rate of 0.95 cm. per sec. and increased in volume by 19%.

Investigation of End Effect

To determine whether adequate allowance for "end" effect had been made, rate of fall was determined using the additional sighting marks. The data (Table I), for triolein falling through aqueous ethanol, show that the lower

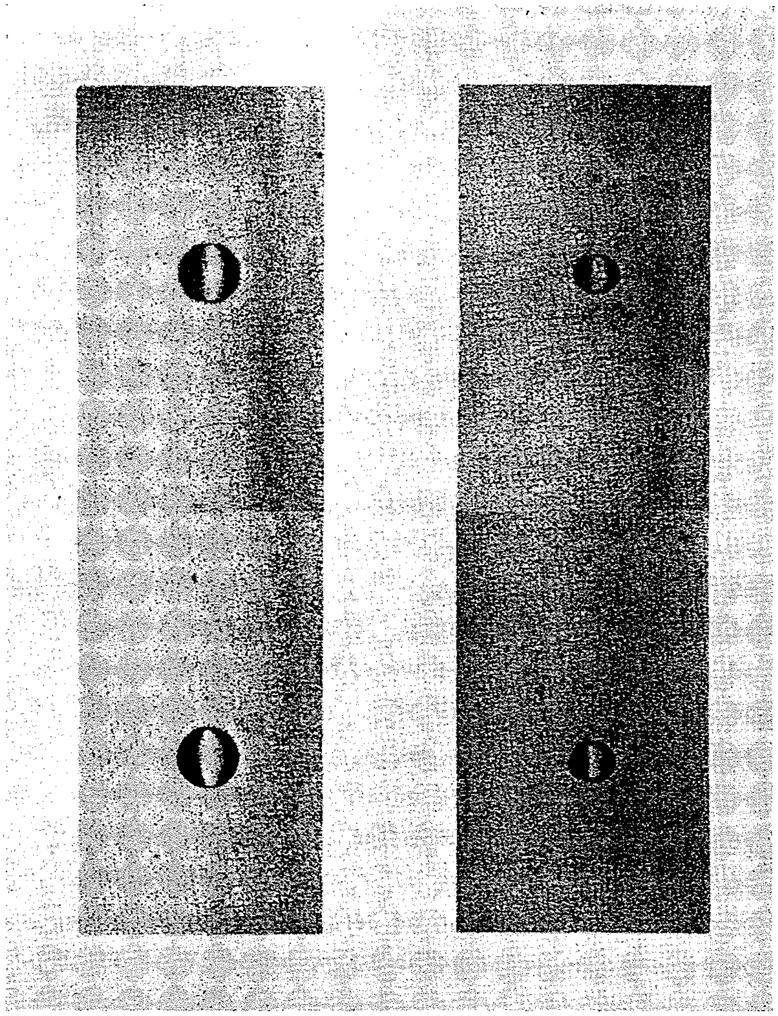

FIG. 1. Photographs of drops falling at a velocity of 0.66 cm. per sec.
a. Triolein, drop volume 0.01 cm^3.
b. Methyl erucate, drop volume 0.005 cm^3.

TABLE I
EFFECT OF END ZONE ON FALLING TIME

Length of end zone, cm.		Interval, cm.	Time, sec.	Rate, cm./sec.
Top	Bottom			
12*	7*	30	45.7	0.656
7	12	30	45.6	0.658
7	7	35	53.5	0.654
7	2	40	61.4	0.651
12	2	35	53.5	0.654
17	2	30	45.7	0.656
17	12	20	30.2	0.662

* *Original end zones.*

the starting point and the higher the finish line, i.e. the longer the end zones, the faster the measured rate of fall. A statistical analysis of the data, not included here, has shown that these differences are significant.

Attempts to circumvent "wall" and "end effects" by use of wider tubes failed. Under these conditions, the drops fell in an irregular manner, presumably because of convection currents.

Interfacial Tension

The interfacial tension between linseed oil and 61% ethanol was 5.9 and 6.9 dynes per cm. respectively for unheated oil and oil heated 20 hr. at 280° C. The tension between surfaces of methyl erucate and 77% ethanol was 2.1 dynes per cm.

DISCUSSION

When falling time was plotted as an arithmetic function of density difference between drops and media, parabolic curves were obtained: $y = 3 + 0.47x + 0.0015x^2$ for glycerides and $y = -2 + 0.5x + 0.0064x^2$ for esters (13). Although the curve for esters was of the same form, it crossed the glyceride plot at high drop velocities.

The parabolic form of the arithmetic plot suggests that the velocities used were too great. Since the velocities correspond to Reynolds numbers ranging from 22 down to 3, with 9 an average value, the flow of medium was generally not streamlined. Although turbulence should be avoided, slower rates of fall could not be used with the apparatus employed because of larger coefficient of variation in longer falling times. However, when the time of fall of various drops was calculated in three ways using Allen's (1) generalized equation for the motion of a sphere in a viscous medium, and the Wadell equation (14) and Newton's equation for the intermediate region of the flow, the results showed that introduction of a squared velocity term still left anomalies. The shape of the plots can therefore be attributed to a combination of excessive velocity and the following constant errors associated with the falling drop method: tangential velocity within the drop, nonspherical shape, "wall" and "end" effects, and the influence of the medium on the drop.

Internal Tangential Velocity

The viscosity of the drop substance in combination with the surface tension determines the magnitude of the internal tangential velocity and the shape of the drop. The ratio of the viscosity of glycerides and C_{18} esters to that of the media is 25 and 5 respectively and the value of the respective interfacial tensions 6.5 and 2.1. Therefore, according to Bond (4), a drop of glyceride behaves as if it were solid. Esters, however, having approximately one-tenth the viscosity of glycerides, could have their drop velocity accelerated by a factor of 1.1. However, as Bond later pointed out (5), the interfacial tension between drop and medium may be sufficient to reduce this acceleration. If the radius of the drop is smaller than a critical radius, the drop behaves as a solid even though its viscosity is less than that of the medium. As the critical radius for methyl erucate was three times the actual radius, a drop of ester should not be accelerated. However, the drops were travelling rapidly, causing increased tangential velocity and the critical radius may well have been less than the calculated value. Such was the case when Miyagi's (12) value for the critical radius of air in water was compared with the value calculated using Bond's expression. This effect might therefore partially account for the ester line apparently crossing the glyceride plot.

Drop Shape

Photographs showed that drops of glycerides were round at all velocities studied and that drops of ester (lower viscosity and surface tension) did not assume spherical shape until they fell at velocities greater than 1 cm. per sec. This change in shape could account for the upward bend of the ester curve at low velocities and the apparent crossing of the glyceride plot.

"Wall and End Effect"

The magnitude of the "wall" and "end effects" was estimated by calculating the velocities of a drop of linseed oil and methyl erucate using Stokes' law, Ladenburg's (9, 10) modification of it, and Bacon's (2) adaptation of Faxen's (7) correction. The following results were obtained.

Drop substance	Drop velocity, cm. per sec.			
	Stokes	Ladenburg	Faxen	Measured
Linseed oil	1.96	1.05	0.69	0.64
Methyl erucate	2.34	1.38	1.05	0.67

These results indicate that "wall" and "end effects" are significant and that, with triglycerides, the Faxen correction is applicable even at high drop velocities. When the ratio of drop radius to tube radius is larger than 0.3, the Faxen correction becomes too great. Since the measured rate of fall was slower than the most severely corrected value, it might be inferred that "end effect" is operative. The data in Table I also suggest, in contradiction of Merrington's statement, that "end effect" is appreciable when "wall effect" is large. They support Ladenburg's observation (10) that "end effect" is appreciable even if only the middle 50% of the tube is used as the timing zone.

The influence of "wall" and "end effect" on the velocity of drops of ester is about 7% less than on the larger glyceride drops. Hence, the ester falls faster than would be anticipated from consideration of drop radius alone. The diminished "wall" and "end effect" may be an additional reason for the apparent intersection of the ester and glyceride curves.

Diffusion

Another constant error was observed when methyl esters were used. Since esters are completely miscible with ethanol and acetonitrile, they might dissolve in the medium or the medium might diffuse into them. Because the rate of fall of methyl oleate through oleate-saturated 77% ethanol solution still showed deceleration, the medium can be presumed to diffuse into the drop. Moreover, the increase in volume of the drop, calculated from photographs, was three times greater than when it fell through unsaturated medium. The more rapid deceleration in aqueous acetonitrile, in which esters are less soluble than in alcohol (13), can be explained by the larger diffusion coefficient and lower specific gravity of acetonitrile. The failure of the Faxen correction with methyl erucate can therefore be attributed to deceleration caused by solvent influence.

With a commercial Falling Drop apparatus high drop velocities must be used. When the medium exerts solvent action on the drop, the resultant turbulent flow of medium affects the drop volume by increasing the mass transfer rate. Drop velocity also governs the shape of the drop if the viscosity of the drop substance is sufficiently low. Excessive rate of fall is also directly responsible for part of the nonlinearity of the calibration curve. "Wall and end effect" are appreciable with apparatus of this type. However, the Faxen correction for "wall effect" appears to be applicable at high drop velocities. "End effect" seems to be a factor even when "wall effect" is large.

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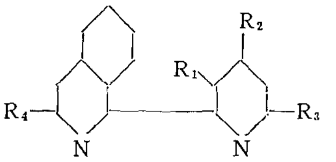
ANALOGUES OF 2,2′-BIPYRIDYL WITH ISOQUINOLINE AND THIAZOLE RINGS. PART I[1]

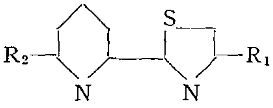
By R. F. Knott and J. G. Breckenridge

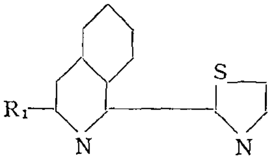
ABSTRACT

Several analogues of 2,2′-bipyridyl, with isoquinoline, thiazole, and pyridine rings in various combinations, have been synthesized, and the effect of substituent groups in certain positions in the molecules studied with respect to their ability to react with cuprous and ferrous ion (the "cuproin" and "ferroin" reactions). The results agree with earlier work, and emphasize the desirability of two substituent groups "ortho" to the nitrogen atoms if a stable and sensitive cuprous ion reagent is wanted. The presence of one ortho substituent makes the reagent ineffective toward reaction with ferrous ion. Two of the compounds synthesized had groups in positions which did not allow a coplanar *cis* configuration of the molecule, and only in these cases were dipicrates formed; this situation is explained by assuming that hydrogen bond formation between the nitrogen atoms is not possible.

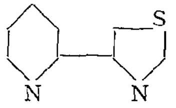
We have been engaged for some time in a study of compounds analogous to 2,2′-bipyridyl, with respect to correlations between structure and the "ferroin" and "cuproin" reactions typical of this class of compounds. The examples we have prepared are illustrated below; to conserve space they are referred to subsequently in the text by Roman numerals.



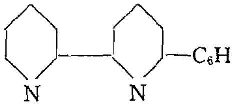




Compound	R_1	R_2	R_3	R_4
I	H	H	H	H
II	H	CH_3	H	H
III	CH_3	H	H	H
IV	H	H	H	CH_3
V	CH_3	H	H	CH_3
VI	H	H	CH_3	CH_3
VII	H	CH_3	H	CH_3
VIII	H	H		
IX	CH_3	CH_3		
X	CH_3	H		
XI	C_6H_5	CH_3		
XII	C_6H_5	H		
XIII	H			
XIV	CH_3			



XV



XVI

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Contribution from the Department of Chemical Engineering, University of Toronto. Abstracted from the Ph.D. thesis of R. F. Knott.

These were prepared by conventional methods, those containing an isoquinoline ring by reaction of the appropriate pyridyllithium or thiazolyllithium with isoquinoline or 3-methylisoquinoline, and the pyridyl-thiazole compounds by ring-closure methods.

In the course of the synthetic work, the bases were characterized by preparation of picrates. It is well known that compounds such as 2,2'-bipyridyl and 1,10-phenanthroline form only monopicrates, for which a possible explanation might lie in the situation discussed by Mann and Watson (8) for some other types of molecule. This involved the effect of a proton attached to one nitrogen atom on the proton-attracting power of a second nitrogen atom. Another possible explanation in the present case is that a hydrogen bond may be formed between the nitrogen atoms by the first proton, but where the two rings are free to rotate about the bond connecting them they will presumably take up the coplanar *trans* configuration; this has been shown to be so for 2,2'-bipyridyl by Cagle (1) and Fielding and LeFevre (5). In such a case the hydrogen bond would have to be sufficiently strong to hold the molecule in the *cis* configuration. In the present work, examination of molecular models has shown that in two cases (compounds III and V) steric hindrance is such that it would be extremely difficult for the two rings to take up the coplanar *cis* arrangement, and thus a hydrogen bond is improbable; in agreement with the hydrogen bond theory, we have found that these two compounds are the only ones which form dipicrates. The ultraviolet absorption spectra of all the compounds were determined in ethanol solution, and in a few cases in dilute acid, in the hope that in the latter a significant difference might appear between, for example, compounds I and III. The molar extinction coefficients at the wave length of maximum absorption are given in Table I, and it is evident that there are no anomalous results.

TABLE I
ULTRAVIOLET ABSORPTION SPECTRA

Compound	95% ethanol		0.05 *N* HCl	
	λ (mμ)	$\epsilon_{max} \times 10^{-3}$	λ (mμ)	$\epsilon_{max} \times 10^{-3}$
I	222	41.8	232	30.0
II	222	42.8	—	—
III	219	49.5	232	32.0
IV	223	47.5	—	—
V	222	54.2	—	—
VI	223	43.8	—	—
VII	223	46.2	—	—
VIII	(232),301	(4.05),13.8	—	—
IX	(233),312	(4.12),13.8	—	—
X	(235),309	(4.83),13.3	—	—
XI	253,(324)	20.8,(10.3)	—	—
XII	251,(322)	25.1,(10.8)	—	—
XIII	233	28.4	234	28.0
XIV	235	29.2	—	—
XV	249,(287)	12.1,(8.52)	—	—
XVI	236	21.4	—	—

Secondary maxima in parentheses.

We have investigated the reactions of the compounds with ferrous and cuprous ion; it was evident from their structures that they could be divided into three classes: (*a*) those with one or two groups in positions "ortho" to the nitrogen atoms (IV, VI, VII, IX, X, XI, XII, XIV, XVI), which would be expected to give only the cuproin reaction, (*b*) those with no "ortho" groups (I, II, VIII, XIII, XV), which should give both ferroin and cuproin reactions, and (*c*) those in which steric hindrance to coplanarity of the rings is such as to preclude formation of any stable chelate product (III, V). The colorimetric work along these lines is summarized below.

The nine compounds in class (*a*) and two compounds (I, II) in class (*b*) gave highly colored complexes with cuprous ion, extractable by isoamyl alcohol; the absorption spectra in the visible region are shown in Figs. 1 and 2. It may be seen that two "ortho" groups result in a complex with a higher extinction coefficient than if only one or no "ortho" group is present, and that a methyl group is more effective than a phenyl. It might be supposed that the ortho groups would make the complex more stable, for example toward oxidation of the cuprous ion. We hope to be able to report values for the stability constants of these complexes soon. The three class (*b*) compounds whose spectra are not given (VIII, XIII, XV) gave unstable cuprous complexes of low color intensity, emphasizing the point that for a stable and sensitive cuprous ion reagent of this type, the two "shielding" groups are apparently a necessity. Molecular models of these complexes show that with tetrahedral co-ordination

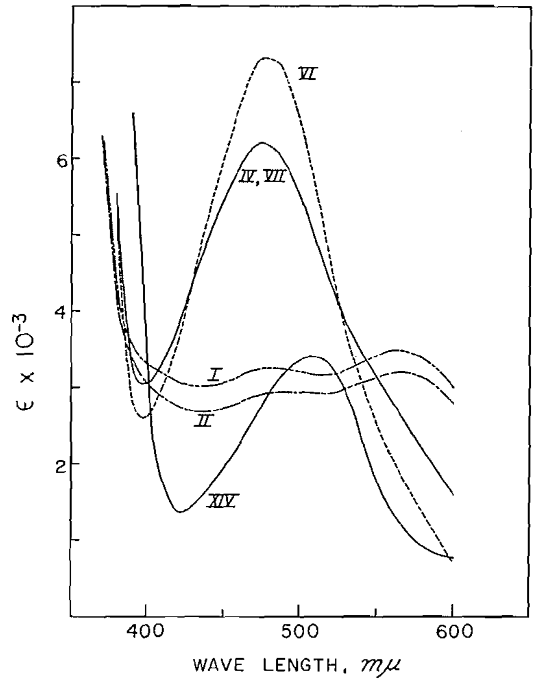

FIG. 1. Absorption spectra of copper complexes of compounds I, II, IV, VI, VII, XIV.

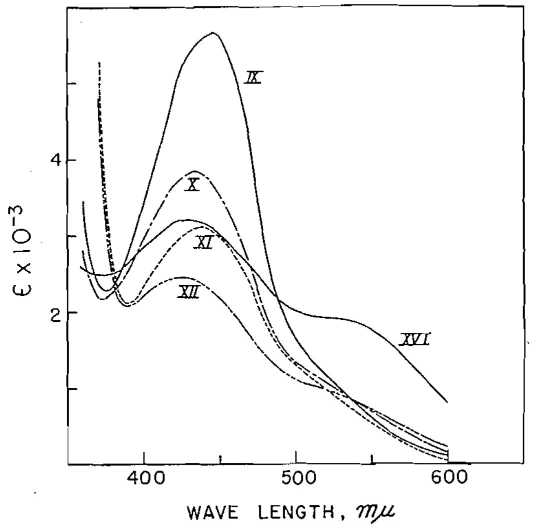

FIG. 2. Absorption spectra of copper complexes of compounds IX, X, XI, XII, XVI.

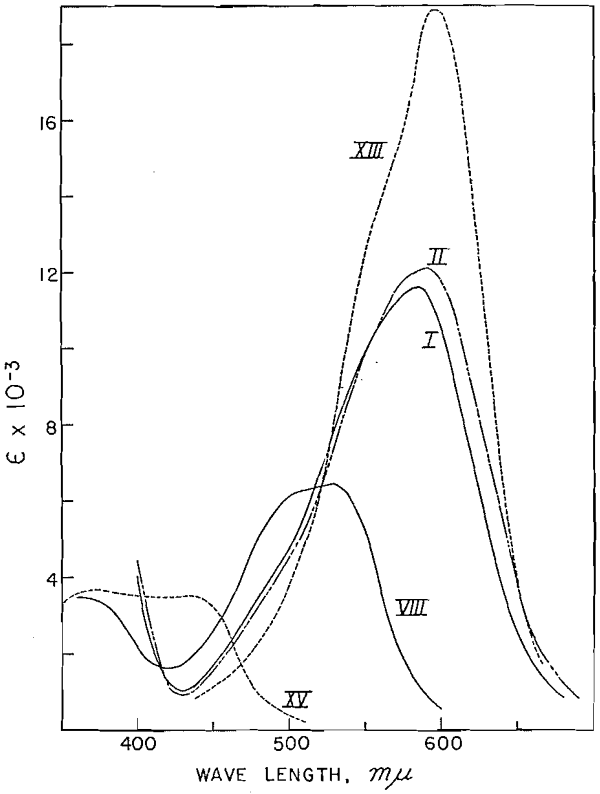

FIG. 3. Absorption spectra of iron complexes of compounds I, II, VIII, XIII, XV.

of the two organic molecules around the cuprous ion, the latter is almost completely shielded from view. It may also be seen that replacement of a pyridine ring by thiazole results in a lowering of the extinction coefficient; compare XII and XVI, and IV and XIV.

The five compounds in class (*b*), as expected, gave colored complexes with ferrous ion, the absorption spectra for which are given in Fig. 3. With these complexes, replacement of pyridine by thiazole leads to a marked increase in extinction coefficient (compare I and XIII). Previous work by Erlenmeyer (4) had shown that 2,2′- and 4,4′-bithiazoles gave no stable colored complexes with ferrous ion, and the result obtained in this work was somewhat unexpected.

The two compounds in class (*c*) gave no color with ferrous ion, and with cuprous ion gave unstable yellow colors of low intensity.

For convenience in comparing the extinction coefficients at the wave lengths of maximum absorption, these are given in Table II.

TABLE II
SPECTRAL DATA FOR IRON AND COPPER COMPLEXES

Compound	Iron complex		Copper complex	
	λ (mμ)	ϵ_{max}	λ (mμ)	ϵ_{max}
I	585	11,600	560	3,500
II	590	12,100	565	3,200
III	—	—	—	—
IV	—	—	475	6,200
V	—	—	—	—
VI	—	—	480	7,300
VII	—	—	475	6,200
VIII	525	6,500	—	—
IX	—	—	445	5,700
X	—	—	435	3,800
XI	—	—	440	3,100
XII	—	—	425	2,500
XIII	600	18,900	—	—
XIV	—	—	510	3,400
XV	370,440	3,600	—	—
XVI	—	—	425	3,200

The ferroin reaction with the five class (*b*) compounds was investigated more fully, and values for their over-all stability constants calculated. Beer's Law was shown to hold for I, II, and XIII, and the method of continuous variations was used to confirm the probability that in the final complex there are three molecules of the reagent per ferrous ion. This was found to be the case with I and XV, and was assumed to be true for the others. To a solution containing known amount of ferrous ion were added increasing quantities of the reagent, and a curve was plotted relating absorbance and moles reagent per mole ferrous ion. This was done for I, II, XIII, and XV; in each case K was calculated from at least three points on the curve, and concordant results were obtained. These of course neglect any light absorption due to the ferrous ion, which at the concentrations used was very small. For compounds I, II, and XV the solvent was 10% aqueous ethanol, buffered to pH 5.1, and for compound XIII the solvent was 60% acetic acid; the temperature was 28° C. The following values for log K were obtained: I, 9.36; II, 9.94; XIII, 8.50; XV, 11.53.

Further work is in progress on the synthesis and examination of other compounds of similar type.

EXPERIMENTAL

All melting points are corrected: microanalyses by Micro-Tech Laboratories, Skokie, Ill. (Table III). A Beckmann Model DU spectrophotometer was used for the colorimetric work.

Compounds I, II, III, IV, V, VI, VII, XIII, XIV

The procedure for all these was essentially that developed by Gilman and co-workers (6); detailed directions are given below only for compound I.

To a solution of 9.1 gm. (0.0577 mole) of 2-bromopyridine in 25 ml. ether at −40° C. was added an equimolar amount of *n*-butyllithium solution. The mixture was stirred gently for 15 min., and then 12.9 gm. (0.1 mole) of isoquinoline in 25 ml. ether was added slowly. The mixture was kept at −35° C. to −20° C. for four hours, with stirring. Slightly less than the equivalent amount of dilute hydrochloric acid was added to effect hydrolysis, and the alkaline aqueous phase extracted with ether. After removing the ether, the red, oily residue was heated with 15 ml. of nitrobenzene at 130° C. for one hour, after which the nitrobenzene was distilled off *in vacuo* (15 mm.). The residue distilled at 135–145° C. at 0.2 mm. pressure, giving a yellow oil which was purified by decolorization and recrystallization from ligroine-ether, yielding 2.44 gm. (20.7%) of white crystals of 1-(2-pyridyl)isoquinoline.

In four cases (II, III, VI, XIII) the crude product could not be crystallized. With two of these (II, XIII) crystals were eventually obtained after conversion to the picrate, purification, and liberation of the free base. With the remaining two (III, VI) even this procedure failed to yield crystals, and the final product was obtained as an oil after redistillation under high vacuum.

Compound XVI

To a solution of phenyllithium prepared from 6.7 gm. (0.043 mole) of bromobenzene and 0.625 gm. (0.09 mole) lithium in 50 ml. ether was added 5 gm. (0.032 mole) of 2,2'-bipyridyl in 50 ml. ether. The dark red solution was stirred and refluxed gently for three hours, and allowed to stand overnight at room temperature. The mixture was hydrolyzed by cold dilute hydrochloric acid, and the ether layer further extracted with acid. The acid extracts were made alkaline and extracted with ether. After removing the ether, oxidation by nitrobenzene and vacuum distillation produced an oil, b.p. 145–155° C. at 0.2 mm. Crystallization from ligroine-ether gave 0.68 gm. (8.9%) of white crystals of 6-phenyl-2,2'-bipyridyl.

2-Cyanopyridine, 2-Cyano-6-methylpyridine

The procedure used by Craig (3) for the preparation of the former was extended to the 6-methyl derivative, which was obtained as white needles, m.p. 72–72.5° C., in 40% yield. Calc. for $C_7H_6N_2$: N, 23.73%. Found: N, 23.93, 23.86%.

Pyridine-2-thiocarboxamide, 6-Methylpyridine-2-thiocarboxamide

The procedure used by Karrer (7) for the preparation of the former was used in both cases. The 6-methyl derivative was obtained in 70% yield as yellow-green plates, m.p. 103–104° C.

Compounds IX, X

Chloroacetone was condensed with the two thiocarboxamides noted above, following the procedure of Karrer (7) for compound X.

TABLE III

Compound	Compounds I–XVI				Picrates		
	Yield	M.p., ° C.	Analyses		M.p., ° C.	Analyses	
			Calc., %	Found, %		Calc., %	Found, %
I	20.7%	74.5–75.3	C, 81.51 H, 4.88 N, 13.62	81.42, 81.45 5.01, 5.03 13.46, 13.60	167.2–168	N, 16.10	16.15, 16.10
II	14.8%	55.2–55.8	C, 81.80 H, 5.49 N, 12.72	81.79, 81.86 5.53, 5.39 12.60, 12.70	161–161.5	N, 15.61	15.55, 15.42
III	29.2%	b.p. 165° C. at 0.35 mm.	C, 81.80 H, 5.49 N, 12.72	81.70, 81.60 5.72, 5.50 12.60, 12.56	156–156.5	*C, 47.80 H, 2.66 N, 16.52	48.01, 47.70 2.62, 2.49 16.54, 16.61
IV	24.4%	75.6–76.3	C, 81.80 H, 5.49 N, 12.72	81.72, 81.65 5.59, 5.40 12.64, 12.44	177–177.6	N, 15.61	15.87, 16.15
V	16.0%	71.5–72	C, 82.01 H, 6.02 N, 11.96	82.13, 82.26 6.13, 6.18 11.76, 11.81	170–170.5	C, 57.00 H, 3.70 N, 15.11	57.55, 57.43 3.51, 3.51 15.33, 15.20
					140–141	*C, 48.56 H, 2.91 N, 16.19	49.03, 49.20 2.83, 2.89 16.27, 16.01
VI	16.5%	b.p. 142° C. at 0.15 mm.	C, 82.01 H, 6.02 N, 11.96	82.03, 81.82 6.25, 5.96 11.86, 11.82	170–171	N, 15.11	15.20, 15.24
VII	16.0%	75–75.6	C, 82.01 H, 6.02 N, 11.96	81.96, 81.79 6.19, 6.11 11.95, 12.10	162–162.5	N, 15.11	15.57, 15.32
VIII	1%	46–46.3	—	—	—	—	—
IX	73.5%	93–93.3	C, 63.11 H, 5.30 N, 14.73	63.04, 63.07 5.24, 5.41 14.28, 14.50	191.5–192	N, 16.70	16.20, 16.43
X	72%	84–84.5	—	—	—	—	—
XI	82%	127–127.5	C, 71.40 H, 4.80 N, 11.11	71.90, 71.76 4.80, 4.86 11.00, 11.10	203–203.5	N, 14.55	14.62, 14.41

* *Calculated values for dipicrate, all others for monopicrate.*

TABLE III (*Concluded*)

Compound	Compound I–XVI				Picrates		
	Yield	M.p., ° C.	Analyses		M.p., ° C.	Analyses	
			Calc., %	Found, %		Calc., %	Found, %
XII	77%	72.5–73	C, 70.54 H, 4.23 N, 11.77	70.74, 70.79 4.32, 4.21 11.52, 11.40	141–142	N, 14.98	14.51, 14.76
XIII	7.8%	73.4–73.7	C, 67.89 H, 3.80 N, 13.20	68.28, 68.26 3.74, 3.90 13.28, 13.15	140–141.3	N, 15.87	15.84, 15.75
XIV	4.2%	68.8–69.2	C, 68.99 H, 4.45 N, 12.38	69.59, 69.68 4.69, 4.56 12.34, 12.40	136–136.5	N, 15.74	15.43, 15.45
XV	18.5%	103–103.5	C, 59.25 H, 3.72 N, 17.28	59.52, 59.65 3.85, 3.93 17.26, 17.47	—	—	—
XVI	8.9%	83.5–84.5	C, 82.72 H, 5.21 N, 12.06	83.02, 82.89 5.23, 5.34 11.66, 11.85	173.8–174	N, 15.22	15.20, 15.20

Compounds XI, XII

A condensation similar to the above, but substituting ω-chloroacetophenone for chloroacetone, was used. Since the procedures were identical, only that for XII is given.

To a solution of 1.5 gm. (0.0108 mole) of pyridine-2-thiocarboxamide in 10 ml. absolute ethanol was added 1.7 gm. (0.0110 mole) of ω-chloroacetophenone; the mixture was refluxed for two hours, and after it had been allowed to stand overnight at room temperature, was refluxed for two more hours. The solution was evaporated to half its volume and cooled; the precipitate which appeared was filtered and washed with dilute potassium hydroxide solution, and then crystallized from ligroine-ether. The white cubic crystals of 2-(2-pyridyl)-4-phenylthiazole weighed 1.99 gm. (77%).

Compound VIII

Pyridine-2-thiocarboxamide (5.1 gm., 0.037 mole) and ethyl α,β-dichloroethyl ether (5 gm., 0.043 mole) were dissolved in 40 ml. 75% ethanol. The solution was refluxed for two hours, concentrated to half its volume, and allowed to stand overnight. The tarry mixture was made alkaline with sodium carbonate, and steam-distilled until the distillate no longer gave a red color with ferrous sulphate; about 400 ml. of distillate was obtained. Ether extraction of the distillate resulted in a small quantity of yellow oil, which darkened slowly on standing, but finally crystallized. Sublimation gave 0.032 gm. (1%) of white crystals of 2-(2-pyridyl)-thiazole. Analyses were not done, but the very great similarity of the ultraviolet absorption spectrum of the product to those of the closely related compounds IX and X left no doubt as to its structure.

Compound XV

A sample of 2-(ω-bromo)acetylpyridine (3.5 gm., 0.0175 mole) was prepared from 2-acetylpyridine by the method of Clemo (2). To this, dissolved in 50 ml. absolute ethanol, was added 1.2 gm. (0.02 mole) of thioformamide in 10 ml. absolute ethanol. A vigorous reaction ensued and the mixture became dark green; it was refluxed gently for four hours, made alkaline with potassium carbonate, and steam-distilled. About 500 ml. of distillate was obtained, which deposited a few crystals on cooling. Slow evaporation produced an additional amount of crystalline material, and purification by sublimation gave 0.503 gm. (18.5%) of 4-(2-pyridyl)thiazole.

Reactions with Cuprous Ion

Standardized aqueous solutions of copper containing 5–30 p.p.m. were prepared.

To 25 ml. of a copper solution of known strength in a separating funnel was added sufficient hydroxylamine hydrochloride to reduce cupric to cuprous ion, and the pH was then adjusted to 6 with a sodium acetate buffer. About 10 ml. of a solution of the reagent in purified isoamyl alcohol (containing about 0.1 gm. of reagent) was added, and the contents of the funnel shaken vigorously. The aqueous layer was removed and the alcohol solution transferred to a 50 ml. volumetric flask. The aqueous layer was extracted with further portions of the alcohol solution until the extract was colorless, and the total alcohol extract was made up to 50 ml. Absorbance values were measured on the alcohol solutions, readings being taken every 5 mμ except near the maxima, where the intervals were 2 mμ. Beer's Law was shown to hold for compound VI, readings being taken at 480 mμ with copper solutions of different strengths.

Reactions with Ferrous Ion

Standardized aqueous solutions of iron were prepared containing 0.7–30 p.p.m. of ferrous ion.

(*a*) *Method of Continuous Variations*

Since the reagents were colorless, and any absorbance due to ferrous ion in the concentrations used was negligible, curves were plotted of absorbance (the "Y" function) against "x". "X" ml. of reagent solution (0.001036 M) were added to $(1 - x)$ ml. of ferrous ion solution of the same concentration, all solutions being buffered to pH 5.1. With the two compounds tested (I, XV) sharp maxima were obtained at $x = 0.75$, i.e. the complexes were of the type FeR_3^{++}.

(*b*) *Stability Constants*

Absorbances were measured of a number of solutions containing 25 ml. of 0.0001945 M iron solution and varying amounts of 0.01459 M reagent solution, buffered to pH 5.1, and made up to 50 ml. at 28° C. Readings were made at 585 mμ, and the results plotted. Calculation of the constant $K = [FeR_3^{++}]/([Fe^{++}]\,[R]^3)$ was done for three points on the sloping part of the curve; the results obtained with I were: 2.22×10^9, 2.37×10^9, and 2.31×10^9. The average value was 2.30×10^9, or $\log K = 9.36$.

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IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH CO^{60} GAMMA-RAYS AND BETATRON X RAYS[1]

By R. W. Hummel, A. B. Van Cleave, and J. W. T. Spinks

ABSTRACT

The production of acid from two commercial brands of chloroform, on exposure to Co^{60} gamma-rays and high energy X rays from a betatron, has been measured. Inhibitor-free chloroform liberates acid in amounts varying linearly with the radiation dose. The specific yield, in micromoles of acid produced per liter of chloroform per kiloroentgen, varies inversely as the square root of the dose rate. The specific yields are slightly less for betatron radiations, compared with Co^{60} gamma-rays. The average lifetime of the free radical chains is about one second.

INTRODUCTION

Polyhalogenated aliphatic and aromatic compounds are radiation sensitive, decomposing chainwise to form halogen acids. The possibilities of adapting chloroform to make a satisfactory dosimeter have been extensively studied, especially concerning its use as a personnel dosimeter (5).

Commercial chloroforms of all grades contain inhibitors such as ethanol which must be removed if high sensitivity to X and gamma radiation is desired. Water and oxygen increase the sensitivity (2). The alcohol is easily removed by multiple extractions with distilled water, and the resulting product, containing water and dissolved oxygen, is highly sensitive to X and gamma radiations. The washed chloroform is, however, sensitive to visible and ultraviolet light and decomposes on heating. The rate of acid production increases with increasing temperature and decreasing dose rate, and is energy dependent in the 50–830 kev. range (5).

The purposes of the present investigation were to determine the energy dependence, if any, of chloroform to electromagnetic radiations from 1–24 Mev. and to determine the nature of the dose rate dependence.

MATERIALS

British Drug Houses AnalaR and Mallinckrodt Analytical Reagent chloroform were used. Each was prepared for irradiation in the same way, by shaking 10 times with equal volumes of distilled water in a separatory funnel. This procedure was followed to remove alcohol, generally included by the manufacturers as a preservative. The washed chloroform was kept under a layer of distilled water, in a brown screw-capped bottle. No appreciable amounts of acid were produced during periods up to a week, nor did the radiation sensitivity change. At least 12 hr. elapsed between washing and irradiating.

The water used throughout was tap water distilled once in an all-Pyrex apparatus from an alkaline permanganate solution. Water redistilled from alkaline manganous hydroxide suspension was used once, but no difference in the results was observed. B.D.H. bromcresol purple was used as an indicator.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

EXPERIMENTAL METHODS

For irradiations with Co^{60} gamma-rays, 3-ml. portions of chloroform were pipetted into glass-stoppered 13 × 100 mm. Pyrex tubes, 2 ml. of distilled water were added, and the samples irradiated. The tubes were not shaken before or immediately after irradiating. After irradiation, the contents of a tube were poured into a 10-ml. Erlenmeyer flask and a glass-enclosed stirring magnet was added. The tube was rinsed twice with 1-ml. portions of distilled water, the rinse waters being added to the flask. Ten drops of bromcresol purple solution (1.5 gm. per liter, pH about 3.5) were added, and the mixture titrated with *ca.* 10^{-2} N sodium hydroxide solution from a microburette until the color of the indicator (just off yellow) matched that of a blank, the latter having received identical treatment except for irradiation. If the pH of the indicator solution had been any higher, the blank color would have been too far off yellow, i.e., the apparent pH would have been greater than about 5.2. It was not feasible to titrate to a purple color (pH about 7.0) since in almost every case the purple color could not be obtained by treating irradiated samples with indicator, base, etc. The nonirradiated chloroform samples could always be taken to the purple color region. It appeared that the greater the dosage received, the more difficult it was to titrate to a purple end point. However, by having the blank at about pH 5.2, it was relatively easy to obtain a color match.

For irradiation with betatron X rays, 2-ml. portions of chloroform overlaid with 2 ml. distilled water were used.

The irradiations were done at 25 ± 2°C. unless otherwise stated.

To determine the average lifetime of the chains leading to acid production, a rotating sector was used. This consisted of a steel cylinder, 12 in. long and $6\frac{1}{4}$ in. in diameter, mounted on roller bearings and rotated, via a variable-speed motor and pulley system, at speeds from about 1–4800 r.p.m. Two sectors, 3.5 cm. deep, were cut out of the cylinder, each subtending an angle

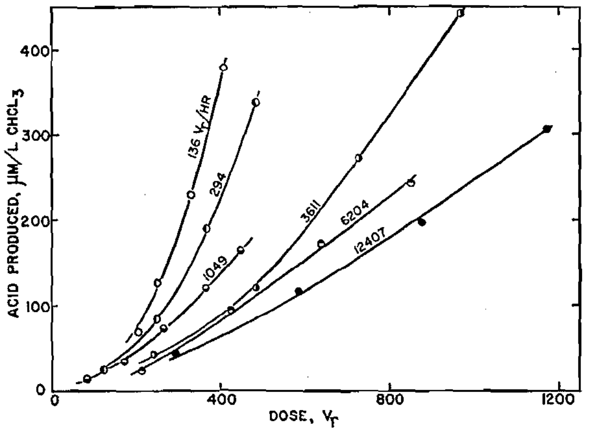


FIG. 1. Irradiation of AnalaR $CHCl_3$ with Co^{60} and betatron radiations. Amounts of acid produced (Y) as a function of Victoreen r.-meter readings, V_r at various dose rates, V_r per hour.

of 60° at the center (see Fig. 7). Rotation rates were determined visually at low speeds and with a tachometer or Strobotac at high speeds. The calculated ratio of the dose rates in the "dark" and "light" periods was 0.0027. The measured ratio was about 0.014. The difference is due presumably to scattered radiation from the walls of the room containing the 1000-c. source.

RESULTS

The results of irradiations of B.D.H. AnalaR chloroform are given in Table I and plotted in Fig. 1. All results are in terms of readings obtained on a Victoreen r.-meter, corrected for temperature and pressure effects. These readings were obtained with the sensitive volume of the thimble chamber inside a glass tube placed, in turn, in a hole in a Lucite block. The details of the experimental arrangements have been given elsewhere (3).

TABLE I

IRRADIATION OF CHLOROFORM–WATER SYSTEMS WITH Co^{60} AND BETATRON RADIATIONS (B.D.H. ANALAR CHLOROFORM)

Source	Photon energy (Mev.)	Dose rate (V_r/hr.)	Dose (V_r)	Yield (μM. acid per liter $CHCl_3$)
1000 c. Co^{60}	1.25	136	205	69.3
			250	126.4
			330	229.8
			409	378.4
1.2 c. Co^{60}	1.25	294	123	25.7
			249	84.2
			366	189.6
			485	338.0
1.2 c. Co^{60}	1.25	1049	83	16.2
			172	35.3
			266	73.6
			366	121.3
			449	164.3
Betatron	24 Mev. peak	3611	242	43.0
			484	119.7
			726	272.0
			968	441.7
Betatron	18 Mev. peak	6204	213	24.2
			426	94.6
			639	172.0
			852	241.7
Betatron	24 Mev. peak	12407	292	44.9
			584	116.9
			876	197.3
			1068	305.4

The square root of the yield (Y) in μM/l. is plotted versus the dose (D) in Victoreen roentgens in Fig. 2. The equations of the lines, calculated by the method of least squares, are given in Table II.

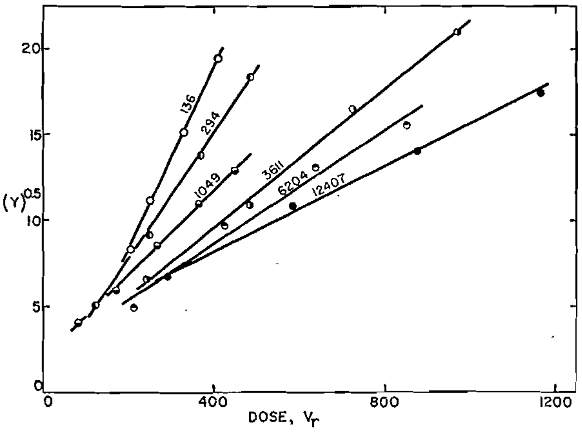


FIG. 2. Irradiation of AnalaR $CHCl_3$ with Co^{60} and betatron radiations. Replot of the data to show the linear relationship between $Y^{\frac{1}{2}}$ and the dose (D) in Victoreen r.-meter readings.

TABLE II

IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH Co^{60} AND BETATRON RADIATIONS—NONLINEAR RELATIONSHIP BETWEEN YIELD AND DOSE (B.D.H. ANALAR CHLOROFORM)

Dose rate (V_r/hr.)	Least squares line
136	$\sqrt{Y} = 0.0534D - 2.35$
294	$= 0.0368D + 0.37$
1049	$= 0.0246D + 1.92$
3611	$= 0.0202D + 1.54$
6204	$= 0.0165D + 2.04$
12407	$= 0.0122D + 3.35$

The results of irradiations of Mallinckrodt A.R. chloroform with Co^{60} and betatron radiations are given in Table III. The individual results used to obtain the least squares lines given in Table III are plotted, together with those

TABLE III

IRRADIATION OF CHLOROFORM-WATER SYSTEMS WITH Co^{60} AND BETATRON RADIATIONS—LINEAR RELATIONSHIP BETWEEN YIELD AND DOSE (MALLINCKRODT A.R. CHLOROFORM)

Source	Dose rate*	Least squares line
Co^{60}	176 V_r/hr.	$Y = 2.85\ D - 65.8$
Co^{60}	292	$= 2.17\ D - 52.8$
Co^{60}	1037	$= 1.25\ D - 10.5$
Co^{60}	4056	$= 0.691D - 25.8$
Betatron (23 Mev. peak)	638 ± 7	$= 1.44\ D - 26$
Betatron (23 Mev. peak)	1245 ± 6	$= 1.04\ D$
Betatron (23 Mev. peak)	2735 ± 54	$= 0.732D + 34.5$
Betatron (23 Mev. peak)	3373 ± 23	$= 0.648D + 7.25$
Betatron (21 Mev. peak)	11850 ± 227	$= 0.397D - 24.5$

**The variation in dose rate during a given betatron irradiation was calculated by timing the "clicks" for short periods throughout the irradiation, a special effort being made to keep the click rate constant by manipulation of the betatron controls. The deviations given in Table III are the standard deviations. Since the dose rate varies across the betatron beam, being greatest at the center, the tubes were placed in the center holes of the rotating Lucite block.*

By "click" is meant the sound heard when a monitor fixed in the X-ray beam is discharged. This occurs when the monitor has received a definite amount of radiation.

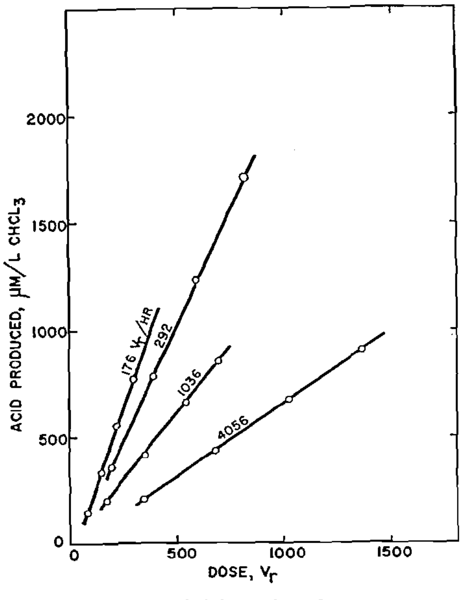
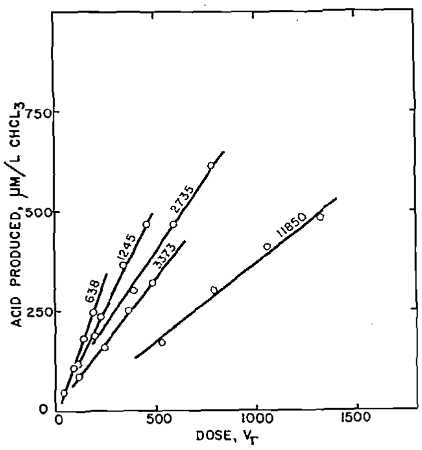


FIG. 3. Irradiation of Mallinckrodt $CHCl_3$ with Co^{60} gamma-rays. Linear relationship between Y and D for various dose rates.

lines, in Fig. 3 (Co^{60}) and Fig. 4 (betatron). The slopes in μM./l./1000 V_r, symbol S, are plotted versus the inverse square root of the dose rate in 1000 V_r/hr., symbol R, in Fig. 5. The equations of the resulting straight lines are given in Table IV.



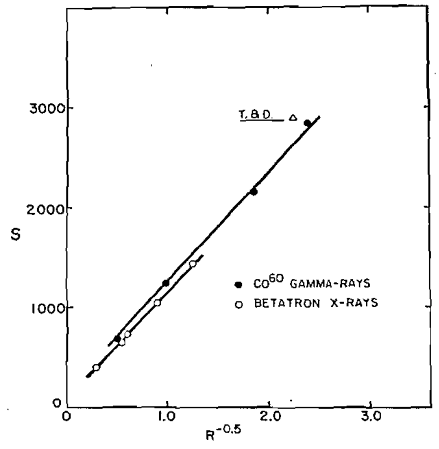


FIG. 4. Irradiation of Mallinckrodt $CHCl_3$ with betatron X rays at various dose rates.

FIG. 5. Irradiation of Mallinckrodt $CHCl_3$ with Co^{60} and betatron radiations. Linear relationships between specific yield (S) and the square root of the reciprocal of the dose rate (R).

The specific yield, S, found by Taplin *et al.* (5) with 200 r./hr. of Ra gamma-rays, is also plotted in Fig. 5.

To determine the average chain lifetime, the rotating sector was operated at rotation rates from 1–2230 r. p. m. Some samples were irradiated for half-

TABLE IV

IRRADIATION OF MALLINCKRODT CHLOROFORM—RELATIONSHIP BETWEEN SPECIFIC YIELD AND DOSE RATE

Source	Least squares line
Co^{60}	$S = 1098 \cdot R^{-\frac{1}{2}} + 172$
Betatron	$S = 1073 \cdot R^{-\frac{1}{2}} + 81.8$

hour periods with the sector stopped; other samples were irradiated with the sector rotating for one and one-half hour periods in order to give each sample the same total exposure to the gamma-ray beam. Actually, Victoreen readings taken under these conditions, agreed within 1.5%. The amounts of base required (A_i) to titrate samples irradiated intermittently were greater than those required (A_s) for samples irradiated with the steady beam. The difference is expressed as a percentage increase in Fig. 6.

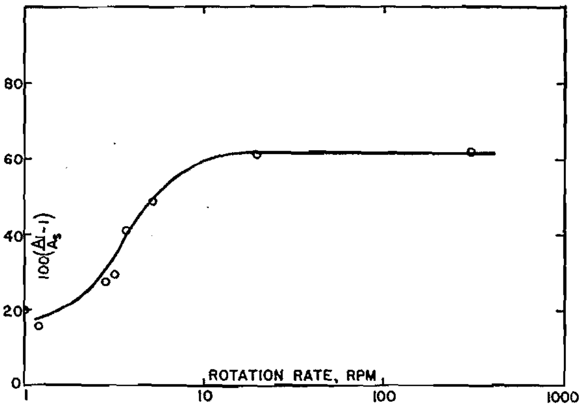


FIG. 6. Effect of intermittent irradiation of Mallinckrodt $CHCl_3$ with Co^{60} gamma-rays.

DISCUSSION

The difference in the results obtained with B.D.H. AnalaR chloroform and Mallinckrodt Analytical Reagent chloroform has been traced to the presence of an unsaturated, water-insoluble compound present in the former. It is removable by shaking the AnalaR chloroform at least five times with portions of slightly basic potassium permanganate solution (*ca.* 0.5 gm. potassium permanganate per liter of solution), followed by one extraction with concentrated hydrochloric acid to remove manganese dioxide, and 10 extractions with distilled water. The results obtained after such treatment were almost exactly the same as were obtained with Mallinckrodt chloroform. Treatment of the latter with potassium permanganate solution did not alter its response to Co^{60} radiations. The foreign substance in the B.D.H. AnalaR chloroform has not been identified.

The mechanism of the radiation-induced reaction has been discussed by Cronheim and Gunther (2). However, their mechanism does not apply to

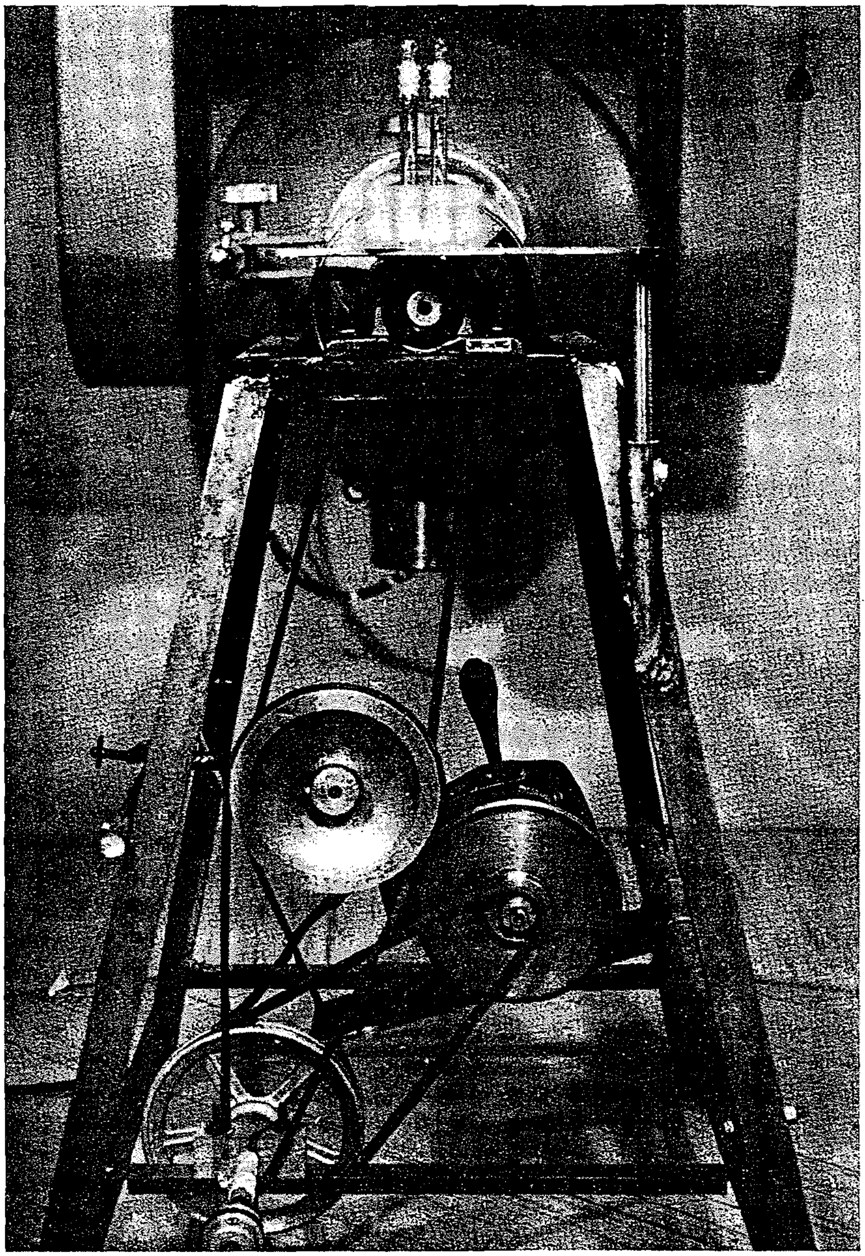


FIG. 7. Rotating sector apparatus and 1000 c. Co^{60} source.

the results reported here, since the over-all acid yield has been found to be inversely proportional to the square root of the radiation intensity, meaning that a recombination process, second order with respect to the radicals important to the chain propagation reaction, must be the principal process by which those radicals disappear (4, p. 197).

The following sequence of reactions leads to a kinetic expression in accord with the observed results. The products, HCl, HOCl, and $COCl_2$ have been identified by others (2).

$$\begin{aligned}
CHCl_3 &\rightsquigarrow CHCl_3^+ + e^- \\
CHCl_3^+ &\longrightarrow CCl_3 + H^+ \\
CHCl_3 + e^- &\longrightarrow CHCl_3^- \\
CHCl_3^- &\longrightarrow CHCl_2 + Cl^-
\end{aligned}$$

$$\begin{array}{lrcll}
(a) & 2\,CHCl_3 & \rightsquigarrow & CCl_3 + CHCl_2 + HCl & \phi I_a \\
(b) & CHCl_2 + O_2 & \longrightarrow & HOCl + COCl & k_1 \\
(c) & COCl + CHCl_3 & \longrightarrow & COCl_2 + CHCl_2 & k_2 \\
(d) & CHCl_2 + CHCl_2 + M & \longrightarrow & CHCl_2{\cdot}CHCl_2 + M & k_3
\end{array}$$

where M is any nonreacting molecule in the system.

A chain reaction involving $CHCl_2$ and O_2 has been given since O_2 is known to promote the production of acid on irradiation, and since the reaction

$$CCl_3 + CHCl_3 \longrightarrow Cl + CCl_3{\cdot}CHCl_2 \quad \Delta H = -2 \text{ kcal./mole}$$

followed by $Cl + CHCl_3 \longrightarrow HCl + CCl_3 \quad \Delta H = +4.6$ kcal./mole

is not so probable on the basis of ΔH values, those for reactions (*b*) and (*c*) being -52 and -2 kcal./mole, respectively. The ΔH values have been taken from Ref. (2).

The phosgene reacts with water to give HCl and CO_2, i.e.,

$$COCl_2 + H_2O \longrightarrow 2HCl + CO_2$$

Letting $A = CHCl_3$, $D_1 = CCl_3$, $D_2 = CHCl_2$, etc., the above equations can be written:

$$\begin{array}{lrcl}
(a) & 2A & \rightsquigarrow & D_1 + D_2 + P_1, \\
(b) & D_2 + B & \longrightarrow & P_2 + D_3, \\
(c) & D_3 + A & \longrightarrow & P_3 + D_2, \\
(d) & D_2 + D_2 + M & \longrightarrow & X + M \\
 & P_3 + C & \longrightarrow & 2P_1 + Y.
\end{array}$$

Assuming steady state conditions, an expression for D_2 can be obtained, i.e.: $dD_2/dt = \phi I_a - k_1D_2B + k_2D_3A - 2k_3D_2^2M = 0$

and $dD_3/dt = k_1D_2B - k_2D_3A = 0$,

so that $\phi I_a = 2k_3D_2^2M$,

and finally, $D_2 = (\phi I_a/2k_3M)^{\frac{1}{2}}$.

The rate of acid production, dP/dt, where $P = P_1 + P_2 + P_3$, is given by $dP/dt = \phi I_a + k_1D_2B + 2K_2D_3A$.

Since $k_2D_3A = k_1D_2B$, then

$$\begin{aligned}
dP/dt &= \phi I_a + 3k_1D_2B \\
&= \phi I_a + 3k_1B \cdot (\phi I_a/2K_3M)^{\frac{1}{2}}.
\end{aligned}$$

By dividing through by I_a the over-all quantum yield is obtained,

$$\Phi = \phi + 3k_1B\cdot(\phi/2k_3I_aM)^{\frac{1}{2}}.$$

The quantity Φ of this expression is proportional to the S of Fig. 5, and I_a is proportional to R. It is seen that the expression obtained for Φ is in accord with the observed results. The intercept on the S axis of Fig. 5 is proportional to the primary quantum yield, ϕ, which here will be the number of chloroform molecules disrupted (by loss or gain of an electron followed by subsequent dissociation to give a free radical) as a result of ionizations produced by interaction of one photon with an electron (primary electron). Since the primary electron may, by collisional processes, produce many secondary electrons, all causing varying amounts of ionization, the primary quantum yield may be very high.

The rotating sector experiments with chloroform are important here mainly in showing that the average lives of the free radical chains are much greater than the time between the pulses of X rays emitted from the betatron. This could also be deduced from Fig. 5 (S vs. $R^{-\frac{1}{2}}$), which shows that the specific acid yields are approximately the same with Co^{60} gamma-rays and betatron X rays. For a radiation-initiated reaction whose measured rate is not directly proportional to the intensity, the effect of pulsed radiation may be important. Dickinson (4; see also Ref. 1) has given a detailed treatment of the theory of the effects of intermittent radiations. If the rate with continuous irradiation is kI_0^n, the rate with intermittent radiations will be either rkI_0^n or $k(rI_0)^n$, depending on whether the intermittency is slow or fast (or the dark periods long or short compared with the average life of the rate-controlling intermediates). The transition between the two cases occurs when the dark periods are of the same order as the average life of the intermediates (4, p. 203). Here r is the ratio of the length of the light period to that of the sum, dark period plus light period, and n is the power of the intensity on which the reaction rate is found experimentally to depend. For betatron radiations emitted in four-microsecond pulses every 1/180th sec., $r = 7.19 \times 10^{-4}$ and $n = 0.5$. Also the average dose rate during a pulse, corresponding to I_0, is $I_m/7.19 \times 10^{-4}$, where I_m is the measured dose rate. Now, if the average life of the intermediates is *less* than 1/180 sec., corresponding to a long dark period, the rate will be given by

$$7.19 \times 10^{-4}\cdot k\cdot(I_m/7.19 \times 10^{-4})^{0.5} = 0.0268\cdot k\cdot I_m^{0.5},$$

while if the average life is *greater* than 1/180 sec. the rate will be given by

$$k(7.19 \times 10^{-4}\cdot I_m/7.19 \times 10^{-4})^{0.5} = k\cdot I_m^{0.5}.$$

Thus, the rate of acid production, using the measured dose rate as a criterion, should be the same with both betatron and Co^{60} radiations *provided* the average life of the rate-controlling intermediates is *greater* than 1/180 sec. The rotating sector experiments with Co^{60} gamma-rays showed that the average chain lifetime, at $I_0 = 1200\,V_r/\mathrm{hr.}$, is about one second. The observed similarity of specific acid yields obtained with intermittent betatron X rays and continuous Co^{60} gamma-rays is therefore consistent with the theory outlined briefly above.

The results obtained with Co^{60} gamma-rays and betatron X rays do not seem to depend on the energies of the radiations. The difference in the positions of the two lines in Fig. 5 probably is not due to the differences in energy, since the percentage difference due to energy dependence, if any, should not increase with increasing dose rate. The difference may be due to breakdown in the dependence of specific yield on (dose rate)$^{-\frac{1}{2}}$ at the very high dose rates such as are obtained during a betatron pulse. The free radical concentrations may then be so high that several chain-termination reactions may become important.

ACKNOWLEDGMENTS

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THE ETHANOLYSIS OF 3-HYDROXY-1-(4-HYDROXY-3-METHOXYPHENYL)-2-PROPANONE IN RELATION TO LIGNIN CHEMISTRY[1]

BY J. A. F. GARDNER

ABSTRACT

The ketol, 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, was subjected to ethanolysis and found to yield the four propylphenols which can be isolated from the ethanolysis products of isolated conifer lignin and of conifer lignin *in situ*. The significance of this finding is briefly discussed.

In the period 1939–1943, a careful investigation of the water soluble phenolic products from the ethanolysis of extractive-free spruce-wood by Hibbert and co-workers (5, 7, 18, 26) resulted in the isolation and identification of four propylphenols, 2-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone (I), 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione (II), 1-ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (III), and 1-(4-hydroxy-3-methoxyphenyl)-2-propanone (IV).

$R\text{–}CO\text{–}CH(OC_2H_5)\text{–}CH_3$ I

$R\text{–}CO\text{–}CO\text{–}CH_3$ II

$R\text{–}CH(OC_2H_5)\text{–}CO\text{–}CH_3$ III

$R\text{–}CH_2\text{–}CO\text{–}CH_3$ IV

R = 4-hydroxy-3-methoxyphenyl

From maple-wood, in addition to these, the syringyl (R = 4-hydroxy-3,5-dimethoxyphenyl) analogues were isolated. The total yield of pure identified products based upon the original Klason lignin of the wood was approximately 5 per cent for spruce-wood and approximately 10 per cent for maple-wood. In spite of the low yields, these findings were of considerable significance in that they provided some direct evidence for the theory that lignin is derived from propylphenol monomers.

In view of the absence of primary alcoholic or terminal ether groups in these products and the evidence for the presence of such groups in lignin provided by analytical results (4) and by the isolation of 3-cyclohexyl-1-propanols from the products of high pressure hydrogenation (3, 12, 15), Hibbert (16) suggested that the propylphenols I–IV were derived from a more reactive β-hydroxyconiferyl alcohol (VI) type of structural element by means of a series of interconversions:

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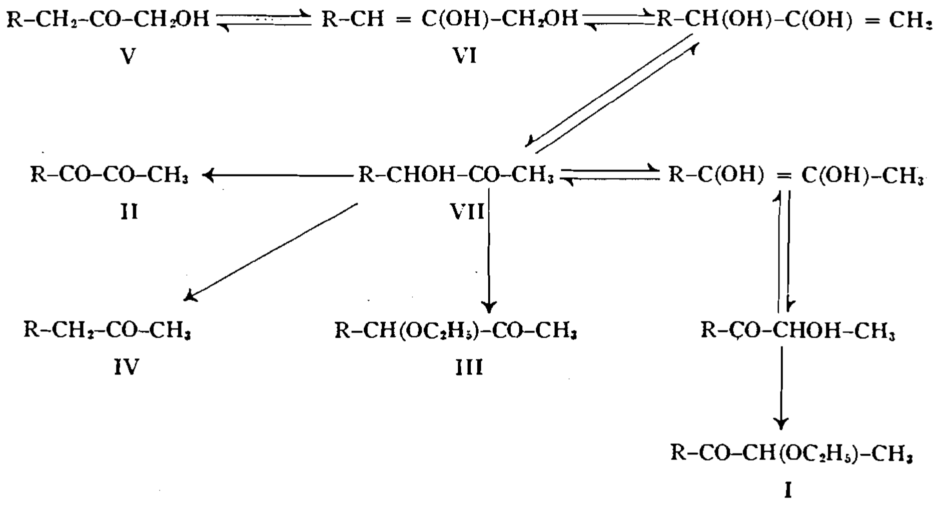
Contribution from Vancouver Laboratory, Forest Products Laboratories of Canada, Forestry Branch, Department of Northern Affairs and National Resources, Canada.
Presented before the Western Regional Conference, Chemical Institute of Canada, Saskatoon, October 24–25, 1952.



This concept was consistent with the absence of C–CH_3 groups in lignin *in situ* as determined by chromic acid oxidation in contrast to their presence in the ethanolysis products and isolated lignins (22). Convincing experimental evidence that such a series of interconversions was capable of yielding the ethanolysis products was provided by extensive studies of the analagous ketols in the veratryl (R = 3,4-dimethoxyphenyl) series (8, 10), and of the diacetate of VII in the guaiacyl series (23). Ethanolysis of the diacetate of VII using the conditions employed on wood yielded the same four propylphenol products, I–IV. A study of the ketol, 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (V), for final proof that it or its enol (VI) could yield the propylphenols (I–IV) by ethanolysis was delayed by difficulties in its synthesis which was finally achieved by Fisher and Hibbert (9).

The ethanolysis of V has now been accomplished. Using the conditions employed on wood, the product was a mixture of the propylphenols, I–IV, and a petroleum ether (30–60°) insoluble polymer in yields of 26, 9, 4.5, 2, and 20% respectively. This result and the isolation of the same propylphenols by ethanolysis of lignin *in situ* and of extracted lignins such as periodate lignin (24), hydrochloric acid lignin (14), and Brauns' "native" lignin (11) provide strong evidence for the presence in the lignin complex of the side chain $-CH_2-CO-CH_2OH$ or its enol form.

The presence in lignin of this side chain as an inner structural element readily freed by hydrolysis would be consistent with other properties of lignin *in situ*. Important examples already noted are the presence in the side chain of primary alcohol and ether groups and the absence of end methyl groups. Rearrangement of the side chain under the influence of a variety of reagents as demonstrated previously (8, 10) and in this work would account for the presence of end methyl groups in isolated lignins. This tendency to rearrange might also account to some extent for the apparent inconsistencies in the literature of lignin concerning the content of other constituent groups such as secondary and tertiary hydroxyls (4).

The theory that the sulphonatable groups of lignin are benzyl alcohols or ethers was originally proposed by Holmberg (17) on the basis of experiments with model compounds. The strong support for this theory provided by the investigations of many others on the sulphonation reactions of lignin and model compounds has been reviewed recently by Lindgren (21). The possibility exists that hydroxyconiferyl alcohol might undergo similar sulphonation reactions by virtue of rearrangement to the benzyl alcohol derivative, VII, as in ethanolysis. This possibility will be explored.

Shorygina and co-workers (25) have provided some additional evidence that hydroxyconiferyl alcohol occurs as a structural element in lignin. By treating cuprammonium lignin with sodium in liquid ammonia, these workers obtained 1-(4-hydroxy-3-methoxyphenyl)-2-propanol in a yield of 12%. They interpreted this result as indicating that the basic structural element in lignin is β-hydroxyhydroconiferyl alcohol or β-hydroxyconiferyl alcohol (VI), the latter being more likely.

No indisputable evidence for the presence of carbonyl groups in lignin *in situ* is available although their presence has been suggested by a number of workers and small amounts have been detected in some isolated lignins (13). If hydroxyconiferyl alcohol groups or structural elements capable of giving rise to such groups are present to any great extent in lignin it is evident that the carbonyl function is hindered or masked in some way by the mode of linkage between elements. Since the experimental portion of this paper was completed, Adler and Yllner (1) have reported on the reactions of veratrylglycerol in relation to lignin chemistry. The results of their experiments on ethanolysis make it evident that a propylphenol containing no ketonic group such as guaiacylglycerol (VIII) is also capable of giving rise to the lignin ethanolysis products via β-hydroxyconiferyl alcohol, VI. They suggested that this alcohol might be formed either by a primary dehydration or by loss of ethanol from an ethyl ether:

$$\begin{tikzcd}
\underset{\text{VIII}}{\text{R-CHOH-CHOH-CH}_2\text{OH}} \arrow[r, "-\text{H}_2\text{O}"] & \underset{\text{VI}}{\text{R-CH} = \text{CH(OH)-CH}_2\text{OH}} \\
\text{R-CH(OC}_2\text{H}_5\text{)-CHOH-CH}_2\text{OH} \arrow[ur, "\text{C}_2\text{H}_5\text{OH}"] &
\end{tikzcd}$$

It may be significant that, as shown in Table I, the yields of monomeric oils from ethanolysis of isolated lignins and lignin *in situ* are roughly one fifth of those obtained from ethanolysis of the ketol, V. If the ethanolysis oils from lignin were assumed to be derived only from one of the phenylpropane building elements, these yields could be taken as an indication that there are approximately five phenylpropane building elements in the average lignin building unit. Considerable evidence favoring an average unit molecular weight in this range is available in the lignin literature (4).

TABLE I
TOTAL YIELDS OF MONOMERIC ETHANOLYSIS PRODUCTS FROM VARIOUS LIGNINS AND THE KETOL, V

Starting material	Yield, %	Reference
Spruce sapwood (extractive-free)	10*	26
Spruce periodate lignin	11.5	24
Spruce hydrochloric acid lignin	11	14
Spruce "native" lignin (Brauns)	10	11
3-Hydroxy-1-(4-hydroxy-3 methoxyphenyl)-2-propanone (V)	50	..

**Based on Klason lignin.*

EXPERIMENTAL

The pure ketol, V, was a colorless crystalline solid, melting point 85–86°*, semicarbazone melting point 147–148° (Fisher and Hibbert reported 81–82° and 147–148° respectively). It was slightly unstable at room temperature and gradually acquired a faint vanillin-like odor and a melting point in the 80–83° range which probably accounts for the low melting point previously reported. Paper chromatographic experiments on a preparation kept a year in the laboratory indicated that vanillin was the contaminant. Only minor changes were made in the method of synthesis from vanillin reported by Fisher and Hibbert (9). Much time was saved by acetylating homovanillic acid by the Chattaway method (6), instead of by boiling for six hours with acetic anhydride, and high yields (90%) of pure product were obtained.

Acetylation of Homovanillic Acid

Homovanillic acid (12.95 gm.) in aqueous sodium hydroxide solution (7.62 gm. in 13 cc.) was treated with crushed ice (40 gm.) and then acetic anhydride (9.5 cc.). The mixture was agitated vigorously for two minutes before acidification with 6 *N* hydrochloric acid (34 cc.) which precipitated the acetate as white fluffy crystals. The product was filtered, washed with water, and dried. Yield 14.5 gm. (92%), melting point 138–139°C.

Ethanolysis of 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, V

Two ethanolyses were run using the same technique as described by Mitchell and Hibbert (23). In the first trial experiment on a small sample (2.045 gm.), after paper chromatography had indicated the presence of the products, I–IV, in the petroleum ether (30–60°) soluble oil (1.02 gm.), it was possible to isolate and identify the two main products, I and II. For the isolation of the small quantities of III and IV produced, the petroleum ether soluble oil (3.9 gm.) obtained from a second ethanolysis of a larger quantity of V (8 gm.) was used.

Paper Chromatography

Samples of the various fractions and isolates were resolved on Whatman No. I filter paper concurrently with synthetic reference samples and mixtures. Solvent systems such as petroleum ether (65°–110°) – water (2:1), diethyl

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**Melting points were determined on Fisher–Johns melting point apparatus and are uncorrected.*

ether – conc. ammonium hydroxide – water (4:1:1), and butanol – conc. ammonium hydroxide (4:1) were found to be useful. With the butanol – ammonium hydroxide solvent it was possible to resolve mixtures of all four propylphenols and vanillin, the approximate R_f values at 25° being: I, .66; II, .51; III, .79; IV, .87; and vanillin, .44. For detection the ferric chloride – potassium ferricyanide reagent of Barton (2) was used.

Isolation of 2-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone, I

After extraction of the bisulphite-soluble fraction with sodium bisulphite the so-called "phenol" fraction (26) was treated with anhydrous ammonia in ether to precipitate the crystalline ammonium salt of I (0.57 gm.). Yield on the ketol was 26%. Methylation of the ammonium salt with dimethyl sulphate gave the crystalline methyl ether. Melting point and mixed melting point with synthetic 2-ethoxy-1-(3,4-dimethoxyphenyl)-1-propanone and an authentic sample isolated from the ethanolysis of western hemlock-wood were identical.

Isolation of 1-(4-Hydroxy-3-methoxyphenyl)-1,2-propanedione, II

The oil (0.325 gm.) recovered from the bisulphite-soluble portion was treated in aqueous solution with hydroxylamine and nickel salts as described previously (18) to give the red nickel glyoxime salt of the diketone. Yield – 0.222 gm. (equivalent to a 9% yield of diketone). Hydrolysis gave II, melting point 69–70°, which gave a quinoxaline, melting point 160–161°. Both II and its quinoxaline showed no mixed melting point depression with authentic samples.

Isolation of 1-(4-Hydroxy-3-methoxyphenyl)-2-propanone, IV

The second ethanolysis experiment (on 8.0 gm. of VI) gave a petroleum ether soluble oil (3.9 gm.) which was separated into a bisulphite-soluble fraction, A, and a "phenol" fraction, B, as before.

Removal of the diketone, II, from A and hydrolysis (20) of the residual oxime gave an oil (0.238 gm.) which paper chromatograms indicated to be IV. Distillation (150–160° at 2 mm.) gave a light yellow oil, n_D^{25} 1.548, 0.16 gm. (2%), from which the semicarbazone, melting point 154–155°, and the thiosemicarbazone, melting point 188–189°, were prepared. A synthetic sample (20), n_D^{25} 1.547, gave the same yield of the same derivatives. There were no mixed melting point depressions.

Isolation of 1-Ethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone, III

The "phenol" fraction B (2.59 gm.) gave paper chromatograms indicating the presence of I and III. After removal of I as the ammonium salt, the residual oil (0.515 gm.), which with several solvent systems gave paper chromatograms indicating it to be III, was distilled (160–180°, 0.5 mm.). Yield, 0.363 gm. of a partially crystalline oil. The semicarbazone (0.08 gm. from 0.17 gm.), melting point 170–171°, gave no mixed melting point depression with the semicarbazone (prepared in similar yield) of a synthetic sample (19), melting point 170–171°.

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THE SYNTHESIS OF 4-DIALKYLAMINOETHYLPYRIDINES[1]

By Anthony J. Matuszko[2] and Alfred Taurins

ABSTRACT

For the synthesis of 4-dialkylaminoethylpyridines two reactions were employed, namely, the Mannich condensation of 4-methylpyridine with formaldehyde and secondary amines, and the addition of secondary amines across the double bond of the 4-vinylpyridine. In the first reaction with diethyl-, di-isopropyl-, di-*n*-butylamine, pyrrolidine, and morpholine, normal Mannich bases (IV-VIII) were obtained. The unsaturated bases (X, XI) were the reaction products when dimethylamine and piperidine were used. The addition of those products 1,3-bis-(dialkylamino)-2-(4′-pyridyl)-propanes (XII, XIII) were formed when dimethyl- and diethylamine were applied.

The structures of the normal Mannich bases were confirmed by the synthesis of several compounds (III, IV, VII–IX) from 4-vinylpyridine and secondary amines.

INTRODUCTION

The Mannich condensation of methylpyridines and -quinolines has been studied only with the substances containing methyl group in the 2-position. Héou-Féo (7) investigated the reaction of 2-methylpyridine with formaldehyde and diethylamine and with formaldehyde and piperidine. The condensation of 2-methylquinaldine has been reported by Kermack and Muir (8), Ger. Pat. 497, 907 (5), Héou-Féo (6), and Boekelheide and Marinetti (1). The Mannich procedure has been recently applied by Sommers, Freifelder, Wright, and Weston (11) to prepare some derivatives of 2-methylpyridine and -quinoline.

The objective of this work was to investigate the reactivity of the methyl group in the 4-position of the pyridine ring in the Mannich condensation and to synthesize certain 4-dialkylaminoethylpyridines. Since similar compounds could be obtained by the addition of secondary amines across the double bond of the 4-vinylpyridine we applied this reaction to confirm the structures of the products obtained in the Mannich reaction.

The addition of nucleophilic reagents with active hydrogen, like secondary amines, to 2- and 4-vinylpyridines was postulated by Doering and Weil (2). They condensed only 2-vinylpyridine with diethylamine, and piperidine, respectively. Similar condensations of 2-vinylpyridine have been carried out using morpholine and 1-methylpiperazine as secondary bases (11). The addition of ketones to 2-vinylpyridine has also been studied by Levine and Wilt (9), and Wilt and Levine (12).

DISCUSSION

The principal product from the condensation of dimethylamine hydrochloride with formaldehyde and 4-methylpyridine (I) was not the normal Mannich base, 4-(β-dimethylaminoethyl)-pyridine (III), but the unsaturated

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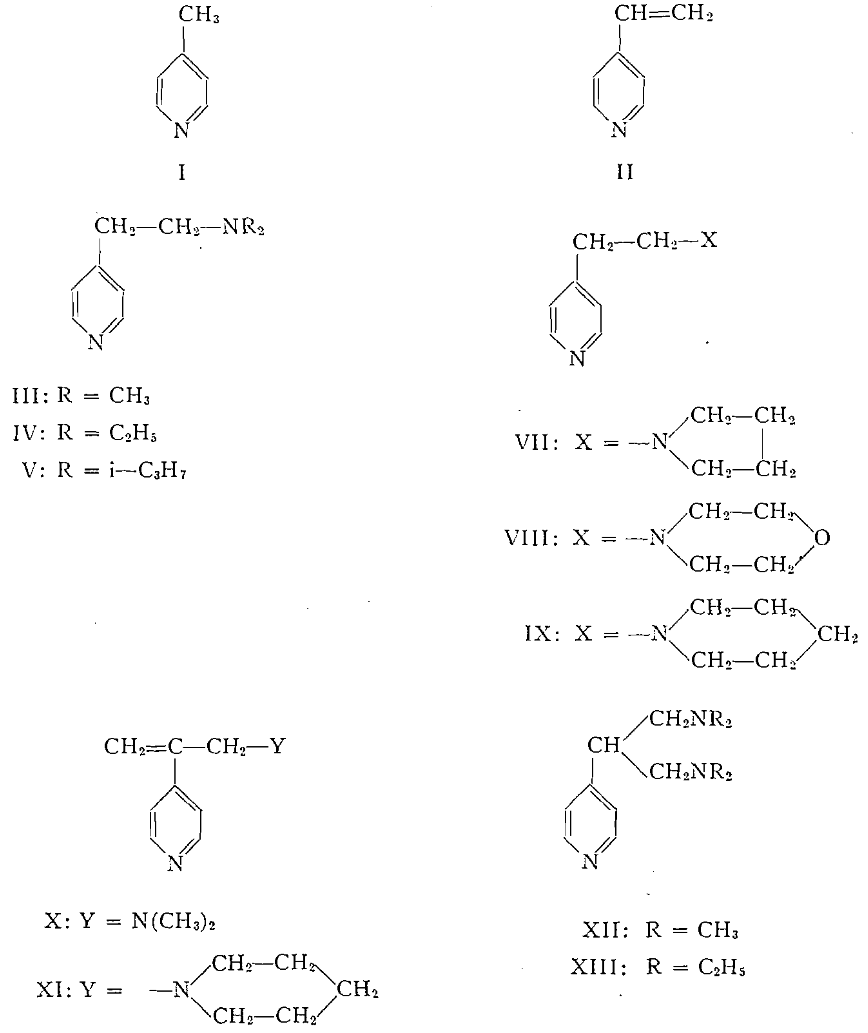
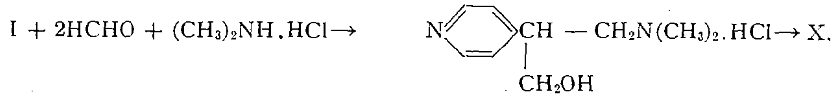


Formulae Scheme

base, 4-(α-methylene-β-dimethylaminoethyl)-pyridine (X). This was substantiated by analyses of X and its chemical behavior. The sample of X was obtained by distillation as a colorless oil which showed a high degree of unsaturation and turned reddish-brown on standing even in a closed container. The terminal methylene group $>C = CH_2$ of the X was determined by ozonolysis according to the method given by Doeuvre (3, 4) and modified by Naves (10). This method is by no means quantitative, therefore it was possible to detect the cleavage of the methylene group to produce formaldehyde to the extent of 34%. The sample of III was prepared by the addition of dimethylamine to the ethylene double bond of the 4-vinylpyridine (II), and it did not show any formation of formaldehyde in the reaction of ozonolysis.

The formation of the methylene base X presumably goes through the methylol compound which loses a molecule of water either by the interaction of a base, or during the vacuum distillation:



The highest yield (45%) of X was obtained when the reaction mixture contained two moles of formaldehyde for one mole of I and dimethylamine. The variation of the reaction time (6–24 hr.) and temperature (50–100°) did not give any indication of formation of III in this reaction. However, the prolonged reaction time of 24 hr. at 60° gave in addition to X a higher boiling compound, 1,3-bis(dimethylamino)-2-(4′-pyridyl)-propane (XII).

The unsaturated methylene base, 4-(α-methylene-β-piperidylethyl)-pyridine (XI) was obtained as the only reaction product in the Mannich condensation of piperidine, formaldehyde, and I. Since piperidine reacted with 4-vinylpyridine to give 4-(β-N-piperidylethyl)-pyridine (IX) it was possible to compare both of the derivatives of piperidine formed in two different reactions. The presence of the methylene group $>C = CH_2$ in XI was detected by the Doeuvre reaction (3, 4) which produced 28% formaldehyde.

In the Mannich condensation I reacted normally with formaldehyde and diethyl-, di-isopropyl-, and di-*n*-butylamine, respectively, to give the corresponding 4-dialkylaminoethylpyridines IV, V, and VI, in low yields. Pyrrolidine and morpholine reacted with I and formaldehyde in a similar manner to yield the bases VII and VIII.

The condensation of 4-vinylpyridine and dimethylamine was carried out by heating a water solution containing both components in molar ratio 1:2 for 24 hr. at 90°. Although the 4-vinylpyridine was not completely soluble in water, enough of it was dissolved at 90° to react with dimethylamine. The yield of 4-(β-dimethylaminoethyl)-pyridine (III) was 40% of the theoretical. A similar procedure was applied in the interaction of 4-vinylpyridine with diethylamine. When the reaction was carried out at reflux temperature for 48 hr., the yield of IV was increased to 70%.

Doering and Weil reported that the reaction of 2-vinylpyridine and diethylamine in the absence of any solvent in a sealed tube gave a poor yield of the 2-(β-diethylaminoethyl)-pyridine. The good yield of IV which we obtained in water solution indicated that a water solvent was favorable for the reaction.

Successful condensation of 4-vinylpyridine was carried out with pyrrolidine, morpholine, and piperidine to obtain the products VII, VIII, and IX. The reaction occurred when the corresponding components were mixed and refluxed for six hours in the absence of water.

Although it was not in the realm of this investigation to study the physiological activity of the compounds prepared, an observation was made which proved to be of interest. Twenty-four hours after performing a series of distillations of the Mannich bases, reddening of certain areas of the face and hands of the worker was observed. This reddening was similar to a caustic burn and it was followed by blistering which continued for five to six days. Once the blistering had subsided and the exposed areas had healed, scars remained which were noticeable even six months later. The reddening and blistering appeared to be similar to that of the shingles, a virus infection. It was not discovered which particular compound caused this behavior, since a number of distillations were carried out at this time.

EXPERIMENTAL*

In the experimental part the Mannich condensation is denoted as the Procedure A and the reaction of 4-vinylpyridine with amines as the Procedure B.

4-(α-Methylene-β-dimethylaminoethyl)-pyridine (X)

A mixture of 4.7 gm. (0.05 *M*) of 4-methylpyridine (I) and 8.2 gm. (0.01 *M*) of dimethylamine hydrochloride was heated to 95–100° while 8.5 gm. of 30% formaldehyde was added with stirring over a period of one hour. The reaction was continued for five additional hours. The reaction mixture was cooled, made alkaline with potassium carbonate, and extracted with ether. The ether solution was dried over anhydrous sodium sulphate and the ether evaporated at reduced pressure. Distillation of the residue yielded 3.5 gm. (43% of the theoretical) of a colorless liquid, boiling point 65–66° at 0.5 mm.; n_D^{24} 1.5170. Anal. calc. for $C_{10}H_{14}N_2$: C, 74.01; H, 8.71%. Found: C, 73.83; H, 8.44%.

The *dipicrate of X* was prepared in ethanol solution and after recrystallization from the same solvent was obtained in the form of orange-yellow needles, melting point 147–148°. Anal. calc. for $C_{22}H_{20}N_8O_{14}$: C, 42.70; H, 3.26; N, 18.13%. Found: C, 43.01; H, 3.28; N, 18.45%.

The *monopicrate of X* was obtained using a smaller ratio of picric acid and was obtained from water as yellow crystals, melting point 124–125°. Anal. calc. for $C_{16}H_{17}O_7N_3$: N, 17.65%. Found: N, 17.82%.

Determination of the Terminal Methylene Group $\rangle C = CH_2$ (*3, 4*)

A solution containing 250 mgm. of the X in 5 ml. of a mixture (3:2) of ethylacetate and glacial acetic acid was cooled to − 15° and treated with ozone for three minutes. One-half milliliter of the ozonized solution was added to a mixture of 30 ml. Grosse-Bohle reagent, 15 ml. hydrochloric acid, and 45 ml. water. After the mixture was shaken and made up to 100 ml., the volumetric flask was stoppered and the mixture allowed to stand for six hours at room temperature. Meanwhile 2 ml., 1 ml., and 0.5 ml. samples of a 0.120% solution of formaldehyde was treated with the Grosse-Bohle reagent and water and diluted to 100 ml. as above. Comparative visual colorimetric tests indicated that in the ozonolysis of X the terminal methylene group had been transformed to formaldehyde to the extent of 34%.

**Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.*

1,3-Bis(dimethylamino)-2-(4′-pyridyl)-propane (XII)

A mixture of 40.5 gm. (0.5 *M*) of I, 40.7 gm. (0.5 *M*) of dimethylamine hydrochloride, 45 gm. of 35% formaldehyde, and 30 ml. of water was stirred at 58° for 24 hr. The further steps in the procedure were similar to those described previously. The residue yielded 20 gm. of X and 5.5 gm. of XII in the form of a colorless oil, boiling point 84–88° at 0.5 mm.; n_D^{24} 1.4998. The yield was 10.8% of the theoretical on the basis of the amount of the amine salt used. Anal. calc. for $C_{12}H_{21}N_3$: C, 69.50; H, 10.22%. Found: C, 69.30; H, 9.92%.

The *tripicrate of XII* was prepared in ethanol and recrystallized from acetone in the form of yellow plates; m.p. 171–172°. Anal. calc. for $C_{30}H_{30}N_{12}O_{21}$: C, 40.24; H, 3.38; N, 18.79%. Found: C, 40.01; H, 3.42; N, 18.93%.

4-(β-Dimethylaminoethyl)-pyridine (III)

A mixture containing 36 gm. of 25% aqueous solution of dimethylamine and 10.5 gm. of 4-vinylpyridine (II) was stirred at 90° for 24 hr. II was not completely miscible with water. The reaction product was extracted with ether, the ether extract dried over anhydrous sodium sulphate, evaporated and distilled at reduced pressure. The yield of III was 6 gm. (40%); boiling point 63–64° at 0.5 mm.; n_D^{24} 1.5023. Anal. calc. for $C_9H_{14}N_2$: C, 71.94; H, 9.40%. Found: C, 72.15; H, 9.60%.

The *dipicrate of III* was prepared in ethanol and recrystallized from acetone; m.p. 159–160°.

4-(β-Diethylaminoethyl)-pyridine (IV)

Procedure A.—Glacial acetic acid (22 gm.) was added dropwise to a mixture of 9.3 gm. (0.1 *M*) of I, 7.3 gm. (0.1 *M*) of diethylamine, and 8.5 gm. of 35% formaldehyde. The reaction mixture was stirred at 60° for 10 hr., made alkaline with 20% potassium carbonate solution, and extracted with several portions of chloroform. The IV was obtained as a colorless liquid, boiling point 80–81° at 0.5 mm.; n_D^{24} 1.4913. The yield of IV was 2.3 gm. (14%). Anal. calc. for $C_{11}H_{18}N_2$: C, 74.09; H, 10.18%. Found: C, 74.27; H, 10.05%.

The *dipicrate of IV* was crystallized from water as yellow crystals, melting point 146–147°. Anal. calc. for $C_{23}H_{24}N_8O_{14}$: C, 43.37; H, 3.80; N, 17.61%. Found: C, 43.25; H, 3.85; N, 17.69%.

The *monopicrate of IV* was recrystallized from water and obtained in the form of yellow crystals, melting point 109–110°. Anal. calc. for $C_{17}H_{21}N_5O_7$: N, 17.11%. Found: N, 17.02%.

Procedure B.—A solution of 14.6 gm. (0.2 *M*) of diethylamine in 30 ml. water was heated to reflux together with 10.5 gm. (0.1 *M*) of 4-vinylpyridine for 48 hr. The ether extract gave 12.5 gm. (70%) of IV, b.p. 80° at 0.5 mm. The dipicrate of IV melted at 146–147° and the mixed melting point of it was not depressed by the dipicrate of IV obtained in the Procedure A.

1,3-Bis(diethylamino)-2-(4′-pyridyl)-propane (XIII)

A mixture consisting of 54.8 gm. (0.5 *M*) diethylamine hydrochloride, 46.5 gm. (0.5 *M*) I, 45 gm. 35% formaldehyde, and 30 ml. water was stirred at 60° for 24 hr. The chloroform extract yielded 10.5 gm. of IV, and 5 gm. of XIII (8.6%), an oil boiling at 98–100° at 0.5 mm.; n_D^{24} 1.5089. Anal. calc. for $C_{16}H_{29}N_3$: C, 72.93; H, 11.10%. Found: C, 72.70; H, 10.78%.

The *tripicrate of XIII* was prepared in ethyl alcohol and, after recrystallization from acetone, melted at 138–139°. Anal. calc. for $C_{34}H_{38}N_{12}O_{21}$: N, 17.68%. Found: N, 17.72%.

4-(*β-Diisopropylaminoethyl*)*-pyridine* (V)

Formaldehyde (16 gm. of 35% solution) was added dropwise with stirring over a period of two hours to a mixture of 13.7 gm. of diisopropylamine hydrochloride and 18.6 gm. 4-methylpyridine. The temperature was kept at 95° and the reaction continued for an additional four hours. V was obtained as a colorless oil, boiling at 116° at 0.5 mm. The yield was 3 gm. (14%). Anal. calc. for $C_{13}H_{22}N_2$: C, 75.68; H, 10.75; N, 13.57%. Found: C, 75.40; H, 10.55; N, 13.60%.

4-(*β-Di-n-butylaminoethyl*)*-pyridine* (VI)

A mixture of 16.3 gm. (0.1 *M*) of dibutylamine hydrochloride and 9.3 gm. (0.1 *M*) of 4-methylpyridine was heated to 92° and stirred while 8.5 gm. of 35% formaldehyde was added dropwise. The reaction was continued for 12 hr. VI was obtained as a colorless liquid, b.p. 111–113° at 0.5 mm. The yield was 2.3 gm. (10%). Anal. calc. for $C_{15}H_{26}N_2$: C, 76.86%; H, 11.18%. Found: C, 76.58%; H, 10.92%.

4-(*β-N-Pyrrolidylethyl*)*-pyridine* (VII)

Procedure A.—A mixture consisting of 10.65 gm. (0.1 *M*) of pyrrolidine hydrochloride, 20 ml. water, 9.3 gm. (0.1 *M*) I was stirred at 80–85° while 9 gm. of 35% formaldehyde was added over a period of two hours and the reaction was continued for four hours. The ether extract gave 4 gm. (22%) of VII, an oil boiling at 93° at 0.5 mm. pressure. Anal. calc. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.90%. Found: C, 74.87; H, 8.95; N, 16.16%.

The *dipicrate of VII* was prepared in ethanol and after recrystallization from acetone, melted at 166°.

Procedure B.—Equimolar amounts (0.1 *M*) of pyrrolidine and 4-vinylpyridine was heated at 80–85° for six hours. The yield of VII was 14.5 gm. (83%). The substance had the boiling point 92–93° at 0.5 mm. Carbon, hydrogen, and nitrogen analyses gave results which were similar to those obtained in the analysis of the previous sample of VI. The dipicrate of VII (recrystallized from acetone) had the melting point 165–166°.

4-(*β-N-Morpholinylethyl*)*-pyridine* (VIII)

Procedure A.—To a solution of 18.6 gm. (0.2 *M*) of I in 10 ml. of water was added 10.6 gm. (0.1 *M*) of morpholine hydrochloride in 10 ml. of water and 8.5 gm. of 35% formaldehyde. The addition was carried out over a period of two hours and the reaction was continued for four hours at 85–90°. VIII was obtained in the form of a colorless liquid, boiling point 117–119° at 0.5 mm. The yield was 3.5 gm. Anal. calc. for $C_{11}H_{16}N_2O$: C, 68.73; H, 8.39; N, 14.57%. Found: C, 68.55; H, 8.50; N, 14.38%.

Procedure B.—An equimolar (0.1 *M*) mixture of morpholine and 4-vinylpyridine was stirred at 105° for six hours. Distillation of the reaction mixture yielded 12.5 gm. (65%) of a colorless liquid, boiling point 116° at 0.5 mm. On cooling the oil solidified, giving crystals melting at 48–49°. Anal. calc. for $C_{11}H_{16}N_2O$: C, 68.73; H, 8.39%. Found: C, 69.02; H, 8.14%.

4-(β-N-Piperidylethyl)-pyridine (IX)

A mixture of 17 gm. (0.2 *M*) piperidine and 10.5 gm. (0.1 *M*) 4-vinylpyridine was heated to reflux (105°) for six hours and then fractionated in vacuum; 10.5 gm. (55%) of IX was obtained as a colorless liquid, b. p. 101° at 0.5 mm.; n_D^{24} 1.5236. Anal. calc. for $C_{12}H_{18}N_2$: C, 75.73; H, 9.54%. Found: C, 75.72; H, 9.37%.

4-(α-Methylene-β-piperidylethyl)-pyridine (XI)

A mixture containing 4.7 gm. (0.05 *M*) of I, 12 gm. (0.1 *M*) of piperidine hydrochloride, and 8.5 gm. of 35% formaldehyde was heated under reflux for six hours. The ether extract gave 3.5 gm. (43%) of XI, which was a colorless oil, boiling at 105–106° at 0.5 mm. pressure; n_D^{24} 1.5298. Anal. calc. for $C_{13}H_{18}N_2$: C, 77.17; H, 8.96%. Found: C, 76.97; H, 9.13%.

The ozonolysis of the XI in order to determine the terminal methylene groups indicated the formation of formaldehyde to the extent of 28%.

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SYNTHESIS OF 1,2-DIALKYLHYDRAZINES AND THE CORRESPONDING AZOALKANES[1,2]

BY R. RENAUD AND L. C. LEITCH

ABSTRACT

The limitations of present methods of synthesizing 1,2-dialkylhydrazines are discussed. A new method of obtaining these compounds in good yields by the reduction of azines with lithium aluminum hydride is reported. Lithium aluminum deuteride was employed as a tracer to investigate the mechanism of the reaction. The 1,2-dialkylhydrazines were oxidized to the azoparaffins in over 90% yields by mercuric oxide in water.

INTRODUCTION

An important source of free radicals for kinetic investigations is the thermal or photochemical decomposition of azoalkanes (11). Up to now the availability of these compounds has been limited on account of the difficulty of obtaining the 1,2-dialkylhydrazines. For example, of the lower azoalkanes only the methyl and isopropyl compounds have long been known, azoethane having been prepared quite recently (15). This work was undertaken to develop a general method of preparing 1,2-dialkylhydrazines and thereby to provide a route to the required azocompounds.

Knorr and Köhler (9) obtained 1,2-dimethylhydrazine by alkaline hydrolysis of dimethylpyrazole and characterized it by means of several derivatives. It had previously been prepared by Harries and Klamt (6) by the methylation and subsequent hydrolysis of 1,2-diformylhydrazine, but their product was probably impure since it boiled over a wide range of temperature; furthermore, no derivatives were reported. The use of dibenzoyl-, instead of diformyl-, hydrazine is a later modification due to Folpmers (4). Hatt (7) subsequently developed the procedure into a useful though still very tedious method of preparing 1,2-dimethylhydrazine dihydrochloride. The over-all yield, which varies between 42 and 54%, is also low.

This route to 1,2-dialkylhydrazines was extended by Harries (5) who obtained 1,2-diethylhydrazine and a high boiling base by ethylation of 1,2-dibenzoylhydrazine and subsequent hydrolysis. The boiling point reported for 1,2-diethylhydrazine, viz. 84–86°C., is almost certainly wrong since Knorr and Köhler (*loc. cit.*) give the boiling point of the lower homologue, 1,2-dimethylhydrazine, as 80–81°C. In a recent paper, Weiniger and Rice (15) mention the preparation of 1,2-diethylhydrazine by ethylation of the copper derivative of 1,2-diformylhydrazine but the properties of the base and its derivatives are not recorded. It seems doubtful, therefore, whether pure 1,2-diethylhydrazine has ever been prepared in quantity.

The reductive alkylation of hydrazine with several aldehydes and ketones was very thoroughly investigated by Taipale (12, 13) during the early twenties

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as a general method of preparing 1,2-dialkylhydrazines. In general, ketones gave moderately good yields, but from aldehydes mixtures of the substituted hydrazines and large amounts of primary amines and ammonia were obtained. When the reaction was carried out in glacial acetic acid, the yields were still only moderate; in some cases the aldazines were rearranged to pyrazolines as had already been observed by Curtius and Zinkeisen (3). Simultaneously with the work of Taipale, the American workers Lochte, Bailey, and Noyes (10) reported the preparation of 1,2-diisopropylhydrazine by the reductive alkylation of acetone with hydrazine hydrochloride in water. More recently, Ugryumov (14) reported the preparation of 1,2-dibenzyl- and 1,2-diheptylhydrazine by the reductive alkylation of hydrazine with benzaldehyde and oenanthaldehyde respectively.

In the present work it was found that the reductive alkylation of acetaldehyde with hydrazine hydrochloride using hydrogen and Adam's catalyst gave a sirupy residue which yielded nothing crystalline besides ammonium chloride. It was then decided to prepare pure ethylideneazine by the method of Curtius and Zinkeisen (3) and to reduce it by the same method. The aldazine was prepared in excellent yield by condensing freshly distilled acetaldehyde and aqueous hydrazine. Reduction of the azine in water with platinum black gave a product which contained a large amount of ethylamine and distilled over a wide range of temperature. Oxidation of the reaction mixture with mercuric oxide in water gave a 20% yield of azobisethane, b.p. 56–58°C. When the reduction of the azine was carried out in the presence of carbon dioxide to maintain the pH of the reaction mixture at or near 7, the amount of ethylamine was considerably reduced but the yield of azobisethane obtained by oxidation was not improved. Reduction in glacial acetic acid gave a high boiling base which was probably the pyrazoline.

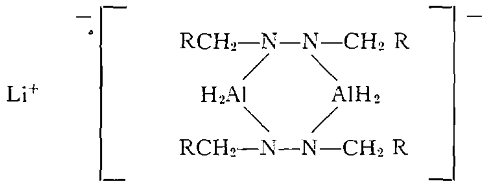
Reduction with Raney nickel alloy in dilute sodium hydroxide gave similar results. In fact, Beregi (1) described the preparation of amines by the hydrogenolysis of the azines of propionaldehyde and butyraldehyde with this alloy.

Since Class and Aston (2) recently reported the reduction of N,N-dimethyl-N′-methylene hydrazine to trimethylhydrazine with lithium aluminum hydride, it was thought ethylideneazine in particular, and azines in general, might be reduced in good yield by this method. The reduction product obtained from ethylideneazine was a base, b.p. 106–107°C. isolated in 80% yield. Its dihydrochloride melted at 168–169°C. and not at 160° as reported by Harries and Klamt (6); it analyzed correctly for diethylhydrazine dihydrochloride. The picrate could not be prepared in the normal way, but the picrolonate was readily obtained. The free base absorbs carbon dioxide from the air. Similarly, 1,2-diisopropylhydrazine was obtained from 2-propylidene azine and 1,2-*n*-propylhydrazine from 1-propylideneazine. The method could probably be extended also to higher homologues. Unfortunately, it is not applicable to the preparation of 1,2-dimethylhydrazine because the azine, $CH_2=N-N=CH_2$, could not be obtained from formaldehyde and hydrazine hydrate. An insoluble polymer was the only product isolable from this reaction.

Reduction of 1,2-diacetylhydrazine with lithium aluminum hydride would likewise lead to 1,2-diethylhydrazine. However, the sparing solubility of acylated hydrazines in solvents suitable for reactions with $LiAlH_4$ prevented reduction in a reasonable time and the reactants were recovered unchanged.

The mechanism of the reduction of azines with lithium aluminum hydride was investigated by means of deuterated reagents. Ethylideneazine was reduced with ordinary lithium aluminum hydride and the complex decomposed by adding deuterium oxide; the 1,2-diethylhydrazine was isolated and oxidized to azobisethane by mercuric oxide in water. Mass spectrometric analysis indicated that the azobisethane contained no deuterium. In a second experiment ethylideneazine was reduced with lithium aluminum hydride containing 25% of the deuteride; the diethylhydrazine and azobisethane were isolated as before. The azobisethane now contained deuterium as shown by the appearance of strong peaks in its mass spectrum at 87 and 88 and a small peak at 89. Of course, the same results would have been obtained if exchange had occurred between the ethylideneazine and lithium aluminum deuteride. However, such an exchange was considered very unlikely since acetone and diacetyl, which contain labile hydrogen, undergo reduction to isopropyl-2-*d*-alcohol and 2,3-butanediol-2,3-d_2 without exchange with this reagent. Finally, dimethylketazine, which contains no hydrogen on the carbon atom adjacent to nitrogen, was converted into 2,2′-azobispropane by the same method. The mass spectrum of the product gave strong peaks at 115 and 116 corresponding to 2,2′-azobispropane with one and two deuterium atoms. The deuterium content was 42.4%.

These results may be explained by representing the complex by the formula



in which one mole of lithium aluminum hydride is utilized per mole of azine. The aluminum adds on to the nitrogen, and hydrogen to the carbon atom. This assumption was further justified by the observation that the 1,2-dialkylhydrazine is contaminated with the hydrazone when less than one mole of reducing agent is employed per mole of azine.

The oxidation of the 1,2-dialkylhydrazines to azoparaffins was best carried out by mercuric oxide suspended in water or ethanol. The yields of azobisethane, 1,1′-azobispropane, and 2,2′-azobispropane from the corresponding hydrazines were nearly quantitative. With 1,2-dimethylhydrazine, azomethane was obtained in 74% yield in contrast with the 25% yield obtained in this laboratory by cupric chloride oxidation of the hydrochloride (8). A further advantage of oxidizing the base with mercuric oxide in water is that the azomethane is free of methyl chloride which is a troublesome impurity in the product obtained by the other method.

EXPERIMENTAL

Ethylideneazine

To a solution of 160 gm. (3.64 mole) of *freshly distilled* acetaldehyde in 400 ml. of ether in a 2 l. round-bottomed flask equipped with a stirrer, a separatory funnel, and a reflux condenser, a solution of 64% hydrazine in water, 92 ml. (1.9 mole), was added dropwise. The flask was immersed in ice-water during the addition of the hydrazine. The reaction mixture was stirred for 10 hr. at room temperature and then treated with 120 gm. anhydrous potassium carbonate in portions. The ether layer was separated, dried over anhydrous potassium carbonate, and distilled off. The residue, distilled through a 12 in. Stedman column, boiled at practically constant temperature, 95.5°C. The yield of colorless product, n_D^{20} 1.4435, d^{26} 0.813, was 134.3 gm. (88%).

1,2-Diethylhydrazine

Lithium aluminum hydride (30.0 gm. of 64% purity) was dissolved in 300 ml. of absolute ether in a 1 l. flask equipped with a stirrer, funnel, and reflux condenser. Ethylideneazine (50 ml.) was added dropwise with stirring to keep the ether refluxing. Stirring was continued under reflux for eight hours thereafter. The complex was decomposed by careful addition of aqueous 40% potassium hydroxide solution. The supernatant liquid was decanted from the inorganic salts into a funnel with a wad of glass wool. The residue was washed several times with small portions of ether. The combined ether filtrate was dried for several hours over pellets of potassium hydroxide, and siphoned into a dry flask for distillation. After the ether had been distilled off, the residue was fractionated through a Stedman column. A tube filled with ascarite was attached to the distilling assembly to prevent absorption of carbon dioxide from the air during distillation, which would cause the boiling point to fluctuate. After collecting a small forerun, b.p. 65–106°, 1,2-diethylhydrazine was collected between 106 and 107°C., n_D^{20} 1.4204, d^{26} 0.797. The yield was 33.7 gm. (80%).

The picrate does not precipitate when equimolecular amounts of 1,2-diethylhydrazine and picric acid in ethanol are mixed. The picrolonate, m.p. 248–250°, after darkening at about 190°C., is readily prepared. The dihydrochloride melts at 168–169°C. Analysis of the dihydrochloride gave C, 29.95%, H, 8.6%. Calc. C, 29.81%, H, 8.7%. Mol. wt. (by iodine titration): Calc. 161, Found 160.2. Free base: Calc. 88.0, Found 87.5.

1,2-Di-n-propylhydrazine

1-Propylideneazine reduced in the same manner gave a 77.5% yield of 1,2-di-*n*-propylhydrazine, b.p. 149.5–150°C., n_D^{20} 1.4287, d_4^{26} 0.7940. Hydrochloride, m.p. 175–175.5°C. Calc. for $C_6H_{16}N_2 \cdot 2HCl$, C, 38.2%; H, 9.53%. Found C, 39.3%, H, 10.17%. Mol. wt. (by iodine titration): Calc. 189.0. Found 188.76.

The picrolonate melted with decomposition at 243–244°C. after darkening at 191–192°C. Calc. for $C_{16}H_{24}N_6O_5$: C, 50.75%, H, 6.32%; N, 22.11%. Found: C, 50.86%; H, 6.35%; N, 22.4%.

1,2-Diisopropylhydrazine

This compound, which had been reported earlier by Lochte, Noyes, and Bailey (10), was obtained in excellent yield (81.4%) from 2-propylideneazine by the present method, b.p. 124–124.5°C., n_D^{20} 1.4160, d^{26} 0.780. Mol. wt. (by iodine titration): Found 115.2. Calc. 116.

Azobisethane

A solution of 10.0 ml. of 1,2-diethylhydrazine in 40 ml. of water was added dropwise to a stirred suspension of 26.0 gm. of yellow mercuric oxide in 40 ml. of water in a flask with a short fractionating column and still head. The reaction mixture was slowly brought to a boil. After an azeotrope of azoethane and water had been collected between 53 and 58°C., the temperature rapidly rose to 90°C., and the distillation was stopped. The yield of product after drying over calcium chloride and distilling off the azoethane on a vacuum manifold was 9.4 ml. (97%), b.p. 58.0°C., n_D^{20} 1.3852.

1,1'-Azobispropane

This compound was prepared by the same method from 1,2-di-*n*-propylhydrazine. B.p. 113.5°C., n_D^{20} 1.4053. Yield: 88%.

2,2'-Azobispropane

This compound was prepared from 1,2-diisopropylhydrazine. B.p. 88.5°C., n_D^{20} 1.3899. Yield: 90%.

Azomethane

To a suspension of 75 gm. yellow mercuric oxide in 120 ml. of water was added slowly through a funnel 22.0 ml. (18.0 gm.) 1,2-dimethylhydrazine in 200 ml. of water. An additional 15 gm. of mercuric oxide was added and the reaction mixture was then stirred continuously at room temperature for two hours. On heating the reaction mixture, azomethane distilled over and was collected in two spiral traps cooled to − 40°C. and − 78°C. Yield: 17.0 ml. in the first trap and 0.5 ml. in the second. The azomethane was dried by slow distillation through a U-tube containing Drierite on a vacuum line. Yield: 12.7 gm. (74% Theor).

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HYDROGEN PEROXIDE AND ITS ANALOGUES

V. PHASE EQUILIBRIA IN THE SYSTEM D_2O–D_2O_2[1]

BY PAUL A. GIGUÈRE AND E. A. SECCO[2]

ABSTRACT

The cooling curves of a number of solutions of deuterium peroxide in heavy water in the concentration range 11% to 95% were measured in order to determine the solid–liquid phase diagram for that binary system. The apparatus of Herington and Handley, which uses a pulsing pressure for stirring the solutions, and a thermistor, was found to be particularly suitable for that purpose. As could be expected the freezing-point curve of the deuterated compounds is closely similar to that of the hydrogen compounds, being shifted up only by about 4° for water-rich solutions and by 2° for peroxide-rich solutions. The melting point of the addition compound, $D_2O_2 \cdot 2D_2O$ very nearly coincides with one of the eutectic points at 46.2% D_2O_2 and −51.5°C.; the other eutectic point is at 60.5% D_2O_2 and −55.1°C. By extrapolation the melting point of pure deuterium peroxide is found to be 1.5°C. as compared with −0.43°C. for hydrogen peroxide. Concentrated solutions of deuterium peroxide exhibit an extreme tendency to supercool, resulting sometimes in formation of glasses even at liquid-air temperature. The previous results of Foley and Giguère for the system H_2O–H_2O_2 were confirmed, specially as regards the melting point of the addition compound $H_2O_2 \cdot 2H_2O$.

INTRODUCTION

For a simple molecule such as hydrogen peroxide substitution of hydrogen by deuterium may be expected to alter noticeably most of the physical properties, and particularly the melting point, by analogy with the case of water and heavy water. Direct determination of this property for the pure isotopic compound was not feasible because of the limited supply of starting material, heavy water, and the difficulty of obtaining an "anhydrous" product. Instead the method of thermal analysis was applied to a number of solutions of various concentrations which led to establishment of the phase diagram of the system D_2O–D_2O_2 and, by extrapolation, to the melting point of deuterium peroxide. Obviously this investigation was patterned after the well established phase diagram of the system H_2O–H_2O_2.

EXPERIMENTAL

The thermometric method used previously in this laboratory (4) was followed but the precision freezing-point apparatus had to be modified because of the small samples available. The improved apparatus devised by Herington and Handley (13) turned out to be especially well adapted to the problem at hand. The major improvement rests in the manner of stirring the sample which allows the freezing curve to be followed until nearly complete solidification. This is achieved by placing the solution in a small U-tube and by applying a gentle pulsing pressure differential over one limb so that the liquid is rocked back and forth past the solid. In addition to a substantial reduction in the size of sample needed (only about 15 gm. was actually used) the new apparatus

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has the further advantage of doing away with mechanical stirrers which would eventually catalyze the decomposition of the peroxide, thus leading to erroneous results.

As in the original apparatus of Herington and Handley the sensitive element was a thermistor (Western Electric, Type 14B) having a resistance of some 2000 ohms at 25°C.; the leads and terminal bead were inserted in a thin-walled glass tubing to avoid contact with the peroxide solution. The resistance was measured with a Wolff potentiometer – Wheatstone bridge combination, used in the latter fashion (23), and a Leeds and Northrup galvanometer with a sensitivity of 0.025 μ amp. per mm. The equation for the temperature coefficient of the thermistor (2)

$$\ln R/R_0 = (B/T - BT_0), \qquad [1]$$

where R_0 is the hypothetical resistance at °K., requires calibration at two points at least. Thus R was found to be 5874.7 ohms at the ice point, realized after the recommended method, and 44,000 ± 10 ohms at −38.87°C., the melting point of mercury. The former datum was checked periodically against a set Beckmann thermometer.

The deuterium peroxide was prepared by dissociation of heavy water in the electrodeless discharge as described elsewhere (12). Some 175 gm. of 99.7% pure heavy water yielded about 130 gm. of a 50% solution of deuterium peroxide. By fractional distillation under reduced pressure this was separated roughly into three portions as follows: 50 gm. of 11%, 50 gm. of 47%, and 30 gm. of 96% D_2O_2. Solutions of various intermediate concentrations were prepared by mixing suitable proportions of these three samples; dilution with heavy water was avoided since it could yield an unstable solution, as was found in the case of hydrogen peroxide (8). The peroxide content was determined by duplicate titrations with 0.1 N potassium permanganate using a microburette and fairly small samples (equivalent to 0.1 gm. of D_2O_2); refractive index measurements (7,20) also served as a first indication. Because of the hygroscopic nature of concentrated peroxide solutions great care was necessary to prevent contamination of the samples by atmospheric moisture during the experiments. Thus the air used in the "pulsing meter" was dried over magnesium perchlorate. A check of the samples by means of infrared spectroscopy after the investigation was completed indicated no significant increase in the original content of ordinary hydrogen.

DISCUSSION OF RESULTS

The cooling curves for each mixture were drawn from temperature readings taken every minute at the beginning of solidification, and less frequently thereafter. It was always necessary to overcome supercooling by seeding the liquid with a few crystals made from the same mixture completely frozen in dry ice or liquid air. Duplicate determinations were carried out and the melting points, as found by the usual extrapolation method, agreed generally within 0.01°C. except in the region of the eutectics where the very high viscosity of the mixtures prevented reaching thermal equilibrium in reasonable time.

TABLE I
FREEZING POINTS FOR THE SYSTEM D_2O–D_2O_2

Experiment No.	Weight % D_2O_2	Freezing point, °C.	Eutectic, °C.
	0.00	+ 3.80	
20	11.00	-3.3_9	
5	20.6_2	-11.6_2	
9	30.4_6	-22.3_4	
8	38.5_1	-35.4_1	
10	43.5_1	-45.0_0	
11	44.6_8	-47.0_0	-51.3_7
12	45.8_4	-50.1_0	-51.3_2
17	46.5_1	-51.5_2	
7	46.9_6	-51.6_2	
14	48.8_4	-51.5_3	
13	50.3_5	-51.6_4	
15	56.0_3	-53.2_8	-55.1_0
22	61.1_7	—	-55.0_6
19	66.5_6	-43.7_6	
18	77.5_4	-25.8_1	
2	80.8_5	-20.9_6	
1	95.0	-4.3_4	
3	95.8_5	-3.0_7	

The various experiments were scattered according to the sequence shown in Table I in order to offset a possible drift in the characteristics of the thermistor, although frequent tests failed to give any such indication. In a few cases it was possible to detect the eutectic halt, and the temperatures thus observed con-

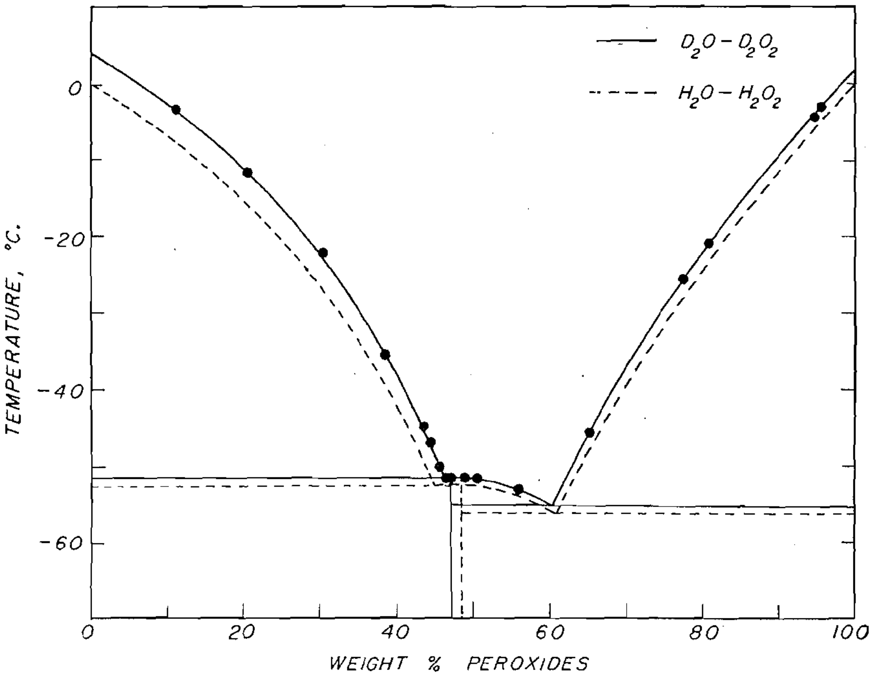

FIG. 1. Phase diagram of the two binary systems D_2O–D_2O_2 and H_2O–H_2O_2.

firmed exactly those found by graphic extrapolation of the three portions of the freezing-point curve. As may be seen in Fig. 1 these curves for the system of deuterium compounds are nearly parallel to those for the hydrogen compounds. For the water-rich mixtures the curve is shifted upwards by about 4°C. whereas for the peroxide-rich mixtures the shift is only half as large. Considering that these temperature differences are the same as between the melting points of the respective pure components the situation is in harmony with the absence of solid solutions in these binary systems as demonstrated otherwise (4, 9, 18).

On the other hand the melting point of the addition compound $D_2O_2 \cdot 2D_2O$, -51.5°C., is only 0.6°C. above that of its hydrogen analogue (4), which may indicate a slightly decreased stability due to isotopic substitution. At any rate both compounds are quite unstable as shown by the very flat maximum of their curve.

Incidentally the present investigation confirms the results of Foley and Giguère (4) for the melting point of the compound $H_2O_2 \cdot 2H_2O_2$, -52.1°C. Their value is some 2°C. lower than that of most previous determinations (10, 15, 17, 18). If the higher value were correct, then the freezing-point curve for the hydrogen system of compounds would cross that for the deuterated compounds, which seems very unlikely *a priori*. As a further check a series of measurements on hydrogen peroxide solutions in the middle range of composition were made using the same apparatus as above. The results (Table II) are in complete agreement with those of Foley and Giguère, and furthermore, they allow a more accurate location of the eutectics (Table III). In particular the failure to observe both the freezing point and the eutectic halt in the same cooling curve for solutions in the concentrations range 45–48.6% H_2O_2 is easily understood in view of the narrow gap, 0.2°C., between these two temperatures.

TABLE II
FREEZING POINTS OF SOME H_2O–H_2O_2 SOLUTIONS

Weight % H_2O_2	Freezing point, °C.	Eutectic, °C.
42.3_1	-46.2	-52.2
47.4_5	-51.9_6	
48.6_2	-51.9_9	
49.8_4	-52.0_2	
52.5_8	-52.5_1	-56.0
55.7_6	-53.4_1	-56.0
66.7_3 (?)	-45.6_0	-56.1
73.8_4	-34.0_0	
76.4_9	-29.2_9	
98.7_5	-1.62	

Replacement of hydrogen by deuterium reduces still further the narrow range of the freezing-point curve of the addition compound because of greater overlapping by the two other curves (Fig. 1). This brings one of the eutectics almost in coincidence with the melting point of the compound $D_2O_2 \cdot 2D_2O$. (The composition difference is only of the order of 1% D_2O_2 and no tempera-

TABLE III
COMPOUNDS AND EUTECTICS IN THE H_2O–H_2O_2 AND D_2O–D_2O_2 SYSTEMS

Weight % H_2O_2	Temp., °C.	Weight % D_2O_2	Temp., °C.	
45.2	−52.2	46.2	−51.5	Higher eutectic
48.55	−52.0	47.35	−51.5	Compound
61.2	−56.1	60.5	−55.1	Lower eutectic

ture difference could be detected experimentally.) By extrapolation from a large plot the melting point of pure deuterium peroxide was found to be 1.5°C. as compared with −0.43° for H_2O_2*. That the isotope effect on the melting point in the case of peroxide is exactly half that in the case of water (3.82°C.) seems quite plausible considering that, (*a*) the molecular mass of the former is nearly double that of the latter and, (*b*) the difference in the zero-point energies of hydrogen and deuterium peroxides is of the same magnitude as that of water and heavy water (21).

Such notable differences in melting points due to substitution of deuterium for hydrogen—a mass increase of merely 6 or 10%—are in contrast with the surprising fact that hydrogen peroxide has nearly the same melting point as water ice despite a much greater relative mass. Now, melting-point relationships are based on considerations of two different kinds: first, the cohesion energy of the lattice and second, the symmetry of the individual molecules. In both water and hydrogen peroxide crystals packing is realized mainly through hydrogen bonds (1), each type of molecule forming the same number of such bonds with its nearest neighbors. From the heat of sublimation of the two solids, 12.2 and 15.6 kcal./mole (5,11) their hydrogen bond energies are found to be of the same magnitude, namely 4.5 (19) and 5.0 kcal./mole. Again comparison of their electric dipole moments 1.84 and 2.16 D and their polarizabilities, 1.48 and 2.31×10^{-24} cm.^{3} (6) shows that their lattice energies cannot be very different. Therefore both compounds are in comparable situations on that account, and their heats of fusion, 1435 and 2987 cal./mole, (9) are roughly in the ratio of their molecular masses as normally expected.

On the other hand, the water molecule, because of its higher symmetry, has fewer possible different orientations on melting and, consequently, its entropy of fusion is only half that of hydrogen peroxide. Furthermore, the constitution of the water molecule is such that it results in an unusually regular and well-balanced structure of the crystal. Although rather open, this structure is so stable that it persists to some extent even after melting. No such anomalies are to be found in hydrogen peroxide. Judging from their respective heat of fusion it appears that twice as many hydrogen bonds are broken on melting in hydrogen peroxide as in water ice (19). Obviously the same considerations apply to the deuterium compounds. So far the indications are that,

**This value from recent very accurate calorimetric measurements (9) is considered more reliable than the thermometric result of Foley and Giguère, −0.46°C. (4). The cause of the discrepancy is now evident, namely, the presence of about 0.03 mole % impurity (water) in the purest sample used by the latter authors. Because of poor thermal equilibrium in their freezing-point apparatus due to inadequate stirring, their calculated freezing points at zero impurity were erratic.*

ceteris paribus, the energy of the deuterium bond is very slightly greater than that of the hydrogen bond (3, 16, 22).

The natural tendency of hydrogen peroxide solutions to supercool was found to be increased further by isotopic substitution. In some cases it became extremely difficult to obtain crystals for seeding the liquid in freezing-point determinations. Concentrated solutions, in particular, could be supercooled not only in dry ice but even in liquid air where they formed glassy transparent solids. Crystallization of these glasses took place only after some time (about 10 min.) and, in one instance, was so sudden that the test tube was shattered and the sample (5 gm. of 77.5% D_2O_2) was lost. It is not clear, at present, why this tendency to supercool should be more pronounced in deuterium peroxide solutions. The increased viscosity of these solutions (20) may be responsible for the very slow rate of crystallization. As in the H_2O–H_2O_2 system it was possible to supercool solutions of deuterium peroxide below the eutectic points even in presence of the "normal" solid phase (8). Dilute solutions of the isotopic peroxide in heavy water follow Raoult's law to the same extent as their hydrogen analogues (5); for instance at 3 mole % D_2O_2 the freezing point lowering is calculated to be 3.0°C. whereas the experimental curve gives 3.4°. No measurement of the heat of fusion of deuterium peroxide has been made yet but a value of about 3030 cal./mole seems reasonable in comparison with the case of water and heavy water (14).

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RÉSUMÉ

On a déterminé par analyse thermique le diagramme des phases du système D_2O–D_2O_2. Comme on pouvait le prévoir la courbe des points de fusion suit de près celle du système analogue H_2O–H_2O_2; la substitution isotopique élève le point de fusion des solutions diluées de peroxyde d'environ 4°C. tandis que pour les solutions concentrées l'effet est la moitié moindre. Par extrapolation on arrive à un point de fusion de 1.5°C. pour le peroxyde de deutérium pur. L'un des eutectiques, à 46.2% de D_2O_2 et -51.5°C., se confond presqu' exactement avec le point de fusion du composé moléculaire $D_2O_2 \cdot 2D_2O$; l'autre se trouve à 60.5% de D_2O_2 et -55.1°C. La tendance à la surfusion est encore plus marquée chez les solutions de peroxyde isotopique que chez celles de peroxyde d'hydrogène.

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THE PRODUCTION OF ISOCYANATES BY THE THERMAL DECOMPOSITION OF PSEUDOUREAS

By J. R. Robinson*

In studies involving an homologous series of 3,3-diphenyl-2-alkylpseudoureas the materials were observed to decompose when distillation was attempted at atmospheric pressure. One of the decomposition products was the corresponding alkyl isocyanate and the other major product was diphenylamine, as indicated by equation [1].

$$(C_6H_5)_2N\cdot C(OR) = NH \xrightarrow{\text{heat}} (C_6H_5)_2NH + RNCO. \qquad [1]$$

The isocyanates distilled over at 250–300°C. and were converted to 1-alkyl-3-*p*-tolylureas by treatment with *p*-toluidine [2] to facilitate identification.

$$p\text{-}CH_3\cdot C_6H_4\cdot NH_2 + RNCO \longrightarrow p\text{-}CH_3\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot R. \qquad [2]$$

The low yields of substituted urea (Table I) indicate correspondingly low yields of isocyanate, and were probably due to polymerization and recombination processes. No precautions were taken to minimize these side reactions.

The pseudoureas were synthesized by the addition of alcohols to diphenylcyanamide, catalyzed by the corresponding alkoxide ion [3].

$$(C_6H_5)_2N\cdot CN + ROH \xrightarrow{RO^-} (C_6H_5)_2N\cdot C(OR) = NH. \qquad [3]$$

The pyrolysis of the methyl homologue has been described elsewhere (3) as producing unsymmetrical diphenylurea. That process occurs when the temperature is kept below 160°C.

EXPERIMENTAL

In each case, 1 to 3 gm. (0.005 to 0.01 mole) of the pseudourea was weighed into a 6 in. soft glass test tube which was then drawn off to a fine delivery tube and bent around to form a semimicro retort. The melting and subsequent thermal decomposition of the material were performed as slowly and at as low a temperature as possible, usually at 250–300°C. The lachrymatory distillate was collected in a cooled 10 ml. Erlenmeyer flask and the pyrolysis was stopped when diphenylamine began to distill over. The crude isocynate was mixed immediately with the theoretically required amount of *p*-toluidine dissolved in 10 ml. of diethyl ether. The resulting solution was left standing in an ice-water bath until crystallization of the substituted urea was complete. The product was crystallized from methanol–water, ethanol–water, and finally from petroleum ether (65–110°), then dried for seven days in a vacuum desiccator containing calcium chloride and shredded paraffin wax.

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The yields and analytical data for the 1-alkyl-3-*p*-tolylureas are shown in Table I.

TABLE I

1-ALKYL-3-*p*-TOLYLUREAS. $p\text{-}CH_3\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot R$

R	Yield,* %	M.p., °C.	M.p. in lit.	Lit. ref.	Calc., % C	Calc., % H	Found, %** C	Found, %** H
Methyl	12	178	178	(1)	65.8	7.37	65.7	7.47
Ethyl	30	143	144	(2)	67.4	7.92	67.6	7.99
n-Propyl	21	125	123	(1)	68.7	8.39	68.7	8.32
Isopropyl	10	157	157	(1)	68.7	8.39	68.9	8.48
n-Butyl	21	119	119	(1)	69.9	8.80	70.0	8.74
Isobutyl	15	153	154	(1)	69.9	8.80	70.0	8.91
n-Amyl	6	103	—	—	70.9	9.15	70.9	9.22
n-Hexyl	11	86	—	—	71.8	9.46	71.7	9.46
n-Heptyl	10	108	—	—	72.5	9.74	72.7	10.03
n-Octyl	6	92	—	—	73.2	9.99	73.6	9.90
n-Nonyl	11	99	—	—	73.9	10.21	73.9	10.32
n-Decyl	3	98	—	—	74.4	10.41	74.6	10.27
n-Undecyl	8	102	—	—	75.0	10.59	74.9	10.68
Lauryl	1	102	—	—	75.4	10.76	75.4	10.70

* *Yields calculated after three crystallizations.*

***Combustion analyses by Mr. R. W. White of the Science Service Laboratory, Department of Agriculture, London, Ont.*

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DEPARTMENT OF CHEMISTRY,
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THE ADSORPTION OF WATER VAPOR BY PROTEINS

BY H. B. DUNFORD AND JOHN L. MORRISON

Bull (3) measured the adsorption of water vapor by a large number of proteins and found that the Brunauer–Emmett–Teller equation (2) fitted the isotherms for the range of relative vapor pressures 0.05 to 0.5. This observation led him to suggest that the water was specifically adsorbed by polar groups in the protein molecule. The B.E.T. surface area measurements indicate that proteins present a large internal surface to water which is not accessible to relatively inert gases such as nitrogen and oxygen (1).

Less is known about the water sorption process at relative pressures greater than 0.5, where the two-constant B.E.T. equation is not applicable. However, solution effects (3) and a spectrum of sorption processes (4) have been postulated.

This note reports the application of the Harkins–Jura equation (5) to Bull's water–protein adsorption isotherms. Some examples of the plotting are given

The yields and analytical data for the 1-alkyl-3-*p*-tolylureas are shown in Table I.

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Less is known about the water sorption process at relative pressures greater than 0.5, where the two-constant B.E.T. equation is not applicable. However, solution effects (3) and a spectrum of sorption processes (4) have been postulated.

This note reports the application of the Harkins–Jura equation (5) to Bull's water–protein adsorption isotherms. Some examples of the plotting are given in Fig. 1. Linear H.J. plots for most of Bull's data are obtained over the relative water vapor pressure range from 0.5 or 0.6 to 0.95. The notable exception is salmin. Salmin, which is not a true protein but a low molecular weight polypeptide, goes into solution at a relative vapor pressure of 0.7 (3). The nylon isotherms yield linear H.J. plots over the shorter range of 0.7 to 0.95.

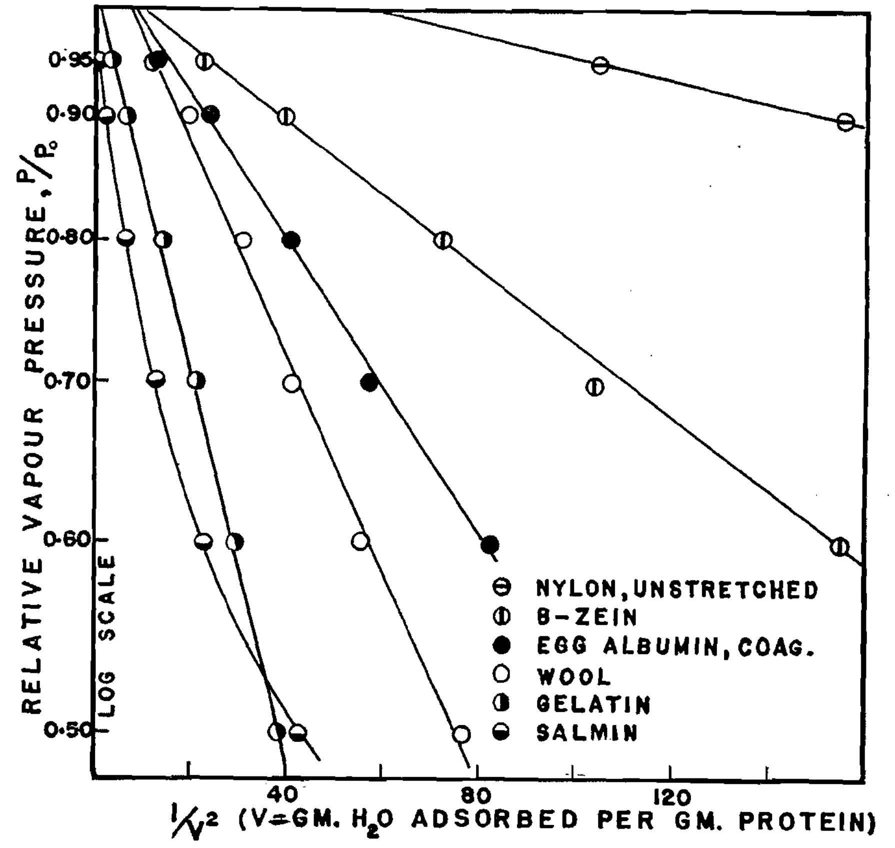

FIG. 1. Harkins–Jura plots of some of Bull's water–protein adsorption isotherms at 25°C.

Liang's method (6) was used to correlate the results of the two equations. Liang has shown that the slope of a linear H.J. plot is related to V_m, the amount in a monomolecular layer as given by the B.E.T. equation. Table I contains the V_m values calculated from the H.J. equation as well as those obtained by Bull from the B.E.T. equation. With the exception of salmin, the values agree with a 5% mean deviation.

The Harkins–Jura equation is based on the assumption that the adsorbed molecules are in a condensed film. Thus it is probable that the adsorption of a condensed film of water by proteins is the predominant process at high vapor pressures.

The general observation that the same V_m is obtained for the upper and lower parts of the isotherms may be explained by one of two possible alternatives.

TABLE I
GRAMS WATER IN MONOLAYER PER 100 GRAMS PROTEIN

Protein	B.E.T. equation (ref. 3)	H.J. equation
Nylon, unstretched	1.92	2.11
Nylon, stretched	1.76	2.02
Silk	4.07	4.11
Wool	6.58	6.26
B-zein	4.10	3.89
C-zein	3.78	4.00
Salmin	5.28	—
Elastin	6.22	6.81
Collagen	9.52	10.4
Gelatin	8.73	8.77
Egg albumin, lyophilized	5.65	5.54
Egg albumin, unlyophilized	6.15	6.09
Egg albumin, heat coagulated	4.97	5.50
β-Lactoglobulin, lyophilized	5.93	6.11
β-Lactoglobulin, wet crystals	6.67	6.48
Serum albumin	6.73	6.48
α- and β-Pseudoglobulin	7.15	7.00
γ-Pseudoglobulin	7.16	7.00

The alternatives are that the complete isotherm represents *either* the formation of a film of one molecule thickness which becomes condensed at higher vapor pressures *or* the formation of a film of at least two molecules thickness, the upper layer being condensed and occupying the same surface area as the underlying monomolecular layer. The concurrence of the V_m values for the two parts of the isotherm means that the same number of adsorption sites are involved. This, together with the observation that in all cases an amount of water greater than V_m is adsorbed well before a relative vapor pressure of 0.5 is reached (3), suggests that the second alternative is the correct one.

The fact that nylon obeys the H.J. equation over a shorter pressure range than the other proteins may be due to the large water-repellant hydrocarbon spacings between the peptide linkages of the synthetic polypeptide hindering condensed film formation.

The concurrence of the V_m values given by the B.E.T. and H.J. equations for the two separate halves of the water–protein adsorption isotherms suggests an interesting extension of Liang's method.

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SPECTRES D'ABSORPTION INFRAROUGES DES URÉES SUBSTITUÉES[1]

PAR JEAN L. BOIVIN ET PAUL A. BOIVIN

RÉSUMÉ

Les spectres d'absorption infrarouges de quelques urées substituées par des groupements alkyles ou aryles ont été déterminés entre 2 et 15 μ. Les urées du type $RNHCONHCH_3$ donnent à 7.05 μ une bande d'absorption constante qui semble caractériser le groupement CH_3NH CONH–. Suit une explication générale des spectres obtenus avec les différents dérivés de l'urée.

INTRODUCTION

Le spectre d'absorption infrarouge de l'urée est bien connu, mais difficile à expliquer. On obtient l'absorption caractéristique des groupements NH et CO, mais non pas aux longueurs d'onde normales des amides. Comme l'urée est une diamide qui possède toutes les propriétés des amides aliphatiques, on devait s'attendre à un comportement identique en spectrométrie infrarouge.

Afin d'expliquer le spectre de l'urée, on a déterminé les spectres infrarouges de quelques urées substituées sur l'azote en position 1 ou 3. Leur préparation a déjà été décrite dans une publication précédente (1).

La littérature fait mention de plusieurs travaux où le spectre infrarouge de l'urée est surtout étudié du point de vue de la mécanique quantique. Peu de travaux sur les spectres d'absorption infrarouges expliquent sa structure chimique.

Récemment, Pristera (2) a publié les spectres de la diméthyldiphénylurée et de la diéthyldiphénylurée et a attribué les bandes obtenues à 6.00 μ et 6.70 μ aux groupements carbonyles et carbamides. La dernière bande d'absorption semble avoir été confondue avec celle du noyau aromatique qui apparaît à 6.25 μ et 6.70 μ.

Mesures spectrophotométriques

On a utilisé un spectrophotomètre Perkin–Elmer, modèle 21 à doubles faisceaux, pour déterminer les spectres d'absorption infrarouges des urées. Les courbes de transmission étaient enregistrées automatiquement sur cet appareil.

Une émulsion des produits dans l'huile minérale servit à la détermination des spectres. Pour obtenir un spectre convenable, l'épaisseur de l'émulsion

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Contribution du Département de Chimie, Université d'Ottawa et du Conseil des Recherches pour la Défense, C.A.R.D.E., Valcartier, Québec.

fut variée de façon à ce que les bandes d'absorption aient une bonne intensité. On ne donne que deux courbes de transmission (fig. 1), celles des cyclohexylurées. Pour les spectres des autres produits, les longueurs d'onde des bandes de bonne intensité seulement sont rapportées dans les tableaux I and II.

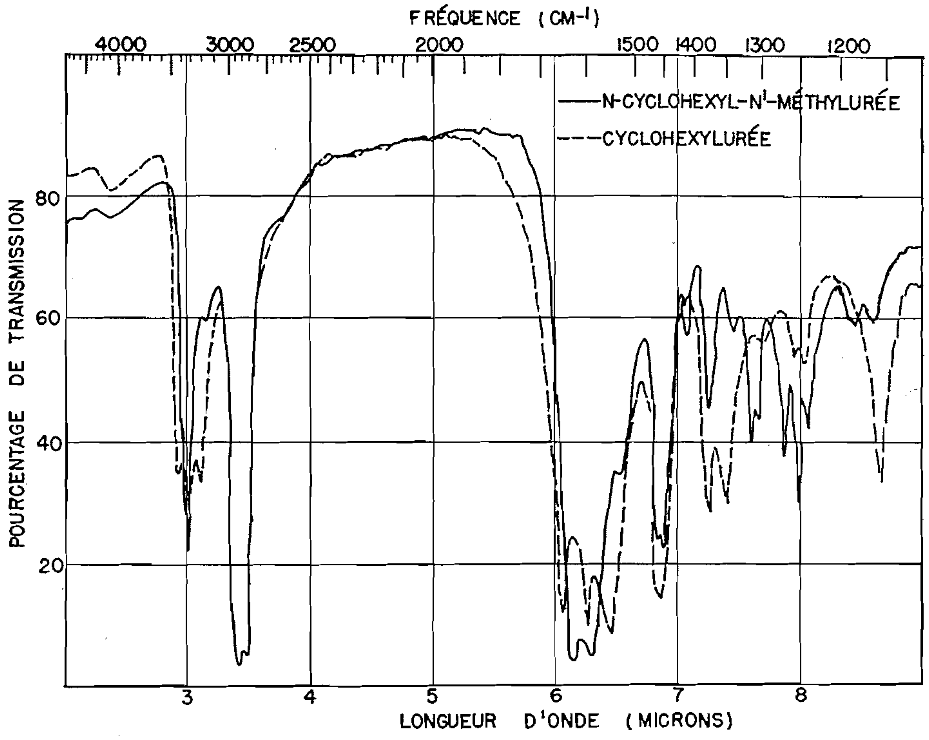
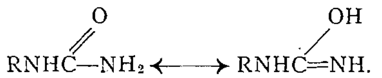


FIG. 1

Urées substituées en position 1

Ces urées (tableau I et fig. 1) donnent des bandes d'absorption dans les régions de 3 μ et de 6 μ qui caractérisent les groupements NH, NH_2 et C=O. Dans la région de 3 μ, la plupart des composés que nous avons étudiés possèdent trois bandes d'absorption; chacune correspond à un mode de vibration entre les atomes d'hydrogène et d'azote. Deux bandes d'absorption et parfois trois sont bien distinctes, mais la troisième est souvent un point d'inflexion. On pourrait attribuer aux vibrations N–H les bandes d'absorption obtenues entre 2.90 μ et 2.96 μ; et aux vibrations NH_2, celles produites entre 2.98 μ et 3.15 μ.

Les possibilités d'avoir des vibrations OH sont exclues, car ces urées ne se tautomérisent pas facilement en milieu neutre:



$$\mathrm{RNH\overset{O}{\overset{\|}{C}}{-}NH_2} \longleftrightarrow \mathrm{RNH\overset{OH}{\overset{|}{C}}{=}NH.}$$

TABLEAU I
URÉES SUBSTITUÉES (RNHCONH$_2$)

Substituants	Position des bandes en microns																				
Méthyle	2.92	3.01		6.08	6.38				7.05				8.58	9.05	11.05	12.80	13.90				
Éthyle	2.92	2.98	3.10		6.05	6.23	6.40		7.45				8.64	9.05	9.27	11.30	12.70	13.90			
n-Propyle	2.95	3.10		6.04	6.22	6.43			7.40	7.72	8.00		8.62	9.00	11.18	11.60	12.80	13.33			
n-Butyle	2.95	3.04	3.17		6.02	6.12	6.54														
n-Amyle	2.95	3.10		6.03	6.12	6.23	6.51	6.75	7.45	7.67			8.68	8.90	12.80	13.65					
n-Hexyle	2.94	3.10		6.03	6.12	6.23	6.53	6.75	7.37	7.55	7.78		8.68	8.90	13.85	13.70					
Cyclohexyle	2.92	2.98	3.10		6.05	6.25	6.45		7.40	7.70	7.95	8.02	8.64	9.70	11.20	13.45	12.82	13.90			
Phényle	2.90	3.00		6.02	6.17	6.25	6.44	6.67	7.36	7.95			8.95	9.28	9.65	11.05	11.65	12.94	13.32	14.40	
Benzyle	2.92	2.98		6.07	6.23	6.38			7.52	7.63	8.27		8.74	9.04	9.25	9.75	10.98	12.10	13.25	13.35	14.40
Anilino	2.92	2.97	3.12		6.02	6.23	6.68		7.00	7.12	7.65	7.88	8.62	9.02	9.28	9.75	11.27	12.90	13.20	13.30	14.50
p-Tolyle	2.92	3.02		6.05	6.27	6.45	6.60		7.12	7.35	7.67	7.95	9.02	12.14	12.32	12.84	14.15				
p-Chlorophényle	2.92	3.00		6.04	6.20	6.28	6.45	6.70	7.62	7.72	7.84	8.00	9.15	9.85	11.50	12.20	12.94	13.70	14.65		

TABLEAU II
1-MÉTHYLURÉES SUBSTITUÉES EN POSITION 3 (RNHCONHCH$_3$)

Substituants	Position des bandes en microns																								
Méthyle	2.98	3.14*		6.15						7.50	7.80						8.52	9.60	10.74	12.90					
Éthyle	2.98		6.12	6.32						7.05	7.90						8.56	9.20	9.50	11.10	12.90				
n-Propyle	3.00	3.15*		6.12						7.05	7.90						8.60	9.35	11.05	11.20	12.90	13.15			
n-Amyle	2.98		6.16							7.05	8.60														
n-Hexyle	2.98		6.02	6.08	6.15	6.25	6.58			7.05	7.70	7.95	8.13				8.60	12.95	13.75						
Cyclohexyle	2.99		6.02	6.08	6.15	6.30	6.52			7.05	7.45	7.60	7.68	7.98	8.07	8.44	8.62	9.23	11.27	11.82	12.94				
Phényle	2.96	3.00*	6.08	6.15	6.25	6.30	6.47	6.65	6.92	7.05	7.60	7.95					8.55	9.25	11.05	11.70	11.84	13.2	13.65	14.35	
Benzyle	2.98		6.15	6.32	6.67	7.02				7.05	7.34	7.78	7.90				8.60	9.27	9.52	9.75	13.65	14.32			
p-Tolyle	2.98		6.05	6.23	6.40	6.60				7.05	7.12	7.62	7.68	7.85	8.08		8.56	9.00	11.90	12.33	12.92	13.17	14.15		
p-Chlorophényle	3.00		6.10	6.22	6.35	6.57	6.72			7.05	7.15	7.70	7.79	8.05			8.56	9.17	9.88	12.02	12.25	13.20	13.50	13.90	14.60

**Point d'inflexion*

Dans la région de 6 μ, qui caractérise les composés à doubles liaisons, une seule bande d'absorption apparaît dans l'analyse de ces urées substituées, entre 6.02 μ et 6.12 μ. On peut donc les apparenter au groupement carbonyle de l'urée. D'ailleurs les amides primaires absorbent habituellement entre 5.90 μ et 6.25 μ.

Une autre bande d'absorption de bonne intensité apparaît aux environs de 6.20 μ. Lorsque R est un radical aliphatique, cette bande semble due à la déformation de NH_2 qui apparaît entre 6.08 μ et 6.25 μ. Mais lorsque R est un résidu aromatique, le noyau benzénique absorbe entre 6.20 μ et 6.25 μ et donne une bande d'intensité variable, mais toujours présente à ces longueurs d'onde.

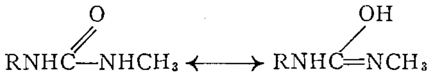
Dans la région entre 8.00 μ et 9.00 μ, il y a absorption caractéristique pour tous les composés substitués par un groupement aliphatique. On peut observer un déplacement bathochromique lorsque l'on passe d'un substituant méthyle à éthyle, propyle, butyle, amyle et hexyle (tableau I).

Il y a plusieurs bandes d'absorption entre 9 μ et 15 μ. Cette région du spectre infrarouge caractérise toute la molécule et ne peut servir qu'à l'identification du composé lui-même.

1-Méthylurées substituées en position 3

Les 1-méthylurées substituées en position 3 donnent des spectres d'absorption infrarouges différents des urées monosubstituées (tableau II et fig. 1).

Dans la région de 3 μ, on obtient des bandes intenses qui indiquent la présence de vibrations NH. Avec les urées, $RNHCONH_2$, on observe trois bandes d'absorption correspondant aux trois modes de vibration entre les atomes d'hydrogène et d'azote. Les urées du type $RNHCONHCH_3$, ayant deux groupements NH ou deux modes de vibration, devraient donner deux bandes d'absorption; mais il n'y a qu'une forte bande d'absorption à 2.98 μ. Toutefois, on obtient un point d'inflexion à une plus grande longueur d'onde (3.10 μ–3.20 μ). La possibilité de tautomérisation de ces urées est encore minime ou inexistante.



$$\mathrm{RNH}\overset{\mathrm{O}}{\overset{/\!/}{\mathrm{C}}}\mathrm{—NHCH_3} \longleftrightarrow \mathrm{RNH}\overset{\mathrm{OH}}{\overset{/}{\mathrm{C}}}\mathrm{{=}NCH_3}$$

Dans la région de 6 μ, i.e. la longueur d'onde normale où les amides ordinaires donnent des bandes d'absorption, les composés du type $RNHCONHCH_3$ donnent tous une absorption intense. Cette bande est due au groupement C=O de ces urées. Il semble y avoir un déplacement de cette bande à mesure que le radical passe de éthyle à hexyle. De 6.20 μ à 6.25 μ et de 6.65 μ à 6.70 μ, on retrouve les absorptions dues aux groupements phényles des urées substituées.

A 7.05 μ, on obtient une bande de bonne intensité qui est présente dans le spectre de toutes les urées du type $RNHCONHCH_3$. Cette bande semble caractériser le groupement $CH_3NHCONH$–. En considérant le tableau I, on constate que la méthylurée donne également une absorption à 7.05 μ.

Etant donné le nombre de composés étudiés et la variété de leurs substituants, il est possible d'identifier le groupement $CH_3NHCONH-$ à l'aide de cette bande.

Entre 8.50 μ et 8.60 μ, on observe également l'effet de la chaîne hydrocarbonée. Ainsi, il y a encore un déplacement bathochromique en passant du groupement méthyle à hexyle.

Si l'on compare les spectres de ces urées, $RNHCONH_2$ et $RNHCONHCH_3$, à celui de l'urée ordinaire, on observe que les bandes à 3.00 μ et 6.00 μ ne sont pas à la même longueur d'onde, bien qu'elles soient présentes dans ces régions du spectre. Ces mesures ont permis d'identifier le groupement méthylcarbamido ($CH_3NHCONH-$) et de conclure que les urées substituées se comportent en spectrographie infrarouge comme des amides ordinaires.

SUMMARY

The infrared spectra of N-substituted ureas and N′-methyl-N′-substituted ureas have been determined in mineral oil emulsion from 2 μ to 15 μ. It was found that all the ureas of formula $RNHCONHCH_3$ gave an absorption band at 7.05 μ which seems to be characteristic of the methylcarbamido group ($CH_3NHCONH-$).

REMERCIEMENTS

Les auteurs désirent remercier monsieur Marcel Bédard, C.A.R.D.E., qui détermina les spectres d'absorption infrarouges et le Conseil des Recherches pour la Défense qui permit la publication de ce travail.

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A STUDY OF THE SULPHATE ESTER OF UNSTABILIZED CELLULOSE ACETATE[1]

By Karl Keirstead and John Myers

ABSTRACT

Evidence for the existence of the ester form of the sulphate in unstabilized cellulose acetate has been examined by ion exchange studies on precipitated and fibrous cellulose acetate. The equilibrium reached during ion exchange is affected by the pH and by the concentration of the salt solution used. The thermal stability of the ester is shown to vary inversely with the sulphate content. A study has been made of the accuracy of the various analyses involved.

INTRODUCTION

Cellulose acetate and cellulose nitrate are normally prepared by treatment of cellulose with the appropriate acid in the presence of sulphuric acid at the appropriate temperature. At one stage in the preparation both esters contain a small amount of sulphate. The amount depends on the composition of the esterifying medium and other factors but usually it is less than 1%. Purification or stabilization, as it is usually called, may be accomplished by partial hydrolysis of the ester in the appropriate medium. It has been established by Malm *et al.* (10) that the sulphate in unstabilized cellulose acetate is in the form of a sulphate ester, RSO_4H, but its form in unstabilized cellulose nitrate has been the subject of discussion for many years. Some direct evidence for the existence of a sulphate ester in cellulose nitrate was presented by Reeve and Giddens (12) in connection with a study of the mechanism of stabilization by ammonia. Freshly prepared samples of cellulose nitrate, rinsed free of superficial acids, were treated with 1% aqueous ammonia at room temperature for 15 min., then thoroughly rinsed and dried for sulphate and ammonia determinations. The results showed that the ammonia–sulphate relation for the unboiled samples was close to unity, suggesting that the sulphate was present in the hemiester form, RSO_4H. Previously Kullgren (9) had estimated the hemiester content of nitrocellulose by the use of an ion-exchange method. The acid liberated from the exchange as indicated below

$$RSO_4H + NaCl \longrightarrow RSO_4Na + HCl \qquad [1]$$

was taken to be a measure of the hemiester content. For one particular sample this value was 25% of the sulphate content. Kullgren (9) concluded that a large part of the sulphate (75%) must be present as the neutral sulphate, R_2SO_4.

The experiments described in this report were undertaken to establish the relative merits of various ion exchange methods for the estimation of the sulphate ester of cellulose acetate. The possibility of applying these methods to the estimation of the acid ester content of cellulose nitrate will be reported in a later communication. While many investigations have been made on ion

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exchange with naturally-occurring minerals and more recently with synthetic organic resins, the only detailed study of ion exchange with cellulose acetate sulphate appears to have been carried out by Araki and Tadenuma (1) who used a "sulphoacetate gel". Because of the present unavailability of the original report it is impossible to make further reference to this study. It should be noted, however, that the present work has been carried out with cellulose acetate sulphate in the precipitated and fiber forms. The term "cellulose sulphoacetate" has been used generally to refer to products with a high sulphate content, but as pointed out by Malm it should be applied only to an ester of cellulose with sulphoacetic acid. Following the terminology used for mixed organic esters of cellulose, the mixed ester of acetic and sulphuric acids will be termed cellulose acetate sulphate.

Cellulose acetate sulphate consists of a high-polymer structure to which sulphate groups with ionizable hydrogen are attached. The whole compound may be regarded as an insoluble acid and its behavior may be studied by determining the change in pH when a suspension is titrated with alkali under various conditions (7, 15). When sodium hydroxide is added to a suspension of cellulose acetate sulphate in the absence of neutral salt the pH changes

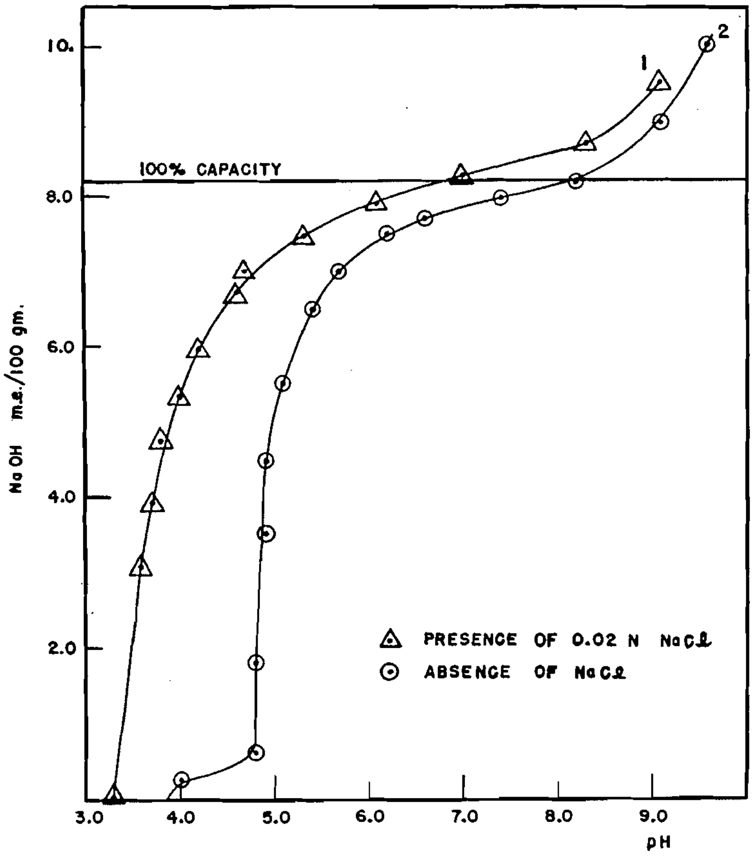

FIG. 1. Titration of cellulose acetate sulphate.

only slowly until the amount added is equivalent to most of the acidic hydrogen on the exchanger, which is known as the full capacity. When 0.2 *N* sodium chloride is added to the system, it becomes acid and the full capacity is realized at pH 7 as shown in Fig. 1. In all the experimental work great care must be taken to avoid or correct for hydrolysis of the sulphate and acetate groups in water. Prior to all experiments hydrolysis was minimized by thorough washing with distilled water, and the effect during an experiment was limited by keeping the duration to a minimum or by estimating the amount of acid formed.

There are a number of methods of studying the ion exchange process quantitatively. If an ion exchange takes place according to the equation

$$RSO_4H + M^+ \longrightarrow RSO_4M + H^+ \qquad [2]$$

the hydrogen ion concentration in the solution after exchange and the metal content of the ester expressed in milliequivalents should each be equal to the sulphate content of the fiber. Malm (10) showed that the sulphate content of unstabilized cellulose acetate sulphate determined by repeated treatment with 1% sodium chloride solution followed by titration of the hydrogen ion liberated in the combined filtrates was 1.01% compared with 1.05% determined by sulphate estimation.

The present paper considers the relations among the sulphate contents as determined by the three possible methods.

EXPERIMENTAL RESULTS

Ion Exchange Experiments

Table I shows the amount of sulphate found in various samples of cellulose acetate by the determination of sulphate gravimetrically as the barium salt, and by ion exchange with sodium or calcium chloride solution and subsequent titration with standard sodium hydroxide.

TABLE I
COMPARISON OF TITRATION AND GRAVIMETRIC METHODS OF DETERMINING SULPHATE ESTER

Batch No.	Type	Cation exchanged	Sulphate, m.e./100 gm.		Per cent difference
			Gravimetric	Ion exchange titration	
28-6	Fiber	Ca	29.3	25.7	−12
33	"	"	23.7	19.5	−18
29-1	"	"	13.6	10.7	−21
29-2	"	"	9.3	6.2	−34
20	Pptd.	"	9.1	8.8	− 3
29-3	Fiber	"	6.5	3.8	−41
32	Pptd.	"	0.20	0.19	− 5
19-13	Fiber	Na	13.6	12.4	− 9
19-1	"	"	13.6	12.4	− 9
17	Pptd.	"	8.0	7.1	−11
23	"	"	6.5	6.1	− 6
27-1	Fiber	"	2.9	2.2	−14
27-2	"	"	2.5	2.3	− 8
27-7	"	"	2.5	2.3	− 8

The normality of the salt solution was 0.2 and the pH was 5.7. In all experiments, the sulphate content determined by ion exchange was less than that found gravimetrically, and it will be shown below that the difference is well outside the expected experimental error. It can be accounted for either by incomplete ion exchange reaction or by adsorption of hydrogen ions on the sample. Table II shows that the second alternative is more likely because the sulphate determined by estimation of the exchanged calcium agreed more closely with the sulphate determined gravimetrically than with that determined by titration of hydrogen ion.

TABLE II
COMPARISON OF CALCIUM AND GRAVIMETRIC METHODS OF DETERMINING SULPHATE ESTER

Batch No.	Type	Sulphate, m.e./100 gm.		Per cent difference
		Gravimetric	Calcium	
28-6	Fiber	29.3	28.6	−2.4
33	"	23.8	24.5	+3.0
45	"	20.5	20.8	+1.0
36	"	17.2	18.2	+6.0
43	"	16.6	16.9	+2.0
40	"	14.9	15.2	+2.0
29-1	"	13.6	13.8	+1.0
30	Pptd.	26.5	26.7	+1.0

The results obtained by the two methods agreed within the limits of experimental error, suggesting that the discrepancies between the gravimetric and titration methods were caused by adsorption of hydrogen ions.

In some of the experiments in which 0.2 *N* sodium chloride solution was used for the exchange, the sodium on the sample after exchange was determined by flame photometry. A few results are shown in Table III. Sample 39-7 was subjected to three rapid washes with distilled water after exchange while no particular care was taken in washing the other three samples. The removal of sodium by washing was confirmed by the increase in ion exchange acidity after washing and the presence of sodium in the filtrate. In one experiment a sample regained 25% of the ion exchange capacity after continuous washing for five hours, followed by contact with water for three days, and in others 100% of the ion exchange capacity was recovered after washing for seven days.

TABLE III
COMPARISON OF SODIUM AND GRAVIMETRIC METHODS OF DETERMINING SULPHATE ESTER

Batch No.	Sulphate, m.e./100 gm.		Per cent difference
	Gravimetric	Sodium	
17-4-a	8.0	4.6	−42.5
17-8-a	7.7	3.5	−55.0
17-8-6	7.7	3.0	−61.0
39-7	11.3	11.3	0

It was found that the physical state of the sample had a considerable influence on the ion exchange process. A sample of batch 29-1 was boiled for five minutes in water and then for 10 min. in 50% alcohol (29-2) while another sample was boiled for five minutes in water followed by five minutes in absolute alcohol (29-3). The sulphate determined by the gravimetric, titration, and calcium methods is shown in Table IV.

TABLE IV
EFFECT OF SAMPLE TREATMENT ON ION EXCHANGE

Batch No.	Sulphate				
	Gravimetric, m.e./100 gm.	Titration		Calcium	
		m.e./100 gm.	Per cent difference	m.e./100 gm.	Per cent difference
29-1	13.6	10.7	−21.0	13.8	+ 1.4
29-2	9.3	6.2	−33.6	9.3	0
29-3	6.5	3.8	−41.5	7.8	+20.0

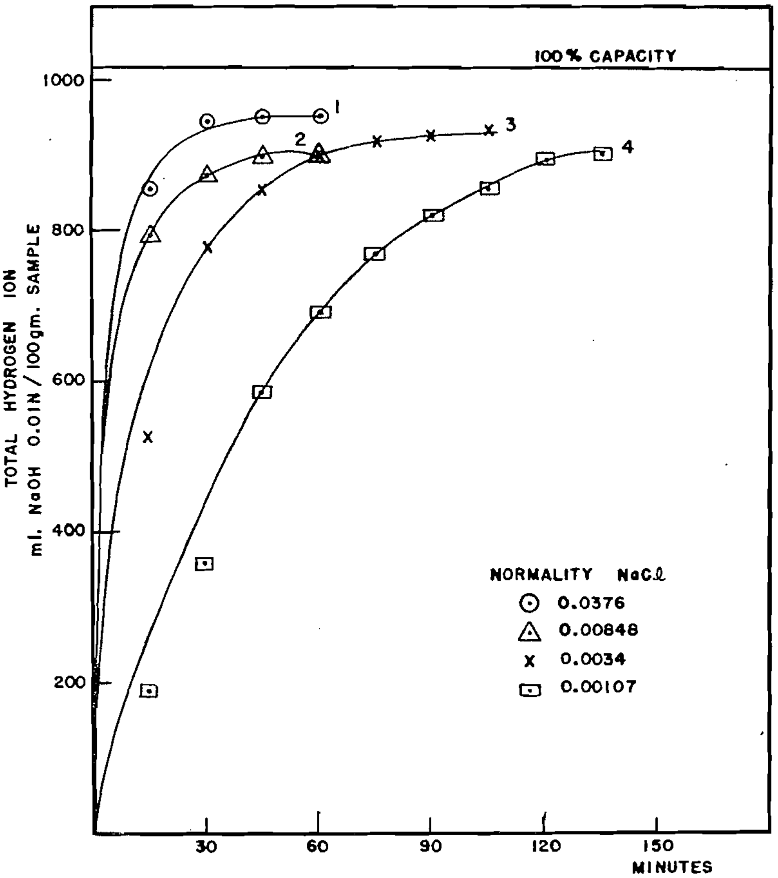

FIG. 2. Effect of salt concentration on Na$^+$–H$^+$ exchange, cellulose acetate sulphate (18-6).

The alcohol treatment modified the exchange process considerably and it can be seen that the errors with the titration method were large. In the third sample the sulphate determined by the calcium method was high, suggesting that the calcium ions may also be adsorbed.

The effect of the normality of the salt solution is demonstrated in Fig. 2, which shows some curves of acidity against time for exchange in sodium chloride solutions. With normalities greater than 0.01, exchange was quite rapid but below this normality the time for exchange increased rapidly.

The effect of pH on exchange in a 0.2 *N* sodium chloride solution is shown in Table V for two samples of ester.

TABLE V
EFFECT OF pH ON ION EXCHANGE

Batch No.	Type	Sulphate, m.e./100 gm., gravimetric	pH	Sulphate, m.e./100 gm., titration.	Per cent difference
19-9	Fiber	13.6	8.6	13.4	− 1
"	"	"	6.7	12.8	− 5
"	"	"	5.75	12.7	− 6
"	"	"	4.5	12.3	− 9
"	"	"	3.8	12.1	−10
21	Pptd.	10.1	10.5	9.3	− 8
"	"	"	8.8	6.1	−40
"	"	"	3.9	5.2	−49
"	"	"	1.9	2.8	−72

The sulphate determined by titration was very sensitive to pH, particularly for precipitated samples.

Heat Stability of Cellulose Acetate Sulphate

Commercial methods for the determination of the thermal stability of cellulose acetate depend either on the charring temperature or the liberation of acetic acid by hydrolysis of the moist sample (4). In the present investigation the stability of the mixed ester was determined by a heat test used previously for unstabilized nitrocellulose. The test has been adapted from the 110°C. test described by Reeve and Giddens (12). Dry air at 65 ± 0.5°C. was used to sweep decomposition products from the sample and an iodometric method used to detect the first traces of volatile acid. The time in minutes taken for a change in the color of the indicator is regarded as a measure of the stability of the sample. Some typical results are shown in Table VI, each value being the mean of several determinations.

The stability of samples of fiber was increased by the substitution of hydrogen by calcium but in one sample of precipitated material examined, ion exchange decreased the stability. The stability of the precipitated material was very much greater than that of the fiber material. Preliminary studies on unstabilized cellulose nitrate using the same test have indicated an increase in stability after ion exchange. In one experiment the stability time for the

TABLE VI
HEAT STABILITY OF CELLULOSE ACETATE SULPHATE

Batch No.	Type	Sulphate content, mgm. H_2SO_4/100 gm.	Stability (minutes)	
			Untreated	Ca treated
56	Fiber	193	13.2	
"	"	228	11.8	
"	"	313	9.2	
52	"	805	8.5	
18	"	944	4.3	
29	"	1340	2.5(2.3, 2.7)*	
40	"	1468	2.0	3.0
28	"	2870	1.7(1.3, 2.1)	3.2
32	Pptd.	195	70.0 (71.0, 71.5, 68.0)	56.8 (56.8, 56.6, 57.0)
51	"	1080	38.4	
44	"	1661	5.0	

**Figures in brackets are duplicate determinations.*

untreated sample was six minutes. After ion exchange with calcium, the stability time was increased to 41 min.

Determination of Dry Weight

The poor stability of cellulose acetate sulphate precludes the use of a heated oven for drying the samples. The decomposition effected by heating resulted in a detectable odor of acetic acid in samples dried at 65°C. It was found that decomposition could be reduced to a minimum by vacuum drying at room temperature. The moisture determined by this method agreed within 1% with that obtained by drying at 40°C., 60°C., and over phosphorus pentoxide at room temperature. The acetyl content of the vacuum-dried material agreed within 1% with the value found on the damp sample. Unlike the product dried in excess of nine hours over phosphorus pentoxide, the vacuum-dried samples showed no change in color. Where possible, experiments were done with a damp sample. Two methods were used to obtain the dry weight. In the first method the dry weight was found by determining the moisture content of a portion of the sample and in the second, the sample was dried after the experiment.

DISCUSSION

The results reported above showed that sulphate content determined by titration of the hydrogen ion liberated by ion exchange with sodium or calcium chloride was always less than that determined gravimetrically as barium sulphate. In most cases the results obtained by estimation of calcium on the sample after ion exchange agreed with the gravimetric results within the limits of the experimental error, but it was found that those obtained by the determination of sodium were usually low and special precautions were essential during the washing of the sample to prevent removal of sodium. It was also demonstrated that treatment of the sample by boiling in alcohol, and the pH of the exchange medium, greatly affected the results. The equilibrium between the sodium and hydrogen ions is apparently quite critical and affected greatly by small changes in experimental technique. There was some evidence to suggest that adsorption of hydrogen ions by the sample was responsible for the low results obtained by the titration method and the results in Table IV show that, under certain conditions, calcium ions were adsorbed. Determination of calcium on the sample after ion exchange with calcium chloride solution gave the best results for the amount of sulphate present as RSO_4H.

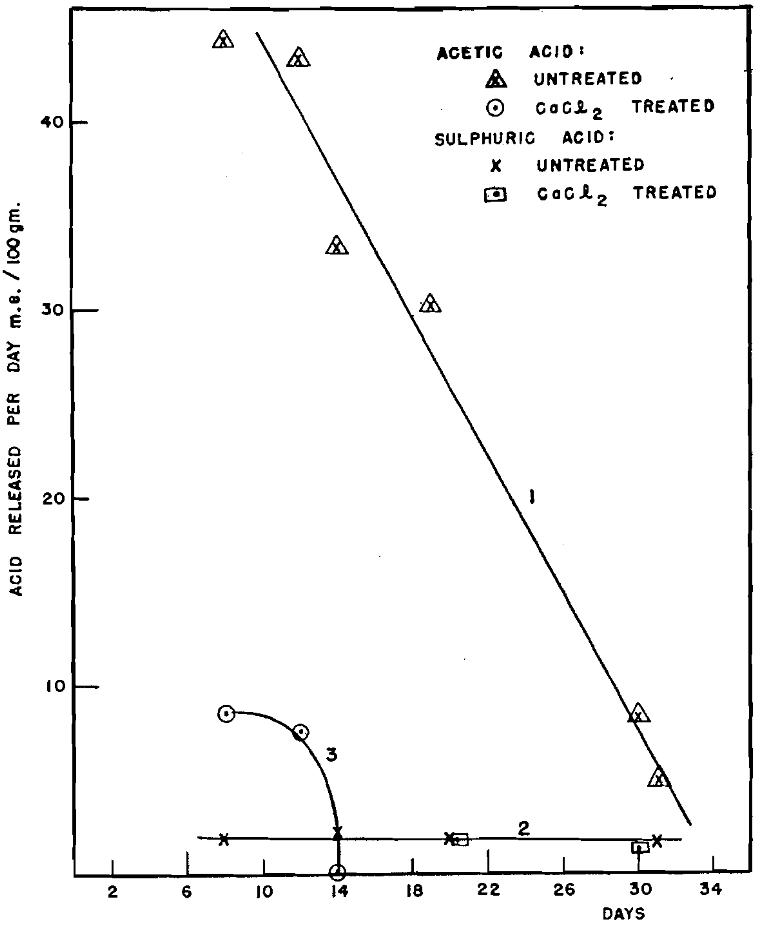

FIG. 3. Hydrolysis of cellulose acetate sulphate.

The greater stability of the calcium-treated fiber samples as determined by the stability test described was in agreement with the greater stability to hydrolysis of the treated material as shown below. Further work is required to determine the decreased stability of the precipitated sample after treatment with calcium chloride, and also to investigate the very large difference between the stability of the fiber and precipitated samples. The difference in physical form may be responsible for the latter effect.

Precision and Accuracy of the Methods

Hydrogen Ion

The amount of free acid in the sample was reduced to a minimum before an experiment by giving 2.5 gm. samples five-minute washes in 100 ml. of distilled water until the acidity was less than the equivalent of 0.80 ml. of 0.01 *N* sodium hydroxide. The rate of formation of acid by hydrolysis from a typical sample containing about 1.6% of sulphate is shown in Fig. 3 for a 30-day period. The amount of acetic acid released per day decreased rapidly while the amount of sulphuric acid decreased only slightly. Another sample was examined after ion exchange with 0.02 *N* calcium chloride. It can be seen that the amount of acetic acid formed was much less and reached zero after a few days, while the sulphate hydrolysis was not affected. The increased stability of the salt form of cellulose esters has been observed previously by Hoffpauir and Guthrie (8). All samples were normally stored in distilled water until required and then used within 4 to 14 days. It was shown that the amount of acid liberated by hydrolysis during an experiment could be regarded as negligible.

Sulphate

Known amounts of standard solution of sulphuric acid were added to samples of a batch of low sulphate content. The total sulphate was determined in triplicate and compared with the figure calculated from the known initial content and added amount. The results are shown in Table VII.

TABLE VII
PRECISION AND ACCURACY OF SULPHATE DETERMINATION IN CELLULOSE ACETATE

Initial sulphate found, mgm. of H_2SO_4	Sulphate added, mgm. of H_2SO_4	Total sulphate	
		Calc.	Found
5.03 ± .25	4.90	9.93	9.96 ∓ .20*
"	9.81	14.84	14.84 ∓ .43
"	14.71	19.74	19.65 ∓ .15
"	19.62	24.65	24.65 ∓ .15
"	24.53	29.55	29.59 ∓ .13

**The 95% confidence level.*

From the 95% confidence level calculated by the method of Dean and Dixon (2) from the triplicate determinations it can be seen that the average value was precise to better than 1% when the sulphate level was greater than 20 mgm. sulphuric acid, which is equivalent to 10.2 m.e./100 gm. It is concluded that the accuracy and precision of the method are better than 1% except for sulphate concentrations below 10 m.e./100 gm.

Calcium

Precision and accuracy were determined by adding known amounts of a standard calcium solution to samples of cellulose acetate sulphate. Determinations were made in triplicate and a correction made for the blank done on the original sample. The results are shown in Table VIII.

TABLE VIII
PRECISION AND ACCURACY OF THE CALCIUM DETERMINATION

Calcium added, mgm.	Calcium found, mgm.
10	9.91 ∓ 0.09
25	24.81 ∓ 0.10

The 95% confidence levels calculated by the method of Dean and Dixon (2) show that the precision was better than 1%, although both results were about 1% low.

EXPERIMENTAL METHODS

Materials

Cellulose

Two kinds of cellulose were used for acetylation:

(*a*) *Wood cellulose.*—B.C. rayon pulp having the following analysis: α-cellulose, 91.7%; ash, 0.07%; iron, 0.0002%. This cellulose was supplied by Canadian Industries Limited.

(*b*) *Cotton linters.*—High grade cotton linters were supplied by the Hercules Powder Company.

Acetone

The acetone, supplied by the Standard Chemical Company, was redistilled before use.

Cellulose Acetate Sulphate (*Solvent Process, Batch No. 21*)

Malm's method (10) was followed.

Cellulose (40 gm., 1 part) was added to acetic acid (96 gm., 2.4 parts) and stirred for one hour at 38°C. A mixture of acetic acid (160 gm., 4 parts) and sulphuric acid (0.352 gm.) was then added. Mixing was continued for 45 min. After cooling to 15°C. a mixture of acetic anhydride (108 gm., 2.7 parts) and sulphuric acid (2.45 gm.) was added. The temperature rose to 30°C. in an interval of two hours by which time the cellulose had dissolved. A drop of the dope when pressed between two microscope slides and examined with a magnifying glass showed only traces of fibers.

A mixture of acetic acid (80 gm., 2 parts) and water (80 gm., 2 parts) was added during a five minute period. After the aqueous acetic acid was added and thoroughly mixed, the dope was transferred to a hydrolysis bath at 35°C. After 24 hr., the dope was slowly poured into distilled water stirred at high speed in a Waring blendor.

The precipitated cellulose acetate sulphate had a moisture content of 92.7% after it had been washed with distilled water, sucked dry on a Buchner funnel, and pressed between filter paper. Analysis: apparent acetyl 32.2%; sulphate, 990 mgm. H_2SO_4/100 gm. The acetyl was determined by a standard method (6). The cellulose acetate sulphate was kept in a large volume of water until required.

Cellulose Acetate Sulphate (*Fibrous Process, Batch No. 28*)

The preparation is similar to U.S. Patent 2,143,332 (by Sindl and Frank (14)). Cellulose (80 gm., 1 part) was treated with 99.5 acetic acid (960 gm., 12 parts) for 12 hr. The excess of liquid was then removed by centrifuging until the weight of the mass was 2.4 parts (192 gm.)

Acetylation was effected by a mixture, preliminarily cooled to 5°C., consisting of benzene (704 gm., 8.8 parts), acetic acid (160 gm., 2.0 parts), acetic anhydride (240 gm., 3.0 parts), and sulphuric acid (12.8 gm., 0.16 parts). The temperature was allowed to rise gradually to 25°C. After 24 hr., the fibrous acetate was soluble in acetone and in a mixture of methylene chloride (9 parts) and alcohol (1 part).

The acetylation medium was removed by centrifuging. The product was washed twice with benzene, once with ethyl alcohol, and repeatedly with distilled water. Analysis: apparent acetyl, 38.5%; sulphate, 2876 mgm. H_2SO_4/100 gm. After ion exchange with calcium, the analysis (for calcium) showed 1.00 equivalent of acidity for each sulphate group.

Determination of Sulphate

The method used was a modification of that developed by Dunnicliff (5) for the determination of sulphate in nitrocellulose. While the method is long and tedious it is capable of good precision and accuracy. A sample of 2 to 3 gm. (dry weight) was weighed and transferred to a 400 ml. tall beaker. Concentrated nitric acid (25 ml.) was added so as to wet the sample thoroughly. The beaker was covered with a watch glass, and the contents boiled gently on a hot plate. When the evolution of brown fumes subsided, small portions of potassium chlorate were added periodically until the liquid became a pale yellow; a total of 1 gm. of potassium chlorate was usually adequate. The contents of the beaker were then evaporated to dryness and the beaker removed from the hot plate. Nitric acid (25 ml.) followed by potassium chlorate (about 0.5 gm.) was added and the contents again evaporated to dryness. If the residue was not then white in color, the process was repeated. Concentrated hydrochloric acid (25 ml.) was added to the beaker and the contents evaporated to dryness. To ensure the complete removal of nitric acid the process was repeated with another 25 ml. portion of hydrochloric acid. The residue was dissolved in water and filtered through fast filter paper. The filtrate and washings were diluted with water to 200 ml., 2 drops of concentrated hydrochloric acid added, and the mixture heated to boiling in a 200 ml. covered beaker. Ten per cent barium chloride solution (10 ml.) was added drop by drop with constant stirring. Boiling was continued for a few minutes and the beaker placed on top of an oven at 100°C. for six hours. The precipitate was collected in a tared porous-bottom porcelain crucible, heated in a muffle furnace at 800°C. for one hour, cooled in a desiccator, and reweighed.

Determination of Calcium

The method was similar to that developed by Schwarzenbach *et al.* (13) for the determination of water hardness and is based on the formation of a soluble chelate with ethylenediaminetetraacetic acid (EDTA) at a pH of 10, the end point being detected by the formation of a colored complex between EDTA, magnesium, and the azo dye eriochrome black. Organic material was first destroyed by digestion with nitric acid and potassium chlorate as described above, and the residue dissolved by warming with distilled water (200 ml.). When larger amounts of calcium sulphate were present, it was sometimes necessary to use a greater volume of water. The resulting solution was neutralized and then buffered by adding 30 ml. of a solution containing 67.5 gm. ammonium chloride and 570 ml. of concentrated ammonia in 1 liter. Eight drops of indicator solution (0.5 gm. of eriochrome black in 50 ml. of triethanolamine) were added and the solution titrated with a solution containing 9.5 gm. of the disodium salt of ethylenediaminetetraacetic acid, 0.1 gm. of anhydrous magnesium chloride, and 0.5 gm. of caustic soda to the liter. The EDTA solution was standardized against a calcium chloride solution containing exactly 1 mgm. of calcium per ml. The indicator solution was prepared by the method proposed by Diskant (3).

Determination of Sodium

A weighed sample (about 1 gm.) was transferred to a 125 ml. Erlenmeyer flask and digested with concentrated nitric acid (15 ml.) on a steam plate until a clear amber-colored solution was obtained. Concentrated sulphuric acid (1 ml.) was added and digestion continued until sulphur trioxide fumes were evolved. Concentrated nitric acid was added drop by drop until all carbonaceous matter had decomposed. The flask was removed from the hot plate, washed down with distilled water, and again heated until evolution of sulphur trioxide almost ceased. The solution was allowed to cool and was made up to 100 ml. Five milliliters of the solution was used for the sodium estimation in the Beckman Model DU Spectrophotometer with the Model 9200 flame attachment. The sodium content was first estimated from the standard curve for the instrument prepared over the range 0 to 200 parts per million of sodium from standard solutions of sodium which were prepared from a master solution containing 5012 parts per million of sodium. All standard solutions were stored in polythene bottles to prevent contamination. The sodium concentration was then determined more accurately by comparing the flame intensity with that of two standard solutions containing respectively slightly less and slightly more sodium and differing in sodium concentration from the unknown by not more than 15 parts per million. The exact sodium concentration was determined by interpolation using the formula:

$$x = A + \frac{(B - A)\,(I_x - I_A)}{(I_B - I_A)}$$

where x = concentration of sodium in the unknown,

A = concentration of sodium in the standard of lower concentration,
B = concentration of sodium in the standard of higher concentration,

I_A = flame intensity of A in transmission dial units,
I_B = flame intensity of B in transmission dial units,
I_x = flame intensity of x in transmission dial units.

The procedure used with the flame photometer was similar to that described in Beckman bulletin 259A. The instrument settings used were:

Selection switch	0.1
Wave length	589 mμ
Slit	0.10 mm.

The average of five separate transmission dial readings was taken when calculating the exact sodium content.

Hydrolysis of Cellulose Acetate Sulphate

A sample of about 15 gm. was shaken with 250 ml. of distilled water at room temperature and allowed to stand for 2 to 14 days depending on the time the original batch had been in contact with water without change. The water was removed and the sample washed, the filtrate and wash water being discarded. The sample was then treated with distilled water for 24 hr., filtered, and washed with three lots of 75 ml. of distilled water. The filtrate and the washings were made up to 500 ml. Sulphate was determined turbidometrically (11) and total acidity by titration with 0.01 *N* sodium hydroxide, using phenolphthalein as indicator. Acetic acid was calculated by difference.

Drying Samples and Determining Moisture Content

The material was dried at room temperature in an evacuated chamber through which a slow stream of dry air was continuously bled. The initial drying was effected by the use of a water aspirator which maintained a vacuum of about 20 mm. with an air flow of one bubble per second. After the removal of the bulk of the moisture, the water aspirator was replaced by a high vacuum pump and drying was continued until constant weight was attained. Several samples (20 gm. damp weight) could be dried in about 24 hr. The equipment consisted of a vacuum chamber (Cenco # 95056) fitted with a needle valve to control the rate of air admitted and with a vacuum gauge to determine the degree of evacuation. The air entering the chamber was dried by passage through an absorption bottle containing sulphuric acid and a drying tower of calcium chloride.

Stability Test

Air, dried and free of carbon dioxide, was passed over the dry sample (0.5 gm.) which was maintained at 65° ± 0.5°C. The volatile decomposition products were carried by the air into the indicator solution. The time lapse between the insertion of the sample and the appearance of the first blue in the indicator solution was recorded as the stability test time. The apparatus is shown in Fig. 4 and consisted of a constant-temperature block in which U-shaped sample tubes were located. The sample tube was connected by means of a ball joint to the indicator tube containing the indicator solution (1 ml.). The air passing over the sample was first passed through towers containing respectively calcium chloride and soda lime. The flow of air was

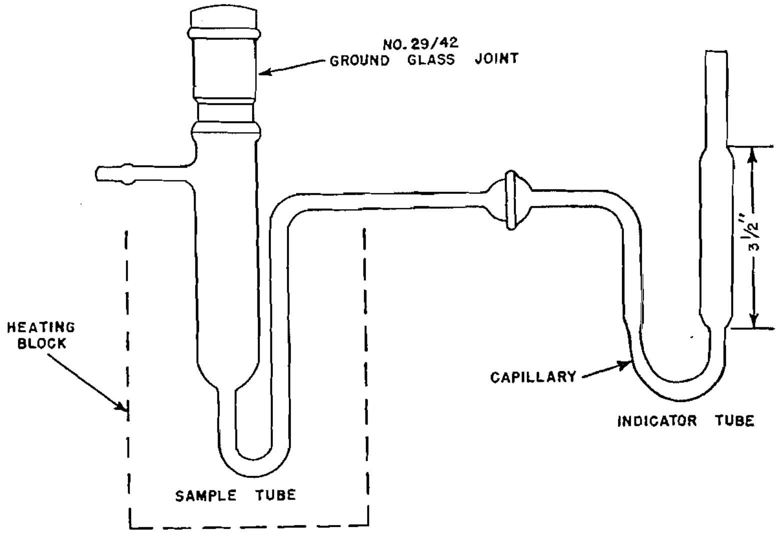

FIG. 4. Apparatus for stability test.

50 bubbles per minute. A sintered glass disk was placed in the line to smooth out the air flow.

The indicator solution contained 20 ml. of each of the following stock solutions: (1) potassium iodide solution (2 gm./100 ml.), (2) potassium iodate solution (1 gm./100 ml.), (3) sodium thiosulphate (0.001 *N*) and 10 drops starch solution (0.5%). The stock solutions were prepared from carbon-dioxide-free water. Ion-free water from a Barnstead Demineralizer was found convenient. Fresh indicator was prepared each day and kept in a brown bottle.

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EFFECT OF GELATIN ON THE CHANGES IN INITIAL CATHODE POLARIZATION DURING ELECTRODEPOSITION OF COPPER[1]

BY B. I. PARSONS[2] AND C. A. WINKLER

ABSTRACT

In the absence of addition agent, the cathode polarization during initial electrolysis of copper from a solution of acid copper sulphate rose almost instantaneously from zero to approximately the steady state polarization. When gelatin was present in the electrolyte, the polarization generally increased to a maximum, $P_{\max}$, (in time $t_{\max}$) then decreased to a minimum, $P_{\min}$, (in time $t_{\min}$) beyond which it increased to the steady state value, P_s. Generally, $P_{\max}$ increased to a steady value with an increase in the time, T_0, the electrode was in contact with the electrolyte before electrolysis was begun. At low, moderate, and high current densities respectively, $t_{\max}$ increased continuously, passed through a maximum, and decreased continuously with T_0. The behavior of $t_{\min}$ approximately paralleled that of $t_{\max}$. The polarization was linear in the logarithm of the current density; $t_{\max}$ and $t_{\min}$ decreased with increase in current density. The polarization values increased and $t_{\max}$ decreased, with increase in gelatin concentration. Increase of temperature had approximately the same effect as decrease in current density. With both chloride and gelatin present, $P_{\max}$ was practically independent of T_0 and chloride concentration, while $P_{\min}$ and P_s showed minimum values at about 2 mgm./l. chloride.

INTRODUCTION

Previous studies have shown that, during electrodeposition of copper in a Haring cell, the cathode polarization generally changes until a steady state value is reached (1, 2). This steady state polarization is increased when gelatin is present in the electrolyte (3). These observations, originally made in cells that permitted convection currents upward past the cathode face, have been substantiated in convection-free systems (7).

A cathode-ray oscillograph has now been used to study the effect of gelatin on the initial, rather than on the steady state polarization, under a variety of conditions. The experimental results obtained are recorded in the present paper.

EXPERIMENTAL

Experiments have been made in both a standard type (horizontal) Haring cell (1) and in the modified (vertical) cell in which convection currents are eliminated (6). Each type of cell contained 150 ml. of air-saturated electrolyte, and in each the apparent area of electrode surface immersed was 10 cm.^{2} Steady or slowly changing potentials were measured with a Leeds and Northrup type K2 potentiometer. The rapidly changing initial potentials were obtained with either a DuMont 304-H cathode-ray oscilloscope or a Brush BL932-BL201 recording oscillograph. The copper sulphate and sulphuric acid were reagent grade, the water was twice distilled, and the gelatin was U.S.P.

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grade. Gelatin solutions, prepared at room temperature, were used within 30 hr.

A standard surface was obtained on each cathode before it was used, by electrodeposition on it at 25°C. from a standard electrolyte (125 gm. $CuSO_4.5H_2O$ and 50 ml. conc. H_2SO_4 per liter of solution) at an apparent current density of 3 amp./dm.^{2} for 30 min., followed by 2 amp./dm.^{2} for one hour. The polarization at the end of this time was 110 ± 5 mv.

The cells and solutions were brought to the desired temperature in a suitable thermostat. The standard surface was laid down on the cathode in one cell, after which the electrode assembly was quickly transferred to another cell containing the electrolyte to be examined. The immersion time, T_0, is defined as the time the electrode was in contact with the electrolyte before current was passed. The cathode compartment of the Haring cell was connected to the oscillograph before the current was turned on. After the initial rapid changes of potential had been determined with the oscillograph, deposition was continued and the change of potential to the steady state followed with the potentiometer. The level of reproducibility in the various experiments to be discussed was generally the order ± 5%.

RESULTS

General Observations

When current was passed in the absence of addition agent the polarization increased almost instantaneously to about 100 mv., then changed more slowly

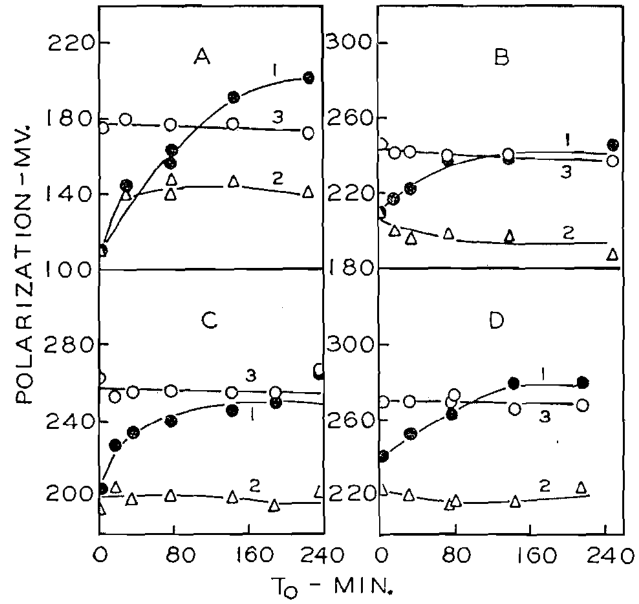

FIG. 1. Typical curves to show the effect of immersion time on P_{max}, P_{min}, and P_s, at different gelatin concentrations. Current density 2 amp/dm.^{2}; temperature 25°C. Curves 1—P_{max}, 2—P_{min}, 3—P_s.
A—1, B—10, C—25, D—100 mgm. gelatin/liter of standard electrolyte.

to the steady state value. However, when gelatin was present in the electrolyte, the polarization generally increased rapidly to a maximum, then decreased to a minimum, beyond which it again increased slowly to the steady state polarization characteristic of the gelatin concentration. For convenience the polarization maximum is designated as P_{max}, the minimum as P_{min}, the steady state polarization as P_s, the time required to attain P_{max} as t_{max}, and the time to attain P_{min} as t_{min}. The observations in the absence of addition agent were independent of T_0 but in the presence of gelatin there were changes in the initial polarization pattern as T_0 was altered.

The Effect of Gelatin

Changes were observed in the polarization pattern with changes in immersion time, gelatin concentration, current density, and temperature. The curves in Fig. 1 are typical for the changes in P_{max}, P_{min}, and P_s with T_0 at different gelatin concentrations. Relations of the same general type were obtained between these quantities when the current density and temperature were varied, although there were differences in matters of detail. For example,

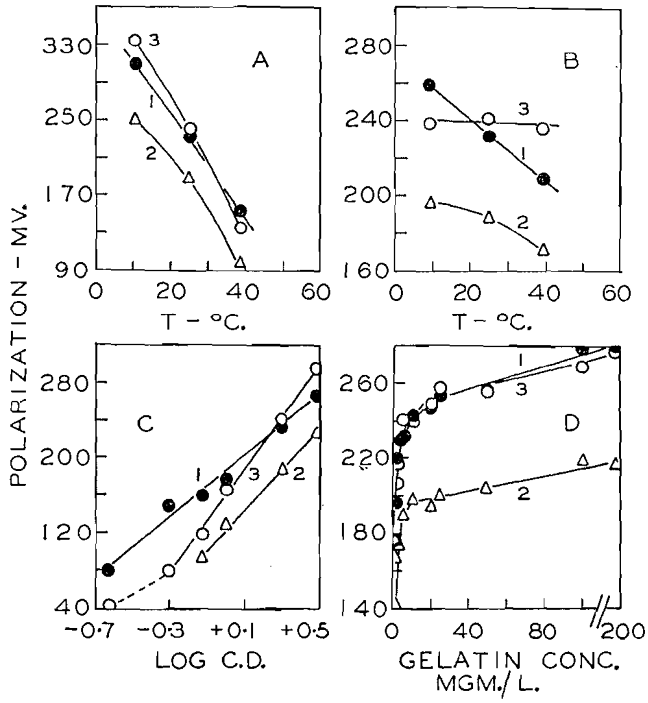

FIG. 2. Summary of the effect of temperature, current density, and gelatin concentration on P_{max}, P_{min}, and P_s. $T_0 >$ 75 min. Curves 1: P_{max}; 2: P_{min}; 3: P_s.
A. Immersion and deposition at temperature plotted.
B. Immersion at temperatures plotted, electrode then transferred to electrolyte at 25°C. and deposition begun at that temperature after 2 min.
For both A and B, gelatin concentration = 5 mgm./l., current density = 2 amp./dm.^{2}
C. Effect of current density. Temp. = 25°C., gelatin concentration = 5 mgm./l.
D. Effect of gelatin concentration. Temp. = 25°C., current density = 2 amp./dm.^{2}

the relative positions of the three curves were altered by suitable changes in current density and temperature, while at sufficiently low current densities (<0.5 amp./dm.^{2}) no minimum at all appeared in the potential-time curve. The influence of the various factors on the potential values may be summarized as in Fig. 2, for values of T_0 (generally >75 min.) where the potential values become practically constant.

The changes in t_{max} and t_{min} with T_0, at different gelatin concentrations, are shown in Fig. 3, as further indication of the reasonably systematic behavior of the initial polarization pattern with alteration of the conditions of electrolysis. The analogous curves at different current densities are shown in Fig. 4. Curves for the effect of temperature on t_{max} and t_{min} are not reproduced but the results may be briefly summarized. With immersion and deposition (2 amp./dm.^{2}, 5 mgm./l. gelatin) at 37°C., t_{max} passed through a maximum (*ca.* 6 sec.) at $T_0 = 80$ min., while t_{min} increased steadily from about 20 sec. at $T_0 = 15$ min. to 55 sec. at $T_0 = 180$ min. A maximum in t_{max} (at 2.5 sec.) was also observed at 25°C. when T_0 was about 80 min., while at this temperature t_{min} passed through a slight minimum (at 10 sec.) for $T_0 = 40$ min. and became essentially constant at 20 sec. for $T_0 > 120$ min. At 10.5°C., t_{max} was much decreased. Both t_{max} and t_{min} showed little change from the values 0.5 sec. and 9 sec. respectively with increase of T_0.

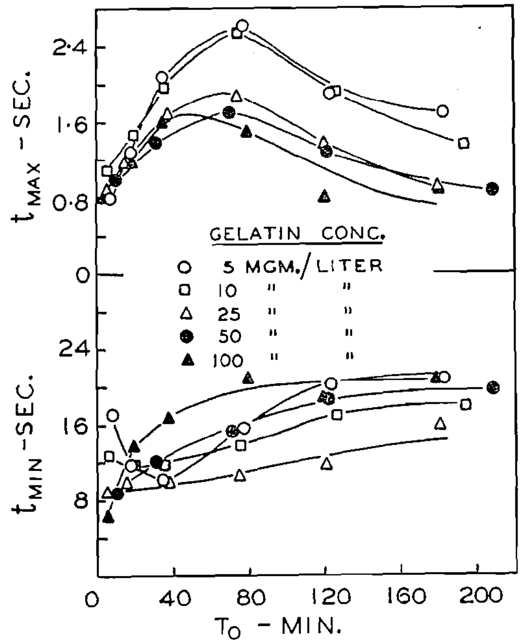

FIG. 3. Effect of immersion time on t_{max} and t_{min}, at different gelatin concentrations. Current density 1 amp./dm.^{2} Temp. 25°C.

Preliminary experiments showed that the absolute values of P_{max} and P_{min} depended upon the method of dissolving the gelatin. The value of P_{max} and P_{min} decreased with

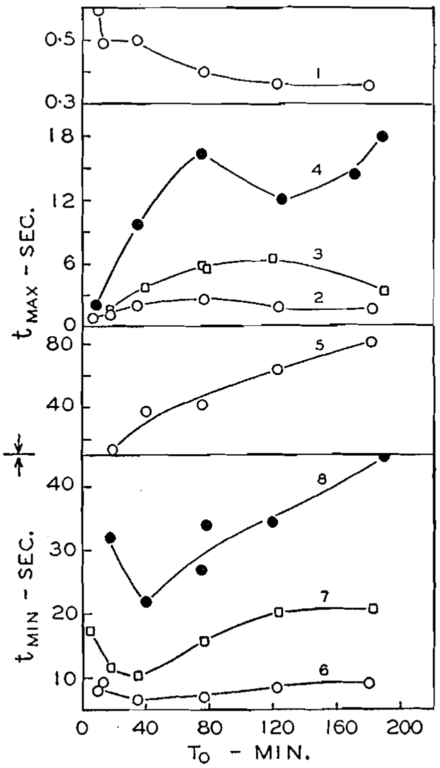

FIG. 4. Effect of current density on t_{max} and t_{min}. Gelatin conc. 5 mgm./l. Temp. 25°C.

CURVE NO.	CURRENT DENSITY (amp./dm.^{2})
1, 6	2
2, 7	1
3, 8	0.75
4	0.50 (No minimum observed)
5	0.25 (No minimum observed)

(*a*) an increase in the age of the electrolyte containing gelatin,

(*b*) an increase in the temperature at which the gelatin solution was prepared.

Extremes in either factor also lowered the steady state polarization.

The effect of molecular weight of the gelatin on the polarization pattern was studied in two ways. Fractionation of the stock gelatin by coacervation (5) gave two portions of molecular weights* 94,500 and 14,500, while average molecular weights ranging from 55,000 to 9,500 were obtained by degrading a 1% gelatin solution at 100°C. for various lengths of time. Except for small changes in the absolute potentials there was little alteration of the initial polarization pattern with a change in the molecular weight of the gelatin.

The effect of the cathode surface on the polarization pattern was also investigated with two types of surface other than the standard. One of these

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The molecular weight of the gelatin was determined by using the relation between the intrinsic viscosity and the molecular weight established by Pouradier and Venet (5) $N = 1.66 \times 10^{-5} M^{0.885}$.

was the base metal of the copper stock after it had been etched in 50% nitric acid. The other was the base metal ground with 120 mesh emery powder. The ground surface was allowed to stand in standard electrolyte for several hours before the experiment was begun.

Whereas with the standard deposited surface the build-up in potential to P_{max} could actually be observed, the polarization at the etched surface in the presence of gelatin showed only a rapid decrease to P_{min} from some higher value, followed by a slow increase to P_s. The initial high value of the potential increased with T_0 in a manner similar to that observed for P_{max} on a deposited surface. Experiments in the absence of gelatin showed no such potential pattern. At 2 amp./dm.^{2} and 25°C. the initial potential observed was approximately 65 mv. and this increased to a P_s value of 100 mv.

The immersion time for the ground surface was varied from 9 to 850 min. At 2 amp./dm.^{2} and 25°C. the polarization in the absence of addition agent rose instantaneously to about 60 mv., then continued to rise slowly towards P_s. The initial polarization pattern observed in the presence of gelatin was exactly the same as that observed in its absence.

To determine whether the observations recorded above were in any way peculiar to the Haring Cell, polarization measurements on a standard surface were made with a probe assembly at 25°C. and 2 amps./dm.^{2} The results paralleled those obtained in the Haring cell, both in the presence and absence of gelatin.

Stirring the electrolyte in the cathode compartment during T_0 exaggerated the deviations of the experimental points from a smooth curve, but the difference between P_{max} and P_{min} still increased as T_0 was increased.

For the experiments in the absence of convection, it was not convenient to prepare the cathode surface by deposition in a separate cell, as in the previous experiments. The same electrode and electrolyte were therefore used throughout and the standard surface was the deposited surface of the previous experiment.

Initially the cathode was etched with 50% nitric acid, rinsed, and placed at the top of the cell. Current was passed until the measured polarization indicated that hydrogen was being evolved. The flow of current was then stopped and the electrolyte mixed by tipping and turning the cell. The immersion time was measured from this time of mixing.

The initial polarization pattern observed in the presence of gelatin with the vertical cell at 0.5 amp./dm.^{2} was similar to the pattern observed with the horizontal cell at 2 amp./dm.^{2} The polarization rose to P_{max}, fell to P_{min}, then slowly increased until hydrogen evolution occurred. An increase of the current density to 2 amp./dm.^{2} in the vertical cell did not change the polarization pattern.

The Effect of Chloride and Gelatin

The steady state polarization measured in an electrolyte containing gelatin is lowered considerably by the addition of a small amount of chloride ion (4). As the amount of chloride is further increased, the polarization again increases. It was obviously of interest to determine whether this behavior might be reflected in the initial polarization values.

The effect of chloride on the initial polarization pattern in the absence of gelatin and in the presence of gelatin is shown in Fig. 5. The chloride ion was introduced into the standard electrolyte from a concentrated sodium chloride stock solution. The effect of the immersion time on the initial polarization pattern in electrolytes containing both gelatin and chloride was determined in two series of experiments. In the first the prepared cathode was transferred, in the usual way, to the Haring cell containing the electrolyte to be examined. After the specified immersion period the current was turned on and the initial polarization recorded. In the second series the cathode was immersed for 75–80 min. in electrolyte containing 25 mgm./l. gelatin, then transferred to the test cell containing gelatin and chloride for further immersion, T_0, before deposition was begun.

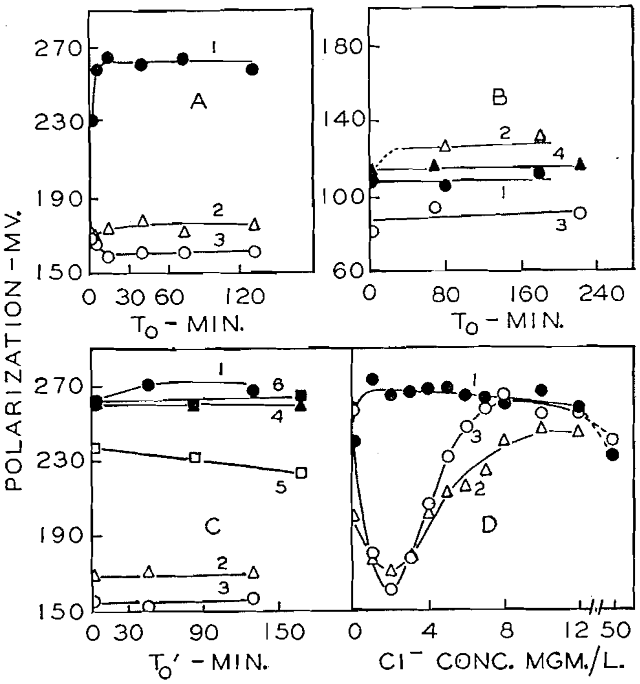

FIG. 5. The effect of chloride on the initial polarization pattern. Current density 2 amp./dm.^{2} Temp. 25°C.

Parts A, C, and D.— Curves 1, 4: $P_{\max}$; 2, 5: $P_{\min}$; 3, 6: P_s.

Part B.—Curves 1, 3: first recorded polarization; 2, 4: P_s.

A. The effect of the immersion time on the polarization pattern. Gelatin concentration: 25 mgm./l. Chloride ion concentration: 2 mgm./l.

B. The effect of chloride in the absence of gelatin. Curves 1, 2: 2 mgm./l. chloride; 3, 4: 10 mgm./l. chloride.

C. The effect of immersion in electrolyte containing 25 mgm./l. gelatin for 75–80 min., then immersion in electrolyte containing both gelatin and chloride for the specified period of time. Curves 1, 2, 3: 2 mgm./l. chloride; 4, 5, 6: 10 mgm./l. chloride.

D. The effect of chloride concentration on the initial polarization pattern. Gelatin concentration: 25 mgm./l. Immersion time: 75–80 min.

While the addition of chloride to electrolyte containing gelatin had a profound effect on the P_{max}–T_0 relation, the most interesting feature of the results is perhaps that, at long immersion times, P_{max} was virtually uninfluenced by chloride ion concentration, whereas both P_{min} and P_s passed through minima corresponding to that observed for P_s in the earlier studies (4).

ANODE POLARIZATION

The polarization pattern at the anode was also observed to reflect the presence of gelatin in the electrolyte.

The standard surface chosen for the anode was the base metal of the copper stock. Initially, the anode was brought to red heat in an oxygen flame, then etched deeply with 50% nitric acid. The final surface was prepared by anodic solution into the electrolyte containing gelatin at 25°C. and 2 amp./dm.^{2} Experiments were made in succession upon the same electrode.

The polarization pattern observed with gelatin-free electrolyte was similar to that obtained in the cathode compartment. The anode polarization at 25°C. and 2 amp./dm.^{2} was observed to rise from zero to approximately 35 mv. within 0.02 sec., and to remain at approximately this value as solution of the anode continued. The immersion time had no effect on the measured quantities.

When the electrolyte contained gelatin the initial anode polarization decreased from a very high value to an essentially steady state value within 0.25 sec. The magnitude of the first polarization value it was possible to record increased with immersion time, from 68 mv. at $T_0 = 2$ min. to 100 mv. at $T_0 = 20$ min., and then remained practically constant with further increase of T_0. The steady state anode polarization showed a slight increase from 50 mv. at $T_0 = 2$ min. to 56 mv. at $T_0 = 10$ min., at which value it remained constant with further increase of T_0.

DISCUSSION

The results of the present study demonstrate a sensitive and reasonably systematic behavior of the initial polarization pattern with changes in conditions of electrodeposition in the presence of gelatin. Preliminary work with other addition agents has indicated that gelatin is not unique in modifying the changes in initial polarization and that the changes observed with different addition agents are of various types. It may be expected, therefore, that further studies of such patterns should be useful in interpreting the action of addition agents generally.

The dependence of P_{max} and t_{max} on T_0 serves to emphasize the processes that occur when the cathode is immersed in the acid electrolyte containing gelatin, and before current is passed. These processes are presumably corrosion and adsorption, and it seems reasonable to suppose that after sufficiently long immersion times, a steady state is attained in respect of these two processes. While adsorption of gelatin, as such, probably occurs, the formation of complexes with cupric and cuprous ions formed during the corrosion process, and their subsequent adsorption might also be important. It is hoped that some indication of the part played by copper ion – gelatin complex formation might be obtained from a study with simple amino acids, now in progress in this laboratory.

It is not proposed to attempt a detailed explanation of the results obtained in the present study, since an unequivocal interpretation has yet to be found for the mere existence of the observed maxima and minima in the polarization–time curves. Even a tentative explanation of these seems to require that, since $P_{\max}$ depends upon T_0, it depends upon the extent to which the electrode surface is covered with gelatin (or copper–gelatin complex), and that this, in turn, is related to the extent that gelatin is depleted in the vicinity of the cathode when deposition is begun. Thus, for relatively large extent of uncovered surface, corresponding to relatively small values of T_0, the supply of gelatin adjacent to the cathode might be considerably depleted when the current is switched on, while the reverse argument would apply for larger T_0 values.

The mechanism by which gelatin might suffer such depletion is not known. It could conceivably involve complex formation with cuprous ions at the cathode surface, or it might be due merely to adsorption on uncovered or newly deposited copper surface, perhaps accentuated by the negative charge on the cathode. Replenishment of gelatin at the cathode–electrolyte interface would be mainly by convection, and should have little influence on the polarization pattern during the initial changes. Eventually, of course, a steady state should be established between the rates at which gelatin is brought up to, and used up at the cathode.

On the basis of the preceding ideas, serious depletion of gelatin might be expected in the immediate neighborhood of a freshly prepared cathode, with its relatively large amount of uncovered surface, when it is immersed in electrolyte containing gelatin and the current turned on after a short interval, i.e. small T_0 value. Hence, the initial rise of potential due to the action of the addition agent should be followed by a tendency for the potential to decrease as deposition is continued in an environment impoverished of gelatin. Accordingly, a maximum in the potential–time curve might be expected. Obviously, the more the electrode is covered with addition agent before the current is turned on, i.e. the larger the T_0 value, the less initial depletion of gelatin there should be at the cathode–solution interface. Hence, with increase of T_0 the values of both $P_{\max}$ and $t_{\max}$ should tend to increase, since the initial potential increase should continue longer and to higher values before depletion of gelatin at the newly deposited surface reverses the trend. This type of behavior was observed at low current densities, but an optimum or slight decrease in $t_{\max}$ with increased T_0 was observed at higher current densities. It is possible, however, that the different relations between $t_{\max}$ and T_0 at different current densities simply reflect the different ways in which gelatin depletion is related to the extent of uncovered surface after T_0 and to deposition of new surface. As indicated previously, larger values of T_0 should correspond to less depletion, hence larger $t_{\max}$, while higher current densities, with concomitant higher rates of deposition of new surface, might correspond to more rapid depletion, hence smaller $t_{\max}$. Appropriate combinations of T_0 and current density conditions might permit the observed range of $t_{\max}$–T_0 relations.

The existence of $P_{\min}$, following $P_{\max}$, can also be accounted for, since gradual establishment of convection past the cathode face should increasingly replenish the gelatin supply and cause a gradual increase of potential again, until the steady state is reached.

The tentative interpretation given above is limited to a few outstanding features of the present results. Its extension to other observations made during the study might be offered, but before this is done it would seem that an attempt should be made to get experimental verification of the ideas involved, particularly with other addition agents.

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A NOTE ON THE USE OF INDIUM FOR REMOVAL OF MERCURY VAPOR IN VACUUM SYSTEMS[1]

By R. D. Heyding and E. A. Flood

ABSTRACT

It is shown that metallic indium adsorbs mercury vapor quite rapidly after a short induction period. It is suggested that indium may be found useful in removing traces of mercury vapor from vacuum systems.

In vacuum systems requiring low mercury vapor concentrations, the conventional liquid-air cooled trap between the system and sources of mercury vapor is often replaced by a trap containing a mercury vapor 'getter', e.g., metallic sodium, gold, or cadmium. Similarly, gold and brass are extensively used in traps into which vapors are condensed, prior to distillation into a weighing vessel, to minimize the transport of mercury into the weighing vessel.

During the course of another investigation, we observed that metallic indium has a considerable affinity for mercury vapor, and we have subsequently made a cursory study of the relative rates of absorption of mercury vapor by several metallic foils.

Small foils of gold, indium, and aluminum (all 99.95% pure) and brass (67% Cu, 33% Zn) were prepared by rubbing with fine emery paper and washing with alcoholic potassium hydroxide and water. The grade of emery paper employed appeared to have little effect on the absorption of mercury vapor when expressed in milligrams per planar square centimeter. The foils were suspended individually on a quartz spiral about 10 cm. above a pool of mercury, and the increase in weight *in vacuo* observed, using a cathetometer in the usual manner. While such an apparatus will not register the absorption of the first few molecular layers, increments of 0.1 mgm. $cm.^{-2}$ could be detected.

At room temperature (25°C.), the absorption of mercury vapor by brass and aluminum foils in 100 hr. was negligible. Indium was found to absorb more readily than gold; this was particularly evident at higher 'surface concentrations'.

Rates of absorption, mgm. $cm.^{-2}hr.^{-1}$

	Surface Concentrations		
	Ca. zero	*Ca.* 5 mgm.$cm.^{-2}$	*Ca.* 8 mgm.$cm.^{-2}$
Gold	0.4	0.02	—
Indium	5.0	2.0	0.6

Spicer and Banick (1) have recently shown that indium amalgams containing 18 to 42% mercury have a liquidus as well as a solidus phase. The

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formation of this liquidus phase on absorption of mercury vapor led to perforation of the foil and, of course, disintegration if the absorption was allowed to proceed. We have prepared a more rigid 'getter' by electrodeposition of indium from the sulphate on fine brass gauze at high current densities. The rate of absorption of mercury vapor by the gauze was comparable to that by the foil, and the droplets of amalgam were retained by the brass.

Unlike gold, indium foil, regardless of preparation, required four to five hours *in vacuo* before absorption began unless some procedure was employed to make an initial deposition of mercury on the surface. Admission of air to the system during absorption imposed a similar induction period before absorption was resumed. Since admission of water vapor or nitrogen to the system did not give this effect, it is attributed to the formation of an oxide film over the foil.

The value of indium as a mercury 'getter' will be a function of the mercury vapor pressure of the amalgams formed on absorption. We have attempted to measure the vapor pressures of amalgams containing less than eighteen per cent mercury (i.e., solidus phase only) by the effusion method, and have found these to be less than 5×10^{-7} mm. Hg, i.e., probably less than a thousandth of that of mercury vapor at room temperature (25°C.). The rate of desorption of mercury from indium foil by a liquid-air cooled trap was found to be less than 0.008 mgm. $\text{cm.}^{-2}\ \text{hr}^{-1}$.

Thus one would expect that under most of the ordinary laboratory conditions indium should be better than gold for removing traces of mercury vapor from vacuum systems. The relatively low cost of indium and the ease with which it can be molded into various shapes, electrodeposited, etc., are also to be borne in mind. It may be remarked that indium adheres tenaciously to glass and consequently castings cannot be removed from glass tubes unless the tubes were previously well oiled.

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THE REACTIONS OF METHYL AND ETHYL RADICALS WITH DIETHYL KETONE[1]

BY P. AUSLOOS[2] AND E. W. R. STEACIE

ABSTRACT

The hydrogen-abstraction reactions of methyl and ethyl radicals from diethyl ketone have been studied in the temperature range 25 to 160°C. Azomethane and azoethane were used as photochemical sources of methyl and ethyl radicals. The activation energies found were 7.0 and 7.6 kcal., respectively, for the reactions:

$$CH_3 + C_2H_5COC_2H_5 \rightarrow CH_4 + C_2H_4COC_2H_5 \qquad [1]$$
$$C_2H_5 + C_2H_5COC_2H_5 \rightarrow C_2H_6 + C_2H_4COC_2H_5. \qquad [2]$$

If the combination of both methyl and ethyl radicals is assumed to occur at every collision, the steric factors for the two reactions are $E_1 = 7.4 \times 10^{-4}$, $E_2 = 7.1 \times 10^{-4}$.

INTRODUCTION

Studies of the photolysis of azomethane (2) and of azoethane (1) have shown that these compounds may be used as sources of methyl and ethyl radicals for the investigation of hydrogen-abstraction reactions of the type:

$$CH_3 + RH \rightarrow CH_4 + R \qquad [3]$$

and

$$C_2H_5 + RH \rightarrow C_2H_6 + R. \qquad [4]$$

One advantage of the use of azo-compounds in this way is that they may be photolyzed by light of wave length greater than 3400 Å, where ketones and most other organic compounds are transparent. Azo-compounds may therefore be photolyzed in their presence without complications due to the simultaneous photolysis of the substances under investigation.

It appeared to be of interest to investigate the reaction of methyl and ethyl radicals with diethyl ketone. In the first place this serves as a check on the values found for the reaction

$$C_2H_5 + C_2H_5COC_2H_5 \rightarrow C_2H_6 + C_2H_4COC_2H_5 \qquad [2]$$

in the photolysis of diethyl ketone itself (3), and in addition it gives an opportunity to investigate the effect of substituting methyl for ethyl radicals, and thus comparing the rates of reactions [3] and [4] for the same substance, RH.

EXPERIMENTAL

Azomethane and azoethane were prepared by Dr. Leitch of this laboratory (4). Diethyl ketone was obtained from Eastman Kodak Co. All compounds were distilled *in vacuo* before use.

The light source was a Hanovia S500 medium pressure mercury arc. The apparatus was essentially similar to that used in previous papers from this laboratory. The fused quartz reaction vessel was a cylinder, approximately

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[2] *National Research Council of Canada Postdoctorate Fellow, 1952–54.*

5 cm. diameter and 10 cm. long. It was completely filled by a parallel light beam. Two types of filter were used to limit the incident radiation to longer wave lengths:

(*a*) A Corning violet ultra No. 7-37, or 586, 6 mm. in thickness, which was opaque at wave lengths below 3150 Å.

(*b*) A Corning filter No. 0-52, or 738, opaque at wave lengths below 3400 Å.

The analytical section of the apparatus was the same as that described elsewhere (1). The $N_2 - CH_4$ fraction was removed at − 195°C., and the $C_2H_6 - C_2H_4$ fraction at − 170°C. Repeated cooling and heating was necessary to separate butane from azoethane at − 125°C. The $N_2 - CH_4$ and $C_2H_6 - C_2H_4$ fractions were analyzed with a mass spectrometer. To avoid complications due to secondary reactions the amount of conversion of azoethane was always kept below five per cent.

RESULTS AND DISCUSSION

(*A*) *The Reaction of Methyl Radicals with Diethyl Ketone*

When azomethane is photolyzed in the presence of diethyl ketone, the following steps in the mechanisms of their respective decompositions have to be taken into account

$$CH_3N_2CH_3 + h\nu \rightarrow 2CH_3 + N_2 \qquad [5]$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [6]$$

$$CH_3 + CH_3N_2CH_3 \rightarrow CH_4 + CH_2N_2CH_3 \qquad [7]$$

$$CH_3 + C_2H_5COC_2H_5 \rightarrow CH_4 + C_2H_4COC_2H_5 \qquad [1]$$

$$C_2H_4COC_2H_5 \rightarrow C_2H_4 + CO + C_2H_5. \qquad [8]$$

If reaction [8] is omitted, a steady-state treatment gives:

$$k_1/k_6^{\frac{1}{2}} = (R_{CH_4}/R^{\frac{1}{2}}_{C_2H_6} - k_7/k_6^{\frac{1}{2}}[CH_3N_2CH_3])/[C_2H_5COC_2H_5].$$

Reaction [8] does not seem to occur to any appreciable extent in the temperature range 25 – 150°C., especially at the rather high intensities used in this work. This was confirmed by the fact that at 150°C. no measurable amount of CO_2 could be detected in the N_2 fraction after it had been passed over hot cuprous oxide. Also, less than one per cent of C_2H_4 was present in the $C_2H_6 - C_2H_4$ fraction.

The values of $k_7/k_6^{\frac{1}{2}}$ which are required in the calculations have been taken from an experimental Arrhenius plot for azomethane alone. For runs with three different samples of azomethane no curvature in the plot could be found in the low temperature region, contrary to previous work (2). The best line through the points was

$$k_7/k_6^{\frac{1}{2}} = 8.5 \times 10^{-9}\, e^{-7300/RT} \text{ cm.}^{3/2} \text{ molecule}^{-\frac{1}{2}} \text{ sec.}^{-\frac{1}{2}}$$

The results for $k_1/k_6^{\frac{1}{2}}$ are given in Table I. In Fig. 1, log $k_1/k_6^{\frac{1}{2}}$ is plotted against $1/T$. An activation energy of 7.0 ± 0.1 kcal. for reaction [4] is obtained from the slope of the curve, if the activation energy for the recombination of two methyl radicals is assumed to be zero. There is again no curvature in this plot at low temperatures. The cause of curvature in such plots will be

TABLE I
REACTION OF METHYL RADICALS WITH DIETHYL KETONE

Temp., °K.	Pressure, cm.		$R_{CH_4} \times 10^4$, cc./min.	$R_{C_2H_6} \times 10^4$, cc./min.	$k_1/k_6^{\frac{1}{2}} \times 10^{13}$, cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$
	Azomethane	Diethyl ketone			
Filter 586					
299	5	1.6	1.98	26.8	2.45
301	4.07	1.5	1.54	20.1	2.4
313	2.85	1.93	1.19	4.67	3.69
315	1.4	1.16	0.56	3.22	3.74
326	3.97	1.45	3.38	16	6.5
330	3.46	1.89	3.62	12	7.25
331	2.16	1.73	1.61	3.7	6.9
354	2.18	2.06	2.55	1.5	15
361	3.78	1.67	6.21	8.55	16.6
407	4.11	1.5	11.06	3.64	56
Filter 738					
370	3.06	1.86	7.39	5.93	23.1
387	2.96	2.42	10.35	4.23	34.7
406	3.24	1.87	10.29	2.59	55.8

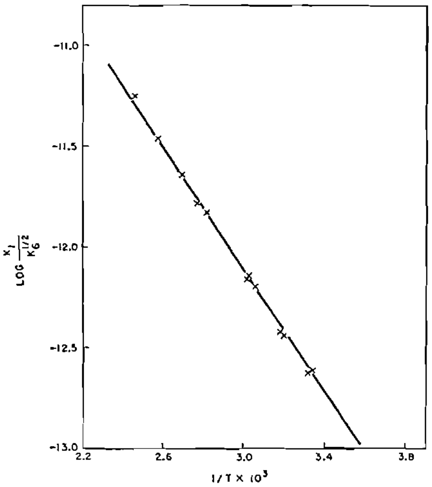

FIG. 1. Arrhenius plot for the reaction of methyl radicals with diethyl ketone.

discussed in a further paper. If the diameters of a methyl radical and a diethyl ketone molecule are assumed to 3.5 and 6.0 Å respectively, a value of 7.4×10^{-4} is obtained for the ratio of the steric factors $P_1/P_6^{\frac{1}{2}}$. Or, assuming $P_6 = 1$, $P_1 = 7.4 \times 10^{-4}$.

(*B*) *The Reaction of Ethyl Radicals with Diethyl Ketone*

The reaction mechanism for the photolysis of azoethane in the presence of diethyl ketone is presumably:

$$C_2H_5N_2C_2H_5 + h\nu \rightarrow 2\,C_2H_5 + N_2 \qquad [9]$$

$$2\,C_2H_5 \rightarrow C_4H_{10} \qquad [10]$$

$$2\,C_2H_5 \rightarrow C_2H_4 + C_2H_6 \qquad [11]$$

$$C_2H_5 + C_2H_5N_2C_2H_5 \rightarrow C_2H_6 + C_2H_4N_2C_2H_5 \qquad [12]$$

$$C_2H_5 + C_2H_5COC_2H_5 \rightarrow C_2H_6 + C_2H_4COC_2H_5 \qquad [2]$$

$$C_2H_4N_2C_2H_5 \rightarrow C_2H_4 + N_2 + C_2H_5 \qquad [13]$$

$$C_2H_4COC_2H_5 \rightarrow C_2H_4 + CO + C_2H_5. \qquad [8]$$

Reaction [8] may again be neglected in the temperature range used here. Reaction [13] can also be ignored since it will only slightly affect the kinetics. (For a discussion of the analogous case in the photolysis of diethyl ketone see (5).)

A steady-state treatment of reactions [9] – [12] and [2] gives

$$\frac{k_2}{k_{10}^{\frac{1}{2}}} = \frac{R_{C_2H_6} - R_{C_2H_4}}{R^{\frac{1}{2}}_{C_4H_{10}}[C_2H_5COC_2H_5]} - \frac{k_{12}[C_2H_5N_2C_2H_5]}{k_{10}^{\frac{1}{2}}[C_2H_5COC_2H_5]}$$

The values of $k_{12}/k_{10}^{\frac{1}{2}}$ were taken from the experimental Arrhenius plot for azoethane (2). The results are given in Table II, and in Fig. 2, log $k_2/k_{10}^{\frac{1}{2}}$ is plotted against $1/T$. From the slope of the curve in Fig. 2 an activation energy of 7.6 kcal. is obtained. If E_{10} is assumed to be zero, the experimental

TABLE II

REACTION OF ETHYL RADICALS WITH DIETHYL KETONE

Temp., °K.	Pressure, cm.		Rate, cc./min. 10^4			$k_2/k_{10}^{\frac{1}{2}} \times 10^{13}$, cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$
	$C_2H_5N_2C_2H_5$	$C_2H_5COC_2H_5$	C_2H_4	C_2H_6	C_4H_{10}	
322	4.2	2.15	1.225	3.2	8.95	1.79
347	3.6	2.11	1.345	5.21	7.77	3.84
372	3.85	2.05	1.52	7.5	8.78	8.1
397	3.6	2.1	0.627	7.54	3.5	16.2
398	8.1	2.0	1.95	21.6	9.3	14.4
431	3.2	2.3	1.35	18.8	6.3	33.2
431	4.03	2.22	1.64	22.5	7.1	33.2

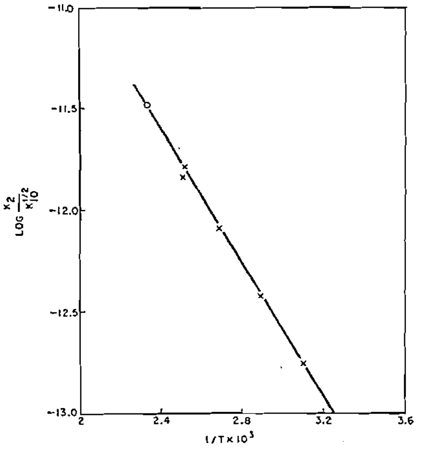

FIG. 2. Arrhenius plot for the reaction of ethyl radicals with diethyl ketone.

value corresponds to E_2. This value is in close agreement with the values found by Kutschke (7.3 kcal.) and Wijnen (7.5 kcal.) in the direct photolysis of diethyl ketone (3). From the experimental value of E_2, the steric factor ratio $P_2/P_{10}^{\frac{1}{2}}$ is calculated to be 7.1×10^{-4}. There is not much direct information about P_{10}, but it is probably not far from unity. Hence $P_2 \approx 7.1 \times 10^{-4}$.

If the results for the two reactions are compared, we have

		E	*P*
(1)	$CH_3 + C_2H_5COC_2H_5$	7.0 kcal.	7.4×10^{-4}
(2)	$C_2H_5 + C_2H_5COC_2H_5$	7.6 kcal.	7.1×10^{-4}.

The steric factors are thus virtually identical, on the assumption that the recombination of methyl and ethyl radicals both occur with the same efficiency. Since the C–H bond is about 4 kcal. stronger in CH_4 than in C_2H_6, reaction [1] is about 4 kcal. more exothermic than reaction [2]. It would therefore be expected that $E_1 < E_2$. The difference found (0.6 kcal.) is, however, rather smaller than might have been expected.

ACKNOWLEDGMENT

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DERIVATIVES OF CHLOROBENZENE-2,4-DISULPHONIC ACID[1]

BY MARSHALL KULKA

ABSTRACT

Chlorobenzene-2,4-disulphonates (II), -disulphones (IV), and -disulphonamides (V) have been prepared from chlorobenzene-2,4-disulphonyl chloride (I). The properties and reactions of I–V have been compared with those of related derivatives of *p*-chlorobenzenesulphonic acid and phenoxybenzene-4,4′-disulphonic acid.

Recent investigations have shown that *p*-chlorophenyl (5) and *β*-chloroethyl *p*-chlorobenzenesulphonates (3) are toxic to insects. In a further search for insecticides, it was decided to prepare for testing derivatives of chlorobenzene-2,4-disulphonic acid. This report of the investigation describes the preparation of II–V from chlorobenzene-2,4-disulphonyl chloride (I) (10); and compares the properties and reactions of I–V with those of related derivatives of *p*-chlorobenzenesulphonic acid (6) and phenoxybenzene-4,4′-disulphonic acid (12). Information regarding the insecticidal activity of these compounds is provided by another communication (8).

Chlorobenzene-2,4-disulphonyl chloride (I) is not affected by chlorine at 160°. This is contrary to the behavior of *p*-chlorobenzenesulphonyl chloride which is converted to *p*-dichlorobenzene under similar conditions (6). The disulphonyl chloride (I) reacts normally with alcohols and phenols to form II when in the presence of sodium hydroxide but only in poor yields or not at all when organic base is used. Thus the reaction products of I, ethylene chlorohydrin, and pyridine were ethylene dichloride and chlorobenzene-2,4-disulphonic acid. Esters of chlorobenzene-2,4-disulphonic acid and allyl alcohol, 1,1,1-trichloro-3-nitro-2-propanol, and 1,1,1-trichloro-2-methyl-2-propanol could not be obtained under any conditions.

Unlike *p*-chlorobenzenesulphinic acid and phenoxybenzene-4,4′-disulphinic acid, chlorobenzene-2,4-disulphinic acid (III) is very soluble in water and liberates sulphur dioxide rapidly when warmed in dilute mineral acid solution. However the sodium salt of III is sufficiently stable to form chlorobenzene-2,4-disulphones (IV) with reactive halogen compounds. *p*-Chlorobenzenesulphinic acid and phenoxybenzene-4,4′-disulphinic acid react readily with aqueous formaldehyde as does *p*-toluenesulphinic acid (2) to form the corresponding hydroxymethyl aryl sulphones but no IV ($R = CH_2OH$) could be isolated from an aqueous solution of III and formaldehyde. Although *p*-chloro- and *p*-nitrobenzenesulphonyl chlorides undergo the Friedel-Crafts reaction with methoxybenzenes to form diaryl sulphones (1) along with other products, diaryl chlorobenzene-2,4-disulphones (IV, R = aryl) could not be prepared from I and anisole, veratrole, and *m*-dimethoxybenzene using zinc chloride as the condensing agent.

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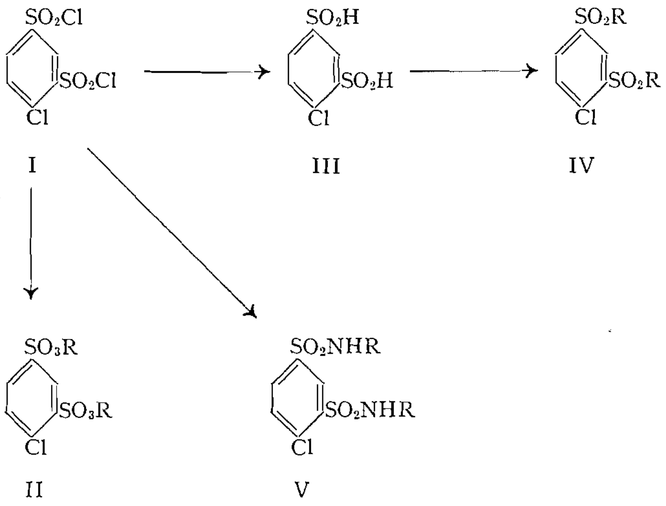
Contribution from the Dominion Rubber Company Limited Research Laboratories, Guelph, Ontario.



No difficulty was experienced in the preparation of chlorobenzene-2,4-disulphonamides (V) from I and excess amine. It must be cautioned that 1,N,N,N′,N′-pentachlorobenzene-2,4-disulphonamide, which was obtained from chlorobenzene-2,4-disulphonamide (V, R = H) (9) and chlorine, is extremely reactive. A solution of the N,N,N′,N′-tetrachloro-V (R = H) in xylene when warmed on the steam bath resulted in a violent explosion.

Aqueous hydrazine can react with chlorobenzene-2,4-disulphonyl chloride (I) to form either chlorobenzene-2,4-disulphonhydrazide (V, R = NH_2) or the disulphinic acid (III) depending on conditions. When I is treated with excess aqueous hydrazine, V (R = NH_2) precipitates and if this is not filtered it gradually dissolves to form the water soluble III. This shows that the hydrazide must be an intermediate when hydrazine is used in the reduction of an arylsulphonyl halide to the corresponding arylsulphinic acid.

EXPERIMENTAL

1. *Chlorobenzene-2,4-disulphonyl Chloride (I)*

A solution of *p*-chlorobenzenesulphonyl chloride (6) (120 gm.) and chlorosulphonic acid (300 ml.) was heated at 130° for 20 hr. The cooled reaction mixture was cautiously poured onto cracked ice and the precipitated solid extracted with benzene. The benzene extract was quickly washed with cold water, dried, and the solvent distilled off. Crystallization of the residue from carbon tetrachloride yielded 120 gm. (69%) of white solid melting 89–90°; Lit. (10) m.p. 90–91°.

In other experiments the use of a lower reaction temperature resulted in incomplete reaction and the use of less chlorosulphonic acid decreased the yield.

2. *Diethyl Chlorobenzene-2,4-disulphonate (II, $R = C_2H_5$)*

To a solution of chlorobenzene-2,4-disulphonyl chloride (I) (31 gm.) in benzene (300 ml.) was added absolute ethanol (125 ml.) and pellet sodium hydroxide (8 gm.) and the reaction mixture stirred at 15–20° for five hours. The resulting mixture was washed with water, the benzene solution dried, and the solvent removed. Crystallization of the residue from ethanol and from benzene – petroleum ether yielded 12 gm. (30%) of white needles melting at 72–73°. Anal. calc. for $C_{10}H_{13}O_6ClS_2$: C, 36.54; H, 3.96. Found: C, 36.52, 36.25; H, 3.85, 4.01.

3. *Dimethyl Chlorobenzene-*2,4*-disulphonate* (*II*, *R* = CH_3)

This was prepared in 55% yield, using methanol instead of ethanol (see section 2), m.p. 118–119°. Anal. calc. for $C_8H_9O_6ClS_2$: C, 31.96; H, 3.00. Found: C, 32.49, 32.35; H, 3.13, 2.95.

4. *bis-*(2*-Chloroethyl*) *Chlorobenzene-*2,4*-disulphonate* (*II*, *R* = CH_2CH_2Cl)

A reaction mixture of chlorobenzene-2,4-disulphonyl chloride (I) (30 gm.), ethylene chlorohydrin (80 ml.), and pellet solid hydroxide (8 gm.) was stirred for two hours, the temperature being maintained at 20–30°. Cooling on an ice water bath was essential at the beginning. After it had been allowed to stand overnight, the reaction mixture was extracted with ether, the ether extract washed with water, and the solvent removed. Crystallization of the residue from methanol yielded 30 gm. (75%) of white prisms melting at 72–73°. Anal. calc. for $C_{10}H_{11}O_6Cl_3S_2$: C, 30.20; H, 2.77. Found: C, 30.38, 30.06; H, 2.98, 2.97.

5. *bis*(2*-Chloroethyl*) *Phenoxybenzene-*4,4′*-disulphonate*

This was prepared in 75% yield from phenoxybenzene-4,4′-disulphonyl chloride (12) and ethylene chlorohydrin (see section 4). It crystallized from benzene–methanol as colorless prisms melting at 82–83°. Anal. calc. for $C_{16}H_{16}O_7Cl_2S_2$: C, 42.20; H, 3.52. Found: C, 42.84, 42.77; H, 3.45, 3.30.

6. *bis*(*p-Chlorophenyl*) *Chlorobenzene-*2,4*-disulphonate* (*II* *R* = *p*-ClC_6H_4)

To a solution of *p*-chlorophenol (35 gm.), sodium hydroxide (9 gm.), and water (35 ml.) was added a solution of chlorobenzene-2,4-disulphonyl chloride (I) (30 gm.) in benzene (300 ml.) and the reaction mixture was stirred for five hours. The temperature was maintained at 25–35° by occasional cooling. The benzene solution was separated, washed with aqueous sodium hydroxide and water, and then concentrated to about 50 ml. On cooling there crystallized 43 gm. (92%) of white prisms which on recrystallization from benzene–methanol melted at 141–142°. Anal. calc. for $C_{18}H_{11}O_6Cl_3S$: C, 43.78; H, 2.23. Found: C, 43.77; H, 2.23.

7. *bis*(*p-Nitrophenyl*) *Chlorobenzene-*2,4*-disulphonate* (*II*, *R* = *p*-$NO_2C_6H_4$)

This compound was prepared in 75% yield from *p*-nitrophenol and I (see section 6). (Reaction time 18 hr.) The white prisms melted at 147–148° after crystallization from benzene. Anal. calc. for $C_{18}H_{11}N_2O_{10}ClS_2$: C, 42.00; H, 2.14. Found: C, 42.24, 42.08; H, 2.28, 2.45.

8. *bis*(8*-Quinolyl*) *Chlorobenzene-*2,4*-disulphonate* (*II*, *R* = C_9H_6N)

This was prepared in 82% yield from 8-hydroxyquinoline and I (see section 6). The light-tan prisms melted at 174–175° after crystallization from acetone.

Anal. calc. for $C_{24}H_{15}N_2O_6ClS_2$: C, 54.70; H, 2.85. Found: C, 54.26, 54.80; H, 2.84, 2.84.

9. *bis(p-Chlorophenyl) Phenoxybenzene-*4,4′*-disulphonate*

This was prepared in 80% yield from phenoxybenzene-4,4′-disulphonyl chloride (12) and *p*-chlorophenol (see section 6). It crystallized from methanol as colorless prisms and melted at 104–105°. Anal. calc. for $C_{24}H_{16}O_7Cl_2S_2$: C, 52.26; H, 2.90. Found: C, 52.34, 52.63; H, 2.74, 2.55.

10. 8-*Quinolyl p-Chlorobenzenesulphonate*

This was prepared in 70% yield, from *p*-chlorobenzenesulphonyl chloride and 8-hydroxyquinoline (see section 6). The light-tan needles melted at 120–121° after crystallization from methanol. Anal. calc. for $C_{15}H_{10}NO_3ClS$: C, 56.34; H, 3.13. Found: C, 56.23; 56.18; H, 3.03, 3.14.

11. *Chlorobenzene-*2,4*-disulphinic Acid (III)*

To a stirred solution of sodium sulphite (175 gm.) in water (500 ml.) was added chlorobenzene-2,4-disulphonyl chloride (I) (50 gm.) and benzene (50 ml.) and the reaction mixture was stirred at 50–60° for five hours. The reaction mixture was allowed to stand overnight, and then was treated with concentrated hydrochloric acid with cooling at 15–20° and the sulphur dioxide was removed *in vacuo* at room temperature. The resulting solution was extracted with five 500-ml. portions of ether and the solvent removed from the extract. The residual oil which was unstable in the presence of warm hydrochloric acid would not crystallize. It was used directly for the preparation of the sulphones (see below).

12. *Dimethyl Chlorobenzene-*2,4*-disulphone* (IV, $R = CH_3$)

A solution of crude chlorobenzene-2,4-disulphinic acid (III) (15 gm.), water (100 ml.), and chloroacetic acid (15 gm.) was treated with sodium carbonate until just alkaline. The resulting solution was heated on the steam bath for two days. The precipitated sulphone (11 gm. or 70%) was filtered, washed, and crystallized from ethanol. The white needles melted at 174–175°. Anal. calc. for $C_8H_9O_4ClS_2$: C, 35.76; H, 3.35. Found: C, 35.79, 35.93; H, 3.47, 3.40.

13. *bis(Chloromethyl) Chlorobenzene-*2,4*-disulphone* (IV, $R = CH_2Cl$)

This was prepared in 25% yield from dichloroacetic acid and III (see section 12). The white solid melted at 137–138° after crystallization from methanol. Anal. calc. for $C_8H_7O_4Cl_3S_2$: C, 28.45; H, 2.07; Cl, 31.56. Found: C, 28.30; H, 1.99; Cl, 31.20.

14. *bis(Chloromethyl) Phenoxybenzene-*4,4′*-disulphone*

This was prepared in 50% yield from phenoxybenzene-4,4′-disulphinic acid and dichloroacetic acid (see section 12). It crystallized from methanol as white needles melting at 139–140°. Anal. calc. for $C_{14}H_{12}O_5Cl_2S_2$: C, 42.53; H, 3.04. Found: C, 42.83; H, 2.80.

15. *Dimethyl Phenoxybenzene-*4,4′*-disulphone*

This was prepared in 75% yield from phenoxybenzene-4,4′-disulphinic acid and chloroacetic acid (see section 12). It crystallized from methanol as white prisms melting at 182–183°. Anal. calc. for $C_{14}H_{14}O_5S_2$: C, 51.53; H, 4.29. Found: C, 52.06, 51.82; H, 3.96, 4.16.

16. *Hydroxymethyl p-Chlorophenylsulphone*

Following the method of von Meyer (7) for the preparation of hydroxymethyl *p*-tolylsulphone, *p*-chlorobenzenesulphinic acid (50 gm.) and 40% formaldehyde (100 ml.) were stirred for one hour. The white solid (52 gm. or 90%) was filtered, washed, dried, and crystallized from benzene, m.p. 111–112°. Anal. calc. for $C_7H_7O_3ClS$: C, 40.67; H, 3.39. Found: C, 40.93, 40.66; H, 3.27, 3.36. Heating this compound with phenyl isocyanate did not yield the urethane.

17. *bis*(*Hydroxymethyl*) *Phenoxybenzene-*4,4′*-disulphone*

This was prepared in 90% yield from phenoxybenzene-4,4′-disulphinic acid (prepared in a manner similar to that of III in section 11) and formaldehyde (see section 16). It crystallized from dilute formaldehyde as a white solid melting at 151–153° (with decomposition). Anal. calc. for $C_{14}H_{14}O_7S_2$: C, 46.92; H, 3.91. Found: C, 47.05, 47.02; H, 3.95, 4.14.

18. *p-Chlorophenyl* 3,4*-Dimethoxyphenylsulphone*

The method of Burton and Hoggarth (1) was employed. A reaction mixture of *p*-chlorobenzenesulphonyl chloride (40 gm.), veratrole (40 gm.), and zinc chloride (30 gm.) was stirred in an open beaker and heated at 120–130° for 15 min. Hydrogen chloride was evolved with considerable frothing. The cooled reaction mixture was treated with dilute hydrochloric acid and then extracted with benzene. The benzene solution was washed with dilute hydrochloric acid, with aqueous alkali, and with water and the solvent was removed. The residue was fractionally distilled yielding essentially two fractions, one boiling at 170–180° (0.2 mm.) and the other at 180–200° (0.2 mm.). The first fraction was crystallized from ethanol to yield white needles (16 gm. or 28%) melting at 99–100° alone or in admixture with *o-methoxyphenyl p-chlorobenzenesulphonate* (see section 19). This is apparently formed through demethylation of veratrole and reaction of the resulting guaiacol with *p*-chlorobenzenesulphonyl chloride.

The second fraction which consisted mainly of *p-chlorophenyl* 3,4*-dimethoxyphenylsulphone* was boiled for three hours with aqueous–alcoholic alkali to free it from *o*-methoxyphenyl *p*-chlorobenzenesulphonate. The alcohol was removed and the precipitate crystallized from ethanol. The white needles (4 gm. or 7%) melted at 140–141°. Anal. calc. for $C_{14}H_{13}O_4ClS$: C, 53.75; H, 4.16. Found: C, 54.17, 54.21; H, 4.33, 4.12.

19. *o-Methoxylphenyl p-Chlorobenzenesulphonate*

This was prepared in 70% yield from *p*-chlorobenzenesulphonyl chloride and guaiacol (see section 6). The white needles melted at 99–100° after crystallization from ethanol. Anal. calc. for $C_{13}H_{11}O_4ClS$: C, 52.26; H, 3.68; OCH_3, 10.39. Found: C, 52.66, 52.46; H, 3.67, 3.77; OCH_3, 10.37, 10.53.

20. *p-Chlorophenyl p-Methoxyphenylsulphone*

This was prepared in 15% yield from *p*-chlorobenzenesulphonyl chloride and anisole (see section 18). The white prisms melted at 70–71° after crystallization from methanol. Anal. calc. for $C_{13}H_{11}O_3ClS$: C, 55.22; H, 3.89. Found: C, 55.41, 55.20; H, 3.58, 4.16.

21. *p,p′-Dichlorobenzhydryl p-Chlorophenylsulphone*

The method of Hinsberg (4) was employed. A solution of *p,p′*-dichlorobenzhydrol (11) (5 gm.), *p*-chlorobenzenesulphinic acid (5 gm.), acetic acid (25 ml.), and two drops of concentrated hydrochloric acid were heated under reflux for four hours. The cooled reaction mixture was poured into water, extracted with ether, the ether extract washed with dilute aqueous sodium hydroxide and with water, and the solvent removed. The residue crystallized from benzene–methanol as white needles (6.1 gm.) which melted at 105–106°. Anal. calc. for $C_{19}H_{13}O_2Cl_3S$: C, 55.41; H, 3.16. Found: C, 55.56; H, 3.24.

22. 1,*N*,*N*,*N′*,*N′-Pentachlorobenzene*-2,4-*disulphonamide*

To a stirred solution of chlorobenzene-2,4-disulphonamide (9) (15 gm.) in sodium hydroxide (6 gm.) and water (250 ml.) was added chloroform (300 ml.) and then excess chlorine was passed in for one hour. The temperature was maintained at 25–30° by occasional cooling. The chloroform layer was separated, washed with water, concentrated to about 30 ml., and allowed to cool. White crystals (16 gm. or 64%) separated which melted at 148–149°. Anal. calc. for $C_6H_3N_2O_4Cl_5S_2$: C, 17.62; H, 0.73. Found: C, 18.01, 18.22; H, 0.94, 1.06.

This compound is a dangerous chlorinating agent. When equimolecular quantities of it and *p*-xylene were mixed and heated on the steam bath a violent explosion resulted.

23. *N*,*N*,*N′*,*N′-Tetramethyl*-1-*chlorobenzene*-2,4-*disulphonamide*

Chlorobenzene-2,4-disulphonyl chloride (20 gm.) and 40% aqueous dimethylamine (100 ml.) were heated on the steam bath and stirred for two hours. The white precipitate was filtered, washed, and crystallized twice from methanol, m.p. 132–133°; yield, 19 gm. or 60%. Anal. calc. for $C_{10}H_{15}N_2O_4ClS_2$: C, 36.75; H, 4.60. Found: C, 37.16; H, 4.69.

24. *N*,*N′-Di*-2-*pyridyl*-1-*chlorobenzene*-2,4-*disulphonamide* (*V*, *R* = 2-*pyridyl*)

To a solution of 2-aminopyridine (35 gm.) in benzene (75 ml.) was added a solution of chlorobenzene-2,4-disulphonyl chloride (25 gm.) in benzene (100 ml.). The resulting reaction mixture was heated under reflux for one-half hour and then poured into cold water. The yellow precipitate was filtered and washed with dilute hydrochloric acid, water, benzene, and acetone. It was then redissolved in dilute aqueous potassium hydroxide, the solution filtered, and the filtrate was acidified with acetic acid. The precipitate (27 gm.

or 80%) was filtered, washed, and dried, m.p. 280° (with decomposition). Anal. calc. for $C_{16}H_{13}N_4O_4ClS_2$: C, 45.21; H, 3.06. Found: C, 44.92, 45.02; H, 3.59, 3.36.

25. *N-2-Pyridyl-p-chlorobenzenesulphonamide*

This was prepared in 80% yield from 2-aminopyridine and *p*-chlorobenzenesulphonyl chloride (see section 24). It crystallized from methanol in the form of white needles which melted at 193–194°. Anal. calc. for $C_{11}H_9N_2O_2ClS$: C, 49.17; H, 3.35. Found: C, 49.21, 49.56; H, 3.29, 3.37.

26. *N,N′-bis(2-Hydroxyethyl)-1-chlorobenzene-2,4-disulphonamide* (*V*, $R = CH_2CH_2OH$)

This was prepared in 35% yield from chlorobenzene-2,4-disulphonyl chloride and ethanolamine using chloroform as solvent instead of benzene (see section 24). It crystallized from benzene–methanol as white needles melting at 127–128°. Anal. calc. for $C_{10}H_{15}N_2O_6ClS$: C, 33.48; H, 4.18. Found: C, 33.70, 33.86; H, 4.12, 4.11.

27. *Chlorobenzene-2,4-disulphonyl-N,N′-bis(1,2,3,4-tetrahydroquinoline)*

This was prepared in 54% yield from 1,2,3,4,-tetrahydroquinoline and chlorobenzene-2,4-disulphonyl chloride (see section 24). It crystallized from benzene as pink prisms melting at 116–117°. Anal. calc. for $C_{24}H_{23}N_2O_4ClS_2$: C, 57.32; H, 4.58. Found: C, 57.34, 57.48; H, 4.48, 4.41.

28. *N-(p-Chlorophenylsulphonyl)-1,2,3,4-tetrahydroquinoline*

This was prepared in 60% yield from 1,2,3,4-tetrahydroquinoline and *p*-chlorobenzenesulphonyl chloride (see section 24). It crystallized from methanol as white needles melting at 94–95°. Anal. calc. for $C_{15}H_{14}NO_2ClS$: C, 58.55; H, 4.55; N, 4.55. Found: C, 58.13, 58.43; H, 4.30, 4.46; N, 4.91, 4.70.

29. *Chlorobenzene-2,4-disulphonyl bis-Hydrazide* (*V*, $R = NH_2$)

To a stirred cold solution of chlorobenzene-2,4-disulphonyl chloride (20 gm.) in benzene (70 ml.) was added a chilled solution of 85% hydrazine hydrate (20 ml.) in water (20 ml.). The reaction mixture was stirred and cooled at 10° for not more than two hours. (Further reaction occurs to form chlorobenzene-2,4-disulphinic acid if more time is allowed.) The white precipitate (16 gm. or 80%) was filtered, washed, dried, and crystallized quickly from pyridine–ether, m.p. 133° (with decomposition). Anal. calc. for $C_6H_9N_4O_4ClS_2$: C, 23.96; H, 3.00. Found: C, 23.90; H, 2.79.

This compound is insoluble in benzene, methanol, ether, and cold water. It is soluble in hot water but decomposition occurs on prolonged heating.

In another experiment twice the amount of hydrazine hydrate was used and the reaction mixture was allowed to stand overnight. The chlorobenzene-2,4-disulphonyl bis-hydrazide, which first precipitated, gradually dissolved. The aqueous solution was separated, acidified with 50% sulphuric acid, the precipitated hydrazine sulphate was filtered, and the filtrate extracted exhaustively with ether. Removal of the ether left the oily chlorobenzene-2,4-disulphinic acid (8 gm.). This, when treated with chloroacetic acid (see section 12), yielded a sulphone which did not depress the melting point of dimethyl chlorobenzene-2,4-disulphone (IV, R = CH_3).

30. *p-Chlorophenylsulphonhydrazide*

This was prepared in 92% yield from *p*-chlorobenzenesulphonyl chloride and hydrazine (see section 29). It crystallized from benzene as white woolly needles melting at 117–118° (with decomposition). Anal. calc. for $C_6H_7N_2O_2ClS$: C, 34.85; H, 3.39; N, 13.56. Found: C, 35.30, 34.72; H, 3.36, 3.74; N, 13.63.

In another experiment where the reaction was carried out at steam bath temperature, a 70% yield of *p*-chlorobenzenesulphinic acid was obtained.

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DIHYDRO-N-*nor*GELSEMINE AND SOME OF ITS DERIVATIVES[1]

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ABSTRACT

Treatment of gelsemine with cyanogen bromide produced N-cyano-*nor*gelsemine which on catalytic hydrogenation gave rise to N-cyanodihydro-N-*nor*gelsemine, identical with the product of the reaction of cyanogen bromide with dihydrogelsemine. N-Cyanodihydro-N-*nor*gelsemine was hydrolyzed with hydrochloric acid to dihydro-N-*nor*gelsemine which readily formed a mono- or a dibenzoyl derivative according to the conditions, and a *p*-toluenesulphonamide. The action of phosphorus pentachloride on the monobenzoyl derivative gave rise to N-benzoylchlorodihydro-N-*nor*gelsemine, hydrolyzable by hydrochloric acid to chlorodihydro-N-*nor*gelsemine. This chloro compound was converted by the action of formaldehyde and formic acid to chlorodihydrogelsemine, identical with the product of the action of phosphorus pentachloride on dihydrogelsemine. Chlorination of dihydrogelsemine with chlorine produced dichlorogelsemine.

It has now been well established that gelsemine is a 3,3-disubstituted oxindole (4,8) but little is known about the structure of the second moiety of the molecule. The basic N(b) carries a methyl group, and there are present a readily reducible double bond which has been claimed to involve an exocyclic methylene group (3,4), and an ether ring. Since gelsemine contains six rings, the unknown moiety must include four of these. The usual conditions of the Hofmann degradation reconvert the metho-base to the original alkaloid, while distillation of the metho-base *in vacuo* does not cause the opening of the ring containing N(b) as first assumed (5) but brings about a transmethylation giving rise to N(a)-methylgelsemine (6,9). It was thought that cyanogen bromide might react with N(b) and thus afford a means of degrading that part of the molecule in which it is contained. Before this work had reached completion, Jones and Stevens (7) reported their investigation of this reaction. We have succeeded, however, in preparing N-benzoyldihydro-N-*nor*gelsemine and shown that phosphorus pentachloride chlorinates the benzene ring present in the alkakoid instead of cleaving the N(b)-containing ring. Furthermore, a number of well defined crystalline derivatives have been obtained which are deemed worth recording.

According to Forsyth *et al.* (2) the action of cyanogen bromide on gelsemine gives rise to a substance yielding imperfectly concordant results which they assumed to be a mixture. In our hands this reaction yielded N-cyano-N-*nor*gelsemine, $C_{20}H_{19}O_2N_3$, which could be hydrogenated catalytically to N-cyanodihydro-N-*nor*gelsemine, $C_{20}H_{21}O_2N_3$, identical with the product obtained directly by the action of cyanogen bromide on dihydrogelsemine. N-Cyanodihydro-N-*nor*gelsemine was first reported by Jones and Stevens (7). On hydrolysis with hydrochloric acid it produced crystalline dihydro-N-*nor*gelsemine, $C_{19}H_{22}O_2N_2$, which formed both a picrate and a perchlorate. Dihydro-N-*nor*gelsemine gave rise to a *p*-toluenesulphonyl derivative and, in

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the Schotten-Baumann reaction, to a monobenzoyl derivative, while it gave a dibenzoyl derivative when treated with benzoyl chloride and pyridine. An attempt to degrade monobenzoyldihydro-*nor*gelsemine with phosphorus pentachloride resulted in the formation of benzoylchlorodihydro-*nor*gelsemine which on hydrolysis with hydrochloric acid produced crystalline chlorodihydro-*nor*gelsemine. This chloro compound could not be recrystallized without some decomposition, although it formed a stable perchlorate and a *p*-toluenesulphonamide.

Chlorine could not be removed from chlorodihydro-*nor*gelsemine either by treatment with chromous chloride or with zinc and acetic acid, both of which reagents left the material unchanged. Catalytic hydrogenation seemed to effect partial dehalogenation only as indicated by examination of the various fractions isolated by chromatography of the product (see experimental). The firmness with which the chlorine is retained makes it likely that it is located in the benzene ring of the alkaloid. At any rate, the infrared spectra of the various compounds (Table I) seem to support this possibility.

TABLE I

INFRARED ABSORPTION OF GELSEMINE DERIVATIVES ATTRIBUTABLE TO SUBSTITUTED BENZENE RING*

Compound	Absorption bands (in wave numbers)				
Gelsemine		742	756		
Dihydrogelsemine	720	740,745	760		
Cyano-*nor*gelsemine		745	750,757		
Cyanodihydro-*nor*gelsemine		743	756		
Dihydro-*nor*gelsemine	738	747	760		
Bz-chlorodihydro-*nor*gelsemine	704			824	
Chlorodihydro-*nor*gelsemine	720			808,818	
Chloro-*p*-toluenesulphonamide	707	748†		815	
Chlorodihydrogelsemine				810	
Dichlorodihydrogelsemine	732	750,769			859

**The infrared spectra were determined on nujol mulls with a Perkin-Elmer double beam spectrometer, model 21.*

†Weak band.

Chlorodihydro-N-*nor*gelsemine was converted by heating with formaldehyde and formic acid to chlorodihydrogelsemine identical with the product obtainable by treatment of dihydrogelsemine with phosphorus pentachloride. Chlorination of dihydrogelsemine with chlorine in chloroform solution gave rise to dichlorodihydrogelsemine, $C_{20}H_{22}O_2N_2Cl_2$.

A comparison of the infrared spectra (Table I) of gelsemine, dihydrogelsemine, cyano-N-*nor*gelsemine, and cyanodihydro-N-*nor*gelsemine with those of benzoylchlorodihydro-N-*nor*gelsemine, chlorodihydro-N-*nor*gelsemine, its *p*-toluenesulphonamide, and of chlorodihydrogelsemine shows that the band at 756 – 760 cm.$^{-1}$ present in the first four and attributable to a disubstituted benzene ring (1) is absent in the spectra of the chloro compounds which all contain a new band at 815 – 824 cm.$^{-1}$ attributable to a trisubstituted benzene ring (1). It is, therefore, very probable that the chlorine has entered the benzene ring of the alkaloid. The infrared spectrum of dichlorodihydrogelsemine contains a band at 859 cm.$^{-1}$ instead of the absorption at 815 – 824 cm.$^{-1}$ so that the substance probably contains both chlorine atoms in the benzene ring.

The ultraviolet spectra of the gelsemine derivatives described show that the introduction of chlorine into the molecule causes a shift of the spectrum in the direction that would be expected from the addition of such an auxochrome to the chromophoric group.

EXPERIMENTAL[2]

*N-Cyano-N-*nor*gelsemine*

A solution of gelsemine containing acetone of crystallization (1.041 gm.) in dry chloroform (20 ml.) was refluxed for six hours with freshly distilled cyanogen bromide (1.5 gm.). The reaction mixture was evaporated to dryness under reduced pressure and the residue taken up in *ca.* 25 ml. of chloroform and filtered. The chloroform insoluble material (359 mgm.) consisted of crude gelsemine hydrobromide, m.p. 315–322°. The chloroform solution, washed with dilute sodium hydroxide solution and evaporated to dryness under reduced pressure, gave 678 mgm. of pale yellow foam which crystallized on the addition of a few drops of methanol, m.p. 217.5 – 219°. Chromatography on alumina from benzene solution and elution with benzene–chloroform mixtures yielded a product which after recrystallization from methanol consisted of colorless prisms, m.p. 217.5–218°. A substance which was probably slightly impure N-cyano-N-*nor*gelsemine is reported in the literature as melting at 216° (2). Calc. for $C_{20}H_{19}O_2N_3$: C, 72.05; H, 5.74; N, 12.61. Found: C, 72.01; H, 5.81; N, 12.70; N·CH_3, 1.28, 1.36%[3].

*N-Cyanodihydro-N-*nor*gelsemine*

(*a*) *By Hydrogenation of N-Cyano-N-*nor*gelsemine*

Cyano-*nor*gelsemine (197 mgm.) dissolved in methanol (15 ml.) was hydrogenated at low pressure in the presence of platinum oxide (45 mgm.). Two-thirds of the calculated volume of hydrogen was absorbed. Chromatography of the product from benzene solution with chloroform elution gave 161 mgm. of colorless foam which was dissolved in hot methanol. On cooling the solution deposited colorless prisms (75 mgm.), m.p. 258–262°. After three recrystallizations from methanol, m.p. 269–270.5° (reported m.p. 269° (7)). Calc. for $C_{20}H_{21}O_2N_3$: C, 71.62; H, 6.31; N, 12.53. Found: C, 71.50, 71.55, 71.68; H, 6.30, 6.19, 6.74; N, 12.19, 12.37%.

(*b*) *From Dihydrogelsemine*

A solution of dihydrogelsemine (4.030 gm.) in dry benzene (75 ml.) to which was added freshly distilled cyanogen bromide (6 gm.) was refluxed for 16 hr. The reaction mixture, worked up as in the preparation of cyano-*nor*gelsemine,

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[2] *All melting points are corrected.*

[3] *The theoretical value for one N-CH_3 is about 4.3%. N-Cyano-N-*norgelsemine* contains no imino methyl, and the small value obtained may be due to some reduction of the cyano group. At any rate the infrared spectra of the* norgelsemine *derivatives contain only a weak band at 1375 cm.$^{-1}$ and no absorption at 2750 cm.$^{-1}$, whereas the spectra of gelsemine and dihydrogelsemine show in both these regions definite absorption attributable to an N-CH_3 group.*

yielded a pale yellow oil (3.819 gm.) which crystallized from methanol (first crop, 2.340 gm.), m.p. 268.5–271° either alone or in admixture with N-cyanodihydro-N-*nor*gelsemine obtained by procedure (*a*).

*Dihydro-N-*nor*gelsemine*

N-Cyanodihydro-N-*nor*gelsemine (4.086 gm.) was hydrolyzed by refluxing with ethanol (75 ml.) and concentrated hydrochloric acid (30 ml.) for 96 hr. The clear yellow solution was concentrated to a small volume, diluted with water, and extracted with ether to remove any nonbasic material. The extracted aqueous solution was alkalized with dilute aqueous potassium hydroxide. This caused the precipitation of a white powder which was filtered and dried (3.726 gm.). A portion of this base (265 mgm.) was crystallized from methanol from which it separated as colorless prisms (103 mgm.), m.p. 299.5–302° and after one further crystallization, m.p. 301.5–302.5°. Calc. for $C_{19}H_{22}O_2N_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.79; H, 7.44; N, 8.92%.

The base formed a picrate which separated from ethanol as yellow prisms, m.p. 275–276°(dec.). The melting point reported in the literature is 281–282° (7).

Dihydro-N-*nor*gelsemine also formed a perchlorate which, twice recrystallized from water, consisted of colorless prisms, m.p. 295.5° (dec.). Calc. for $C_{19}H_{22}O_2N_2HClO_4$: C, 55.52; H, 5.65; N, 6.84. Found: C, 54.89, 54.73; H, 6.09, 6.18; N, 6.50%. (The salt invariably exploded during the initial stages of the analysis, and this may account for the low figures obtained.)

*N-p-Toluenesulphonyldihydro-N-*nor*gelsemine*

The uncrystallized base (365 mgm.) dissolved in pyridine (5 ml.) was allowed to stand for 24 hr. with *p*-toluenesulphonyl chloride (410 mgm.). The solvent was then distilled under reduced pressure, the residue dissolved in chloroform, and the solution washed with dilute hydrochloric acid. After evaporation of the chloroform a residue was obtained which was dissolved in benzene and chromatographed on alumina. Elution with benzene gave a small first fraction consisting of a pale yellow oil which was likely *p*-toluenesulphonyl chloride and a main fraction. After evaporation of the solvent the main fraction was a colorless foam (332 mgm.) which crystallized on the addition of methanol, m.p. 209.5 – 212°. Two further recrystallizations from methanol raised the melting point, 214–214.5°. Calc. for $C_{26}H_{28}O_4N_2S$: C, 67.15; H, 6.07; N, 6.02. Found: C, 67.57; H, 6.18; N, 6.10%.

*Benzoylation of Dihydro-*nor*gelsemine*

(*a*) A solution of dihydro-*nor*gelsemine (1.145 gm.) in chloroform (30 ml.) and dioxane (5 ml.) was shaken with 5% aqueous potassium hydroxide (5 ml.) and benzoyl chloride (0.5 ml.). The addition of alkali and benzoyl chloride in the same quantities was repeated twice at 15 min. intervals. When the odor of benzoyl chloride had disappeared, the chloroform layer was washed with dilute sulphuric acid, dried, and evaporated. It left a colorless foam which on addition of methanol gave crystalline N-monobenzoyldihydro-N-*nor*gelsemine, m.p. 268–274° (1.344 gm.).

(*b*) To a solution of dihydro-*nor*gelsemine (615 mgm.) in pyridine (7 ml.) was added benzoyl chloride (1 ml.). After two hours at room temperature, the solution was refluxed for 15 min. and subsequently evaporated to dryness under reduced pressure. The residue was dissolved in chloroform, washed first with dilute potassium hydroxide solution and then with dilute sulphuric acid. After evaporation of the chloroform the residual oil was dissolved in benzene and chromatographed on alumina. Elution with benzene and methylene chloride gave 727 mgm. of colorless foam which crystallized from methanol as colorless prisms, m.p. 227.5 – 228.5°. One further recrystallization gave dibenzoyldihydro-*nor*gelsemine, m.p. 229– 229.5°. Calc. for $C_{32}H_{30}O_4N_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.61; H, 6.15; N, 5.53%.

Further elution with chloroform brought down 224 mgm. of a pale yellow foam which crystallized from methanol, m.p. 274 – 276°, identical with monobenzoyldihydro-*nor*gelsemine prepared by the Schotten-Baumann reaction. Two further recrystallizations from methanol raised the melting point to 279–280°. Calc. for $C_{26}H_{26}O_3N_2$: C, 75.34; H, 6.32; N, 6.76, Found: C, 75.61; H, 6.73; N, 6.65%.

*Attempted Degradation of Benzoyldihydro-*norgelsemine *With Phosphorus Pentachloride*

A mixture of monobenzoyldihydro-*nor*gelsemine (301 mgm.), freshly sublimed phosphorus pentachloride (718 mgm.) and dioxane (10 ml.) was refluxed for eight hours. After the addition of a few drops of water, the solvent was removed under reduced pressure, the residual gum dissolved in chloroform, and the solution washed first with dilute hydrochloric acid and afterwards with dilute ammonia. Evaporation of the chloroform left a pale yellow foam (272 mgm.) which crystallized from methanol as colorless prisms, m.p. 297–302°. Three recrystallizations from methanol gave pure benzoylchlorodihydro-*nor*gelsemine, m.p. 312.5 – 313.5°. Calc. for $C_{26}H_{27}O_3N_2Cl$: C, 69.24; H, 6.04; N, 6.21. Found: C, 70.78, 70.25; H, 6.16, 5.73; N, 6.53, 6.23%.

*Chlorodihydro-N-*norgelsemine

Benzoylchlorodihydro-*nor*gelsemine (68 mgm.) was dissolved in ethanol (10 ml.) and concentrated hydrochloric acid (5 ml.). The solution was refluxed for 16 hr. and evaporated to dryness under reduced pressure. The residue was dissolved in water and the solution extracted with chloroform and then alkalized with sodium hydroxide. The precipitated base was collected by extraction with chloroform. Evaporation of this chloroform extract left a foam which crystallized from acetone as colorless needles, m.p. 244 – 248°. Further crystallization lowered the melting point to 240 – 243° and caused the appearance of a yellow color in the mother liquor. The perchlorate of this base separated from methanol as colorless needles, m.p. > 340°. Calc. for $C_{19}H_{21}O_2N_2Cl.HClO_4$: C, 51.25; H, 4.98; N, 6.29. Found: C, 51.50; H, 5.07; N, 6.46%. The base also yielded a *p*-toluenesulphonamide prepared as described for that of dihydro-*nor*gelsemine. It was chromatographed in benzene solution on alumina and eluted with ether. The eluate yielded the product which after two crystallizations from methanol consisted of elongated prisms which on slow heating gave off solvent at 130°, resolidified and melted at 204–204.5°. Calc. for $C_{26}H_{27}O_4N_2SCl$: C, 62.58; H, 5.46; N, 5.62. Found: C, 62.81; H, 5.88; N, 5.62%.

*Attempted Reduction of Chlorodihydro-N-*norgelsemine

(*a*) *With Chromous Chloride*

A solution of chlorodihydro-N-*nor*gelsemine (350 mgm.) in absolute ethanol (10 ml.) was refluxed under nitrogen for three hours with an ethanolic solution of chromous chloride prepared from chromic chloride hexahydrate (4 gm.), amalgamated zinc (3 gm.), and concentrated hydrochloric acid (5 ml.). The reaction mixture was concentrated under reduced pressure, diluted with water (50 ml.), alkalized with ammonia, and extracted with three portions of ether. The combined dried extract when evaporated to dryness left a residual powder (271 mgm.) which was dissolved in benzene–chloroform (1:1) and chromatographed on alumina. Elution with chloroform containing 5% of methanol brought down the product which on evaporation of the solvent consisted of a pale yellow foam (269 mgm.). This only partially crystallized on addition of a few drops of methanol (m.p. 196–219°). The solid impure base was therefore benzoylated under Schotten-Baumann conditions and the product crystallized from methanol, m.p. 310–313.5°, either alone or in admixture with benzoylchlorodihydro-N-*nor*gelsemine.

(*b*) *By Catalytic Hydrogenation*

Chlorodihydro-*nor*gelsemine (288 mgm.) dissolved in methanol was hydrogenated at low pressure in the presence of platinum oxide (29 mgm.). In two hours 80% of the calculated volume of hydrogen was absorbed. The solution was filtered to remove the catalyst and evaporated to dryness. It left a residue which was dissolved in chloroform and the solution after washing with dilute aqueous potassium hydroxide was evaporated to dryness. The residual colorless foam was dissolved in benzene and chromatographed on alumina. Elution with benzene containing increasing concentrations of ether, then with chloroform, failed to give well defined fractions. The fractions eluted with benzene containing 10% of ether gave material which crystallized partially on addition of a few drops of methanol. This material still contained chlorine and its infrared absorption spectrum still contained a band at 810 cm.$^{-1}$ indicative of an unsymmetrically trisubstituted phenyl ring. The fractions eluted with benzene containing 50% of ether yielded material containing a mere trace of halogen and had infrared absorption spectra no longer showing absorption at 810 cm.$^{-1}$, but containing two bands at 740 and 760 cm.$^{-1}$ characteristic of the *o*-disubstituted benzene ring.

(*c*) *With Zinc and Acetic Acid*

Chlorodihydro-*nor*gelsemine (213 mgm.) was refluxed with granular zinc (1.5 gm.) and glacial acetic acid (8 ml.) for three hours. The reaction mixture was diluted with water and the liquor decanted from the zinc which was washed by decantation. The combined decantate was alkalized with concentrated aqueous potassium hydroxide and extracted with chloroform. Evaporation of the chloroform extract left a white solid (197 mgm., m.p. 204.5–211°) which was converted to the *p*-toluenesulphonamide by the method already described. Chromatography on alumina in benzene solution and elution with ether yielded a product (217 mgm.) which after crystallization from methanol consisted of colorless prisms which lost solvent at 130° and melted at 202–203.5°, either alone or in admixture with N-*p*-toluenesulphonylchlorodihydro-N-*nor*gelsemine.

Chlorodihydrogelsemine

(*a*) *By Methylation of Chlorodihydro-N-*nor*gelsemine*

A mixture of chlorodihydro-N-*nor*gelsemine (408 mgm.), 90% formic acid (3 ml.) and 37% formaldehyde solution (3 ml.) was heated on the steam bath under reflux for six hours, then allowed to stand overnight, and heated again for 30 min. after the addition of concentrated hydrochloric acid. The reaction mixture was evaporated to dryness under reduced pressure and the residue taken up in water (50 ml.). The solution was filtered to remove some insoluble material and washed with ether. The aqueous solution was alkalized with aqueous potassium hydroxide and extracted with chloroform. Evaporation of the chloroform extract left a yellow foam (366 mgm.) which was dissolved in benzene containing 5% of chloroform and chromatographed on alumina. Elution with benzene containing 2% methanol gave a substance (184 mgm.) which was rechromatographed in methylene dichloride solution on the same adsorbent. Elution with methylene dichloride yielded the compound (47 mgm.) which crystallized from acetone as colorless plates, m.p. 218.5 – 221.5°. Calc. for $C_{20}H_{23}O_2N_2Cl$: N, 7.81; $N \cdot CH_3$, 4.19. Found: N, 7.96; $N \cdot CH_3$, 3.82%. The base could not be benzoylated under Schotten-Baumann conditions.

(*b*) *By Chlorination of Dihydrogelsemine*

To a solution of dihydrogelsemine (677 mgm.) in dioxane (25 ml.), phosphorus pentachloride (2.34 gm.) was added and the mixture refluxed for six hours. The reaction mixture was concentrated under reduced pressure, diluted with water, alkalized with dilute aqueous sodium hydroxide, and extracted with chloroform. The extract was shaken with dilute sulphuric acid and the aqueous acidic solution alkalized with aqueous sodium hydroxide and extracted with chloroform. Evaporation of the chloroform left a pale yellow foam (686 mgm.) which crystallized as plates from acetone, m.p. 214 – 217.5°. Recrystallization from acetone raised the melting point to 215 – 218° and this was unaltered by mixture with chlorodihydrogelsemine obtained by method (*a*). Calc. for $C_{20}H_{23}O_2N_2Cl$: C, 66.93; H, 6.46; N, 7.81. Found: C, 67.01; H, 6.08; N, 7.70%.

Dichlorodihydrogelsemine

A solution of dihydrogelsemine (719 mgm.) in chloroform (25 ml.), to which amalgamated aluminum (from 280 mgm. of granular aluminum) had been added, was chlorinated by the addition of a chloroform solution of chlorine (30 ml.). The mixture was allowed to stand for one hour in an ice bath and then at room temperature for four hours. Dilute aqueous sodium hydroxide was added until the mixture was basic and the separated chloroform solution was extracted with dilute sulphuric acid. The free base obtained by extraction after alkalization of the acid solution with aqueous sodium hydroxide consisted of a colorless foam (491 mgm.) which separated as needles from acetone, m.p. 241–245°, after two recrystallizations from acetone, m.p. 249–250.5°. Calc. for $C_{20}H_{22}O_2N_2Cl_2$: C, 61.06; H, 5.64; N, 7.12. Found: C, 61.69; H, 5.80; N, 7.24%.

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THE ISOLATION AND OXIDATION OF ASPEN LIGNINS[1]

By J. M. Pepper and D. C. Hagerman

ABSTRACT

A study has been made of the conditions affecting the isolation of a lignin fraction by a procedure involving a moderate temperature catalytic hydrogenation of pre-extracted aspen wood meal. The effect of varying the initial hydrogen pressure, the catalyst, the time and maximum temperature of reaction, and the nature and acidity of the suspending medium were studied. The weight of the residual pulp, the effectiveness of lignin removal, the weight and methoxyl content of the resulting chloroform-soluble fraction containing the lignin, and the yields of vanillin and syringaldehyde obtained by the alkaline nitrobenzene oxidation of this same fraction were the factors serving as the bases for comparison.

Initial hydrogen pressures greater than 500 p.s.i.g. were not required, although below this value there was some loss of efficiency. Neither the use of water or dioxane alone was satisfactory as a suspending medium, but the mixed aqueous–organic medium was required to remove the released lignin. Considering the resultant slight acidity of the reaction product, it is suggested that in such an isolation two separate stages are involved: that of the water functioning to wet and permeate the wood and serve as the acidic medium and that of the organic solvent phase functioning to remove the liberated lignin after the hydrolytic cleavage.

Data are presented and interpreted to indicate the existence of a lignin–carbohydrate complex which is cleaved under the conditions of catalytic hydrogenation. Under the conditions of these experiments practical temperatures for lignin removal are in the range 170 – 180°C. for an aqueous–organic solvent medium, but some thirty degrees lower for an 85% acetic acid medium. Although it has been possible to isolate all the lignin, with good methoxyl recovery, consistently no more than approximately fifty per cent of the required aldehydes is obtainable on oxidation. The increasing value of the syringaldehyde – vanillin ratio with increasing temperature is due to a decreased vanillin yield.

Indications are that the use of copper chromium oxide may be preferred over Raney nickel as a catalyst for this isolation procedure.

The need for the isolation of a representative lignin fraction which has undergone no or only very slight chemical change remains a foremost problem for those interested in the fundamental chemical structure of this component. Many attempts have been made to prepare such a lignin (3). The isolation of the residual product from the periodate oxidative treatment of wood meal known as "periodate" lignin and the extraction of a lignified portion, "native" lignin, by means of cold ethanol have created the greatest interest. However it has been pointed out that the former product may have undergone partial oxidation, and the latter product unfortunately represents only a small portion, less than 10%, of the original lignin. By previously subjecting various wood samples to the decaying action of wood rot organisms, Nord has managed to increase markedly the percentage of native lignin thus obtainable (3). Whether any such pretreatment has any effect on the lignin structure is, of course, open to question.

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Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan.

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A method of lignin isolation that has led to the identification of interesting lignin degradation products is the catalytic hydrogenation of whole wood meal. By this method, solvent-extracted wood meal is suspended in an aqueous–organic solvent medium and heated at a moderate temperature of 165–175°C. in the presence of hydrogen gas and a nickel catalyst for two to four hours. The residual pulp may be removed by filtration and the lignin isolated from the filtrate. This product has been shown to be essentially aromatic and to consist partly of substituted phenyl ethane and phenyl propane derivatives (4, 12, 13). Although admittedly these earlier investigations have led to a highly degraded lignin fraction, the method has resulted in all of the lignin being obtainable in chloroform solution, from which it may be readily recovered for further chemical investigation. It was felt that a comprehensive study of the conditions of such an isolation technique might lead to a greatly modified process whereby the effective separation is achieved but with little chemical change in the isolated lignin fraction.

Part A. Preliminary Isolation Experiments

A series of preliminary experiments were made with a view to studying the effect on lignin removal of the nature of the suspending medium, the presence or absence of a catalyst, the initial pressure of hydrogen, and the time of reaction. A temperature of 160–180°C. was used throughout since in this range aromatic derivatives had been obtained and above which it was feared extensive ring hydrogenation would occur. The importance of this temperature range on the ease of lignin separation procedures has often been observed and is further supported by results reported herein. Samples of solvent-extracted aspen wood meal were suspended in the solvent medium, the catalyst added and the mixture heated in a high pressure reaction vessel in the presence of hydrogen gas at elevated temperatures for short periods of time. The reaction conditions for each run are outlined in Table I.

The cold reaction mixture was filtered, the acidity of the filtrate determined, and the residual pulp washed with the same solvent mixture before it was dried, weighed (allowance being made for the weight of catalyst), and a small sample tested for lignin removal using the Mäule reaction (17). For those cases in which water alone had been used as the medium a secondary extraction of the pulp with a hydrophilic organic solvent removed a further appreciable amount of product. The chloroform-soluble portions of the combined filtrate and pulp washings, and also of the secondary pulp extractives mentioned above, were obtained and dried to constant weight. Details of these observations on the reaction products are also found in Table I. The use of a total chloroform solubility as the criterion of lignin isolation was considered suitable, as a first approximation, as a comparative method of estimating lignin removal. Previous work had indicated that a chloroform extraction effected a reasonable separation of lignin products from water-soluble carbohydrate fractions.

Notwithstanding the difficulty in trying to assess the value of the variation of these conditions merely on the basis of the chloroform-solubility of the

TABLE I

Preliminary experiments on lignin isolation[a]

Run No.	Reaction conditions					H_2 absorption, moles/100 gm. lignin	Reaction products						
							Filtrate		Residual pulp				Total $CHCl_3$-sol. fractions[e]
	Medium[b]	Raney nickel,[c] gm.	Initial H_2 pressure, p.s.i.g.	Temp., °C.	Time at temp., hr.		Acidity[d]	$CHCl_3$-[e] sol. fraction	Recovery, %[f]	Mäule test[g]	Extraction solvent	$CHCl_3$-sol. fraction[e]	
1	Dioxane	35.2	2850	160–170	2	—	6	0	—	Pos.	—	—	0
2	Dioxane	18	2850	160–170	2	2	6	0	—	Pos.	—	—	0
3	Water	17.5	2900	160–170	2.5	4	5	41[h]	72	Pos.	Dioxane	59	100
5	Ethanol–water	18	3000	160–170	4	6	5	64	80	Pos.	—	—	64
6	Dioxane–water	18	3075	160–180	5	—	6	84	77	Pos.	—	—	} 100
6*a*	Dioxane–water	18	625	170–180	6	0.2	5.5	16	71	Sl. pos.	—	—	
7	Ethanol–water	18	425	165–175	3.5	0.2	5.5	68	80	Pos.	—	—	68
8	Dioxane–water	36	650	160–170	2.0	0.8	5.5	48	85	Pos.	—	—	48
9	Dioxane–water	18	500	170–180	5	1.4	5.0	100	55	Neg.	—	—	100
10	Dioxane–water	18	500	170–180	5	1.2	5.5	97	65	Sl. pos.	Dioxane	0	97
12	Water	18	600	170–180	5.5	2.2	4.5	52	64	Pos.	Ethanol	24	76
13	Dioxane–water	18	575	170–180	5	2.6	5.5	94	60	Sl. pos.	—	—	94
14[i]	Water	18	575	170–180	5	2.6	4.5	48	67	Pos.	Ethanol	14	62
15	Dioxane–water	18	550	170–180	5	2.8	5.5	120	58	Neg.	—	—	120
16	Dioxane–water	0	525	170–180	5	1.4	5.0	118	62	Neg.	—	—	118
17	Ethanol–water	0	550	170–180	5	0	4.5	128	63	Sl. pos.	—	—	128
18	Water	0	525	170–180	5	0	4.0	34	72	Pos.	Ethanol	56	90
19	Water	0	0	170–180	5	—	4.0	24	73	Pos.	Ethanol	50	74
20	Ethanol–water	0	0	170–180	5	—	5	120	64	Sl. pos.	—	—	120
21	Dioxane–water	0	600	170–180	5	1.0	5	130	53	Neg.	—	—	130
22	Dioxane–water	0	575	160–170	5	0	5	100	60	Sl. pos.	—	—	100

[a] *For each run, air-dried, extracted poplar wood meal (32.4 gm.); solvent medium (300 ml.).*

[b] *Binary mediums all on an equal volume basis.*

[c] *Wet weight including solvent prepared according to Pavlic and Adkins (11).*

[d] *Acidity determined by using Hydrion paper.*

[e] *Reported as percentage by weight of the original Klason lignin.*

[f] *Air-dried residue corrected for weight of catalyst.*

[g] *Distinct red coloration (pos.); red coloration on isolated fibers (sl. pos.); no coloration of fiber or solution (neg.). In no case did the Mäule reaction change on those pulps that were further extracted.*

[h] *On an ether-soluble basis.*

[i] *Charge was refluxed with Raney nickel (9 gm.) before balance (9 gm.) of nickel added.*

filtrate and Mäule reaction on the residual pulp, the following conclusions appear significant. The variation in the initial hydrogen pressure above 500 p.s.i.g. has little effect on the lignin removal, whilst below 500 p.s.i.g. there is some loss of efficiency. Then, too, the marked higher hydrogen absorption at the higher pressures would suggest a more highly hydrogenated product and therefore one of less value for future structural studies. In terms of ease of isolation there was no apparent advantage to be gained by using Raney nickel as a catalyst. In fact, the observed higher hydrogen absorption in those runs using the nickel catalyst would probably lead to a more highly reduced product. It is significant, though, that for those runs in which no catalyst was used the weight of the total chloroform-soluble fraction was consistently higher than that for those runs in which catalyst was used. This may be interpreted to indicate that there was, in the former case, the extraction into chloroform of a lignin-carbohydrate complex fraction, which, under the conditions of catalytic hydrogenation, has been cleaved to leave only the lignin as the primary chloroform-soluble portion.

The nature of the liquid medium had a marked effect on the completeness of lignin removal. The use of dioxane alone was unsatisfactory as illustrated by its failure to remove any lignin. Water alone was also ineffective as indicated by the small chloroform-soluble extract of the original filtrate. However, in these cases it is interesting to note that a subsequent extraction of the residual pulp with an organic solvent (dioxane or ethanol) removed considerably more material which must have been released under the conditions of the experiment. The most useful solvent medium was a dioxane–water (1:1) mixture, by the use of which at 170–180°C. for five hours at an initial hydrogen pressure of 500 p.s.i.g. the lignin was completely removed. Under such conditions solubility in the liquid phase is complete as illustrated by the failure of the mixture to remove any further product by a subsequent pulp extraction (Run 10).

Although the recorded acidity of the reaction filtrate does not represent a true pH value except maybe for those cases in which water alone was used, there is little doubt that some acidic component is released under the conditions of these experiments. Moreover the preferred use of the aqueous–organic medium would suggest that two separate effects are involved: that of the water functioning to permeate and wet the wood meal to later serve as the acidic medium promoting lignin separation, and that of the organic solvent phase functioning to remove the liberated lignin following the acid catalyzed hydrolytic reaction. The apparent importance, in lignin solubility studies, of the nature of the solvent has been emphasized by Schuerch (15).

Part B. Further Experiments on the Isolation and Oxidation of Aspen Lignins

It appeared that a promising method of lignin removal involved the treatment of wood meal under the conditions similar to those of Runs 10, 13, or 15. However, since this conclusion was based merely on the absence of residual lignin (Mäule test) and on the weight of the chloroform-soluble fraction, much further work was required to determine whether this fraction did contain all the lignin and whether this lignin had been altered appreciably by this extrac-

TABLE II
ISOLATION AND OXIDATION OF ASPEN LIGNINS[a]

		Atmosphere			Residual pulp[c]		Chloroform-soluble products					
									Oxidation products			
Run No.	Raney nickel, gm.	Nature	Init. press., p.s.i.g.	Filtrate acidity[b]	Yield	Mäule test	Yield[d]	OCH_3, %	Syringaldehyde, %	Vanillin, %	Total S+V	Ratio S/V
25	18	H_2	3100	5	67	Sl. pos.	102	20.1	12.4	2.85	15.25	4.35
26	18	H_2	550	5	64	Neg.	95	21.6	14.4	3.37	17.77	4.27
27	0	H_2	3025	4.5	60	Sl. pos.	145	16.4	10.4	3.37	13.77	3.1
(27 *Calculated on basis of lignin only*)								23.8			19.6	
28[e]	18	H_2	575	4.5	63	Pos.	53	23.5	13.0	1.71	14.71	7.57
							18[f]	21.2	12.1	2.40	14.5	5.04
29	0	H_2	575	5	58	Neg.	150	14.2	10.1	3.27	13.37	3.08
(29 *Calculated on basis of lignin only*)								21.3			20.0	
30	18	H_2	0	5	70	Pos.	81	19.7	14.2	4.2	18.4	3.4
31	0	H_2	0	5	68	Pos.	72	17.0	15.1	5.01	20.1	3.0
33	0	N_2	500	2	60	Pos.	128	14.2				
34[g]	0	N_2	500	2	71	Pos.	82	14.2	13.2	5.0	18.2	2.6
35[g,h]	18	H_2	500	4	86	Pos.	100	24.3	20.2	5.3	25.5	3.8
Aspen native lignin[i]								19.4	20.0	10.2	30.2	2.0
Aspen Klason lignin								17.2	Trace	.Trace		
Aspen extractive free, oven-dried, based on Klason lignin content									32.5	11.5	44.0	2.82

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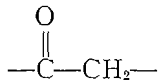
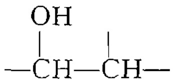
[a] *For each run, air-dried, solvent-extracted poplar wood meal (32.4 gm.); dioxane–water (1:1)(300 ml.), temperature 175–180°C., time five hours.*
[b] *Acidity measured using Fisher alkaloid test paper.*
[c] *See Table I (f, g).*
[d] *Reported as percentage, by weight, of the original Klason lignin.*
[e] *Water only used as suspending medium, time 10 hr.*
[f] *Chloroform extract of the residual pulp.*
[g] *Temperature 165–175°C.*
[h] *Glacial acetic acid (25 ml.) added to the suspending medium.*
[i] *Kindly donated by Dr. F. E. Brauns.*

tion technique. Assuming that the major part at least of the original methoxyl content of the wood was associated with the lignin, then the methoxyl content of the chloroform-soluble fraction may be considered as a good indication of lignin removal. As a test of the chemical nature of this isolated lignin the product was oxidized with alkaline nitrobenzene and the yields of syringaldehyde and vanillin determined. Since such an oxidation of the original wood gave rise to high yields of these aldehydes, 32.5 and 11.5% of the Klason lignin, respectively, similarly obtained values from the oxidation of the isolated lignins would indicate in one respect at least the extent to which the lignin had been modified.

A second series of runs was therefore made in which the products were isolated as before but on which the above mentioned further analytical observations were made. The reaction conditions and the analyses of the various isolated lignins from each run are reported in Table II. All the chloroform-soluble fractions were fairly viscous oils at room temperature and, although originally amber to red in color, darkened considerably on standing.

Unfortunately none of the products so isolated gave the high yields of aldehydes that were obtainable from the wood itself, indicating that some chemical change had occurred which involved to some extent the groupings responsible for aldehyde formation on nitrobenzene oxidation. With the exception of Run 35, which may be significant in that acetic acid was added to the reaction mixture and gave a product of high methoxyl content and better yields of aldehydes, the total production of syringaldehyde and vanillin on oxidation was in the range 15 to 20% instead of the possible 44%. It has been pointed out by Leopold (10), in a study of this oxidation reaction, that such linkages, β-γ to the guaiacyl nucleus, as —C=C— or potentially unsaturated groupings such as  $-\overset{O}{\overset{\|}{\mathrm{C}}}-\mathrm{CH_2}-$ and  $-\overset{OH}{\overset{|}{\mathrm{C}}}\mathrm{H}-\overset{|}{\mathrm{C}}\mathrm{H}-$ are required in order to obtain high yields of vanillin. The destruction of some of these groupings is readily visualized under these reducing conditions.

The methoxyl content (20–24%) of the isolated chloroform-soluble fractions shows a high recovery of this fragment. If allowance be made for an approximate 15% of the methoxyl of aspen wood to be associated with the holocellulose (7), the actual Klason lignin has a methoxyl analysis of around 26.5%. This decreased methoxyl content may be due to direct ether cleavage and could be another factor in the decreased aldehyde yield.

The results of Runs 27 and 29 for which a significantly larger chloroform-soluble fraction of low methoxyl was obtained lend support to the belief that in those cases for which no catalyst was used some uncleaved lignin–carbohydrate complex has been removed from the wood. The methoxyl contents of the product of these two runs, if calculated as a percentage of the lignin only, assuming all the lignin to be present, are increased to 23.8 and 21.3%, respectively, and are then in agreement with those of the other runs. As an indication, too, that these fractions may represent a less changed product there are the higher total yields of aldehydes obtainable and the better syring-

TABLE III

LIGNIN ISOLATION BY HYDROGENATION

Run No.	Temp., °C. ±2.5°	Hydrogen absorption, moles per 100 gm. lignin	Residual pulp[b]		Chloroform-soluble products					
			Yield	Mäule test	Yield[c]	OCH_3, %	Oxidation products			
							Syringaldehyde, %	Vanillin, %	Total S+V	Ratio S/V
Using Raney nickel catalyst (18 gm.)[a]										
38	103	0.4	110	Pos.	4.2	7.6	8.9	3.5	12.4	2.6
39	132	0.2	112	Pos.	10.0	14.8	12.5	6.0	18.5	2.1
66	133	0.6	98	Pos.	5.9	22.1	16.7	6.5	23.2	2.6
59	137	0.0	91	Pos.	7.9	20.5	18.3	6.7	25.0	2.7
58	145	0.6	85	Pos.	20.6	24.0	19.2	4.8	24.0	4.0
61	150	0.6	77	Pos.	30.2	19.6	15.4	3.9	19.3	3.9
57	151	0.6	76	Pos.	10.2	22.2	19.4	5.0	24.4	3.9
65	153	—	74	Pos.	30.2	25.9	16.3	5.4	21.7	3.0
56	157	0.4	63	Pos.	30.0	24.3	17.8	4.3	22.1	4.2
63	160	—	81	Pos.	26.0	26.6	18.0	5.1	23.1	3.6
55	162	0.4	64	Pos.	45.5	25.5	18.6	4.4	23.0	4.3
64	166	0.0	77	Pos.	42.0	22.3	18.3	4.3	22.6	4.3
54	166	0.0	75	Pos.	31.4	24.4	18.8	4.6	23.4	4.1
60	173	0.8	60	Neg.	41	24.0	18.9	3.8	22.7	4.9
45	173	1.0	89	Sl. pos.	30	21.5	14.4	4.0	18.4	3.6
26	177	1.2	64	Neg.	94.6	21.6	14.4	3.4	17.8	4.3
62	197	2.0	58	Neg.	117	22.3	14.4	2.9	17.3	5.0
Using copper chromium oxide catalyst (12 gm.)[a]										
42	103	1.9	94	Pos.	0.8	13.7	15.5	7.4	22.9	2.1
41	133	1.2	87	Pos.	7.2	15.0	15.2	7.2	22.4	2.1
40	166	1.7	74	Pos.	38.0	14.3	16.9	5.9	22.8	2.8
52	166	1.5	50	Neg.	88	16.0	10.1	3.6	13.7	2.8
37	167	1.9	70	Sl. pos.	70	16.7	18.5	5.4	23.9	3.4
44	174	2.2	62	Neg.	—	15.0	15.4	5.5	20.9	2.8
46	175	2.8	58	Neg.	134	13.9	7.8	2.6	10.4	2.9

TABLE III (*Concluded*)

Run No.	Temp., °C. ±2.5°	Hydrogen absorption moles per 100 gm. lignin	Residual pulp[b]		Chloroform-soluble products					
							Oxidation products			
			Yield	Mäule test	Yield[c]	OCH_3, %	Syringaldehyde, %	Vanillin, %	Total S+V	Ratio S/V
36	176	1.7	72	Neg.	101	16.6	16.3	5.0	21.3	3.3
51	177	1.9	55	Neg.	128	15.8	8.2	2.8	11.0	2.9
43	187	2.9	50	Neg.	118	13.6	10.5	3.8	14.3	2.8
50	198	2.3	37	Neg.	188	11.9	4.6	1.9	6.5	2.4
48[d]	177	2.3	—	Neg.	168	14.3	5.18	2.3	7.5	2.2
49[d, e]	177	—	51	Neg.	171	13.8	5.65	2.1	7.7	2.7
Using zinc chromium oxide catalyst (12 gm.)[a]										
47	177	0.6	70	Pos.	80.5	17.2	16.9	4.7	21.6	3.6
Using acetic acid (85%) medium, Raney nickel catalyst (18 gm.)[f]										
70	106	0.8	106	Pos.	36.4	20.5	13.8	6.0	19.8	2.3
71	120	0.6	97	Pos.	58.5	19.2	15.7	4.6	20.3	3.4
69	130	0.8	100	Pos.	56.5	20.2	19.4	6.3	25.7	3.1
68	140	1.0	76	Neg.	147	16.5	10.5	3.6	14.1	2.9
67	150	2.4	90	Neg.	163	15.8	6.4	1.2	7.6	5.4

[a] *For each run, air-dried, solvent-extracted, aspen wood meal (32.4 gm.) (lignin, 5 gm.), dioxane–water (1:1) (300 ml.), Raney nickel catalyst (18 gm.) or copper chromium oxide catalyst (12 gm.); initial hydrogen pressure (cold) 500 p.s.i.g. and time, five hours at stated temperature.*

[b] *See Table I (f, g).*

[c] *Reported as percentage by weight of the Klason lignin.*

[d] *Glacial acetic acid (10 ml.) added.*

[e] *Time, 9.5 hr.*

[f] *For each run, air-dried, solvent-extracted, aspen wood meal (19.5 gm.), glacial acetic acid (155 ml.), water (27 ml.), Raney nickel catalyst (10.8 gm.); initial hydrogen pressure (cold) 500 p.s.i.g. and time, five hours at stated temperatures in a Pyrex glass liner (capacity 660 ml.) were placed inside the steel bomb which was described previously.*

aldehyde to vanillin ratio if the ratio is compared to that of the whole wood oxidations. For the other runs, the much higher ratio appears as a result of a decreased vanillin production, suggesting that the linkages associated with the guaiacyl nuclei are more readily destroyed.

Runs 33 and 34 were designed to determine whether a good isolation, albeit a lignin–carbohydrate complex, could be achieved in a nonreducing (nitrogen) atmosphere. However, delignification was not complete nor were the analyses of the isolated products of any added interest. The high acidity of the filtrate cannot be explained. The oxidations of samples of aspen "native" lignin and of aspen Klason lignin were included to indicate that by this criterion of aldehyde formation both these types of isolated lignins are not representative of the lignin in the wood.

Part C. Effect of Temperature and Catalyst on the Isolation and Oxidation of Aspen Lignins

From the foregoing experiments it appeared that a successful isolation of an only moderately changed lignin might still be possible as long as the conditions could be modified so that undue destruction of certain linkages was prevented. The effect of varying the reaction temperature and changing the type of catalyst now seemed to be the two most important studies. Lower temperature would decrease the possibility of reduction although it was realized that there was a minimum temperature for effective lignin removal. Copper chromium oxide catalyst was studied because of its known decreased tendency to reduce unsaturated linkages (1). The chemical nature of the isolated chloroform-soluble products was investigated as before. The experimental conditions for these series of runs along with the analyses of the resultant products are given in Table III.

Using the dioxane–water medium and Raney nickel catalyst, the isolated products were oils which varied in color from dark yellow to dark brown as the temperature was increased. The chloroform solutions always darkened if allowed to stand exposed to the air, but no discoloration of the solute occurred if the chloroform were removed even after prolonged exposure. In nearly all cases some crystallization occurred on long standing. From the runs made using the copper chromium oxide and zinc chromium oxide catalysts, the products were originally dark brown in color but rapidly changed to dark red on contact with air. These viscous oils slowly solidified to flaky solids but showed no signs of crystallization. The products from those experiments using 85% acetic acid and a nickel catalyst were dark red but fairly fluid oils which darkened rapidly and which showed a tendency towards crystallization.

From a consideration of the results presented in Table III a few general observations may be made. Under the conditions of these experiments, the importance, for lignin isolation, of practical temperatures in the range 170–180°C. is indicated for the use of both the nickel and copper chromium oxide catalysts in the dioxane–water medium. However, with nickel in an 85% acetic acid mixture this temperature has been lowered by some 30°C. It may be concluded that neither the presence or nature of catalyst is important for lignin separation, but that this effect is primarily a combined result of the temperature and the acidity of the medium. The lack of sensitivity of the method and the rather empirical nature of the chloroform-solubility do not allow at this time a more accurate critical temperature to be established.

The increasing yield of the chloroform-soluble fraction with increasing temperature is consistent and to be expected. However, the methoxyl content of this fraction appears dependent to some extent on the catalyst and nature of the medium. With Raney nickel and dioxane–water, the methoxyl value parallels the increasing chloroform-solubility until a maximum is reached around 160 ± 5°C. This value is in fair agreement with that expected for the original lignin. Then as the temperature increases the methoxyl content decreases, owing possibly to partial demethylation or to dilution of the fraction with nonlignin derivatives. Under similar conditions, but replacing the nickel by copper chromium oxide catalyst, the percentage methoxyl of the isolated fractions remains quite constant (15 ± 2%) regardless of the amount extracted. This could be the result of the isolation of a definite lignin–carbohydrate fraction with a therefore lower methoxyl content than that of a similar fraction obtained using nickel which, as it has been suggested earlier, may permit the cleavage of such fragments. With nickel in acetic acid (85%) the similarly obtained methoxyl contents are again high, which tends to support the statement above.

For the great majority of the runs reported in Table III the total yield of aldehydes, expressed as a percentage of the chloroform-soluble fraction, remained between 20 and 25%, a value representing only about half that obtainable by the direct oxidation of the wood meal. For all cases in which nickel was used there is a noticeable increase in the syringaldehyde to vanillin ratio at the expense of the vanillin content, a fact that was noted in Part B. The better ratio of the aldehydes obtained using the oxide catalyst is again indicative of a less changed product.

Two other observations were made which pointed to the apparent lesser degree of hydrogenation when copper chromium oxide was used instead of nickel. One was the extra sensitivity to air oxidation of the products portrayed by their rapid darkening on standing. The second was the isolation from the filtrate of Run 52 of a chemically reactive product, no similar product being found in any runs using nickel as a catalyst. During the concentration of this filtrate, the distillate was tested with several reagents to determine whether any products were thus being removed. Positive carbonyl, Fehling's, and iodoform tests were obtained, but a phenolic test was negative. From this distillate was obtained a dark yellow oil which rapidly changed to a green, gummy substance before any further study to identify it could be undertaken. The observed properties of this substance agreed with those of methyl glyoxal but no positive identification was made. A discussion of the possible role of methyl glyoxal in plant metabolism has been given by Hibbert (8).

In review then, it appears that the sensitivity to chemical change of at least a large portion of the lignin as it exists in the wood will make its total isolation by any variation in the technique of catalytic hydrogenation a difficult task.

However, the change may not be very extensive as evidenced by the fact that a fraction containing all the lignin may be isolated. This does give rise to approximately 50% of the required aldehydes on nitrobenzene oxidation. An interesting possibility therefore arises; the separation of such an isolated lignin into two portions, depending on whether it does or does not yield aldehydes. Further chemical studies on these two portions might lead to an understanding of the linkages that have been destroyed by this method of isolation. It is realized that some of the conclusions which have been drawn from the results of this research, e.g., the isolation of a lignin–carbohydrate complex, have not been supported completely by experiment. It is possible therefore that other interpretations of the data may be made. It is hoped that subsequent investigations will permit a clearer understanding of the reactions involved.

EXPERIMENTAL

Description of Reactants

Aspen wood.—Native Saskatchewan aspen sapwood (*Populus tremuloides*) was ground in a Wiley mill (20 mesh), extracted with ethanol–benzene (4:1) for 48 hr., then with ethanol for 36 hr., thoroughly washed with water, and air dried. Anal.: Klason lignin, 16.4; moisture, 5.8; methoxyl, 5.16%.

Catalysts.—The following catalysts were prepared according to previously reported procedures: Raney nickel (11) (the washing in a hydrogen atmosphere was deleted), copper chromium oxide (2), and zinc chromium oxide (14).

Solvents.—Dioxane was purified according to Fieser (6).

General Reaction Procedure

The previously reported (12) procedure for hydrogenation was followed. The solvent extractions were made exhaustively and solvent removal procedures were continued until constant residual weights were obtained. The reaction products were studied as outlined below.

Part A.—The cooled charge, on removal from the bomb, was filtered and the acidity of the filtrate tested with Hydrion paper. The pulp was washed by stirring with two separate 250 ml. portions of the same solvent medium. These washings and the original filtrate were combined, and reduced to incipient precipitation under reduced pressure (water pump) with sufficient heat to give a moderate rate of distillation. This solution was then extracted with chloroform (5 × 300 ml.) and the chloroform layer back-extracted with water (150 ml.). The excess chloroform was removed as before and the product dried at steam bath temperature and reduced pressure (water pump). A small sample (0.1 gm.) of the pulp after being washed was retained for a Mäule test (17) and the remainder dried for 24 hr. at 100°C. A correction for the presence of nickel was made by subtracting five eighths of the weight of the wet catalyst used. The secondary pulp extractions were carried out at the reflux temperature of the extracting solvent while the mixture was being stirred mechanically. The solvent was used in as many 250 ml. portions as was necessary for complete extraction, each portion being refluxed for three hours. The solution was reduced to incipient precipitation or a volume of 50 ml., whichever occurred the sooner, and added to chloroform (750 ml.). This mixutre was then extracted with an equal volume of water and the product recovered in the same way as that from the chloroform extract of the filtrate.

Part B.—To the charge in the bomb sodium hydrosulphite (0.5 gm.) and chloroform (50 ml.) were added as soon as the bomb was opened. The residual pulp, after removal by filtration, was extracted in a Soxhlet extractor with chloroform (200 ml.) for 10 hr. The pulp was dried at 106°C. for 24 hr., and the weight of the recovered pulp was then calculated, a correction being made for the nickel if present. A small sample (10 mgm.) of this pulp was used for the Mäule test. The original filtrate, after the acidity was determined, was extracted with three separate (50 ml.) portions of chloroform which were together back-extracted with water (50 ml.). The combined pulp and filtrate extracts were concentrated under reduced pressure (N_2 atmosphere, 30–35°C.) and finally dried to constant weight in a vacuum desiccator. This product was then analyzed for methoxyl (9), and the values reported (Table II) represent the mean of two determinations which differed from each other by less than one per cent of the Klason lignin. The alkaline nitrobenzene oxidations were made on small samples (*ca.* 10 mgm.) of this product and analyzed for the resulting aldehyde content by the method of Stone and Blundell (16).

Part C.— After filtration of the bomb contents, the pulp was washed with water (250 ml.). The volume of combined filtrate and washings was reduced to approximately 50 ml. (35°C. at 27 mm.). To the product were added water (50 ml.) and chloroform (75 ml.). The mixture was shaken and the chloroform layer removed. The water layer was further extracted with two 75 ml. portions of chloroform and these three extracts combined. The pulp was extracted in a Soxhlet extractor with chloroform (200 ml.) until no further color was removed (five hours). After drying at 100°C. for 24 hr. the weight of the recovered pulp was calculated, correction being made for the catalysts present, and a small sample used in the Mäule test. The combined pulp and filtrate extracts were dried over anhydrous sodium sulphate for 24 hr., and reduced in volume to 25 ml. (25°C. at 27 mm.). At this point the solution was transferred to a 50 ml. Erlenmeyer flask and the remaining chloroform removed under similar conditions. This product was analyzed for methoxyl content and for aldehyde production by alkaline nitrobenzene oxidation according to the methods given in Part B. The procedure and reagents used in the methoxyl determination were periodically checked by trial determinations on vanillin and those used in the aldehyde analyses were checked by repeated determinations on the extracted wood meal. Some idea of the reproducibility of this procedure is given by the following sets of analyses made at different times. The yields of syringaldehyde and vanillin, expressed as percentage of the Klason lignin, were: 31.1, 11.3; 33.2, 11.7; 31.8, 11.8; and 33.9, 11.0%.

All the reduced pressure distillations referred to above were carried out using two small "film evaporators" constructed, with modifications, according to the assembly described by Craig *et al.* (5). The main difference involved the use of only one rotating flask, which was connected by an adapter to a ball and socket joint. A pulley system attached to this adapter provided the necessary rotation through this ball and socket joint. The socket joint was attached at a slight inclination to the center of a vertical system carrying an efficient condenser on top and a receiver flask on the bottom. A water aspirator was attached through the top of the condenser. The advantages arising from the use of such equipment with respect to the use of low temperatures, rapid concentration, and decreased foaming, were significant.

Examination of the Distillation of Run 52

During the reduction in volume of the filtrate from Run 52 (Table III), portions of the distillate were tested with several reagents to determine whether any of the products of hydrogenation were being removed. An orange red precipitate was obtained with 2,4-dinitrophenylhydrazine and positive Fehling's and iodoform tests were also obtained. A negative test for phenols was obtained using the ferric chloride – potassium ferricyanide test mixture. To recover this carbonyl containing fraction, the distillate was extracted with ether (5 × 50 ml.). The resulting ether–dioxane solution was shaken with moist solid sodium bisulphite until the ether solution no longer gave a positive test with 2,4-dinitrophenylhydrazine. To the solid addition product, after filtration, were added water (50 ml.) and ether (50 ml.), and the mixture was acidified with hydrochloric acid. The aqueous layer was extracted with 5×50 ml. ether and the combined ether extracts dried and concentrated at room temperature to leave a dark yellow to orange colored oil. On standing this product changed to a green, gummy substance.

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TWO SYNTHESES OF 1,5:3,6-DIANHYDRO-2,4-*O*-METHYLENE-D-GLUCITOL: STABILITY OF THE METHYLENE ACETAL BRIDGE TOWARD AQUEOUS ACID[1]

By Samuel B. Baker[2]

ABSTRACT

1,5:3,6-Dianhydro-2,4-*O*-methylene-D-glucitol has been synthesized by two wholly independent routes. The methylene acetal bridge was found to be stable in hot water and dilute aqueous acid and thus differs from the methylene bridges in 1,4:3,6-dianhydro-2,5-*O*-methylene-D-mannitol and in the D-iditol analogue of the latter compound. It is suggested that this difference may be due to the ease of folding of the glucitol derivative as compared to the rigidity of the mannitol and iditol structures.

A previous (1) publication has indicated that extreme molecular rigidity occurs in cyclic compounds such as 1,4:3,6-dianhydro-2,5-*O*-methylene-D-mannitol (I) and 1,4:3,6-dianhydro-2,5-*O*-methylene-D-iditol (II) so that the strain within the bonds of I and II cannot be dissipated by folding or twisting of these bonds. It follows that these substances should be unstable and cleavage of the most highly strained group within the molecules I and II would occur. It was shown (1) that the methylene acetal groups in I and II were extremely unstable and hydrolytic cleavage occurred with great facility.

It was suggested (1) that the substance 2,5-*O*-methylene-D-mannitol (III), being capable of folding and twisting to overcome internal strain, should be stable to the hydrolytic conditions used for I and II. This was found to be the case.

Further work was undertaken to investigate the feasibility of the hypothesis and a dianhydro-*O*-methylene hexitol was synthesized that would not possess great molecular rigidity. This substance, 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol (IV), was found to be very stable toward hot water and 0.01 *N* hydrochloric acid. This stability was expected on the basis of the views postulated previously (1), as examination of a model of IV shows that the tricyclic structure may fold or twist to overcome internal strain within the molecule and the methylene acetal group should then be stable.

Vargha (2) showed that 2,4-*O*-benzylidene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (V), on treatment with one molecular equivalent of sodium methoxide, lost one *p*-tolylsulphonyl group with the formation of the ethylene oxide derivative, 5,6-anhydro-2,4-*O*-benzylidene-1-*O*-*p*-tolylsulphonyl-D-glucitol (VI). Application of Vargha's method to 2,4-*O*-methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (VII) yielded 5,6-anhydro-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (VIII). The ethylene oxide ring was very easily cleaved by dilute hydrochloric and sulphuric acids to yield 6-chloro-6-deoxy-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (IX) and 2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (X) respectively. The 6-chloro derivative (IX) on treatment with

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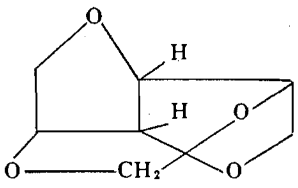
[1] *Manuscript received January 19, 1954.*
Contribution from The Research Institute, Montreal General Hospital, Montreal, Quebec.
[2] *In charge, Division of Organic Chemistry.*



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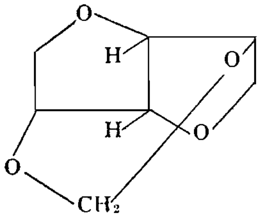

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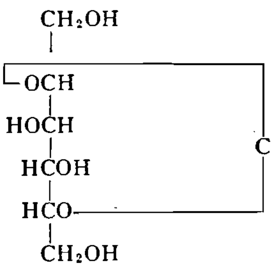

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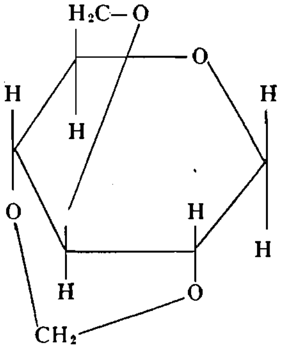

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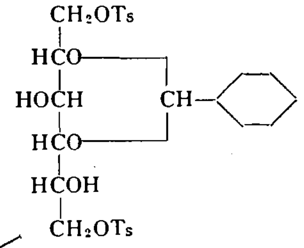

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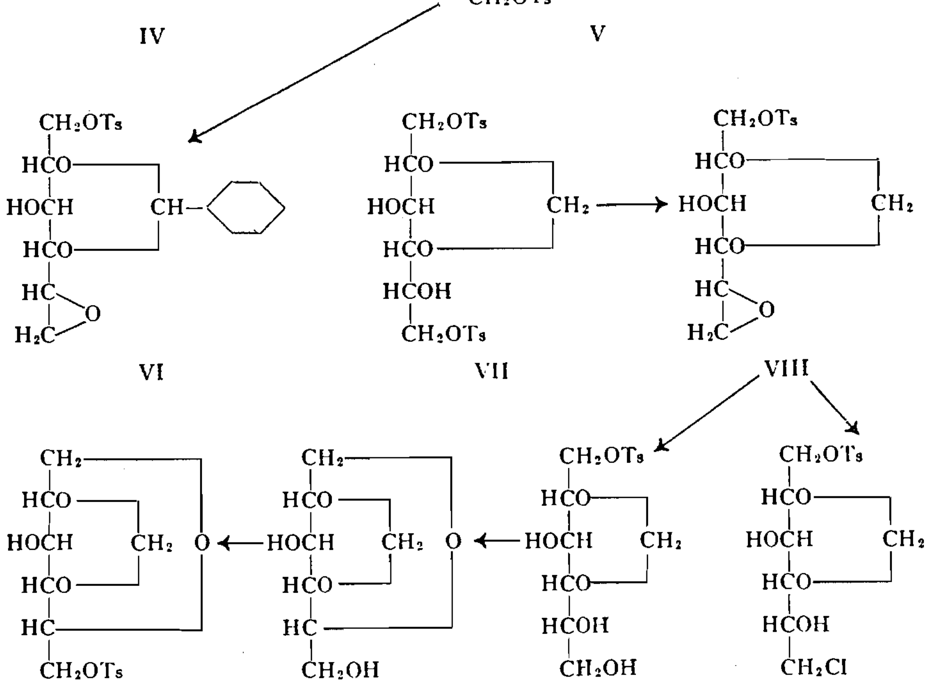
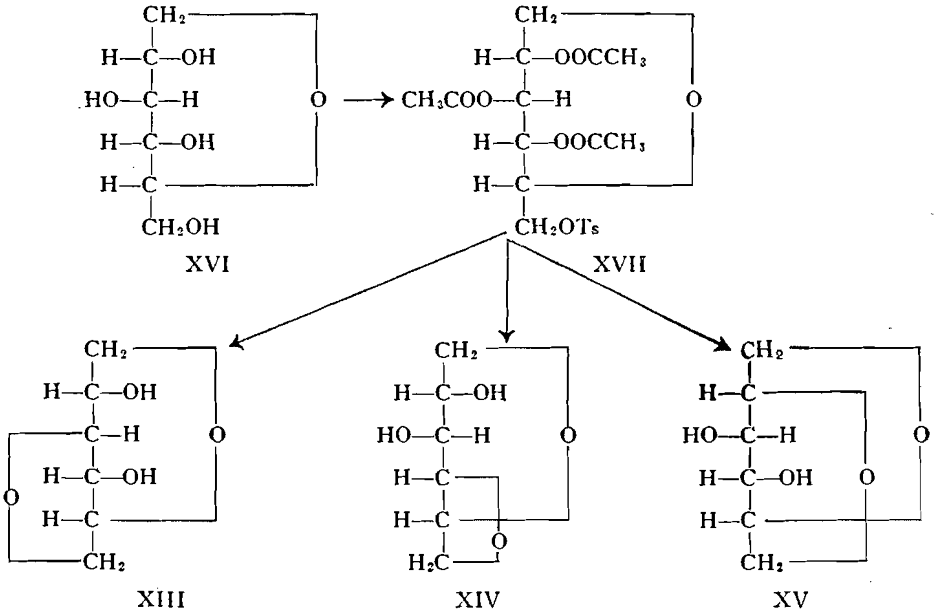


one molecular equivalent of sodium methoxide yielded VIII. This showed that the chlorine atom was situated either on the terminal carbon atom or on C-5, but most probably on the terminal position since otherwise an L-iditol derivative would be obtained. Additional proof of the absence of an hydroxyl group on C-6 was obtained when tritylation of the chloro derivative IX did not occur.

The substance (X) reduced a glacial acetic acid solution of lead tetraacetate to the extent of one mole per mole oxidant thus showing the presence of vicinal hydroxyl groups in X. Monotosylation of X with tosyl chloride in pyridine yielded 2,4-*O*-methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (VII). Therefore X was a glucitol derivative, which was expected since cleavage of an anhydro ring which is on a terminal carbon atom occurs without Walden inversion. Saponification of X with aqueous sodium hydroxide yielded an anhydro derivative (XI) that reacted readily with trityl chloride in pyridine. Lead tetraacetate was not reduced, thereby indicating the absence of vicinal hydroxyl groups. Thus the anhydro ring could not be either 1,6 or 1,3. The latter ring would be unlikely on steric grounds. Therefore the substance had to be 1,5-anhydro-2,4-*O*-methylene-D-glucitol (XI). Treatment of XI with tosyl chloride in pyridine yielded the monotosylate XII, 1,5-anhydro-2,4-*O*-methylene-6-*O*-*p*-tolylsulphonyl-D-glucitol, which on saponification with sodium methoxide yielded 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol or 2,4-*O*-methylene-*neo*glucide* (IV). This latter substance on treatment with hot water or 0.01 *N* hydrochloric acid was recovered unchanged. Hydrolysis of



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*The prefix "neo" is used here to indicate analogous ring structure with neo-mannide, which is 1,5:3,6-dianhydro-D-mannitol.

the methylene group occurred only on prolonged heating in 1 *N* hydrochloric acid. The tricyclic ring structure of IV is therefore relatively stable.

Synthesis of 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol (IV) by a different route served to confirm its structure. The D-glucitol derivative D-*neo*-glucide* (XIII) was synthesized by a route that made possible one of three structures (XIII, XIV, XV). 1,5-Anhydro-D-glucitol (polygalitol) (XVI), whose structure is known with certainty, was condensed with one molecular equivalent of tosyl chloride in pyridine and then acetylated with acetic anhydride. Isolation of the reaction product yielded a crystalline derivative that had three acetyl groups. Saponification of the latter, 2,3,4-tri-*O*-acetyl-1,5-anhydro-6-*O*-*p*-tolylsulphonyl-D-glucitol (XVII), with sodium methoxide yielded a product that could be XIII, XIV, or XV. The compounds XIV and XV having 1,2-glycol groups should be oxidized by lead tetraacetate. However, since this substance was stable to the action of this oxidant, it is very probably XIII. The product of the reactions described above,1,5:3,6-dianhydro-D-glucitol (XIII), was treated with formaldehyde solution and hydrochloric acid and the isolated product proved to be identical with 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol (IV), prepared earlier.

EXPERIMENTAL

5,6-Anhydro-2,4-O-methylene-1-O-p-tolylsulphonyl-D-glucitol (VIII)

2,4-*O*-Methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (VII) (47.4 gm.) was dissolved in chloroform (500 cc.). Methanol (75 cc.) in which sodium (2.2 gm.) had been dissolved was added to the cold (0°) chloroform solution. A gel formed immediately and the mixture was allowed to stand overnight at 5°. The small excess of sodium methoxide was converted to carbonate, and water (100 cc.) was added to dissolve the sodium salts. The chloroform layer was separated, dried over anhydrous sodium sulphate, and concentrated *in vacuo* to a thick sirup which was then dissolved in a small volume of 99% ethanol. The solution was kept at −15° overnight and the crystalline mass, thus obtained, was washed with a little cold 99% ethanol and finally dried. The yield was 24 gm. (80%) and melting point was 94–95.5°. This substance was pure enough for subsequent work.

A sample was dissolved in a hot mixture of ethyl acetate – isopropyl ether (1:3) and, after cooling slowly to 20°, crystallization occurred in the form of clusters of rosettes. The melting point was 95–95.5°; $(\alpha)_{\text{D}}^{24°}$–4.4° ($CHCl_3$; *c*, 5.6724). Anal.: Calc. for $C_{14}H_{18}SO_7$: C, 50.91; H, 5.45; S, 9.69. Found: C, 50.80; H, 5.86; S, 9.6.

Effect of Hydrochloric Acid on 5,6-Anhydro-2,4-O-methylene-1-O-p-tolylsulphonyl-D-glucitol (VIII)

The compound above (5 gm.) was heated to boiling for about one minute with 8% hydrochloric acid (120 cc.). The starting material melted, dissolved, and precipitation occurred. The precipitate was filtered, washed with water to remove all traces of acidity, and then air-dried. The yield was 4.1 gm. (74.5%). The crude product was recrystallized from ethyl acetate and the melting point was 162–162.5° and rotation $(\alpha)_D^{25°}$–21.2° (pyridine; *c*, 2.9048). Anal.: Calc. for $C_{14}H_{19}SClO_7$: C, 45.75; H, 5.17; S, 8.7. Found: C, 45.68; H, 5.22; S, 8.7.

A sample (1 gm.) of the above, 6-chloro-6-deoxy-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (IX), was suspended in chloroform (100 cc.) and 0.3 *M* sodium methoxide in methanol (10 cc.) was added. The solid dissolved and precipitation of sodium chloride occurred. The reaction mixture was allowed to stand overnight at 5°, the small excess sodium methoxide converted to carbonate, and the mixture washed once with a small volume of water to remove sodium salts. The chloroform solution was dried over anhydrous sodium sulphate, the solvent removed *in vacuo*, and the resulting sirup dissolved in a little 95% ethanol and the solution cooled to −15°. Precipitation occurred and water was added so that most of the product separated as a crystalline mass. The air-dried substance melted broadly at 82–92° and was recrystallized from 250 cc. of boiling isopropyl ether in a yield of 0.7 gm. (77%). Alone or in admixture with 5,6-anhydro-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol it melted at 95–96°.

*Nonreaction of Trityl Chloride with 6-Chloro-6-deoxy-2,4-O-methylene-1-O-p-tolylsulphonyl-*D*-glucitol (IX)*

A sample (0.3 gm.) of the above substance was dissolved in anhydrous pyridine (5 cc.) and trityl chloride (0.23 gm., 1 mol. equiv.) was added. The mixture was allowed to stand for three days at 24° and was then added to cold water. The crystalline substance that separated was removed by filtration and washed well with water to remove most of the pyridine. After drying in air, the solid was extracted for one hour in boiling isopropyl ether (50 cc.) and filtered. The insoluble fraction (0.24 gm.) melted at 160–162° when mixed with the starting material. The isopropyl ether filtrate was concentrated to dryness and the solid was found to be slightly impure tritanol by a mixed melting point determination with authentic tritanol. This experiment proved that the terminal carbon atom did not have an hydroxyl group and the starting material was thus 6-chloro-6-deoxy-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (IX).

*2,4-O-Methylene-1-O-p-tolylsulphonyl-*D*-glucitol (X)*

5,6-Anhydro-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (52 gm.) was added to boiling water (1500 cc.). Concentrated sulphuric acid (15 cc.) dissolved in water (60 cc.) was added and the molten glucitol derivative (X), dissolved in about 10 min. The clear solution was quickly neutralized with barium carbonate and the barium sulphate and carbonate were removed by filtration through a thin layer of decolorizing charcoal. The clear filtrate was then concentrated *in vacuo* to a thick sirup and the latter was dissolved in hot 95% ethanol and a slight turbidity removed by filtration through a layer of charcoal. The alcoholic filtrate was then concentrated to dryness and traces of water were removed by codistillation with 99% ethanol. The colorless sirup was dissolved in 99% ethanol, petroleum ether (30–60°) was added to turbidity, and the solution cooled at −15°. Soft, feathery crystals melting at 113–

114.5° separated. The crude product was recrystallized from the same solvent mixture with practically no loss and then melted at 115–115.5°. It was soluble in acetone, ethanol, methanol, chloroform, and hot water. It was insoluble in ether and petroleum ether. It rotated $(\alpha)_D^{24°}$–0.24° (acetone; *c*, 2.2876). Anal.: Calc. for $C_{14}H_{20}SO_8$: C, 48.27; H, 5.75; S, 9.2. Found: C, 48.15; H, 5.91; S, 9.1.

*Conversion of 2,4-O-Methylene-1-O-p-tolylsulphonyl-*D*-glucitol (VIII) into 2,4-O-Methylene-1,6-di-O-p-tolylsulphonyl-*D*-glucitol (VII)*

2,4-*O*-Methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (1 gm.) was dissolved in anhydrous pyridine (10 cc.). The solution was cooled to −5° and tosyl chloride (0.55 gm.) was added. The solution was allowed to stand for three hours after warming up to room temperature (24°) and it was then added to cold water. The crystalline product that separated was removed by filtration, washed with water on the filter, dried, and then recrystallized from 95% ethanol. It melted at 129–130° and the mixed melting point with authentic 2,4-*O*-methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol was 128–130°.

*Lead Tetraacetate Oxidation of 2,4-O-Methylene-1-O-p-tolylsulphonyl-*D*-glucitol*

A sample of the compound above (0.2727 gm.)was dissolved in 0.0329 *M* lead tetraacetate in glacial acetic acid in a 100.0 ml. volumetric flask and made up to volume with the tetraacetate solution. After 1, 2, and 24 hr. 0.94, 0.99, and 1.06 mol. equiv. of lead tetraacetate were consumed.

*1,5-Anhydro-2,4-O-methylene-*D*-glucitol (2,4-O-Methylene-polygalitol)*

2,4-*O*-Methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (10 gm.) was dissolved in freshly boiled water (200 cc.). Sodium hydroxide (1.1 gm.) was added and the solution heated on the steam bath in the absence of carbon dioxide. A few drops of 1% phenolphthalein was added and after two hours the reaction mixture became neutral. The solution was then concentrated *in vacuo* and traces of water were removed by codistillation with 99% ethanol. The white crystalline residue was heated with chloroform (400 cc.) and filtered to remove the insoluble sodium *p*-toluenesulphonate. The chloroform filtrate was concentrated to about 200 cc. and petroleum ether (30–60°) was added until a faint turbidity was formed. Crystallization occurred almost immediately and the mixture was cooled to −15° overnight to assure complete crystallization. The product was found to be pure, as an additional recrystallization did not change the melting point of 135–135.5°. It rotated $(\alpha)_D^{19°}$–24.2° (H_2O; *c*, 2.0632). Anal.: Calc. for $C_7H_{12}O_5$: C, 47.72; H, 6.82. Found: C, 47.50; H, 6.93.

*1,5-Anhydro-2,4-O-methylene-6-O-trityl-*D*-glucitol*

1,5-Anhydro-2,4-*O*-methylene-D-glucitol (3 gm.) and trityl chloride (4.7 gm.) were dissolved in anhydrous pyridine (30 cc.). The reaction mixture was allowed to stand three days at room temperature (24°). About 5 cc. water were added to dissolve the separated pyridinium chloride and the mixture was then added to cold water. The sirup that separated was dissolved in chloroform and the chloroform solution washed several times with water. The chloroform solution was dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo* to remove the solvent and traces of pyridine. The light-yellow sirup was dissolved in 99% ethanol (100 cc.) and the solution was treated with decolorizing charcoal and finally filtered. The colorless residue formed a glass that would not crystallize from any of the solvents used. Yield was 4.8 gm. (68%) and decomposition of 1.13 gm. of the substance with concentrated sulphuric acid yielded 0.68 gm. tritanol, showing the presence of one terminal hydroxyl group as the theoretical yield is 0.70 gm.

*1,5-Anhydro-2,4-O-methylene-6-O-p-tolylsulphonyl-*D*-glucitol* (*XII*)

1,5-Anhydro-2,4-*O*-methylene-D-glucitol (20 gm.) was dissolved in anhydrous pyridine (200 gm.) and the solution was cooled to 0°. *p*-Toluenesulphonyl chloride (21.0 gm.) was added and the mixture was allowed to stand four hours at 24°. The mixture was concentrated to $\frac{1}{4}$ vol. and the sirupy residue mixed with cold water (500 cc.). The sirup did not solidify; it was dissolved in chloroform and the chloroform solution washed twice with ice-cold 2% sulphuric acid to remove pyridine and once with water. The chloroform solution was dried over anhydrous sodium sulphate, filtered, and concentrated to dryness. A white crystalline substance separated in a yield of 31 gm. (81%). This was dissolved in hot 95% ethanol (200 cc.) and a trace of color removed by means of decolorizing charcoal. The clear solution was allowed to cool and crystallization occurred. The product melted at 118–119°. Further recrystallization from ethanol did not change the melting point. It rotated $(\alpha)_D^{23°}$ $-16.6°$ ($CHCl_3$; *c*, 6.0092). Anal.: Calc. for $C_{14}H_{18}SO_7$: C, 50.91; H, 5.45; S, 9.69. Found: C, 50.83; H, 5.66; S, 9.7.

*1,5:3,6-Dianhydro-2,4-O-methylene-*D*-glucitol* (*IV*)

1,5-Anhydro-2,4-*O*-methylene-6-*O*-*p*-tolylsulphonyl-D-glucitol (15 gm.) was dissolved in chloroform (250 cc.) and sodium (2 gm.) in methanol (100 cc.) was added. The mixture became milky and after about 10 min. glistening crystals of sodium *p*-toluenesulphonate separated. The slight excess of sodium methoxide was converted to carbonate with carbon dioxide and the mixture was then concentrated to dryness *in vacuo*. The dry solid mass was broken up and extracted twice with boiling chloroform and the mixture filtered. The clear, colorless filtrate was concentrated to dryness and the solid residue was soluble in hot ether and hot ethyl acetate. Recrystallized once from ethyl acetate and twice from ether it melted at 79.5–80° and rotated $(\alpha)_D^{22°}$ $-44.9°$ ($CHCl_3$; *c*, 1.112). The yield after recrystallization was 5.7 gm. (79%). Anal.: Calc. for $C_7H_{10}O_4$: C, 53.16; H, 6.33. Found: C, 53.07; H, 6.47.

*2,3,4-Tri-O-acetyl-1,5-anhydro-6-O-p-tolylsulphonyl-*D*-glucitol* (*XVIII*)

2,3,4-6-Tetra-*O*-acetyl-1,5-anhydro-D-glucitol (24.5 gm.) was dissolved in chloroform (300 cc.). Methanolic sodium methoxide (25 cc. of 0.2 *N*) was added and the mixture allowed to stand 36 hr. at 5°. The sodium methoxide was converted to carbonate and the solvents removed *in vacuo*. The thick sirupy product containing sodium carbonate and bicarbonate was dissolved in hot anhydrous pyridine (45 cc.) and after the solution was cooled to 0°, tosyl chloride (13.0 gm.) was added. The reaction mixture was then allowed to stand for two hours at 22° and again cooled to 0°. Acetic anhydride (30 cc.) was added and the reaction mixture allowed to stand overnight at room temperature. The mixture was added to cold water and a sirup separated. The sirup did not crystallize after two days and it was therefore extracted with chloroform. The chloroform solution was washed with cold 5% hydrochloric acid to remove pyridine, washed twice with water, and finally dried over anhydrous sodium sulphate. The mixture was filtered and the chloroform filtrate concentrated *in vacuo*. The resulting sirup was dissolved in ether and the ether solution on cooling and scratching deposited crystals. Petroleum ether (30–60°) was added to force complete crystallization. The crude product was then recrystallized from 95% ethanol and it melted at 143.5–144.5°. It rotated $(\alpha)_D^{24°}$ 62.2° ($CHCl_3$; 1,2; *c*, 1.3816). The yield was 19.9 gm. (61%). Anal.: Calc. for $C_{19}H_{24}SO_{10}$: C, 51.35; H, 5.45; S, 7.27; Acetyl, 26.8. Found: C, 51.1; H, 5.7; S, 7.3; Acetyl, 26.5.

*Conversion of 2,3,4-Tri-O-acetyl-1,5-anhydro-6-O-p-tolylsulphonyl-*D*-glucitol to 1,5:3,6-Dianhydro-*D*-glucitol* (D*-Neoglucide*) (*XIII*)

2,3,4-Tri-*O*-acetyl-1,5-anhydro-6-*O*-*p*-tolylsulphonyl-D-glucitol (11.4 gm.) was dissolved in anhydrous methanol (150 cc.) containing sodium (0.5 gm.) in solution. The reaction mixture was allowed to stand two hours at 24° and then heated to boiling under reflux for an additional two hours. The solution was cooled to 10°, the slight excess of sodium methoxide neutralized with dilute sulphuric acid, and the neutral solution concentrated to dryness *in vacuo*. The resulting gummy mass was heated with chloroform (250 cc.) and filtered. The residue consisting mainly of sodium *p*-toluenesulphonate was extracted once with hot chloroform (75 cc.) and the combined filtrates were concentrated *in vacuo*. The resulting sirup, which was soluble in ethyl acetate, chloroform, methanol, ethanol, acetone, water, and dioxane, was heated with isopropyl ether (120 cc.) and the solution was slowly concentrated until it became turbid. Scratching the flask caused immediate precipitation. The solid mass was removed by filtration and it was recrystallized once more from a large volume of isopropyl ether. The melting point was 150–152° and the rotation was $(\alpha)_D^{24°}$ 4.1° (water: 1; 2; *c*, 1.6116). The yield was 4.9 gm. (67.5%). Anal.: Calc. for $C_6H_{10}O_4$: C, 49.25; H, 6.87. Found: C, 49.08; H, 6.97.

Lead Tetraacetate Oxidation of D*-Neoglucide* (*XIII*)

A sample (0.4062 gm.) of D-neoglucide was dissolved in 0.543 *M* lead tetraacetate in glacial acetic acid solution and then made up to 100.0 ml. in a volumetric flask with the same solution. The lead tetraacetate solution was not reduced after 2, 24, and 48 hr. This indicated the absence of a 1,2-glycol group.

Methyleneation of D*-Neoglucide*

A sample (0.3 gm.) of D-neoglucide was dissolved in 37% aqueous formaldehyde (1 cc.) and concentrated hydrochloric acid (1 cc.). The reaction mixture was allowed to stand for 20 hr. at 40–45° and the hydrochloric acid removed with silver carbonate. Water (50 cc.) was added and the mixture filtered. The filtrate was treated with hydrogen sulphide to remove dissolved silver ions and the silver sulphide removed by filtration through a thin layer of charcoal. The filtrate was concentrated to dryness *in vacuo* and the resulting colorless sirup was dissolved in ether (3 cc.) and seeded with a crystal of 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol. The mixture was cooled to −20° for 48 hr. The crystalline product was filtered and recrystallized once more from a small volume of ether. The yield was 0.11 gm. (35%) and the product, in admixture with a sample of 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol, prepared as described earlier, melted at 77–80°.

*Effect of Sodium Periodate and Lead Tetraacetate on 1,5:3,6-Dianhydro-2,4-O-methylene-*D*-glucitol (IV)*

Samples of the above (IV) did not reduce either standard periodate or lead tetraacetate. This showed the absence of 1,2-glycol groups.

*Effect of Acetic Anhydride on 1,5:3,6-Dianhydro-2,4-O-methylene-*D*-glucitol (IV)*

A sample (2 gm.) of (IV) was dissolved in acetic anhydride (5 cc.) and anhydrous pyridine (5 cc.) was added. The reaction mixture was allowed to stand for 72 hr. at 23° and then converted to a thick sirup *in vacuo.* The sirupy residue was dissolved in chloroform and the chloroform solution washed once with ice-cold 2% sulphuric acid, once with saturated ice-cold sodium bicarbonate, and then with water. The chloroform solution was dried over anhydrous sodium sulphate, filtered, and concentrated to dryness *in vacuo.* The white solid residue was recrystallized once from hot ether. The yield was 1.6 gm. (80%) and the mixed melting point with the starting material (IV) was 79–80°. This indicated the absence of hydroxyl groups.

*Effect of Hot Water on 1,5:3,6-Dianhydro-2,4-O-methylene-*D*-glucitol (IV)*

A sample of the above (0.4 gm.) was dissolved in water (50 cc.) and boiled under reflux for one hour. The water was removed *in vacuo* and the distillate did not give a dimethone test for formaldehyde. The residue on recrystallization from ether was found to be unchanged starting material in a yield of 0.38 gm. (96%).

*Effect of 0.01 N Hydrochloric Acid on 1,5:3,6-Dianhydro-2,4-O-methylene-*D*-glucitol (IV)*

A sample of the above (0.35 gm.) was heated under reflux in 0.01 *N* hydrochloric acid (50 cc.) for one hour. The solution was neutralized with silver carbonate and then filtered. The filtrate was treated with hydrogen sulphide to remove traces of silver ions and after filtration the filtrate was concentrated to dryness and the white residue recrystallized from ether. The yield was 0.28 gm. (82%) and the mixed melting point with starting material was 78–80°.

Effect of 1 N Hydrochloric Acid on IV

The above experiment was repeated with 0.3 gm. of IV and 1 *N* hydrochloric acid. After one hour a trace of formaldehyde was formed. The solution was then slowly distilled in a stream of nitrogen and the volume was kept constant by addition of distilled water. After six hours all the formaldehyde was evolved and 0.47 gm. (86%) of the dimethone of formaldehyde was isolated, washed, and dried. It melted at 187–189° and the melting point was not depressed with authentic formaldehyde dimethone. The residue in the distilling flask was neutralized with silver carbonate and after filtration the traces of silver ions were removed as sulphide. The filtrate was concentrated to dryness and the cloudy sirup dissolved in chloroform; the latter solution was treated with charcoal and then filtered. The clear, colorless filtrate was concentrated *in vacuo* to a thick sirup. The sirup was extracted with a large volume of boiling isopropyl ether. The solvent was allowed to evaporate slowly and crystallization occurred. The oily crystals were filtered and recrystallized once more from isopropyl ether. The yield was 0.13 gm. (48%) and the melting point was 150–152°. A mixed melting point determination with authentic 1,5:3,6-dianhydro-D-glucitol showed identity.

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BENZIDINE-REARRANGEMENT DURING THE TITRATION OF AZO-COMPOUNDS WITH TITANOUS CHLORIDE

BY STIG VEIBEL

Fainer, Myers, and Keirstead (1) recently mentioned that on attempting the estimation of some chlorinated azobenzenes with titanous sulphate according to the method of Knecht and Hibbert (2), using a procedure similar to that recommended by Siggia (4), they found that in some instances, viz. when the *p*-positions to the azo-group were unsubstituted, only two equivalents of titanous sulphate were used instead of the expected four equivalents; and when the *p*-positions were blocked nearly four equivalents (reported 3.27 equivalents) were used, benzidine rearrangement taking place when the *p*-positions are free.

The authors mention that Veibel (5) has reported similar rearrangements when azo-compounds are titrated with titanous chloride. They call attention to the strongly acid medium in which the reaction takes place, pointing out that this will favor the benzidine rearrangement. Evidently a procedure such as that recommended by Siggia will favor the benzidine rearrangement, but we should like to stress that a strongly acid medium is not necessary for obtaining this rearrangement during the titration. We have for more than 25 years used the technique recommended by Kolthoff and Robinson (3), in which the reaction of the medium is nearly neutral, the reaction mixture being strongly buffered with sodium citrate. The titration is carried out at room temperature and is finished in two to three minutes. Notwithstanding this, only two equivalents of titanous chloride are used when azobenzene is titrated. From this is clearly seen that even under reaction conditions not favoring the rearrangement of hydrazobenzene into benzidine such a rearrangement may take place during the titration.

Other azo-compounds may use more than two equivalents. We found, for example, that 3-nitro-azobenzene uses 8.5 equivalents of titanous chloride, which means six equivalents for the nitro function and 2.5 equivalents for the azo function. 4-Carboxy-azobenzene uses 2.05 equivalents of titanous chloride, and in estimating azo-compounds where both *p*-positions are blocked we found a consumption of three to nearly four equivalents of titanous chloride, in excellent agreement with the statement of Feiner, Myers, and Keirstead that 4,4′-dichloro-azobenzene uses only 3.27 equivalents of titanous sulphate.

When azo-compounds in which one or both *p*-positions are blocked use less than four equivalents of Ti^{+++} it means that not only a benzidine rearrangement, but a semidine or a diphenyline rearrangement as well, may take place under the conditions of the experiment, i.e. in nearly neutral solution.

The rate with which the titration is carried through may influence the number of equivalents of Ti^{+++} used. When a solution of *o*-azo-toluene is titrated in the usual manner slightly over two equivalents of titanous chloride are used, but when an excess of the titanous chloride solution is added in one batch or when, with even greater efficiency, the solution of the azo-compound is added to an excess of titanous chloride, up to three equivalents of titanous chloride are used. This result indicates that two reactions, viz. reduction to an aniline and rearrangement to a benzidine, proceed simultaneously when the initial reduction of the azo-compound to a hydrazo-compound has taken place. In the estimation of nitro-compounds we have so far never met this complication.

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THE PREPARATION OF 2,2,2-TRIFLUOROETHYLAMINE[1]

By A. F. McKay and G. R. Vavasour

2,2,2-Trifluoroethylamine hydrochloride has been prepared (1) by the catalytic hydrogenation of 2,2,2-trifluoroacetonitrile which was obtained from 2,2,2-trifluoroacetamide on treatment with phosphorus pentoxide. The highest over-all yield by this method was 59% based on the acetamide. 2,2,2-Trifluoroethylamine hydrochloride can be produced consistently in 68–75% yields, in one step, by the reduction of trifluoroacetamide with lithium aluminum hydride.

EXPERIMENTAL

2,2,2-Trifluoroethylamine Hydrochloride

Trifluoroacetamide (50 gm., 0.44 mole) (prepared by the method of Gilman and Jones (1)) was dissolved in 200 cc. of anhydrous ether and added slowly, with stirring, to a suspension of lithium aluminum hydride (42 gm., 1.1 mole) in 600 cc. of anhydrous ether so as to maintain gentle reflux[2]. An atmosphere of nitrogen was maintained in the flask. After the addition was complete, refluxing and stirring was continued for one hour, then the theoretical amount

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[1] *Issued as D.R.C.L. Report No. 141.*

[2] Caution: *The referee has warned that when concentrated ether solutions of lithium aluminum hydride and trifluoroacetamide are mixed, the reaction may be violent. Thus it is essential that the solutions be diluted and the additions made with extreme care.*

The rate with which the titration is carried through may influence the number of equivalents of Ti^{+++} used. When a solution of *o*-azo-toluene is titrated in the usual manner slightly over two equivalents of titanous chloride are used, but when an excess of the titanous chloride solution is added in one batch or when, with even greater efficiency, the solution of the azo-compound is added to an excess of titanous chloride, up to three equivalents of titanous chloride are used. This result indicates that two reactions, viz. reduction to an aniline and rearrangement to a benzidine, proceed simultaneously when the initial reduction of the azo-compound to a hydrazo-compound has taken place. In the estimation of nitro-compounds we have so far never met this complication.

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THE PREPARATION OF 2,2,2-TRIFLUOROETHYLAMINE[1]

By A. F. McKay and G. R. Vavasour

2,2,2-Trifluoroethylamine hydrochloride has been prepared (1) by the catalytic hydrogenation of 2,2,2-trifluoroacetonitrile which was obtained from 2,2,2-trifluoroacetamide on treatment with phosphorus pentoxide. The highest over-all yield by this method was 59% based on the acetamide. 2,2,2-Trifluoroethylamine hydrochloride can be produced consistently in 68–75% yields, in one step, by the reduction of trifluoroacetamide with lithium aluminum hydride.

EXPERIMENTAL

2,2,2-Trifluoroethylamine Hydrochloride

Trifluoroacetamide (50 gm., 0.44 mole) (prepared by the method of Gilman and Jones (1)) was dissolved in 200 cc. of anhydrous ether and added slowly, with stirring, to a suspension of lithium aluminum hydride (42 gm., 1.1 mole) in 600 cc. of anhydrous ether so as to maintain gentle reflux[2]. An atmosphere of nitrogen was maintained in the flask. After the addition was complete, refluxing and stirring was continued for one hour, then the theoretical amount

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[1] *Issued as D.R.C.L. Report No. 141.*

[2] Caution: *The referee has warned that when concentrated ether solutions of lithium aluminum hydride and trifluoroacetamide are mixed, the reaction may be violent. Thus it is essential that the solutions be diluted and the additions made with extreme care.*

of water (79 cc.) was added gradually with stirring and cooling. During the addition of water the effluent hydrogen was passed through a trap cooled with dry ice – chloroform mixture. Additional water (45–60 cc.) was added slowly until the precipitate appeared white and granular. The precipitate was allowed to stand overnight and then separated by centrifugation. The solid was washed with ether, after which the washings, the contents of the trap, and the centrifugate were combined and the ethereal solution dried over Drierite. Dry gaseous hydrogen chloride was passed over the filtered ether solution and the precipated 2,2,2-trifluoroethylamine hydrochloride was recovered and dried *in vacuo* over phosphorus pentoxide, yield 44.5 gm. (75.1%). Calc. for $CF_3CH_2NH_3Cl$: Cl. 26.2%. Found: Cl, 26.35%.

2,2,2-Trifluoroethylamine

2,2,2-Trifluoroethylamine (b.p. 37.8–38.0°C. (757 mm.)) was prepared from its hydrochloride in excellent yield by the method of Gilman and Jones (1). Analysis by titration indicated that it was 99% pure.

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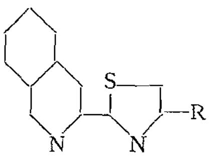
ANALOGUES OF 2,2′-BIPYRIDYL WITH ISOQUINOLINE AND THIAZOLE RINGS. PART II[1]

By F. R. Crowne and J. G. Breckenridge

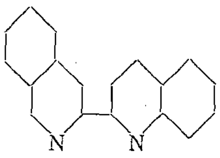
ABSTRACT

In continuation of the work reported in Part I, several more bipyridyl analogues have been prepared and the absorption spectra of the cuprous and ferrous complexes determined. The results follow the pattern of the previous series of compounds.

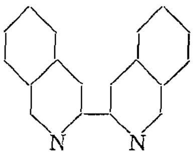
In an earlier paper (5) we reported the synthesis of a number of bipyridyl analogues and their reactions with cuprous and ferrous ion. Some of these were 1-isoquinolyl derivatives. In the present paper we report the synthesis of several analogues with the isoquinoline ring connected in the 3-position. Examples of this type in the literature are confined to 3,3′-biisoquinolyl, prepared by Case (1), who reported that it gave an orange color with ferrous ion, but gave no further details. We have repeated his synthesis, and have prepared in addition four new compounds; the structures of all these are shown below. In order to avoid confusion with those described earlier, the present compounds are numbered XVII to XXI, in continuation of the previous series.



XVII R = H
XVIII R = CH_3
XIX R = C_6H_5



XX



XXI

On the basis of our present knowledge of this type of compound, those with no "ortho" blocking groups (XVII, XXI) should react with ferrous ion, while the remainder should react only with cuprous ion; this was confirmed. Experimental work on the absorption spectra of the complexes was carried

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Condensed from the M.A.Sc. thesis of F. R. Crowne.

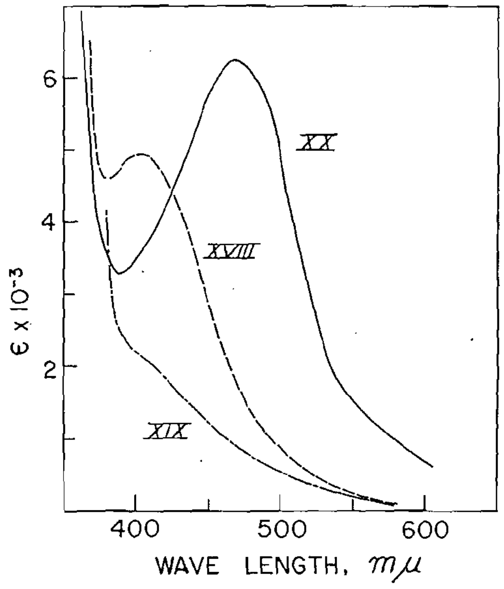
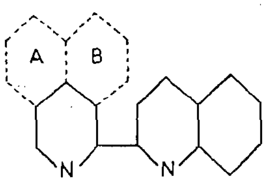


Fig. 1. Absorption spectra of copper complexes of compounds XVIII, XIX, XX.

out in the same manner as for the previous group; Fig. 1 shows the absorption spectra in the visible region for the cuprous complexes of compounds XVIII, XIX, and XX, all of which were extractable by isoamyl alcohol.

The depressing effect of a phenyl group in the "ortho" position (as compared to a methyl group) on the value for $\epsilon_{\max}$ is evident (compare XVIII and XIX); this is the same as was observed in the previous series. The two compounds (XVII, XXI) with no "ortho" group gave weakly colored unstable complexes, the spectra of which were not determined. It is of interest to compare the value for $\epsilon_{\max}$ for XX with that found by Hoste (3) for the isomeric 1-(2-quinolyl) isoquinoline:



Cuprous complexes
A—$\epsilon_{\max}$ = 6230 at 470 mμ
B—$\epsilon_{\max}$ = 2550 at 495 mμ

The fused ring in position B should not result in any appreciable hindrance to planarity, so that the steric situation in the immediate vicinity of the metal ion should be the same in both cases.

Compounds XVII and XXI behaved in a similar manner toward ferrous ion; both gave orange complexes which were highly dissociated, and we were unable to calculate accurate values for the molar extinction coefficients. The absorption spectra are shown in Fig. 2. Irving and Williams have predicted (4) that XXI should give an extractable complex with ferrous ion,

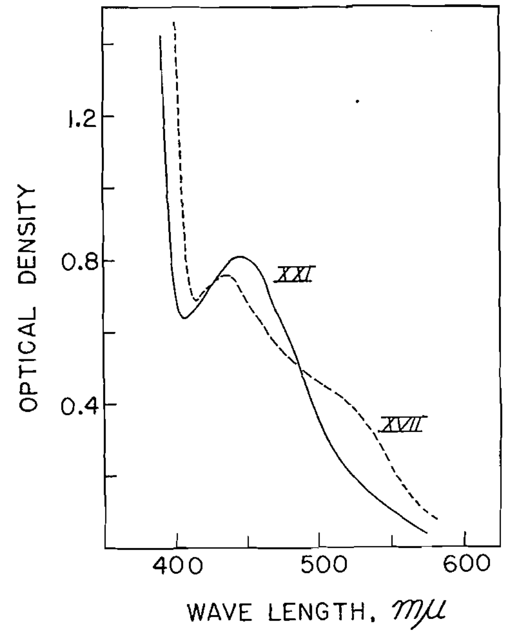


FIG. 2. Absorption spectra of iron complexes of compounds XVII, XXI.

and that it should be a more sensitive reagent than 2,2′-bipyridyl, which has a value of ϵ_{max} of 8700 at 522 mμ (6). We have confirmed this, since the complex is indeed extractable by isoamyl alcohol, and an approximate value for ϵ_{max} is 14200 at 445 mμ.

EXPERIMENTAL

Melting points are corrected: microanalyses by Micro-Tech Laboratories, Skokie, Ill.

Isoquinoline-3-aldoxime

Isoquinoline-3-carboxaldehyde, prepared from 3-methylisoquinoline by the method of Case (1), was condensed with an equimolar amount of hydroxylamine hydrochloride in aqueous ethanol. The mixture was made alkaline and poured into water, and the product recrystallized from ethanol. Yield nearly theoretical, m.p. 197–197.5°C. Calc. for $C_{10}H_8ON_2$: C, 69.75; H, 4.68; N, 16.27%. Found: C, 69.80, 69.83; H, 4.54, 4.65; N, 15.94, 16.07%.

3-Cyanoisoquinoline

The aldoxime, (19.5 gm.) was warmed with acetic anhydride (25 gm.), and after the vigorous reaction had subsided, the mixture was refluxed for two hours and then poured into water. The product was extracted with petroleum ether and recrystallized from ethanol in 80% yield, m.p. 127.5–128°C. Calc. for $C_{10}H_6N_2$: C, 77.90; H, 3.92; N, 18.17%. Found: C, 78.23, 78.34; H, 3.98, 3.97; N, 17.91, 18.00%.

Isoquinoline-3-thiocarboxamide

Five grams of the cyano compound was dissolved in 200 ml. ethanol, and ammonia was bubbled through the solution, followed by hydrogen sulphide. The yellow precipitate which appeared on standing was crystallized from ethanol. Yield theoretical, m.p. 198–198.5°C. Calc. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.80%. Found: C, 63.90, 64.14; H, 4.48, 4.40; N, 14.97, 15.13%.

3-(2-Thiazole)isoquinoline (XVII)

Isoquinoline-3-thiocarboxamide (5 gm.) and ethyl α,β-dichloroethyl ether (5 gm.) were dissolved in 230 ml. 75% ethanol and the solution refluxed for 12 hr. A further 4 gm. of the ether was added and refluxing continued for eight hours more. The solution was concentrated to 100 ml., made alkaline, and extracted with petroleum ether. Evaporation of the extract left an orange oil, which was crystallized from petroleum ether. Yield 10%, m.p. 116–117°C. Calc. for $C_{12}H_8N_2S$: C, 67.90; H, 3.80; N, 13.20%. Found: C, 67.86, 68.06; H, 3.85, 3.94; N, 12.87, 12.77%.

3-(4-Methyl-2-thiazole)isoquinoline (XVIII)
3-(4-Phenyl-2-thiazole)isoquinoline (XIX)

These were prepared by condensation of the thiocarboxamide with chloroacetone and ω-chloroacetophenone in ethanol. The products were recrystallized from ethanol; yield about 80% in both cases. Data for XVIII: m.p. 150–151°C.; calc. for $C_{13}H_{10}N_2S$: C, 69.00; H, 4.46; N, 12.38%; found: C, 69.00, 69.01; H, 4.55, 4.53; N, 12.34, 12.11%. Picrate m.p. 184.5–185°C.; calc.; N, 15.38%; found: N, 14.92, 15.06%. Data for XIX: m.p. 173.5–174°C.; calc. for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.20; N, 9.72%; found: C, 75.13, 75.15; H, 4.11, 4.16; N, 9.70, 9.84%. Picrate m.p. 191.5–192°C.; calc.: N, 13.54%; found: N, 13.40, 13.60%.

3-Acetylisoquinoline

To a Grignard reagent in ether prepared from 2.6 gm. magnesium and 14.8 gm. methyl iodide was added 11 gm. 3-cyanoisoquinoline in 600 ml. ether. The mixture was warmed gently and shaken, a voluminous precipitate appearing. Most of the ether was distilled off, 200 ml. dry benzene added, and the mixture refluxed for one hour and then cooled. Crushed ice and 50 ml. cold 50% sulphuric acid were added slowly, an orange precipitate appearing in the aqueous layer. The benzene layer was extracted with acid, and the combined acid portions made alkaline and steam-distilled. The product was recrystallized from ethanol, yield 60%, m.p. 92–92.8°C. Calc. for $C_{11}H_9ON$: C, 77.17; H, 5.30; N, 8.23%. Found: C, 77.21, 77.31; H, 5.18, 5.34; N, 8.21, 8.40%. Clemo and Popli (2) report m.p. 88°C. for this compound.

3-(2-Quinolyl)isoquinoline (XX)

To a solution of 3.4 gm. *o*-aminobenzaldehyde in 25 ml. 95% ethanol was added a solution of 4.5 gm. 3-acetylisoquinoline in 75 ml. 95% ethanol. Potassium hydroxide in ethanol (1.5 ml., 1 *N*) was added, and the mixture refluxed for two hours and cooled. The product was recrystallized from ethanol, yield 50%, m.p. 151.5–152°C. Calc. for $C_{18}H_{12}N_2$: C, 84.35; H, 4.72; N, 10.93%. Found: C, 84.40, 84.52; H, 4.80, 4.77; N, 11.11, 11.10%. Picrate m.p. 245.5–246°C.; calc.: N, 14.43%; found: N, 14.68, 14.55%.

ACKNOWLEDGMENT

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THE BIOGENESIS OF ALKALOIDS

X. THE ORIGIN OF THE N-METHYL GROUPS OF THE ALKALOIDS OF BARLEY[1]

By Edward Leete[2] and Léo Marion

ABSTRACT

Sodium formate-C^{14} and C^{14}-methyl-D- and L-methionine were each fed to sprouting barley under identical conditions and radioactive alkaloids were isolated from the leaves and roots. Degradation of these alkaloids showed that the D- and L-methionines were an equally efficient source of the methyl groups of N-methyltyramine and hordenine, the root alkaloids; but D-methionine was a less efficient source than L-methionine of the methyl groups of gramine, from the leaves. The formate was a source of the methyl groups of all the alkaloids, however, less efficient than the methionines, and a very poor source for the methyl groups of gramine. The significance of these results is discussed.

In view of the recent work on the biological methylation of the alkaloids hordenine (9, 14), nicotine (3, 4), ricinine (7), and protopine (18), it was of interest to see whether the N-methyl groups of the alkaloid gramine which occurs in the leaves of sprouting barley also arose from formate and methionine. The efficiency of D- and L-methionine as methyl donors was also compared. Comparatively little work has been carried out on the utilization of D-amino acids by the higher plants. In one case (19) it has been shown that while the L forms of certain amino acids produce toxic effects on *Nicotiana* species, the D-amino acids have no ill effect. With microorganisms more work has been done, some are apparently able to utilize both forms of the amino acids equally while others fail to utilize the D form, presumably owing to the absence of a D-amino acid oxidase in such organisms (11). Thus it was found (17) that *Lactobacillus arabinosus* did not utilize D-methionine whilst the same organism in the presence of pyridoxal was able to use it (5) presumably by racemization to DL-methionine via a chelate ring formation involving the pyridoxal (16).

In the present work the sodium formate-C^{14} and the C^{14}-methyl labelled D- and L-methionines were fed to identical dishes containing the germinating barley and after a suitable period the alkaloids were isolated and separated as previously described (1, 10, 12). In all cases the alkaloids were radioactive and they were degraded by established methods (12, 13) in order to locate the positions of activity. The hordenine from the formate and L-methionine feeding experiments was not degraded since previous work (14) had shown all the activity to reside in the methyl groups.

Table II shows that all the activity of the radioactive alkaloids was present in the N-methyl groups. Considering first the root alkaloids, formate is seen to be a less efficient source of methyl groups than methionine. This is in accordance with results previously obtained (3, 14) and favors the hypothesis that

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

formate is a precursor of the methyl groups of methionine. The D- and L-methionines are equally effective as a source of the methyl groups. The appreciably higher activity of the N-methyltyramine, which only contains one methyl group, over hordenine, which contains two, confirms the stepwise methylation (i.e., tyramine → N-methyltyramine → hordenine) since, if the N-methyltyramine were produced by the demethylation of hordenine, analogous to the formation of nornicotine from nicotine (6) in *Nicotiana glutinosa*, one would expect it to have a lower specific activity than hordenine.

In so far as gramine was concerned, D-methionine was significantly less efficient than L-methionine, and it is suggested that the leaves which are assumed to be the site of synthesis (2) are not capable of inverting the D-methionine. Thus the active gramine from the D-methionine feeding experiments results from D-methionine which has been inverted to L-methionine in the roots. The higher activity of the leaf extract (Table I) in this experiment is presumably due to D-methionine which has bypassed the enzymes causing inversion and which cannot be utilized in the leaves as a source of methyl groups. On the other hand, formate was a very poor source of methyl groups for this alkaloid. The inability of formate to serve as a precursor of N-methyl groups in ricinine has been reported by Dubeck and Kirkwood (7) who suggested that this inability was due to the state of development of the *Ricinus* plants used in their experiments. In barley, however, formate does serve as a precursor of the N-methyl groups of hordenine and N-methyltyramine, although with gramine this action is very much less marked. This might indicate that the transfer of methyl groups by formate to methionine takes place in the root but not in the leaves in which the methylation of the nitrogen of gramine can only take place by the action of methionine translocated from the roots. Such an interpretation of the result would also indicate that the enzyme systems are less developed in the leaves of barley than in the roots.

The activity of the gramine from the formate feeding experiments is of the same order as that of the gramine obtained from the feeding experiment with doubly labelled tryptophan-2-β-C^{14} in the presence of large amounts of mold (13). In the latter experiment the gramine isolated from the plant had appreciable activity in its N-methyl groups, and the postulate made then that the activity in the methyl groups had arisen by attack of the tryptophan by mold to yield formylkynurenine, which gave rise to the active formate by hydrolysis, is thus consistent with the present result.

EXPERIMENTAL

D- and L-C^{14}-methyl Labelled Methionines

S-Benzyl-DL-homocystine was resolved via the formyl derivative with brucine as described by Du Vigneaud and Patterson (8) and the two isomers converted to the methionines by treatment with sodium followed by C^{14}-methyl iodide in liquid ammonia (15).

Feeding of Labelled Substances and Isolation of the Alkaloids

L-Methionine was fed to 720 gm. of barley in 12 trays on the fourth day of germination when the shoots were 1–1.5 cm. long, the temperature of the germination cabinets varied between 15 and 21°C. D-Methionine and formate were also fed to identical batches of barley under the same conditions. In each case the plants were harvested on the 10th day of germination, the roots and leaves separated, dried, and the alkaloids extracted as previously described (1, 10, 12). Details of the amounts of tracers fed and the yields of the various

TABLE I

WEIGHTS AND ACTIVITIES OF LABELLED SUBSTANCES FED AND ALKALOIDS ISOLATED FROM THE BARLEY (720 GM. IN EACH EXPERIMENT)*

	Tracer		
	Sodium formate	L-Methionine	D-Methionine
	Weight fed		
	22.8 mgm.	50 mgm.	50 mgm.
	Total activity		
	4.13×10^7	4.58×10^7	4.55×10^7
Roots			
Wt. of roots	113 gm.	126 gm.	113 gm.
Activity of methanol extract	8.1×10^5	5.0×10^6	7.8×10^6
Wt. of hordenine	66.5 mgm.	41.3 mgm.	77.9 mgm.
Wt. of N-methyl-tyramine	48.6 mgm.	16.4 mgm.	20.1 mgm.
Leaves			
Wt. of leaves	57 gm.	44 gm.	45 gm.
Activity of methanol extract	7.3×10^4	1.33×10^6	3.04×10^6
Wt. of gramine	65.2 mgm.	46.0 mgm.	46.2 mgm.

Activities expressed as disintegrations per minute.

TABLE II

ACTIVITIES OF THE ALKALOIDS AND THEIR DEGRADATION PRODUCTS*

	Tracer		
	Sodium formate	L-Methionine	D-Methionine
Hordenine	2.98×10^4	8.06×10^4	7.80×10^4
Hordenine hydrochloride	3.10×10^4	7.91×10^4	7.75×10^4
Hordenine methiodide			7.95×10^4
Methylhordenine methiodide	Not degraded	Not degraded	7.65×10^4
Trimethylamine picrate			8.10×10^4
p-Vinylanisole			0
N-Methyltyramine	9.45×10^4	1.20×10^5	1.12×10^5
N-Methyltyramine hydrochloride	10.1×10^4	1.22×10^5	1.27×10^6
Hordenine methiodide	9.45×10^4	1.21×10^5	1.11×10^5
Methylhordenine methiodide	10.0×10^4	1.23×10^5	1.04×10^5
Trimethylamine picrate	9.54×10^4	1.23×10^5	1.11×10^5
p-Vinylanisole	0	0	0
Gramine	4.38×10^3	1.72×10^5	8.61×10^4
Dimethylethylamine picrate	4.10×10^3	1.62×10^5	8.22×10^4
3-Ethoxymethylindole	0	0	0

All activities are for carrier free material and are expressed as distintegrations per minute per millimole.

extracts are given in Table I. Table II summarizes the results obtained on assay of the alkaloids and their degradation products obtained as previously described (12, 13).

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KINETICS OF THE REACTION $H + CH_4 = CH_3 + H_2$[1]

BY M. R. BERLIE[2] AND D. J. LE ROY

ABSTRACT

The reaction $H + CH_4 = CH_3 + H_2$ has been studied in the temperature range 99° to 163°C. The rate constant is given by the expression $k = 1.7 \times 10^{-14} \exp(-4500/RT)$. The data are in agreement with the results, but not the interpretations, of previous work. The entropy of the methyl radical has been calculated for several temperatures.

INTRODUCTION

In a recent publication (13) preliminary data were reported for the kinetics of the reaction $H + CH_4 = CH_3 + H_2$. The significant feature of the results was the fact that the steric factor and activation energy were found to be very much lower than had been previously suspected. The results have been subjected to a careful analysis and will be presented here together with a comparison with the data obtained by other workers.

EXPERIMENTAL

The method has already been described (2, 8). Particular care was taken to purify the methane and hydrogen. Matheson C.P. methane (99.0%) was passed through two towers containing Fieser's solution, three containing concentrated sulphuric acid, and one containing Drierite. It was then subjected to trap-to-trap distillation using "pumped down" liquid air traps. The resulting gas was found to contain 0.3% ethane and 0.03% ethylene. To reduce these impurities below the limit of detection the gas was allowed to bubble slowly through liquid methane at the temperature of liquid air and then through mercury, which fixed the pressure over the liquid at approximately 20 mm. The gas was then frozen in a "pumped down" liquid air trap at −206°C. It was estimated that the final gas contained less than 0.01% impurities.

Some ethane was formed in the reaction. It was partially removed from the gas stream by passage through a "pumped down" liquid air trap; additional amounts were removed by isolating samples of the gas which came through this trap, removing the hydrogen by diffusion through a palladium thimble, and circulating the residual gas, which was largely methane, through a smaller "pumped down" liquid air trap. The total amount of ethane collected was negligible, however, in comparison with the amount of atomic hydrogen that reacted with the methane. It seems justifiable, therefore, to neglect combination of methyl radicals under the conditions used in the present experiments.

RESULTS

A number of experiments were done in the temperature range 99° to 163°C. using various pressures of methane and of molecular hydrogen. The reaction

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was considerably slower than that with ethane (2) and consequently great care had to be taken in making the correction for H atoms consumed by combination to form H_2. It has been pointed out (8) that the combination of atomic hydrogen under our experimental conditions appears to have an order between one and two. The partial pressure of methane would be expected to have an effect on the second order combination reaction, and hence the results reported here are only for experiments in which the ratio of methane to hydrogen was kept approximately constant.

The interpretation of the results is based on consideration of the following reactions:

$$\mathrm{H} + \mathrm{CH_4} = \mathrm{CH_3} + \mathrm{H_2}, \qquad [1]$$

$$\mathrm{H} + \mathrm{CH_3}\ (+\ \mathrm{M}) = \mathrm{CH_4}\ (+\ \mathrm{M}), \qquad [2]$$

$$2\mathrm{CH_3} = \mathrm{C_2H_6}, \qquad [3]$$

$$\mathrm{CH_3} + \mathrm{H_2} = \mathrm{CH_4} + \mathrm{H}. \qquad [4]$$

In view of the negligible amount of ethane formed, reaction [3] may be neglected. If [1] were followed by [4] no H atoms would be consumed (other than by combination to form H_2). If only [1] and [2] occur then, aside from the combination reaction, the rate of consumption of H atoms would be given by the relation

$$-d(\mathrm{H})/dt = 2k_1(\mathrm{H})(\mathrm{CH_4}). \qquad \text{(i)}$$

If, in addition, [3] and/or [4] take place the value of k_1 calculated on the basis of (i) would be too small. Since it will be assumed that only [1] and [2] occur, the values of k_1 will be minimum values. If [4] occurs at all under the present experimental conditions it will become more important at the higher temperatures. This possibility will be examined more fully in the following section.

When allowance is made for first and second order combination of H atoms the rate equations take the form

$$-d(\mathrm{H})/dt = k_c'(\mathrm{H}) + 2k_1(\mathrm{H})(\mathrm{CH_4}), \qquad \text{(ii)}$$

$$-d(\mathrm{H})/dt = k_c''(\mathrm{H})^2 + 2k_1(\mathrm{H})(\mathrm{CH_4}), \qquad \text{(iii)}$$

in which k_c' and k_c'' are the first and second order rate constants for H atom combination, respectively. It might be expected that k_c'' would be different for a hydrogen–methane mixture than for hydrogen alone.

As described previously (2) the H atom concentration at any position in the reactor was determined by measuring the rate of liberation of the heat of combination on the detector; this was measured as a wattage and given the symbol W. The method of determining the constant of proportionality f in the expression $(\mathrm{H}) = fW$ has also been described (2). The reaction time t was calculated from the linear flow rate in the reactor and the distance of the detector from the point where the methane was added.

In terms of the measured quantities, equations (ii) and (iii) become

$$-dW/dt = k_c'W + 2k_1W(\mathrm{CH_4}), \qquad \text{(iv)}$$

$$-dW/dt = k_c''fW^2 + 2k_1W(\mathrm{CH_4}). \qquad \text{(v)}$$

In the integrated form they are

$$\log W = -0.4343\{k_c' + 2k_1(\mathrm{CH_4})\}t + \text{constant}, \qquad \text{(vi)}$$

$$\log\{1 + 2k_1(\mathrm{CH_4})/(k_c''fW)\} = 0.4343 \times 2k_1(\mathrm{CH_4})t + \text{constant}. \qquad \text{(vii)}$$

On the basis of (vi) log W should be a linear function of t, or for a given linear flow rate, of the distance d from the point of mixing. From (vii) a plot of log W vs. t would not be linear. A typical plot is shown in Fig. 1.

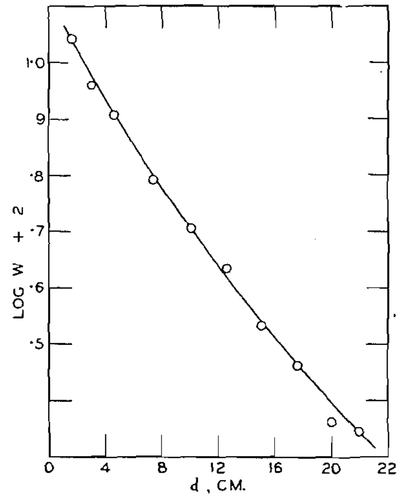

FIG. 1. Plot of log W vs. d for experiment 7Me. The linear flow rate was 98.4 cm. sec.$^{-1}$, and hence $t = d/98.4$ sec.

In Table I the values of k_1 calculated from (vi) are given the symbol k_1', those from (vii) the symbol k_1''. The means of the values calculated by the two methods are given in the last column.

TABLE I

Expt.	Temp., °C.	$(\mathrm{H_2})$ $\times 10^{-15}$	$(\mathrm{CH_4})$ $\times 10^{-15}$	$(\mathrm{H})_0$ $\times 10^{-15}$	k_c' sec.$^{-1}$	k_c'' $\times 10^{15}$ (a)	k_c'' $\times 10^{15}$ (b)	k_1' $\times 10^{17}$	k_1'' $\times 10^{17}$	k_1 $\times 10^{17}$, mean
7Ma	99	143	34.6	1.07	3.13	2.88	4.85	3.27	4.70	3.98
7Me	139	132	32.0	0.99	3.25	3.18	7.22	6.95	7.55	7.25
7Md	163	122	30.6	0.91	2.83	3.00	6.55	9.08	10.15	9.62

(a) *In the absence of methane.*
(b) *With methane present.*
Concentrations are expressed in atoms or molecules cm.$^{-3}$, k_c'' *and* k_1 *in cm.*^{3} *molecule*$^{-1}$ *sec*$^{-1}$.

The values of k_1' were obtained by subtracting the slopes of the best straight lines through log W vs. t plots for experiments with and without methane, but otherwise under identical conditions.

A lower limit for the value of k_c'' was obtained by plotting $1/W$ vs. t for an experiment with no methane present; the slope of this curve, $k_c''f$, would give a smaller value of k_c'' than would apply to an experiment in which methane was present since, presumably, methane would be more efficient than hydrogen as a third body. A first approximation to k_1'' was the value k_1', obtained as described above. By a method of successive approximations the ratio of k_1 to k_c'' in the log term was adjusted until the best straight line fitting equation (vii) was obtained; the values of k_1'' in Table I were obtained from the slopes of such lines.

The values of the first order rate constant for the recombination of H atoms are given in column six of Table I; they are very similar to those obtained previously (8), and correspond closely with the recombination coefficient of 2×10^{-5} found by Smith (16) for a metaphosphoric acid surface. On the other hand, the second order rate constants for H atom recombination given in column seven are in fairly good agreement with the data of Farkas and Sachsse (10) quoted by Morikawa, Benedict, and Taylor (14). Their third order rate constant, 3.4×10^{16} cm.^{6} mole^{-2} sec.$^{-1}$, corresponds to a value of k_c'' of 13.4×10^{-15} cm.^{3} molecule^{-1} sec.$^{-1}$ at a hydrogen concentration of 143×10^{15} molecules cm.$^{-3}$, compared to the value 2.88×10^{-15} given in Table I.

An Arrhenius plot of the data in the last three columns of Table I is shown in Fig. 2. The following expressions are obtained from the straight line corresponding to the mean values of k_1:

$$k_1 = 1.7 \times 10^{-14} e^{-4500/RT},$$
$$k_1 = 1.3 \times 10^{-5} Z e^{-4100/RT}.$$

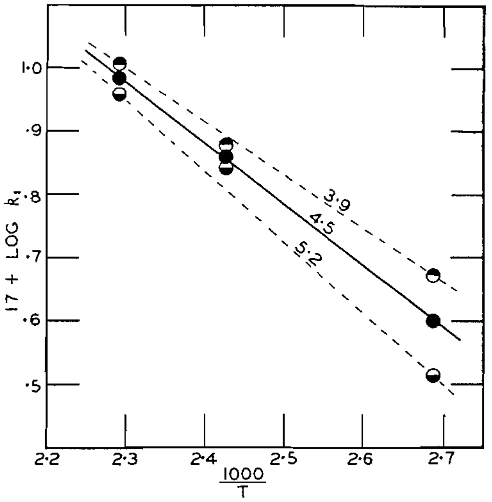

FIG. 2. Arrhenius plot for k_1. ◒ k_1', assuming first order recombination of H atoms; ◓ k_1'', assuming second order recombination of H atoms; ● mean of k_1' and k_1''.

ACCURACY OF THE RESULTS

The present results differ somewhat from those quoted in the preliminary note (13), viz. $p_1 \backsim 10^{-4}$, $E_1 \backsim 6.6$ kcal. per mole. However, the original values were obtained on the basis of first order recombination of H atoms only, and it can be seen from Fig. 2 that this leads to high values of E_1. The original values of k_1 were also in error to a slight extent because no allowance had been made for the change in pressure and flow rate on adding methane to the hydrogen stream.

In estimating the accuracy of the present results it is necessary to make a distinction between the accuracy of the actual rate constants, on the one hand, and the accuracy of p_1 and E_1 on the other. We believe it unlikely that the value of k_1 for any temperature will be in error by more than a factor of two from any or all of the following causes: (*a*) errors in measurement, which are relatively small, (*b*) uncertainty in making the correction for H atom recombination, (*c*) neglect of reactions [3] and [4].

Neglect of reaction [3] could, at the most, cause an error of a factor of two in k_1, and this would require that all of the methyl radicals formed in [1] be used up in [3]; the small amount of ethane formed makes this unlikely. Some justification for eliminating reaction [4] from the present scheme is obtained from the data of Whittle and Steacie (25). For the lowest temperature quoted in their work, 210°C., they obtained the value $k_4/k_3^{1/2} = 22 \times 10^{-13}$, or, in terms of actual reaction rates, $R_4/R_3^{1/2} = 22 \times 10^{-13}(\mathrm{H_2})$. It follows that at 163°C., the highest temperature used in the present work,

$$R_4/R_3^{1/2} < 22 \times 10^{-13}(\mathrm{H_2}),$$

and hence

$$R_4/R_1 < \frac{22 \times 10^{-13}(\mathrm{H_2})}{k_1(\mathrm{H})(\mathrm{CH_4})} R_3^{\frac{1}{2}}.$$

However, we have found that $R_3 < R_1$, and hence, using the data for experiment 7Md and assuming the average value of (H) to be one tenth of the initial value,

$$R_4/R_1 << \frac{22 \times 10^{-13}(\mathrm{H_2})}{\{k_1(\mathrm{H})(\mathrm{CH_4})\}^{\frac{1}{2}}} << 1.6 \times 10^{-2}.$$

It therefore seems justifiable to neglect reaction [4] in the present experiments.

Probably the greatest source of error in the determination of k_1 is in making the correction for H atom recombination. This error will be greatest at low temperatures, since recombination will then account for a greater proportion of the H atoms consumed; this is seen from Table I and Fig. 2.

A conservative estimate of the possible error in E_1 can be made by assuming an error of half the difference between k_1' and k_1'' for the highest and lowest temperatures used; this works out to be ±1.2 kcal. per mole. The corresponding error in the exponent of A_1 in the expression $k_1 = A_1e^{-E_1/RT}$ or of p_1 in the expression $k_1 = p_1Z\,e^{-E_1/RT}$ is approximately 0.7. The actual errors in E_1, A_1, and p_1 may be somewhat greater.

DISCUSSION

The activation energy obtained in this investigation is considerably lower than previous estimates (18, 19). It is therefore appropriate to discuss at some length the methods and conclusions of previous investigators.

Bonhoeffer and Harteck (4), v. Wartenberg and Schultze (24), and Chadwell and Titani (5), using the discharge tube method, found no evidence of products at room temperature, and Geib and Harteck (11) found none at temperatures up to 183°C. These negative results were taken to indicate that k_1 was too small to measure, since no ethane appeared to have been formed by the combination of methyl radicals. However, we have found in the present work that the rate of ethane formation at low pressures is very much less than the rate of reaction [1]. Furthermore, the present data and those for ethane (2) show that at, say, 183°C. k_1 would be approximately equal to 0.04 k_5,

$$H + C_2H_6 = C_2H_5 + H_2, \qquad [5]$$

and hence for conditions which would lead to the measurable decomposition of hydrocarbons such as ethane, the amount of ethane produced from the methane reaction would be too small to measure. The present results are therefore not in disagreement with those obtained by the earlier workers.

Under certain conditions the use of D atoms affords a sensitive test for the occurrence of reaction [1], or more correctly reaction [1*a*],

$$D + CH_4 = CH_3 + HD. \qquad [1a]$$

This method has been used in the more recent work, but it will be seen from a detailed examination of the various papers that the authors have been reluctant to accept an interpretation of their data which would indicate a low value for E_{1a}.

Geib and Steacie (12) studied the reaction of D atoms with methane at 20° and at 100°C. by the discharge tube method. The amount of methane exchanged ranged from zero to 4.3%, but there appeared to be no correlation between the per cent exchange and the temperature. They attributed the apparent lack of reaction to E_{1a} being at least 11 kcal. per mole, taking the steric factor to be 0.1. It is significant that for a temperature of 100°C. this estimate corresponds to an activation energy of 4.1 kcal. per mole combined with a steric factor of 10^{-5}. In a similar investigation Steacie and Phillips (20) reported 1.9% exchange, in essential agreement with the results of Geib and Steacie.

Steacie (17) used the discharge tube method to investigate the reaction of D atoms with methane up to 500°C. The per cent exchange was corrected for what appeared to be exchange resulting from back diffusion of methane into the discharge. The correction was made by subtracting the average exchange at room temperature (4.3%) from all the values for higher temperatures. It seems not unreasonable to suppose that the small temperature coefficient of exchange at low temperatures might, at least in part, be attributed to reactions [1*a*] and [2*a*].

$$D + CH_3\ (+ M) = CH_3D\ (+ M) \qquad [2a]$$

At the higher temperatures the rate of exchange would increase more rapidly by reason of reaction [4*a*], which would regenerate D atoms.

$$CH_3 + D_2 = CH_3D + D \qquad [4a]$$

The most recent value of E_{4a}, 11.8 kcal. per mole (25), is in line with this suggestion.

Trenner, Morikawa, and Taylor (22), also using the discharge tube method, reported no exchange of methane below 310°C. under conditions similar to those in which the reaction of D atoms with ethane caused 24.2% of the latter to be consumed. However the present value of k_1 at, say, 163°C. is less than 1/20 of the value of k_5, and hence the amount of exchange to be expected would only be of the order of one per cent; this was close to the limit of error of the method used to determine C–D bonds.

While the present method involves, essentially, the measurement of the rate of exchange of methane without the use of D atoms, the actual rate of consumption of H atoms is a much more sensitive measure of the rate of [1] or [1*a*] than would be the determination of the per cent exchange. For example, it can be calculated that at 163°C. the per cent of methane exchanged in experiment 7Md would have been only 0.85.

Morikawa, Benedict, and Taylor (14) studied the $Hg(^3P_1)$ photosensitized exchange between D_2 and CH_4 over the temperature range 98° to 488°C. From 98° to 196°C. the temperature coefficient was very small; at the higher temperatures it corresponded to an activation energy of 12 kcal. per mole. They attributed the low-temperature activation energy of 4.5 kcal. per mole to the reaction

$$Hg(^3P_1) + CH_4 = CH_3 + H + Hg(^1S_0) \qquad [6]$$

rather than to reaction [1*a*].

This appears to be the only case in which an appreciable activation energy has been assigned to the dissociative quenching of a hydrocarbon. However their interpretation can only be made by disregarding the published quenching data for CH_4 and/or D_2 (1, 9). Taking into account the molecular weights of the two gases, these data predict that the quenching efficiency of D_2 should be almost 250 times that of CH_4. The maximum quantum yield for exchange through reaction [6] would then be only 0.004 at 98°C. The observed quantum yields at 98° were 0.42, 0.59, and 0.25. The predicted quantum yield could be raised to a maximum of 0.016 by postulating exchanges of the type

$$D + CH_3 = CH_2D + H \qquad [7]$$

but this would mean that most of the exchanged methane would be in the form of CD_4, contrary to their observations. If the low-temperature activation energy is assigned to reaction [1*a*] then the results of Morikawa, Benedict, and Taylor are in good agreement with the present results.

Darwent and Roberts (7) have pointed out what would appear to be an inconsistency between our results on reaction [5] (2) and our preliminary results on reaction [1] (13). Their work was based on the following mechanism:

$$\begin{aligned} D_2S + h\nu &= D + DS, & [8]\\ D + CH_4 &= CH_3 + HD, & [1a]\\ D + C_2H_6 &= C_2H_5 + HD, & [5a]\\ D + D_2S &= D_2 + DS. & [9] \end{aligned}$$

The method consisted in measuring the ratio $(HD)/(D_2)$; with methane this should be proportional to $(CH_4)/(D_2S)$ with slope k_{1a}/k_9, with ethane it should be proportional to $(C_2H_6)/(D_2S)$ with slope k_{5a}/k_9. The determination of activation energies of reactions such as [1*a*] or [5*a*] by this method requires the determination of the effect of temperature on these slopes, and a knowledge of E_9 (and the steric factor p_9, if steric factors are to be calculated as well). The difference in activation energy for reaction [10],

$$D + H_2 = H + HD, \qquad [10]$$

and reaction [9] was evaluated from the effect of temperature on the slope of the $(HD)/(D_2)$ vs. $(H_2)/(D_2S)$ curve for experiments in which H_2 was substituted for the hydrocarbon. E_9 (as well as p_9) was calculated by adopting the values $E_{10} = 5$ kcal. per mole, $p_{10} = 0.07$ (6). These latter values have recently been questioned (3), and hence the most reliable method of comparing our results with those of Darwent and Roberts would seem to be in terms of rate constants, rather than activation energies.

At 400°C. Darwent and Roberts found a considerable increase in $(HD)/(D_2)$ for an increase in $(C_2H_6)/(D_2S)$, but not for an increase in $(CH_4)/(D_2S)$. However, on the basis of our present results the slope of the latter curve would be only about 1/35 of that for ethane. The values of $(HD)/(D_2)$ would therefore not be expected to rise much above the "background" value of 0.25, to which all of their curves extrapolated (although according to theory all of the curves should extrapolate to zero).

Space does not permit further consideration of the results of other workers on reactions [1] and [1*a*]. The earlier literature has been covered by Steacie (18).

Although more reliance can be placed on the values of k_1 than on the calculated values of E_1, it is of interest to compare our value of E_1 with bond dissociation energy data. The C–H bond dissociation energy in methane has been estimated to be 102 ±1 kcal. per mole (21), although the temperature to which this value applies is not certain. The dissociation energy of H_2 at 25°C. is 104.2 kcal. per mole (15). It is probably safe to assume that the change in internal energy for reaction [1] is approximately 2.2 ± 1 at temperatures of the order of 150° to 200°C. Whittle and Steacie (25) quote a value of 10.0 kcal. per mole for E_4. Since we have found E_1 to be 4.5 kcal. per mole, there would appear to be a noticeable discrepancy in the results in so far as agreement with the relation

$$E_4 - E_1 = -\Delta E^0 \qquad \text{(viii)}$$

is concerned. However, taking into consideration the uncertainty in each of the activation energy values, the uncertainty in $-\Delta E^0$, and the uncertainty in the validity of (viii) as applied to activation energies calculated in a particular way, the discrepancy may be more apparent than real.

ENTROPY OF THE METHYL RADICAL

More rigorous than (viii) is the relation

$$RT \ln (k_1/k_4) = T\,\Delta S^0 - \Delta E^0, \qquad \text{(ix)}$$

from which it is possible to calculate ΔS^0 at any temperature for which values of k_1, k_4, and $-\Delta E^0$ are known. The largest source of error is probably in the last quantity. Unfortunately the temperature ranges for our data and those of Whittle and Steacie do not overlap, but a negligible error should arise in extrapolating the latter data to 163°C., at which temperature k_1 is 9.62×10^{-17}. Whittle and Steacie obtained data for $k_4/k_3^{1/2}$, rather than for k_4. They found $p_4/p_3^{1/2}$ to be 1.6×10^{-3} and $E_4 - \frac{1}{2}E_3$ to be 10.0 kcal. per mole, but since p_3 is undoubtedly in the range 0.01 to 1.0, and E_3 is approximately equal to zero, the value of k_4 at 163°C. can be estimated with some certainty to be in the range 1.08×10^{-18} to 1.08×10^{-17}. Assuming, as before, that $-\Delta E^0 = 2.2 \pm 1$ kcal. per mole, it can be shown that $\Delta S^0 = 1.6 \pm 4.6$ e.u. From thermodynamic data for H, CH_4, and H_2 (15) it follows that S^0 for the free methyl radical is 44.9 ± 4.6 e.u. at 163°C.

Extrapolation of the data of Whittle and Steacie to 99°C., the lowest temperature used in the present experiments, yields the value 45.3 ± 5.0 e.u. for the entropy of the methyl radical at that temperature. If the present data on reaction [1] are extrapolated to 210°C., the lowest temperature quoted by Whittle and Steacie, using the values $A_1 = 1.7 \times 10^{-14}$, $E_1 = 4.5$ kcal. per mole, the entropy of the methyl radical at that temperature is found to be 49.3 ± 4.4 e.u. A higher value at this temperature is to be expected on thermodynamic grounds.

Some years ago Zeise (26) calculated the entropy of the methyl radical to be 47.345 at 298°K., 49.80 at 400°K. The values calculated from kinetic data on reactions [1] and [4] are in satisfactory agreement. Trotman-Dickenson (23) has recently estimated a value of 45.5 e.u. at room temperature.

Trotman-Dickenson (23) has utilized the equation

$$R \ln (A_1/A_4) = \Delta S \tag{x}$$

to calculate ΔS, but this procedure is less reliable than the use of (ix) because of the assumptions of a theoretical nature involved, and because errors in A and E are complementary.

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STRESSES AND STRAINS IN ADSORBENT–ADSORBATE SYSTEMS[1]

By E. A. Flood and R. D. Heyding[2]

ABSTRACT

From thermodynamic considerations a simple equation is derived which correlates length changes of a porous rigid adsorbent with its elastic and adsorptive properties. The equation contains a structure factor which is a constant characteristic of the adsorbent. Calculated and observed results agree reasonably well and suggest that, in the cases concerned, the assumptions underlying the derivation of the equation are valid. The underlying assumptions are: (*a*) both adsorbate and adsorbent can each exist separately in equilibrium with externally applied forces in states that are thermodynamically identical with their states in the adsorbate–adsorbent system, (*b*) adsorption isotherms represent paths of thermodynamic reversibility.

INTRODUCTION

In previous papers we have shown that the pore dimensions of both micropore and macropore systems of certain activated carbons may be estimated from permeability data (7). The dimensions of the micropore systems were related to micropore permeability by means of equations derived from the thermodynamic conditions for equilibria of single component fluids in potential fields. Thus micropore permeability equations were based upon the assumption that, in the adsorption reaction, the adsorbate and adsorbent retain their own individual properties.

This paper is mainly concerned with stress–strain inferences derivable from this assumption, as well as with the plausibility and limitations of the assumption. More particularly, the basic assumption is: Assemblies of volumes of the pure adsorbable gas and assemblies of volumes of the pure adsorbent can each exist separately, in equilibrium with externally applied forces, in states that are thermodynamically identical with their states in the adsorbent–adsorbate system. When and only when this assumption holds, is it theoretically possible to determine the change in the state of stress of the adsorbent resulting from the adsorption reaction, and to correlate this change in state of stress with the elastic constants of the pure adsorbent and with its dimensional changes.

When this assumption is applied to an isotropic porous adsorbent the following very simple equation (Equation 16) can be deduced:

$$\delta l/l = -\tfrac{1}{3}\beta(1 + \phi K - \phi K\alpha)\delta p.^{3}$$

This equation thus provides a basis for a fairly sensitive experimental test of the validity of the assumption that in the adsorption reaction the adsorbate

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[2] *National Research Council Postdoctoral Fellow, 1951–53.*

[3] $\delta l/l$ = *length change per unit length;* β = *coefficient of cubical compressibility of the solid adsorbent;* ϕ = *ratio of void volume to solid volume;* K = *ratio of linear average stress to volumetric average stress;* α = *mean number of volumes adsorbed averaged over the pressure interval* δp; p = *hydrostatic pressure of fluid surrounding the adsorbent–adsorbate system.*

and adsorbent retain their own individual properties. Accordingly, some experiments have been carried out, the results of which suggest that this assumption is reasonably valid as applied to large adsorptions by certain activated carbons.

It may be remarked that Hill (10) has pointed out some of the difficulties in distinguishing clearly between the thermodynamics of adsorption processes which are essentially "solution" processes and those special cases which are in conformity with the above assumptions.

In what follows, a simple theoretical development of some inferences derivable from the above assumption is presented, together with some experimental results and relevant discussion.

THEORETICAL

For a process of transformation of two separate systems into a single system containing the same matter where the temperatures, pressures, surface tensions, etc. of the systems are to remain constant during the process, the condition that it shall be reversible is,

$$F_1 + F_2 = F_{12}, \tag{1}$$

where F_1, F_2, and F_{12} are the free energies[4] of the first, second, and combined systems, respectively. Accordingly, in order that the process of transformation of the separate systems into the combined system shall remain reversible at any point along a path of variation of the three systems, the path of variation is subject to the condition,

$$dF_1 + dF_2 = dF_{12}. \tag{2}$$

Applying this equation to the isothermal reaction between a gas and an almost incompressible solid of very low vapor pressure, p_{2s}, which forms a solid product under a hydrostatic pressure very nearly equal to that of the pure gas with which it is in equilibrium, that is, applying Equation 2 to conditions analogous to those which prevail during gas adsorption measurements, we can write,

$$v_1 dp_1 + dF_2 = v_{12} dp_{12}, \tag{3}$$

where v_1 is the volume of the pure gas at the equilibrium pressure, p_1, corresponding to the mass, n_1, of gas adsorbed and v_{12} is the volume of the combined system whose hydrostatic pressure is p_{12}.

Equation 3 thus describes a point of the path of variation for changes in the pressures p_1 and p_{12} along which $\Delta F = 0$ for the process of transformation of the pure components into the combined system. Integrating Equation 3 between appropriate limits we can describe the path of variation, corresponding to a constant mass of sold, n_2, interacting with any quantity of gas, n_1, and thus obtain,

$$\int_{p_1=0(n_1=0)}^{p_1=p_1(n_1=n_1)} v_1 dp_1 + \int_{p_{2s}(n_2)}^{p_2(n_2)} dF_2 = \int_{p_{2s}(n_1=0,n_2=n_2)}^{p_{12}(n_1=n_1,n_2=n_2)} v_{12} dp_{12}. \tag{4}$$

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[4] *$F = E = - TS + pv + \gamma\Sigma$, where E = energy, S = entropy, γ = surface tension, Σ = surface area, etc.*

Since p_{2s} is assumed very low, $p_{12} \approx p_1$, accordingly, we can write,

$$[5] \qquad \Delta F_2 = \int_{p_{2s}}^{p_1} v_{12} dp_{12} - \int_0^{p_1} v_1 dp_1$$
$$= \bar{v}_{12} \cdot p_1 - \bar{v}_1 \cdot p_1$$

where $\bar{v}_1$ is defined by $\bar{v}_1 \cdot p_1 \equiv \int_0^{p_1} v_1 dp_1$ and $\bar{v}_{12}$ is similarly defined.

In the case of large adsorptions, $\bar{v}_1$ will be, in general, much larger than $\bar{v}_{12}$, the latter being of the order of the volume of the solid. Hence for large adsorptions we can neglect $\bar{v}_{12} \cdot p_1$ in comparison with $\bar{v}_1 \cdot p_1$ and assuming the gas ideal over the given pressure range, we can write,

$$[6] \qquad \Delta F_2 = -\int_0^{p_1} v_1 dp_1 = -\frac{RT}{Mv_0} \int_0^{p_1} \frac{v_0'}{p_1} dp_1,$$

where v_0' is the volume of gas adsorbed expressed as cc. reduced to N.T.P., p_1 is the equilibrium gas pressure, and v_0 is the volume per mole of adsorbate at N.T.P. Free energy per gram, F_2.

ΔF_2, as given in Equation 6, is the change in free energy of pure adsorbent when changed from its initial state under its own vapor pressure to its combining state. Thus for a given mass of a particular solid and gas at a given temperature, ΔF_2 is usually a function of p_1 alone and is uniquely determined by the observed value of the integral $\int_0^{p_1} v_1 dp_1$ provided that the observed integral represents an integral along the path of thermodynamic reversibility corresponding to minimum free energies of the combined systems. ΔF_2 may be expressed in a number of more or less arbitrary ways. Thus we may suppose the solid of volume v_c to be subjected to a change in hydrostatic pressure Δp_c or we may suppose that the solid of surface area Σ has undergone a change in surface tension, $\Delta\gamma$, and thus write $\Delta F_2 = \bar{v}_c \cdot \Delta p_c$ or $\Delta F_2 = \bar{\Sigma} \cdot \Delta\gamma$ according as we prefer to suppose that the change in potential of the solid is mainly due to a change in its volume free energy or in its surface free energy. Hence we may write,

$$[7] \qquad \bar{v}_c \cdot \Delta p_c = \bar{\Sigma} \cdot \Delta\gamma = -\frac{RT}{Mv_0} \int_0^{p_1} \frac{v_0'}{p_1} dp_1,$$

which is the equation commonly used (8, 9) in discussing these problems.

If we now suppose that $\bar{v}_c \cdot \Delta p_c$ or $\bar{\Sigma} \cdot \Delta\gamma$ refers *not only* to the combining state of the pure adsorbent separately, but actually describes its condition exactly in the mixed system we can attempt to correlate the values of $\bar{v} \cdot \Delta p_c$ and/or $\bar{\Sigma} \cdot \Delta\gamma$ to the dimensional changes of the adsorbent–adsorbate system and to the elastic constants of the pure solid. Both Δp_c and $\Delta\gamma$ are measures of changes in states of stress and since the solid is almost incompressible, its elastic constants will be much the same in the stressed and unstressed states.

Equations of the form of Equation 7 have been used with considerable success by a number of investigators (1, 2, 3, 4, 8, 9) to correlate dimensional changes, resulting from adsorption, with calculated "spreading pressures" and with the compressibilities of various adsorbent materials. Thus there appears to be some validity in the supposition that in these cases $v_c \cdot \Delta p_c$ or $\Sigma \cdot \Delta\gamma$ refers not only to the state of stress of the pure adsorbent separately but refers, as well, to its state in the mixed system. This supposition is equivalent to the assumption that the combined system consists of two pure substances which exert mechanical or similar forces upon one another while each substance retains its original equation of state. In order to bring out more clearly the physical nature of this very important assumption, as well as to indicate something as to its plausibility and limitations, it seems worth while to look into the problem in a little more detail.

In Equations 3 and 4, v_{12} represents the total volume of the porous solid. This volume consists of the sum of the volumes of solid and void space, namely, the sum of the volumes v_c and v_a, respectively.

It is, accordingly, convenient to rewrite Equation 4 in the form

$$[8] \qquad \int_0^{p_a} v_a dp_a + \int_{p_{2s}}^{p_c} v_c dp_c = \int_{p_{2s}}^{p_1} v_{12} dp_{12},$$

where $v_{12} = v_a + v_c$, and p_a is the pressure of the pure adsorbate in a volume v_a. p_c and v_c represent the pressures and volume of the solid, respectively, and p_1 is the pressure of the gas surrounding v_{12}, i.e., the equilibrium pressure and also the hydrostatic pressure of the combined system.[5]

Equation 8 is subject to the condition,

$$[9] \qquad \int_0^{p_1} v_1 dp_1 = \int_0^{p_a} v_a dp_a.$$

Thus the volume v_a is separated from v_1 by the potential energy difference $\int_{p_1}^{p_a} v dp$.

Equation 8 is valid for any type of equilibrium since the integrals on the left are more or less arbitrary expressions of the free energy changes of the pure components from specified initial states. In the case of a two component chemical compound or in the case of a two component solution, no very definite meaning can be given to "v_a" and "v_c", the volumes of the components in the compound or in the solution, while in the case of mechanical mixtures, these volumes are quite definite. The assumption that the mixed system consists literally in the mechanical combination of the two separate systems or assemblies of systems of pure substances without change of their volumes or their forms, pressures, entropies, or any of their properties except their positions with respect to

[5] *If we prefer to regard the solid in its initial state as existing under a condition of stress corresponding to, say, p_c', we can add the integral $\int_{p_c'}^{p_{2s}} v_c dp_c$ to both sides of Equation 8.*

one another, distinguishes this special case of "reaction" from the more general type of reaction where there are various heat and other effects accompanying the equilibrium conversion of the separate systems into the combined system. In the latter more general type of reaction, neither of the separate systems can exist in a state or assembly of states in equilibrium with externally applied forces that shall be identical with their states in the combined system. In the special type of reaction which we are considering, the volume v_a in the adsorbent is to be regarded as containing the same substance as the equilibrium gas, and the equilibrium conditions as between the adsorbate in v_a and the gas in equilibrium therewith as resembling the equilibrium conditions which persist between two volumes of gas at different heights in a gravitational field. While the potential difference separating the two volumes in the latter case is a constant and independent of the temperature and pressure and of the nature of the gas, in the former case, although the potential difference between the volumes v_a and v_1 is constant during the transformation of the separate systems into the combined system, in general, this potential difference is dependent upon p_1 and upon the temperature and upon the natures of the gas and solid. Under these conditions, in order that an equilibrium exist at constant temperature as between the gas outside of v_a and that within v_a, as we vary the pressure, p_1, of the gas outside, we must have $v_a dp_a = v_1 dp_1$, hence,

[10] $$p_a = \int_0^{p_1} \frac{\rho_a}{\rho_1}\, dp_1,$$

where ρ_a is the mean density of the substance in v_a and ρ_1 is the density of the gas.

If within the volume v_a the densities vary, the equation is still valid, p_a representing the volumetric average pressure. Thus consider v_a made up of the sum of the small volumes v_i, where in each elementary volume v_i the density can be regarded as uniform. Then for each small volume we may write

[10a] $$p_{ai} = \frac{1}{v_i}\int_0^{p_1} \frac{m_i}{\rho_1}\, dp_1,$$

where m_i is the mass of material in the constant elementary volume v_i and $m_i/v_i = \rho_{ai}$. Thus we obtain

$$\sum v_i p_{ai} = \int_0^{p_1} \frac{\sum m_i}{\rho_1}\, dp_1$$

and hence,

$$\frac{\sum v_i p_{ai}}{\sum v_i} = p_a = \frac{1}{v_a}\int_0^{p_1} \frac{\sum m_i}{\rho_1}\, dp_1 = \int_0^{p_1} \frac{\rho_a}{\rho_1}\, dp_1.$$

Since ρ_a/ρ_1 is inherently positive, the integral must be positive for increasing values of p_1. Accordingly, along a path of thermodynamic reversibility p_a cannot become negative as p_1 increases. However, if at some point along the path of $\int_0^{p_1} v_1 dp_1$, a phase change occurs so that a second path of reversible variation[6] intersects the path of increasing pressure at some point, say, p_1', then as the equilibrium pressure is reduced from p_1', the system may pass along the second path and p_a will be given by,

$$[11] \qquad p_a = \int_0^{p_1'} \frac{\rho_a}{\rho_1}\,dp_1 + \int_{p_1'}^{p_1} \frac{\rho_a'}{\rho_1}\,dp_1.$$

Thus p_a may become negative if the second integral is larger than the first. For example, if the volume, v_a, is filled with liquid at p_1' and the pressure is then reduced, the liquid may persist and the value of ρ_a'/ρ_1 exceeding ρ_a/ρ_1, p_a may become negative.

Since the volumes v_a, v_c, and v_{12} are practically constant we can write Equation 8 in the form

$$[12] \qquad v_a \cdot p_a + v_c \cdot p_c = v_{12} \cdot p_1 = (v_a + v_c)p_1.$$

If the volumes v_a and v_c are made up of regions under varying stresses, it is to be understood that p_a and p_c are volumetric averages, i.e.,

$$v_{ai}p_{ai} + v_{ci}p_{ci} = (v_{ai} + v_{ci})p_1,$$

and

$$\sum v_{ai}p_{ai} + \sum v_{ci}p_{ci} = (v_a + v_c)p_1,$$

hence, in Equation 12,

$$p_a = \sum v_{ai}p_{ai}/\sum v_{ai} \text{ and } p_c = \sum v_{ci}p_{ci}/\sum v_{ci}.$$

Thus we can write

$$p_c = p_1 + (v_a/v_c)p_1 - (v_a/v_c)p_a,$$

and since

$$p_a = \int_0^{p_1} \rho_a/\rho_1 \cdot dp_1 = \overline{(\rho_a/\rho_1)} \cdot p_1 = \alpha p_1,$$

defining α, and putting $v_a/v_c = \phi$, we get the very simple basic equation

$$[13] \qquad p_c = (1 + \phi - \phi\alpha)p_1.$$

Equation 13 gives the average volumetric change in pressure or stress of the solid adsorbent from its state of stress where the adsorbable gas pressure is zero, to its state of stress when in equilibrium with the gas whose pressure is p_1.

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[6] *In general this second path of reversible variation is not one for which the free energy of the whole system is a minimum for given values of the potential of the adsorbate and given quantities of adsorbent. If the state of the system "jumps" from one of these paths to the other, the process is thermodynamically irreversible.*

The formation of surfaces of tension within a given volume, along a path where the equilibrium pressure increases from zero, will, in general, render observed values of $\int_0^{p_1} v_1 dp_1$ *an inexact measure of* ΔF_1. *Once a surface is formed, changes in the area and form of the surface may be perfectly reversible. Under these conditions,* $\Delta F_1'$ *is measured by the observed values of* $\int_{p_1}^{p_1'} v_1 dp_1$, *and the pressure changes within the system containing the interface are given by*

$$\Delta p_a = \int_{p_1}^{p_1'} \rho_a/\rho_1 \cdot dp_1.$$

Where hysteresis occurs, whether due to the mechanism usually implied by the term "capillary condensation" or to such a mechanism as proposed by Pierce and Smith (11), or to any other mechanism consistent with our basic assumptions, the above considerations are equally applicable.

If we wish to correlate length changes with the changes in stress resulting from adsorption we introduce Hooke's Law and assuming isotropy, we can write

$$\delta v/v = 3\delta l/l = -\beta\delta p$$

where v is the volume of the porous solid, l its length, β the compressibility, and p the uniform state of stress or pressure. If the pressures are not uniform along the length l, we must write

$$[14] \qquad \delta l/l = -\tfrac{1}{3}\beta \sum l_i\delta p_i/\sum l_i = -\tfrac{1}{3}\beta\overline{\delta p}$$

where $\overline{\delta p}$ is the change in linear average state of stress. In general, the linear average stress of linear average pressure will differ by a more or less constant factor from the volumetric average pressure unless the pressures are practically uniform. If the pressures on the solid adsorbent are uniform, we can write

$$[15] \qquad \delta l/l = \tfrac{1}{3}\beta(1+\phi-\phi\alpha)\delta p_1$$

where the symbols are as indicated previously. α is the mean value of ρ_a/ρ_1(i.e. the mean value of the number of volumes adsorbed) averaged over the pressure interval δp_1.[7] Where the solid pressures are not constant, we must write

$$[16] \qquad \delta l/l = \tfrac{1}{3}\beta(1+\phi K-\phi K\alpha)\delta p_1$$

where K is a small numerical factor dependent upon the structure of the porous solid and upon more detailed considerations which we shall discuss later with reference to particular models (cf. Appendix II). In general, ϕK should be more or less independent of the nature of the adsorbate, but a characteristic of the structure of the adsorbent and the nature of the surface forces involved in adsorption; K may thus be regarded as a structure factor.

If the porous rod is immersed in an incompressible liquid which fills the void space completely and the pressure of the surrounding liquid is increased by δp_1 the value of α will be unity over this pressure range and Equation 16 reduces to,

$$\delta l/l = -\tfrac{1}{3}\beta\delta p_1,$$

which should therefore apply approximately to the case where the rod is immersed in liquid water. For no adsorption, i.e., $\alpha = 1$, the equation also reduces to the above simple form, as of course it should. For large adsorptions, i.e., $\alpha \gg 1$, the equation becomes,

$$[16a] \qquad \delta l/l = \tfrac{1}{3}\beta\phi K\alpha\delta p_1 = \tfrac{1}{3}\beta\phi K\delta p_a,$$

and hence $\delta l/l$ becomes proportional to $\int_0^{p_1} \rho_a/\rho_1 \cdot dp_1$, and where the equilibrium gas is ideal, $\delta l/l$ is proportional to $\int_0^{p_1} v_0'\, d(\log p_1)$ and hence, where the quantity adsorbed is comparatively constant, $\delta l/l$ becomes proportional to $\log p_1'/p_1$ over the interval p_1 to p_1', as found by Amberg and McIntosh (1).

It is to be emphasized that Equation 16 is valid for any type[8] of adsorption by any virtually incompressible solid provided that the adsorbate (and hence

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[7] *The calculation of p_a from isotherm data according to Equation 10 is very simple. From the isotherm, values of ρ_a/ρ_1 are calculated and plotted against p_1, the equilibrium gas pressure. p_a is the area under the curve from 0 to p_1. In the case of hysteresis loops p_a is the difference of the areas under the curve from 0 to p_1' and the area under the curve p_1' back to p_1, preferably along the "scanning curve".*

[8] *Any shape of adsorption isotherm can be consistent with Equation 16.*

also the adsorbent) behaves as a single pure substance and also provided that no irreversible processes occur, i.e., provided $\int_0^{p_1} v_1 dp_1$ does in fact measure ΔF_1.

CALCULATED AND OBSERVED EXTENSIONS

As a test of the validity of these assumptions as applied to real systems, we have made use of some published data to compare observed extensions with those calculated by means of Equation 16*a*.

In Figs. 1, 2, and 3 calculated extensions are compared with those obtained experimentally by Haines and McIntosh (8) for activated carbon rods. The numerical value of βK is chosen to make the equation fit the observed result for saturated water vapor. The same value of βK is used for dimethyl ether and for ethyl chloride. It will be noted that βK is somewhat greater than the compressibility of graphite. In Fig. 4 calculated values are compared with those obtained experimentally by Wiig and Juhola (12) for a long column of short carbon rods placed end to end, while in Fig. 5 calculated extensions are compared with the precise extension measurements of Amberg and McIntosh (1) using porous glass rods, the value of βK again being taken so as to fit the extension at saturation. Evidently Equation 16*a* fits these data as well as could be expected since (*a*) none of the samples were known to be isotropic; (*b*) in the data of Haines and McIntosh the adsorption isotherm for water refers to a different sample from that used to measure extensions, (*c*) in Wiig

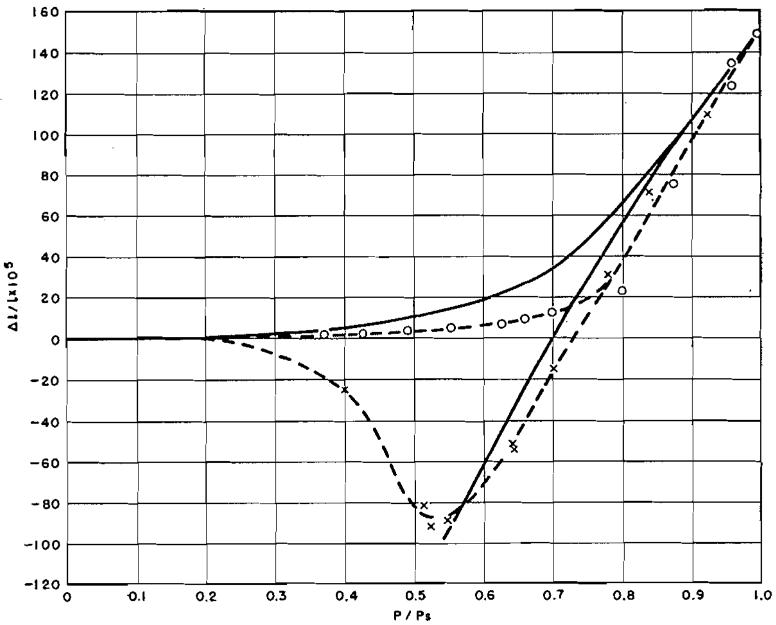

FIG. 1. Adsorption extension: Water vapor on carbon (data of McIntosh and Haines). Broken line drawn through experimental points. O, Adsorption; ×, Desorption. Solid line calculated from: $\delta l/l = +\frac{1}{3}\beta\phi K\alpha p_1 = 3.43\cdot10^{-7}\cdot\alpha p_1.(\beta K = 4.76\cdot10^{-7}/\text{p.s.i.};\ \phi = 2.16.)$

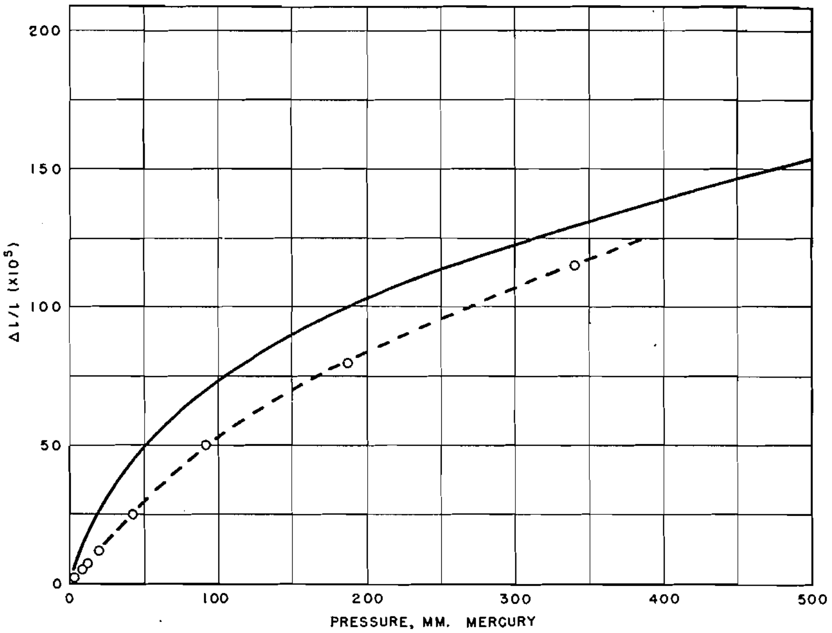

FIG. 2. Adsorption extension: Dimethyl ether on carbon (data of McIntosh and Haines). Broken line drawn through experimental points. Solid line calculated from: $\delta l/l = 3.43 \cdot 10^{-7} \cdot \alpha p_1$.

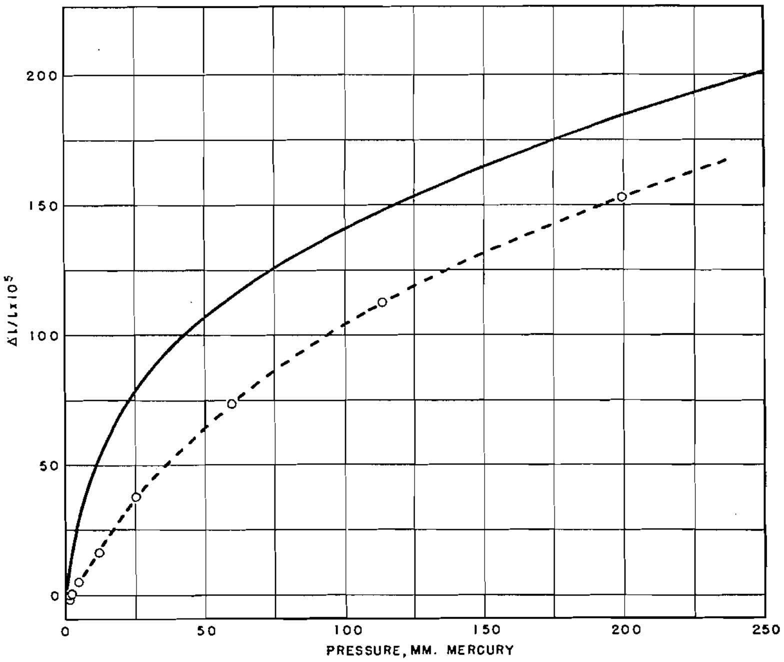

FIG. 3. Adsorption extension: Ethyl chloride on carbon. (data of McIntosh and Haines). Broken line drawn through experimental points. Solid line calculated from $\delta l/l = 3.43 \cdot 10^{-7} \cdot \alpha p_1$.

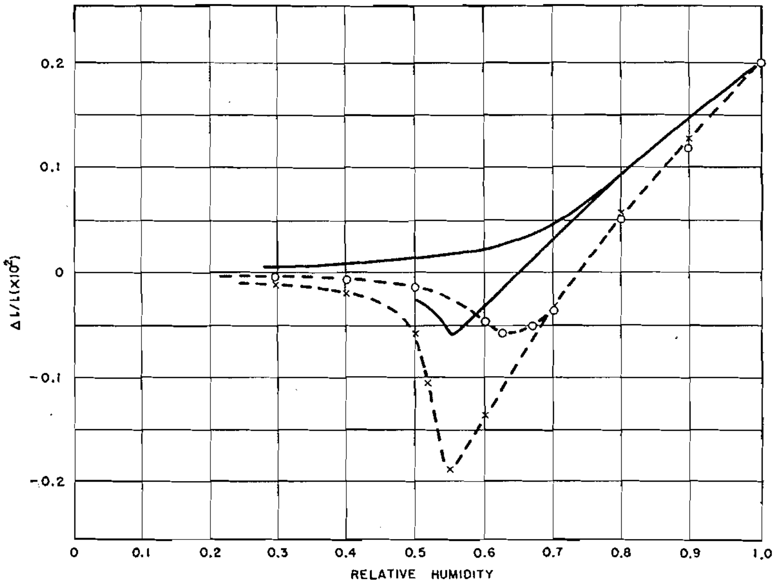

FIG. 4. Adsorption extension: Water vapor on carbon (data of Wiig and Juhola). Broken line drawn through experimental points. ○, Adsorption, ×, Desorption. Solid line calculated from: $\delta l/l = +\frac{1}{3}\beta K\phi\alpha p_1 = 3.49\cdot10^{-7}\cdot\alpha p_1$. ($\beta K = 6.54\cdot10^{-7}$/p.s.i.; $\phi = 1.60$.)

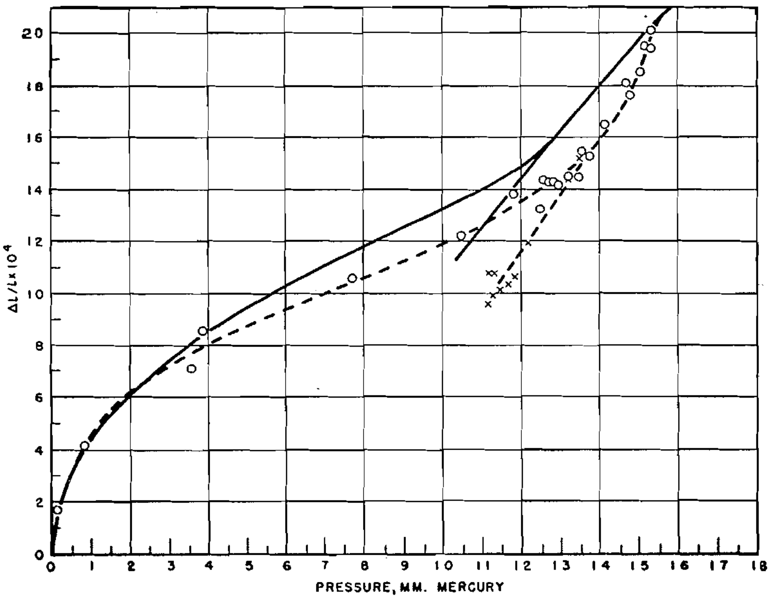

FIG. 5. Adsorption extension: Water vapor on porous glass (data of Amberg and McIntosh). Broken line drawn through experimental points. ○, Adsorption; ×, Desorption. Solid line calculated from: $\delta l/l = +\frac{1}{3}\beta\phi K\alpha p_1 = 3.69\cdot10^{-7}\cdot\alpha p_1$. ($\beta K = 5.76\cdot10^{-7}$/p.s.i.; $\phi = 1.92$.)

and Juhola's experiments there was some lack of reproducibility of the data, and finally, (*d*) because of the high surface tension of liquid water, irreversible processes are apt to occur within the adsorbent and consequently $\int_0^{p_1} \rho_a/\rho_1 \cdot dp_1$ is apt to give an inaccurate measure of p_a.

As an additional check on the validity of Equation 16 we have made some measurements of the extensions in length of a long thin activated carbon rod, when exposed to various pressures of helium, nitrogen, water vapor, and liquid water at room temperature. Measurements of radial extensions of the same rod when exposed to water vapor have also been made. Relevant adsorption isotherms were determined and the values of β and ϕ and K determined from the data.

In general terms, the results obtained may be summarized as follows:

(*i*) No appreciable change in length of the rod could be detected as between its length when in equilibrium with water vapor very close to the saturation pressure and when immersed in liquid water.

(*ii*) When immersed in liquid water the length decreases with increasing pressure of the surrounding water. The mean compressibility (0–2000 p.s.i.) in liquid water is close to that of pure graphite (5) but shows a tendency to increase with increasing pressure. If liquid water does not fill the void space completely, the value of α will tend to increase as a result of forcing water into empty spaces, thus reducing the apparent compressibility. Further, since water is slightly compressible, the compressibility decreasing with increasing pressure, α will approach unity more closely the higher the pressure. Thus in both of these cases the apparent compressibility should increase with increasing pressure. Evidently the observed behavior is consistent with Equation 16.

(*iii*) In the case of helium, the length also decreases with increasing pressure up to 1600 p.s.i. However, the apparent mean compressibility is considerably less than that of graphite (about one half) suggesting some adsorption of helium (5–10%) and/or adsorption of traces of water vapor from the helium. The accuracy of the measurements was not sufficient to make any reliable estimate of the helium adsorption.

(*iv*) In the case of nitrogen, the rod increases in length as the pressure of the nitrogen is increased from 0 to 1600 p.s.i. The increases in length can be calculated with surprising accuracy by Equation 16, making use of the adsorption isotherm data. Even if K is taken as unity in Equation 16 and the apparent value of β taken from the extension of the rod in saturated water vapor the calculated extension in nitrogen at 1600 p.s.i. is within 10% of the observed value. It will be noted that in these two cases the numerical values of α are very different, being of the order of 3 for nitrogen and of the order of 10^4 in the case of saturated water vapor.

(*v*) When exposed to water vapor at low relative humidities, the rod contracts slightly ($\sim 0.03\%$), the contraction increasing with increasing pressure up to 10 to 11 mm. Hg, and subsequently expands considerably. The extension (0.36%) at saturation (23.65 mm. Hg) although agreeing fairly well with calculated values is too large to be quite consistent with those obtained with nitrogen. The desorption behavior is practically identical with the adsorption behavior. (These carbon rods show comparatively little adsorption hysteresis.) Changes in diameters of the rod due to water vapor adsorption were found to be essentially similar to the changes in length.[9]

Details concerning experimental methods and materials are given in Appendix I, the experimental results being recorded in Figs. 6 to 9.

Evidently, Equation 16 describes the general extension behavior of the carbon rod very well but fails to describe the extensions when the carbon rods are exposed to water vapor at low relative humidities (cf. Wiig and Juhola's data). While this failure may be due to the system behaving as a two-component system or to rather bizarre structural effects, we believe that the failure of Equation 16 in this region is due to the irreversible formation of liquid-vapor menisci. While adsorption at a few isolated regions might easily give rise to a contraction in one direction and to expansions in directions perpendicular thereto, the net effect of the surface forces still corresponding to a net compression of adsorbate and extension of adsorbent, a net compression of adsorbate can hardly be consistent with contractions in both the length and diameter of the rod, i.e., it seems unlikely that non-isotropic solid tensions will give rise to contractions of the rod along its three principal axes. The contractions, when the rods are exposed to low relative humidities of water vapor, are thus considered to be due to the adsorbate having a net negative pressure—a condition consistent with reversible *desorption* paths *only*, i.e., paths involving some reduction in equilibrium pressure. Thus we believe that in these cases the isotherm of thermodynamic reversibility, the true measure of $\Delta\ F_1$ and of $\int_0^{p_1} \rho_a/\rho_1 \cdot dp_1$, lies to the right of the observed isotherm (i.e. the isotherm ordinate, x/m, should be smaller for given equilibrium pressures).

Assuming the compressibility of the rod to be practically the same as that of graphite (5), i.e., taking 3.3×10^{-7}/p.s.i. as the value of β, and assuming 4.8 as the axial value of ϕK, all of our data are reasonably self-consistent as well as being consistent with what is to be expected in such cases. The calculated axial extensions in the cases of nitrogen, liquid water, and water vapor, Figs. 8 and 9, are based on these values of β and ϕK (cf. Appendix II).

DISCUSSION

Evidently the view that the adsorbate may be regarded as the same substance as the pure gas which it adsorbs is qualitatively in agreement with the facts in these cases. However, there are undoubtedly many other cases of "adsorption" where real bonds are formed between adsorbent and adsorbate and where a considerable fraction of the molecules of the adsorbed material are in energy states that are not attainable by molecules of either the adsorbate or adsorbent alone. Such a situation might be expected in the case of the highly specific catalytic activity of many adsorbing catalysts. However,

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[9] *In view of these small initial contractions, the extension behavior of the rod on exposure to nitrogen was reexamined with considerable care especially in the low pressure region. No contractions could be detected.*

if the bonds of the adsorbent are very strong, the residual orbital fields and any Van der Waals or Lennard-Jones type forces might have little specific character and the resultant field within a narrow capillary space behave as an almost wholly nonquantized attractive force field of considerable range. In such a case any work done by the field would cause a change in the state of stress of the material that could be very closely paralleled by the application of external forces. However, if the surface is very large it seems very improbable that no regions are formed where the state of the adsorbate–adsorbent system is essentially a two-component system. The known effects of various adsorbates on the formation of surface complexes indicate that in activated charcoals there are undoubtedly regions which cannot be identical thermodynamically with two separate components in any pure state. However, in general, where large adsorptions occur in fine-grained rigid porous adsorbents there is a good deal of evidence that indicates that by far the larger part of the adsorbate may be regarded as a single substance. Thermodynamically, a clear distinction between chemisorption and physical adsorption can be made, if by physical adsorption we restrict the adsorption reactions to those where assemblies of the separate systems of adsorbate and adsorbent can each exist separately in equilibrium with externally applied forces in states which are identical thermodynamically with their states in the adsorbate–adsorbent system.

APPENDIX I—EXPERIMENTAL DETAILS

1. *Materials*

Activated Carbon Rods

Except where noted, all of the experiments were carried out with Carbon Rod No. 1. This rod was nearly straight, 88 mm. in length, and 1.78 mm. in diameter. Apparent (mercury) density, 0.753; helium density, 2.00; total void volume per cc., 0.623; micropore void volume (H_2O adsorption) per cc., 0.302; carbon volume per cc., 0.377.

The carbon rod used was one taken from a group of long straight rods supplied through the courtesy of the National Carbon Company. The rods are believed to have been made by extruding a zinc chloride – wood meal plastic mix to which had been added activated coconut shell charcoal fines. After extrusion and baking, these rods were remarkably straight but during the subsequent activation (~ 900°C.) considerable distortion occurred. However, a number of reasonably straight rods were selected for this work. Although the properties of the rods were similar, isotherms of the individual rods studied were all somewhat different. Water isotherms showed comparatively little hysteresis. The adsorption behavior of these rods differed considerably from the behavior of zinc chloride activated carbons with which we are familiar.

Helium

An especially pure commercial hydrogen-free helium was used (Air Reduction Sales Ltd., 99.99+% He). The helium was taken from a cylinder found satisfactory for use in a helium cryostat after passage through a liquid-air-cooled charcoal trap. The helium was dried in our experiments by passage over solid KOH contained in a suitable high pressure vessel.

Nitrogen

Highest grade obtainable commercially (Dominion Oxygen Co., 99.7+%; < .03% O_2). The nitrogen was passed over KOH as in the case of helium.

2. *Experimental Procedures and Methods*

Water adsorption isotherms were determined by the McBain technique. Vessels containing the quartz spirals, manometers, etc. were all immersed in a large oil thermostatic bath maintained at about 25°C., but constant to within ±0.001°C. within short time intervals and probably to within ±0.1°C. during the eight month period of all of the experiments reported herein. Water vapor at controlled pressures was introduced into the adsorption apparatus by evaporation from a thoroughly outgassed water reservoir immersed in a second thermostatic bath.[10]

Nitrogen adsorption at high pressures was determined by expanding the gas at various pressures from a small high pressure capillary into a large volume attached to the vacuum system. The volumes were known and by comparison of the pressure relations between expansions with the carbon rod present and those with the rods absent, the "apparent" increase in volume of the capillary due to the presence of adsorbing carbon could be calculated for the various pressures. (Estimated error at higher pressures 5%, lower pressures 10%). At low pressures (down to 3×10^{-3} mm. Hg) expansions were made into a small capillary containing the active carbon on a different vacuum system. (Estimated error at pressures below 0.1 mm. Hg, about 20%.) In the case of helium similar measurements were made but the experimental errors were too large to give even qualitatively reliable adsorption data. The carbon rod helium density of 2.00 quoted above is that obtained at pressures of about half an atmosphere and not being corrected for helium adsorption is perhaps 5–10% too low.

Length Changes

The carbon rod was placed in a horizontal, heavy walled, large bore, pyrex capillary which was connected through a short length of high pressure steel tubing to a three way high pressure steel valve. The capillary could be opened to the high vacuum system and also to either a hydraulic high pressure oil pump and mercury separator, or to a cylinder containing gases at fairly high pressures.

The capillary containing the carbon rod (the ends of the rod were filed flat) was itself contained within a glass tube through which oil from the thermostat was circulated.

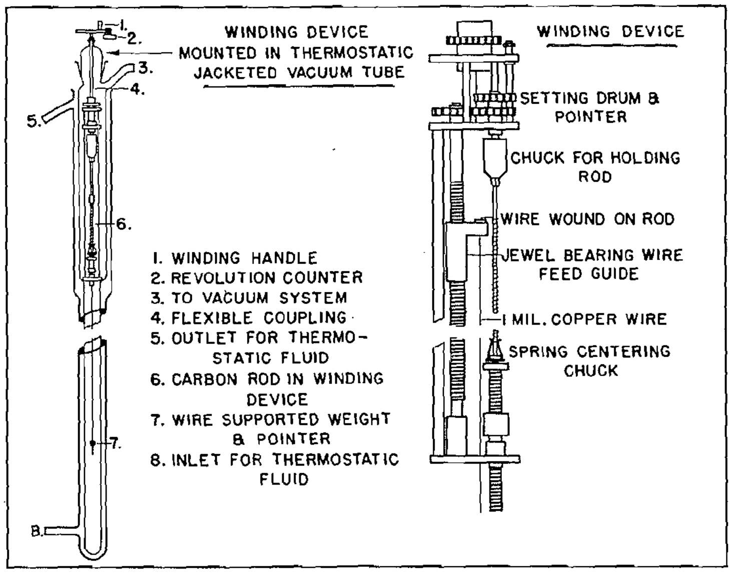
Length changes were observed by means of a travelling microscope. Reproducibility of individual length measurements was usually within $\pm 2 \times 10^{-3}$

[10] *The isotherm as plotted in Fig. 7 is based on the carbon weight obtained after a four day evacuation period following the water vapor equilibrations. This weight was less than the initial evacuated weight. The loss in weight is considered to be due to loss of chemisorbed or other material. The values of x/m used in the calculations were reduced by 0.014.*

mm. while reproducibility of length changes for various pressures was perhaps within 5×10^{-3} mm. Reproducibility of length measurements of the rod in vacuum on dismantling and reassembling the apparatus was $\pm 3 \times 10^{-2}$ mm.

It is considered that larger values of $\delta l/l$ are within ± 5%; small values, for example maximum contraction, within ± 20%.

Radial extensions were measured by means of a small winding device with which it was possible to observe the change in height of a small weight which was raised by winding a fine supporting wire on the carbon rod. Reproducibility in linear lift per 100 turns was usually within the reproducibility of the cathetometer, i.e., ± 0.05 mm., the total lift being of the order of 600 mm. The winding device was contained within a long vacuum tight glass tube which was surrounded with circulating thermostatic oil pumped from the large thermostat (25°C.). It may be remarked that considerable trouble was encountered owing to breakage of the bare one mil copper wire. The wire was tested for elastic deformation, elastic fatigue, etc., by making trial runs of 200 "winds" of 100 turns each in a number of ways which were more apt to cause breakage (e.g. larger weight, pulling wire over iron and glass rods, etc.). However, the trials were not made in vacuum. It was found that protection of the wire and winding apparatus from Hg vapor by means of a trap containing indium metal (liquid air cooled on evacuation) considerably prolonged the life of the wire. However, as a result of the frequent breakage of the wire, values of $\delta l/l$ corresponding to various changes in water vapor pressures as given in Fig. 9 do not represent a continuous series of extensions with a given setting. Considerable care was taken in the examination of the minimum and it is considered that it is real, the very small contraction being reliable perhaps within ± 50%. The extension at saturation is thought to be reliable within ± 20%. The winding apparatus is shown diagrammatically in the following sketch.



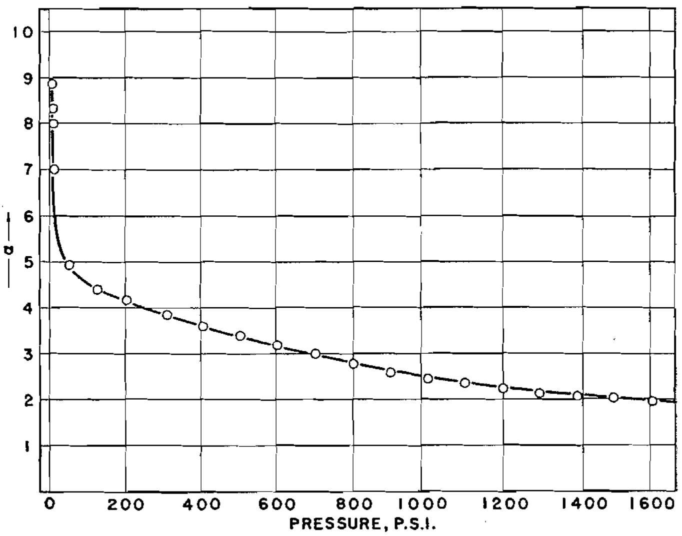


FIG. 6. Adsorption isotherm: Nitrogen on carbon rod No. 1 (25°C.). Ordinate, $a = \rho_a/\rho_g = \dfrac{\text{apparent void volume}}{\text{void volume}}$. Abscissa, nitrogen pressure.

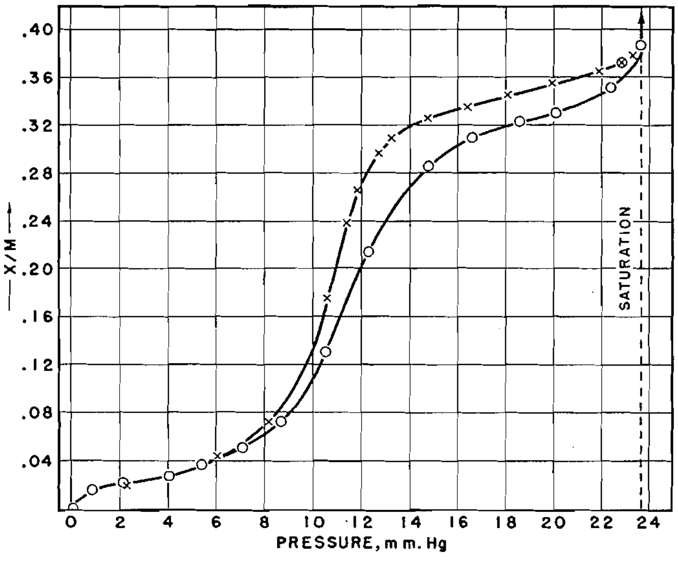


FIG. 7. Adsorption–desorption isotherm: Water vapor on carbon rod No. 1 (25°C.). Ordinate, weight of water adsorbed per gram carbon. Abscissa, water vapor pressure. (Cf. footnote 10)

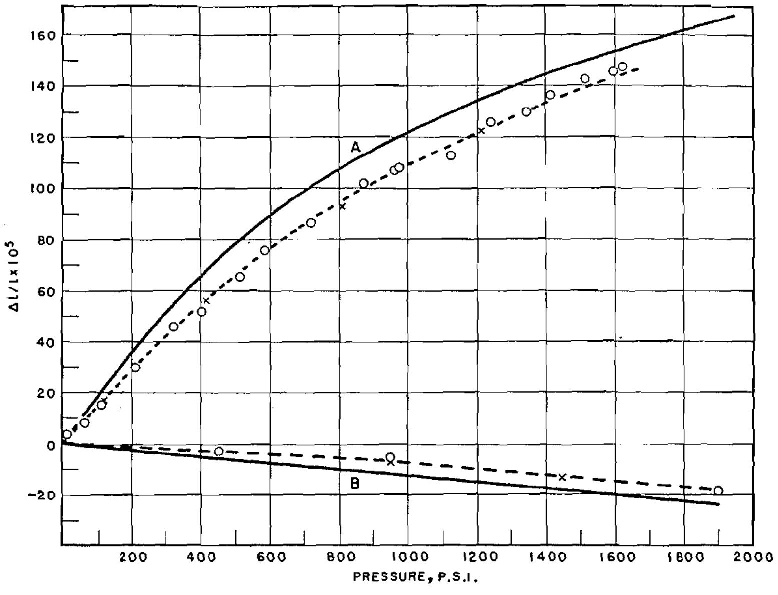


FIG. 8. Adsorption extension: Carbon rod No. 1 (25°C.); A, nitrogen; B, liquid water. Broken line drawn through experimental points; O, adsorption; X, desorption. Solid line calculated from: $\delta l/l = \frac{1}{3}\beta(1 + \phi K - \phi K\alpha)p_1$, $\beta = 3.3\cdot10^{-7}$/p.s.i.; $K = 2.91$; $\phi = 1.65$.

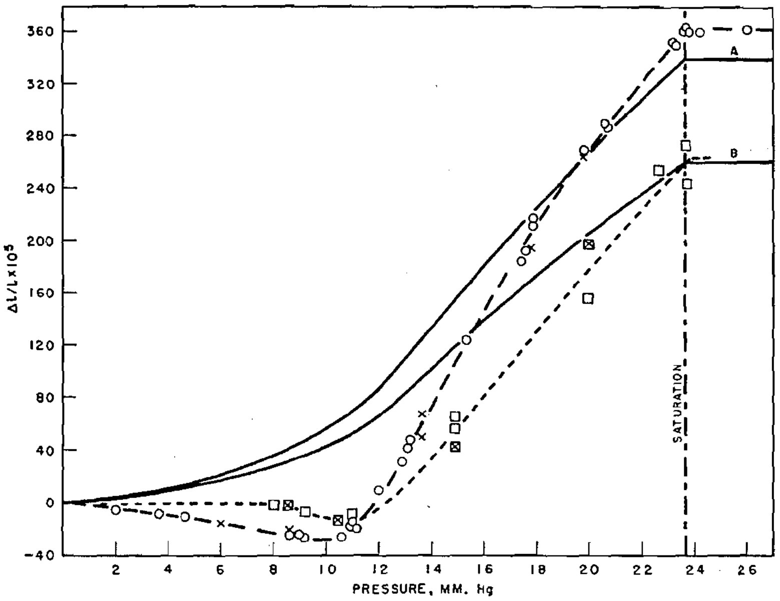


FIG. 9. Adsorption extension: Water vapor on carbon rod No. 1 (25°C.); A, axial extensions; B, radial. Broken line drawn through experimental points. Solid line calculated, Axial A, as for Fig. 8. Radial B, as for Fig. 8, but $K = 2.23$.

APPENDIX II—MODEL PORE SYSTEMS

The influence of pore shapes on the extensions of solids for given values of the changes of volumetric mean pressures, i.e., the relation of linear average pressures to volumetric average pressures, is, perhaps, best illustrated by reference to particular models.

Consider a thin section of a porous solid. Let the section have a thickness l_i and an area A_i consisting of the sum of the areas a_i and c_i. The area a_i represents the area of holes filled with fluid while the area c_i represents solid material. Let F_i be the total force acting normally on the area A_i so that the corresponding pressure $P_i = F_i/A_i$. Let F_{a_i} and F_{c_i} be the forces acting on the areas a_i and c_i respectively, the corresponding pressures being $p_{a_i} = F_{a_i}/a_i$ and $p_{c_i} = F_{c_i}/c_i$. Then we have $F_i = F_{a_i} + F_{c_i}$, and $A_iP_i = a_ip_{a_i} + c_ip_{c_i}$, and summing over all the sections,

$$\sum l_iA_iP_i = \sum l_ia_ip_{a_i} + \sum l_ic_ip_{a_i},$$

hence,

$$vP = v_ap_a + v_cp_c,$$

where $\sum l_iA_i = \sum v_i = v$ and $\sum v_iP_i = vP$ and p_a and p_c are similarly defined volumetric averages.

Let us now assume that the fluid-filled areas (i.e., the holes in the porous solid) are of two distinctly different kinds: (1) a number of small holes where the influence of the attractive forces is relatively large and where the pressures of the fluid differ from the hydrostatic pressure of the whole system, and (2) a smaller number of large holes where the effect of the attractive forces is small and the pressures are the same as that of the hydrostatic envelope. Thus we write

$$A_i = a_{1i} + a_{2i} + c_i$$

where A_i is subject to a net hydrostatic pressure P independent of l_i, while the area a_{1i} is subject to the pressure $P + p_{a_{1i}}$, the area a_{2i} to the pressure P, and the solid area c_i to the pressure $p_{c_i} = P + p_{c_i}'$. Then balancing forces in each section and summing over all of the sections l_i we get

$$P\sum l_iA_i = P\sum l_ia_{1i} + \sum l_ia_{1i}p_{a_{1i}} + P\sum l_ia_{2i} + P\sum l_ic_i + \sum l_ic_ip_{c_i}',$$

hence,

$$c_ip_{c_i}' = -a_{1i}p_{a_{1i}}$$

and

$$v_{a_1}p_{a_1} = v_a(p_a - P).$$

In order to introduce these relations into the compressibility formula

$$\delta l/l = -\tfrac{1}{3}\beta\sum l_ip_{c_i}/\sum l_i,$$

we must know a good deal about the actual structure of the material as well as something concerning the relations between fluid and solid stresses. If, for example, we assume that the hydrostatic pressure of the fluid within a micropore is uniform, so that the force per unit area within a given pore is the same in all directions, it implies that the corresponding equilibrium stresses in the walls of long thin capillaries are different in different directions. On the other hand, if we assume that the tensions in the solid surface are everywhere the same, the hydrostatic pressure of the fluid in equilibrium with these tensions will differ in different directions. In the case of a comparatively very large capillary filled with liquid having concave menisci at its ends the bulk of the liquid will be under an almost uniform hydrostatic pressure, but the axial stress on the capillary wall will be considerably less than the radial stress. If, on the other hand, the change of the surface stress of the solid is assumed uniform, the corresponding change in axial and radial mean pressures of the fluid will not be the same. The former is a condition analogous to "capillary condensation" in large pores, the latter a condition describing adsorption in layers on a macroscopically uniform surface.

In addition to assumptions concerning the nature of the stresses, it is necessary to construct some sort of representative model pore system. For this purpose we assume that the porous body can be described as an assembly of rectangular or cubical cells of various sizes where the dimensions of the void space in each cell have constant relations to the cell dimensions. And we assume (*a*) that the fluid pressure $p_{a_{1i}}$ is constant everywhere within the void space of the cell, i.e., independent of l_i and independent of the cell dimensions, or we assume (*b*) that $c_i p_{c_i}' = \gamma\lambda_i$ where λ_i is the common perimeter of the areas a_{1i} and c_i, and where γ is the change in surface tension and is independent of l_i and independent of the cell dimensions. The latter assumption seems much more plausible generally as applied to active adsorbents, although as we have pointed out, for relatively large pores all of which were liquid filled and separated from vapor by menisci of constant curvature the former might be a fair approximation.

With these assumptions, we obtain for the two cases:

(*a*)
$$p_{c_i} = P - (a_{1i} p_{a_{1i}}/c_i),$$
$$\therefore \sum l_i p_{c_i} / \sum l_i = P - p_{a_1} [(\sum l_i a_{1i}/c_i)/ \sum l_i]$$
$$= P - (v_a/v_{a_1})(p_a - P)[\sum l_i a_{1i}/c_i)/ \sum l_i],$$
which with the compressibility relation leads to

[2*a*]
$$\delta l/l = -\tfrac{1}{3}\beta(1 + \phi K_p - \phi K_p \alpha)\delta P$$
where $\delta p_a = \alpha \delta P,\ \phi = v_a/v_c,$

and $K_p = (v_c/v_{a_1})[(\sum l_i a_{1i}/c_i)/ \sum l_i],$

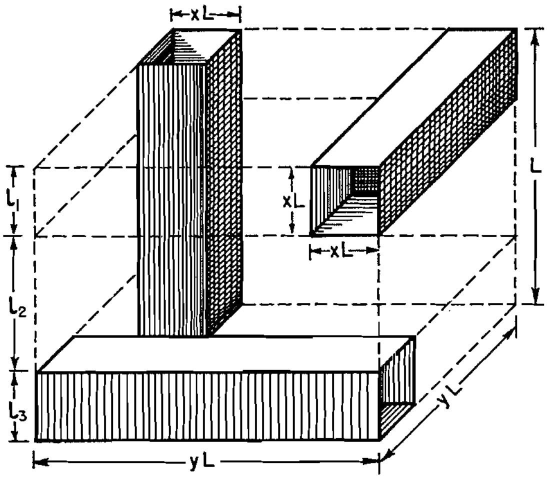
and α is defined by $p_a = \int_0^P \rho_a/\rho_1 \cdot dP = \alpha P.$

(*b*)
$$p_{c_i} = P + \gamma\lambda_i/c_i,$$
$$\therefore \sum l_i p_{c_i} / \sum l_i = P + \gamma[(\sum l_i \lambda_i/c_i)/ \sum l_i$$
and
$$\gamma = - \sum l_i a_{1i} p_{a_{1i}} / \sum l_i \lambda_i = - v_a\, p_{a_1} / \sum l_i \lambda_i = - v_a(p_a - P)/ \sum l_i \lambda_i,$$
$$\therefore \delta l/l = -\tfrac{1}{3}\beta(1 + \phi K_\gamma - \phi K_\gamma \alpha)P \qquad (2b)$$
where
$$K_\gamma = v_c \cdot [(\sum l_i \lambda_i/c_i)/ \sum l_i \lambda_i \cdot \sum l_i].$$

In both cases when c_i is constant, i.e., independent of l_i, $K_p = K_\gamma = 1$. Thus K_p and K_γ measure the ratios of the linear average pressures to the volumetric average pressures.

It will be noted that these formulae are dependent wholly on the relation of the micropore and solid structures and are independent of the macropore structure. If we are interested in relating these extensions to extensions produced by the application of a force of tension to the whole system, as in measurements of Young's modulus, we must include both the macropore and the micropore structures in determining $\sum l_i p_{c_i} / \sum l_i$. It is further to be noted that if we suppose that the porous body can be described as an assembly of rectangular or cubical cells of various sizes where the void space in each cell has a constant shape, the extensions are independent of the distribution of cell sizes but dependent only on the elastic behavior of the individual cell. The "average shaped cells" are more or less arbitrary representations of structural irregularities. We shall suppose the cells orientated so that the faces of the cells are parallel to the principal planes of stress. It will be noted that whatever the state of stress of a body, there will always exist three mutually perpendicular planes for which the tangential stress-components are zero; the stresses acting normally on these principal planes of stress behave essentially as pressures.

To illustrate the influence of cell shape on numerical values of K_p and K_γ we will consider two rather different model cells. The first model will be representative of a system of nonintersecting straight capillaries running through the specimen as shown in the following figure.



The capillaries are assumed square in cross section and of area x^2L^2. The cell has the dimensions $yL \cdot yL \cdot L$ (providing for lack of isotropy). Taking the axial length as L, the dimensions as function of l_i are

$l_1 = Lx \qquad \lambda_1 = L(4x + 2y) \qquad a_1 = L^2(x^2 + xy) \qquad c_1 = L^2(y^2 - x^2 - xy)$
$l_2 = L(1 - 2x) \qquad \lambda_2 = L4x \qquad a_2 = L^2x^2 \qquad c_2 = L^2(y^2 - x^2)$
$l_3 = Lx \qquad \lambda_3 = L(4x + 2y) \qquad a_3 = L^2(x^2 + xy) \qquad c_3 = L^2(y^2 - x^2 - xy)$

The values of x and y are limited by the following: Volume of void space (micropore) $= L^3x^2(1 + 2y)$. Volume of solid plus volume of micropore, i.e., the cell volume, $= L^3y^2$. (The cell structure is representative of the structure of the material surrounding the macropore space.) Hence, in the case of our carbon rods, $x^2(1 + 2y)/y^2 = 0.445$. Assuming the most unsymmetrical arrangement consistent with the model, i.e., taking $x = 0.5$, then $y = 1.5$, and

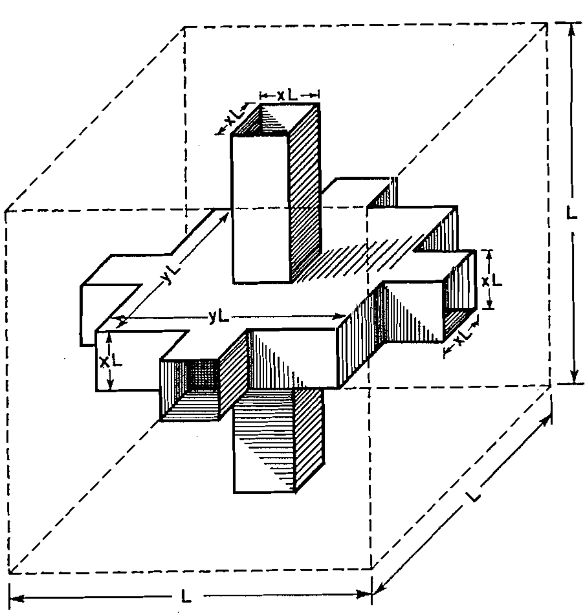
$$\phi K_p(\text{axial}) = 1.65,\ K_p = 1,$$
$$\phi K_\gamma(\text{axial}) = 1.65,\ K_\gamma = 1.$$

The corresponding expressions for radial extensions are:

$$\phi K_p = 2.20,\ K_p = 1.33,$$
$$\phi K_\gamma = 2.03,\ K_\gamma = 1.23.$$

The values for capillaries of circular cross section are essentially similar.[11]

X-ray diffraction studies indicate that the micropore system of activated carbon is a box-like structure formed from imperfect graphite-like platelets (6), the micropore void space constituting about one half of the void structure. The tensile strength of impervious graphite (Karbate) as given in the handbooks is about 2500 p.s.i. while the tensile strength of our samples is of the order of 400 p.s.i. The macropore system of many active carbons are fairly regular interstitial structures (our rods before activation have a tensile strength of $\sim$ 1000 p.s.i.). Thus it would appear that there should be areas along the axis where the micropore void space is about 80% of the micropore-solid system. The following model is representative of such a system.



For the model, taking $x = 0.395$ and $y = 0.90$, we get,

$$A \text{ axis},\ \phi K_\lambda = 9.34,\ K_\gamma = 5.66,$$
$$B \text{ axis},\ \phi K_\lambda = 1.42,\ K_\gamma = 0.860.$$

We may suppose the structure made up of filaments of cells of this type, a

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[11] *It may be remarked that in the case of a cubical cell ($y = 1$), the elongation, due to a single capillary (square cross section x^2L^2) parallel to the axes of elongation, varies from 1/2 to 1/3 of that due to two similar capillaries whose axes are perpendicular to the elongation, i.e., K_p in the former case is $1/2(1 + x)$ times the value of K_p in the latter case.*

fraction of them arranged so that the A axes of the cells are parallel to the filament axes and the remainder of the cells arranged so that the B axes of the cells are parallel to the axes of the filament. Taking the fraction, 0.427, arranged so that the A axis of the cell is parallel to the axes of the filaments, we get

$$K_\gamma \text{ (axial)} = 2.91,$$
$$K_\gamma \text{ (radial)} = 2.23.$$

The plots of calculated extensions shown in Figs. 8 and 9 are based on these values of K_γ.[12] Thus the model micropore system is reasonably consistent with the strength of the material, its elastic properties and, in addition, consists of a box-like structure such as might be formed from graphite platelets. Of course, a great many alternative models can be devised that will describe the behavior of the rods, but these models are not by any means entirely arbitrary.[13]

It must be pointed out that if the shape of the average pore is not statistically independent of the surface free energy of the solid enclosing the average micropore, then K will become a function of p_1 and will probably vary with the nature of the adsorbable gas. Further, since the compressibility is not a true constant, but is unsymmetrical with respect to large compressions and expansions, Equation 16 must be regarded as an approximate representation of a more general formula which we may represent empirically as follows:

$$\delta l/l = -\tfrac{1}{3}\beta\bar{\delta}p_c\cdot e^{-h\overline{\delta p}_c}$$

and

$$\overline{\delta p}_c = \{1 + \phi K[1 + f(p)] - \phi K[1 + f(p)]\alpha\}\delta p_1.$$

While we might expect that in most cases $f(p)$ will be practically zero, the lack of constancy of the compressibility will not be negligible in cases where adsorption is large and the corresponding changes in states of stress of the solid are large. In the case of graphite the compressibility at 5000 p.s.i. is about 2% less than its compressibility at zero pressure (5). If activated carbon can be regarded as consisting essentially of graphite under stress, the stresses being largely removed when the rods are immersed in liquid water, the pure active carbon must be regarded as graphite under a compressive stress intensity of more than 5000 p.s.i., this large stress practically vanishing on immersion in liquid water.

It is important to note that the frequency distribution of cell sizes does not influence the values of $\delta l/l$ appreciably. This is in marked contrast to the influence of the frequency distribution of cell sizes on surface areas and permeabilities. These latter properties are dominated by the frequency distribution of cell sizes. While the elastic properties are almost wholly dependent

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[12] *ϕ = total void volume/volume of carbon = 1.65 for this particular carbon. ϕ is independent of the model.*

[13] *It will be noted that the above treatment of the distribution of stress in the particular models assumes that stress contours in each section can be treated independently. This assumption ignores shearing and other distortional stresses and is, of course, a crude approximation. However, in the case of fine-grained isotropic porous material where deformations are very small, the mean stresses obtained by the above method will differ very little from those obtained by the much more laborious but more rigorous methods of the classical theories of elasticity.*

on the shape of the average micropore, the surface areas and permeabilities are almost entirely dependent on the ratios of the various statistical moments of the pore diameters, i.e., on the relative values of the mean pore diameter, the mean square, the mean cube, and the mean fourth power of the pore diameters. Thus adsorption–extension measurements can provide information concerning micropore structure that cannot be obtained directly from almost any other simple measurement, nearly all of the more readily measurable properties of active adsorbents being strongly dependent on frequency distributions of pore diameters. Adsorption–extension measurements and measurements of micropore permeability combined with B.E.T. surface area measurements and the results of X-ray diffraction studies should provide sufficient information from which to construct model micropore systems that are reasonably reliable representations of the real structure of some of these complex systems.

ACKNOWLEDGMENT

The authors are indebted to Dr. J. A. Morrison, Dr. M. Huber, and Dr. P. H. Sterling for valuable criticism and useful suggestions.

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THE SPECTRA OF SATURATED AND α-β UNSATURATED SIX-MEMBERED LACTAMS[1]

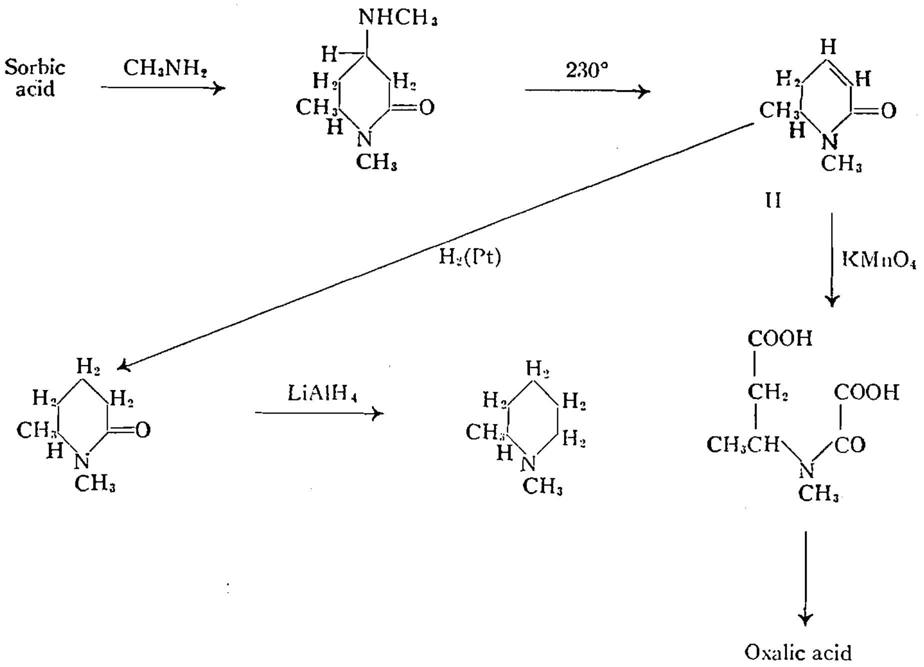
By O. E. Edwards and Tara Singh[2]

ABSTRACT

The ultraviolet and infrared spectra of some saturated and unsaturated six-membered lactams are described, and the unusual features in the 3μ and 6μ regions discussed. A comparison is made of these spectra with those previously ascribed to α-β unsaturated lactams.

On the basis of ultraviolet and infrared spectra, α-β unsaturated lactam structures have been assigned to products of Beckmann rearrangement of unsaturated oximes (8, 14) and to the alkaloid bakankosine (1). In addition an α-β unsaturated lactam structure has been considered for one of the transformation products of lycoctonine (5). It thus became of interest to examine the spectra of authentic α-β unsaturated lactams for comparison with those of the above compounds.

6-Methyl-5,6-dihydro-2-pyridone (I) and 1,6-dimethyl-5,6-dihydro-2-pyridone (II) were prepared by a method similar to that of Fischer and Schlotterbeck (7). The preparation and characterization of the latter is outlined below.



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[2] *National Research Council Postdoctorate Fellow.*

Since hydrolysis of the oxidation product from the unsaturated lactam gave oxalic acid in 75% yield, the lactam contained at least this percentage of the α–β unsaturated isomer.[3]

The 1,2-dimethyl piperidine gave a picrate analyzing correctly, and melting at 242° (the literature gives 241° (12)).

The ultraviolet spectra of the various compounds which have been assigned α–β unsaturated lactam structures are recorded in Table I. Our observations with 6-methyl-5,6-dihydro-2-pyridone contrast with the broad band (236–251 mμ) or series of maxima recorded by Linstead and co-workers (6). The positions of the maxima of all the compounds are similar, occurring at much longer wave lengths than for acyclic α–β unsaturated amides (2). As an example of the latter we have examined N-crotonylpiperidine,[4] and find it to have only a shoulder around 235 mμ.

The intensity of the maxima of the two six-membered α–β unsaturated lactams is considerably lower than those recorded for the seven-membered analogues and the bakankosine derivatives. Indeed, the spectra of the compounds related to bakankosine are more like those of α–β unsaturated ketones except that no long wave length (300–330 mμ) maxima are recorded.

The "iso" compounds derived from the periodate cleavage products of lycoctonine (5) have λ_{max} 219 mμ, 20 mμ lower than the simple α–β unsaturated lactams which have been studied. This raises doubt as to the unsaturated lactam postulate.

The origin of the bands in the 3μ and 6μ regions in the infrared spectra of amides has been the subject of considerable controversy (9, 15, 16). The strong band in the 6μ region observed with aliphatic amides has been associated with the C=O stretching vibration (9,13,15). Saturated N-alkyl six-membered lactams have a strong band near 1640 cm.$^{-1}$ when in carbon disulphide solution or in the liquid or solid state (mull). This band is displaced to near 1625 cm.$^{-1}$ in chloroform solution (Table II). The peak is often asymmetric but in the simple compounds so far examined no second band has been clearly resolved. In contrast to these the spectrum of N-crotonylpiperidine has two bands, and the spectra of the two α–β unsaturated lactams have three bands

TABLE I
ULTRAVIOLET SPECTRA IN ETHANOL

Compound	λ_{max} in mμ	ϵ_{max}	Reference
Bakankosine derivatives	236–242	12,000–18,000	1
3,5,5-Trimethyl-7-amino-2-heptenoic acid lactam	237	7,320	14
3,5-Dimethyl-7-amino-2-heptenoic acid lactam	241	—	8
6-Methyl-5,6-dihydro-2-pyridone	241	1,470	
1,6-Dimethyl-5,6-dihydro-2-pyridone	251	1,120	

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[3] *The equilibrium between acyclic α–β and β–γ unsaturated acids and esters at moderate temperatures lies over 65% on the α–β side (11). The position of the equilibrium in the above dihydropyridone seems the same at 230° as at room temperature, since no change in* ϵ_{max} *was observed when I was left at room temperature in 1 N alkali for six hours.*

[4] *The authors are indebted to Dr. F. A. L. Anet for a sample of this amide.*

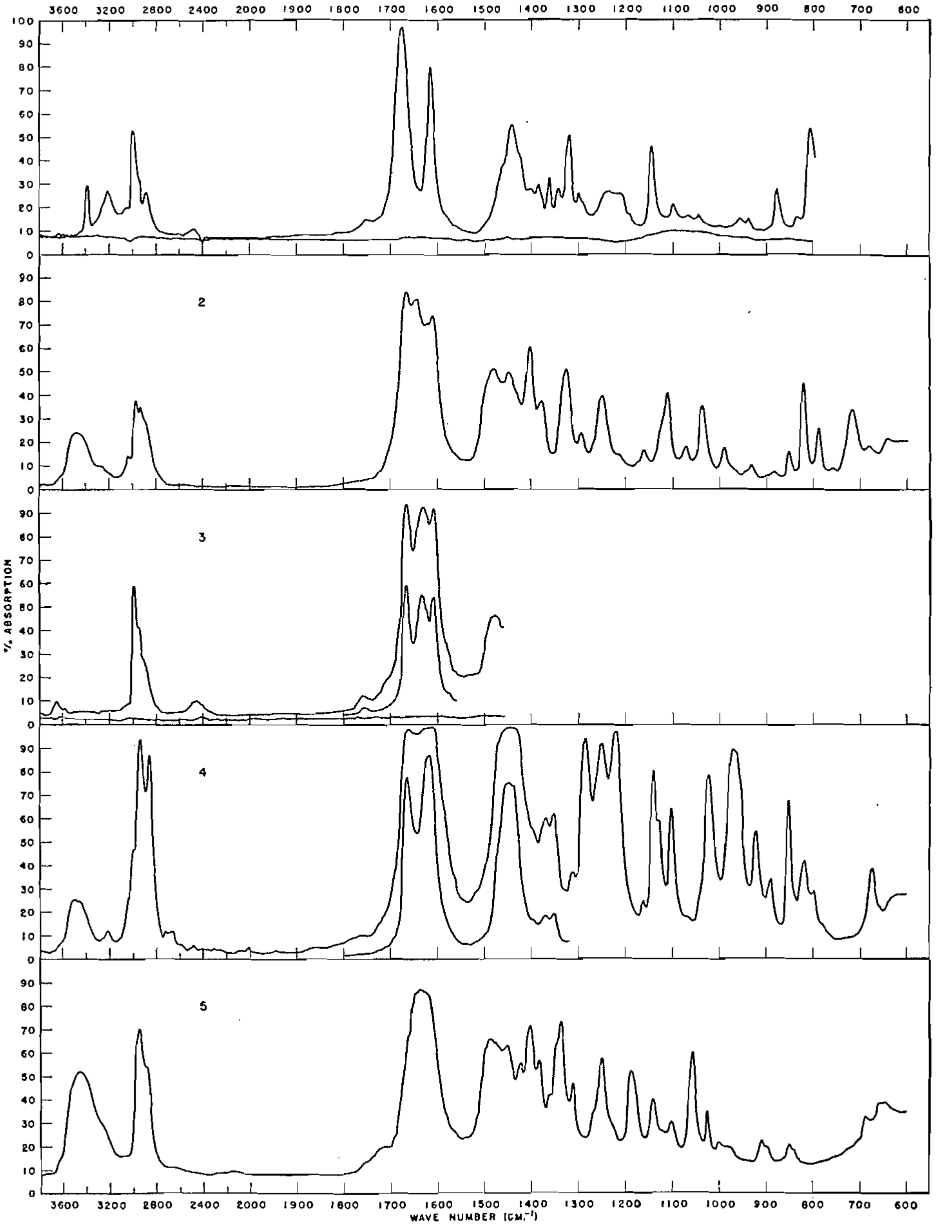

FIG. 1. Infrared spectra of: 1. 6-methyl-5,6-dihydro-2-pyridone (chloroform), 2. 1,6-dimethyl-5,6-dihydro-2-pyridone (liquid), 3. 1,6-dimethyl-5,6-dihydro-2-pyridone (chloroform), 4. N-crotonylpiperidine (liquid), 5. 1,6-dimethyl-2-piperidone (liquid). The background trace in 1 and 3 is that obtained when both cells were filled with pure chloroform.

in the 1600–1700 cm.$^{-1}$ region (Fig. 1). No bands occur in the 1500–1600 cm.$^{-1}$ region in the saturated or unsaturated lactams.

The $C=C$ and $C=O$ stretching bands in the α–β unsaturated amides would be expected to lie in the 1610–1630 cm.$^{-1}$ region since conjugation usually shifts

This page has been reprinted to include the correction pointed out in the Errata that appear at the end of the volume.

both toward smaller wave numbers. The C = C band should as usual be very much weaker than the C = O band. The CN band according to Letaw and Gropp (10) should lie between 1600 and 1650 cm.$^{-1}$. A possible explanation of the spectra actually found is that the three vibrations have very close to the same fundamental frequency, and that resonance between them results in split bands of higher and lower frequency with very much modified relative intensity.

The "iso" compounds derived from lycoctonine have single bands near 1650 cm.$^{-1}$ which lends no support to the unsaturated lactam suggestion.

The infrared spectra of bakankosine derivatives resemble that of N-crotonylpiperidine more than that of 6-methyl-5,6-dihydro-2-pyridone (the 1610 cm.$^{-1}$ band is more intense than the 1670 cm.$^{-1}$ band). However, the alkaloid spectra could as readily be interpreted as that of α–β unsaturated ketones (1670 cm.$^{-1}$) with an isolated hydrogen bonded lactam (1610 cm.$^{-1}$). (See the discussion of ultraviolet spectra.)

The hydrogen on the double bonds (*cis* disubstituted in I and II) shows up in the infrared near 3040 cm.$^{-1}$ (CH stretching) and probably (3) in the strong band at 805–820 cm.$^{-1}$ (CH bending). It is interesting that the 3040 band does not appear in the spectrum of the N-alkyl lactam II taken in chloroform.

The band at 2800 cm.$^{-1}$ in 4-methylamino-1,6-dimethyl-2-piperidone can most probably be assigned to the C–H stretching of the methyl group on the basic nitrogen since the N-methyl lactams do not show it.

The 3400–3500 cm.$^{-1}$ bands in the spectra of liquid films of N-dialkyl amides have been noted by Letaw and Gropp (10). They consider them to be overtones of the 1600–1700 cm.$^{-1}$ bands. We have observed with lupanine (4) and in the present work that this band does not appear in the spectra in chloroform or carbon disulphide solutions. It is much too intense for an overtone, and in addition, it is at too high a wave number (first overtones usually appear at a wave number very close to double the parent wave number). Thus the only simple explanation of this band appears to be that in the liquid state N-alkyl lactams exist to a considerable extent as the enol. Although lupanine gave no methane in the Zerewitinoff determination, freshly distilled II and 1,6-dimethyl-2-piperidone gave close to one mole at 100°, indicating the mobility of the hydrogens α (or γ) to the carbonyls.

The two lactams with an NH (I and 2-piperidone) in chloroform solution had sharp bands near 3400 cm.$^{-1}$ (free NH) and broader bands of similar intensity near 3200 cm.$^{-1}$ (bonded NH). In the spectra of the pure substances, however, the 3400 cm.$^{-1}$ band was absent but the 3200 cm.$^{-1}$ one was much more intense.

A study of saturated N-alkyl lactams in which enolization is blocked by alkyl substitution, or which contain N^{15}, and α–β unsaturated N-alkyl lactams with the double bond carbons substituted might clarify the origin of the infrared spectra in the 3 and 6μ regions.

A summary of the position of the bands in the 1600–1700 cm.$^{-1}$ region of some saturated and α–β unsaturated six-membered lactams is given in Table II.

TABLE II

Lactam	Position of band, cm.$^{-1}$	State[a]
Saturated —CONHR		
2-Piperidone[b]	1670	Liquid film
	1665	Chloroform solution
Saturated —CON~~H~~R$_2$		
3-Carbethoxy-4-quinolizidone[b]	1643	Liquid film
	1631	Chloroform solution
Lupanine[c]	1642	Liquid film
	1624	Chloroform solution
Oxysparteine[c]	1640	Carbon disulphide solution
4-Methylamino-1,6-dimethyl-2-piperidone	1637	Liquid film
1,6-Dimethyl-2-piperidone	1637	Liquid film
α-β Unsaturated —CONHR		
6-Methyl-5,6-dihydro-2-pyridone	1610, 1677	Nujol mull
	1615, 1675	$CHCl_3$ solution
α-β Unsaturated —CON~~H~~R$_2$		
1,6-Dimethyl-5,6-dihydro-2-pyridone	1611, 1643, 1667	Liquid film
	1609, 1634, 1664	Chloroform solution

[a] *The concentration of the chloroform solutions was approximately 30 mgm. per ml.*

[b] *The authors gratefully acknowledge the gift of samples from Dr. L. Marion and Dr. H. J. Vipond.*

[c] *See Reference* (*4*).

EXPERIMENTAL

The ultraviolet spectra were taken on a Beckmann model D.U. spectrophotometer using 95% ethanol as solvent. The infrared spectra were determined on a Perkin-Elmer model 21 double-beam spectrophotometer with a sodium chloride prism. Percentage absorption is indicated in brackets after the wave number in cm^{-1}.

4-Methylamino-1,6-dimethyl-2-piperidone

Twelve grams of methylamine was condensed into a pressure tube containing 2 cc. of water and 4.0 gm. of sorbic acid. The tube was sealed and heated at 150° for 60 hr. The contents of the tube were transferred to a distilling flask and the methylamine boiled off, finally under reduced pressure. Preliminary experiments showed that only a trace of free acid was left after the 60 hr. treatment. The residual liquid was distilled and a fraction was collected at 93–94° under 0.3 mm. pressure (4.5 gm., 80%). Found: N, 17.56. Calc. for $C_8H_{15}ON_2$: N, 17.95. Infrared spectrum (liquid film): 3460 (40), 3300 (46), 2950 (56), 2800 (39), 1637 (87), 1490 (60), 1475 (58), 1458 (60), 1425 (46), 1402 (61), 1377 (55), 1330 (63), 1286 (36), 1260 (34), 1241 (42), 1170 (29), 1135 (44), 1120 (40, shoulder), 1084 (33, shoulder), 1060 (31), 1032 (25), 973 (19). The spectrum in the fingerprint region was not sharp. The amino lactam did not readily give a crystalline hydrochloride or perchlorate. It formed a crystalline picrate when picric acid in benzene was added to a benzene solution of the base. This was recrystallized from 50% ethanol–water from which it separated as long stout prisms, m.p. 187–189°. Found: C, 43.77; H, 4.78. Calc. for $C_{14}H_{19}O_8N_5$: C, 43.64; H, 4.97.

1,6-Dimethyl-5,6-dihydro-2-pyridone

When 4-methylamino-1,6-dimethyl-2-piperidone was refluxed with a solution of 3 gm. of barium hydroxide octahydrate in 20 cc. of water, methylamine was slowly evolved. However, after eight hours the bulk of the amine was recovered unchanged.

At 150° the amino lactam evolved methylamine but the conversion was very slow.

The amino lactam (17.0 gm.) was decomposed by refluxing for seven hours in a nitrogen atmosphere and then slowly distilling the product at one atmosphere. The weight loss on the refluxing was 3.0 gm. (theory for 1 mole of methylamine 3.38 gm.). The distillate was dissolved in 10 cc. of 50% sulphuric acid. Fifty grams of sodium sulphate was added, the solid broken up, and then thoroughly extracted with methylene chloride. The solvent yielded 13.0 gm. of neutral oil. This was distilled at 155–157° under 130 mm. pressure, giving 10 gm. (73%) of colorless oil with a pleasant odor. Five grams of the oil was fractionated at one atmospheric pressure giving

Cut 1, b.p. up to 225°, $n_D^{26}1.4952$;
Cut 2, b.p. 225–228°, $n_D^{26}1.4953$;
Cut 3, b.p. 228–230°, $n_D^{26}1.4960$.

Cut 2 had λ_{max} 251 mμ, log ϵ 3.05, and cut 3 had λ_{max} 251 mμ, log ϵ 3.12. Cut 2 was analyzed. Found: C, 66.69; H, 8.98; active hydrogen, 0.627, 0.646. Calc. for $C_7H_{11}ON$: C, 67.17; H, 8.86; one active hydrogen, 0.805. Infrared spectra (see Fig. 1). Liquid film: 3480 (24), 3040 (14), 2980 (38), 2940 (35), 1667 (84), 1643 (81), 1610 (74), 1483 (51), 1450 (50), 1403 (60), 1377 (38), 1326 (51), 1294 (24), 1250 (40), 1162 (17), 1111 (41), 1073 (18), 1038 (35), 990 (18), 931 (10), 883 (7), 853 (16), 821 (45), 788 (26), 758 (9), 715 (34), 682 (19), 692 (22). Chloroform solution, 1 mm. cell: 3660 (10), 2980 (59), 2460 (10), 1755 (12), 1666 (94), 1631 (92), 1608 (92). Cut 1 (400 mgm.) was dissolved in 1 cc. of 0.1 *N* sodium hydroxide and allowed to stand at 25° for six hours. The solution was made just acid, six grams of sodium sulphate added, and the lactam extracted with methylene chloride. The resulting oil was distilled at a bath temperature of 65–70° under 0.2 to 0.3 mm. pressure. The distillate had λ_{max} 251 mμ, log ϵ 3.05.

The unsaturated lactam (625 mgm.) was oxidized at 0° in aqueous solution with 2.1 gm. of potassium permanganate. After filtration and acidification the solution was extracted continuously with ether. The 1.1 gm. of thick oily acid which was extracted could not be induced to crystallize. A sample of this oil (150 mgm.) was refluxed with 4 cc. of 10% sodium hydroxide solution for six hours. The solution was cooled, acidified with hydrochloric acid, and filtered from a trace of white precipitate. A solution of 0.5 gm. of calcium chloride in 1 cc. of water was added, and the mixture made alkaline to litmus with aqueous ammonia. The white gelatinous precipitate was coagulated by boiling and collected by centrifuging. After washing by suspension in water and centrifuging again, the precipitate was dried to constant weight. Yield: 75.6 mgm. (75% of theory for calcium oxalate). The salt from hydrolysis of 450 mgm. of oily acid was decomposed with 2 cc. of 6 *N* hydrochloric acid and the organic acid extracted into ether. The ether on evaporation left a crystalline mush. This was recrystallized from hot water after which it melted at 95–100°, resolidified, and melted at 189° (dec.). A mixture of this with oxalic acid hydrate behaved in an identical manner.

1,6-Dimethyl-2-piperidone

A solution of 130 mgm. of 1,6-dimethyl-5,6-dihydro-2-piperidone in 10 cc. of ethanol in the presence of platinum from 30 mgm. of platinum oxide (Adams') absorbed 26.1 cc. of hydrogen at 21°C. and 760 mm. pressure in 15 min. The rate of hydrogen uptake then fell off very markedly. The solution was filtered and concentrated below room temperature under reduced pressure. The residual liquid was distilled at a bath temperature of 80–85° under 1 mm. pressure. The distillate had n_D^{24}1.4802. Found: C, 66.04; H, 10.18; active hydrogen, 0.487. Calc. for $C_7H_{13}ON_2$: C, 66.10; H, 10.30; one active hydrogen, 0.792. Infrared spectrum (liquid film, Fig. 1): 3460 (52), 2950 (70), 1637 (87), 1490 (65), 1475 (64), 1451 (63), 1422 (55), 1402 (71), 1382 (57), 1337 (73), 1311 (46), 1250 (57), 1186 (52), 1140 (40), 1101 (30), 1056 (60), 1026 (35), 1000 (21), 909 (22), 850 (20), 688 (32), 657 (38), 645 (39).

1,2-Dimethylpiperidine (*N-Methyl pipecoline*)

The above 1,6-dimethyl-2-piperidone (300 mgm.) was dissolved in 15 cc. of anhydrous ether and 1 gm. of lithium aluminum hydride added. Fifteen cubic centimeters of dioxane was added, and the ether boiled off. The dioxane solution was then refluxed for 30 min. The excess hydride was decomposed by slow addition of methanol, following which the dioxane, methanol, and amine were distilled together under reduced pressure (boiling point around 70°). Twenty cubic centimeters of dioxane was added to the residue and this distilled. To the combined distillate was added 500 mgm. of picric acid. When this solution was concentrated to 10 cc., 600 mgm. of picrate crystallized. The picrate crystallized from ethanol as yellow feathery crystals, m.p. 242° (literature m.p. 240–241°). Found: C, 45.76; H, 5.34. Calc. for $C_{13}H_{15}N_4O_7$: C, 45.61; H, 5.30.

6-Methyl-5,6-dihydro-2-pyridone

This was prepared as described by Fischer and Schlotterbeck (7). When recrystallized from ethyl acetate – petroleum ether it separated as needles, m.p. 105–106°. Found: C, 65.02; H, 7.98. Calc. for C_6H_9ON: C, 64.84; H, 8.16. Ultraviolet spectrum: λ_{min} 235 mμ, log ϵ 3.15; λ_{max} 241 mμ, log ϵ 3.17. Infrared spectrum (nujol mull): 3180 (71), 3060 (54), 2930 (52), 1677 (90), 1660 (81, shoulder), 1610 (79), 1475 (41), 1447 (43), 1420 (67), 1381 (30), 1370 (33), 1355 (26), 1326 (77), 1300 (34), 1210 (19), 1199 (21), 1153 (42), 1100 (20), 1075 (19), 981 (11), 939 (22), 885 (34), 820 (57, shoulder), 812 (72), 757 (29), 697 (30), 655 (23). Chloroform solution (31 mgm. per ml., 0.1 mm. cell): 3400 (29), 3220 (27), 3000 (53), 2890 (27), 1675 (97), 1615 (80), 1442 (55), 1400 (28), 1385 (30), 1363 (33), 1345 (28), 1321 (51), 1300 (26), 1145 (46), 1100 (21), 878 (28), 807 (54).

N-Crotonylpiperidine

This boiled at 117–119° under 10 mm. pressure, and had n_D^{25}1.5090. Ultraviolet spectrum: log ϵ 4.04 (215 mμ); 3.82 (235 mμ). Infrared spectrum (liquid film) (see Fig. 1): 3500 (25), 3220 (12), 2940 (93), 2860 (87), 1664 (98), 1617 (99), 1449 (75), 1369 (60), 1353 (62), 1314 (37), 1285 (94), 1253 (92), 1220 (97), 1162 (25), 1140 (80), 1129 (59), 1103 (64), 1024 (78), 971 (90), 922 (54), 891 (34), 851 (68), 819 (42), 798 (29), 675 (39).

2-Piperidone

A sample of the lactam was purified by dissolving in 3 *N* sulphuric acid, salting out with anhydrous sodium sulphate, and extraction into methylene chloride. After distillation under 10 mm. pressure the compound crystallized readily. The hygroscopic solid melted at 38°. Infrared spectrum: (*a*) Thin liquid film: 3220 (45), 3090 (31), 2950 (53), 2880 (41), 1670 (89), 1500 (58), 1475 (36), 1452 (34), 1415 (44), 1356 (55), 1330 (49), 1310 (44), 1273 (23), 1182 (25), 1170 (35), 1115 (34), 1060 (17), 990 (17), 939 (28), 829 (31), 769 (30), 656 (33). (*b*) Chloroform solution (32.4 mgm. per ml., 0.1 mm. cell): 3400 (28), 3290 (18), 3220 (26), 3000 (57), 3970 (57), 2890 (34), 1665 (97), 1499 (59), 1474 (36), 1454 (32), 1416 (32), 1395 (32), 1356 (59), 1334 (47), 1309 (38), 1274 (30), 1182 (22), 1170 (40), 1106 (27), 1060 (18), 988 (18), 936 (21), 825 (17).

3-Carbethoxy-4-quinolizidone

A chloroform solution of the compound was washed with dilute acid and with sodium carbonate solution. The residual oil after removal of the chloroform was distilled under 0.2 mm. pressure (bath temperature, 130°). Found: C, 64.31; H, 8.81; N, 6.35. Calc. for $C_{11}H_{19}O_3N$: C, 63.97; H, 8.50; N, 6.22. Infrared spectrum (liquid film): 3450 (12, broad), 2940 (68), 2860 (49), 1736 (84), 1644 (90), 1470 (66), 1446 (71), 1392 (32), 1370 (56), 1351 (51), 1320 (55), 1300 (45), 1263 (69), 1219 (58), 1180 (75), 1120 (44),1100 (51), 1145 (43), 1135 (44), 985 (21), 975 (22), 916 (11), 897 (11), 850 (27).

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THE MECHANISM OF PERSULPHATE OXIDATIONS[1]

By R. L. Eager and K. J. McCallum

ABSTRACT

It has been found that exchange between persulphate and sulphate, in both concentrated acetic acid as solvent and in aqueous solution, is not more than one half of one per cent complete in 12 hr. at 34.2°C. This indicates that the equilibrium proposed by Levitt, $S_2O_8^{=} \rightleftarrows SO_4^{=} + SO_4$, probably plays no part in persulphate oxidations.

INTRODUCTION

It has been proposed by Eager and Winkler (1) that the first and rate controlling step in the reaction between potassium persulphate and mercaptans, using concentrated acetic acid as solvent, is

$$S_2O_8^{=} \rightleftarrows 2SO_4^{\dot{-}}. \qquad [1]$$

Recently, Levitt (4) suggested, for both this solvent and aqueous systems, a new mechanism for persulphate oxidations in which the above reaction is replaced by the following:

$$S_2O_8^{=} \rightleftarrows SO_4^{=} + SO_4. \qquad [2]$$

According to either mechanism, the reactive intermediate, $SO_4^{\dot{-}}$ or SO_4, may then react with mercaptan. For high mercaptan concentrations the rate at which persulphate disappears will be equal to that of the forward reaction of [1] or of [2]. Levitt applied his mechanism to the data of Eager and Winkler and found good agreement between the observed and calculated dependence of the specific rate constant on the initial mercaptan concentration. However, this same dependence is required by the mechanism of Eager and Winkler if the Franck–Rabinowitsch "cage effect" (2) is assumed to apply to Reaction 1.

Levitt points out that according to his proposed mechanism sulphate ions should retard the rate of reaction of persulphate. Actually, Eager and Winkler found that sulphate ions increased the rate constant, apparently through a salt effect. Moreover, in some cases at least, when retardation by sulphate ions occurs, it might be due to a mechanism other than that proposed by Levitt. Green and Masson (3) found, in their investigations on the decomposition of aqueous solutions of various persulphates and of persulphuric acid, that sulphate ions caused a retardation of the rate of decomposition which was attributable to a salt effect.

Apart from the above considerations there appears to be a simple way in which to determine whether Levitt's suggestion at least represents a possible mechanism. It is implicit in his mechanism that equilibrium must be established between $S_2O_8^{=}$ ions and $SO_4^{=}$ ions in times that are short compared with those used in the rate studies (1). Otherwise the predicted and the observed kinetics would not agree. This means that if sulphate ions labelled with radioactive sulphur are present in solution with inactive persulphate ions, there should be rapidly established a uniform distribution of radioactive sulphur between sulphate and persulphate ions.

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Previous work in these laboratories (5) indicated that, in aqueous solution and at room temperature, no exchange of radioactivity occurred between sulphate ions labelled with radioactive sulphur and inactive persulphate ions over a period of a few hours. The present paper presents the results of a more detailed study of the exchange in both aqueous solution and in the concentrated acetic acid solvent used by Eager and Winkler.

EXPERIMENTAL AND RESULTS

Exchange Experiments

A solution of S^{35}-labelled sodium sulphate and inactive potassium persulphate was allowed to stand for a given length of time at 34.2°C.* An excess of barium chloride was then added and the precipitated barium sulphate removed by centrifugation. The remaining solution, containing the persulphate and excess barium chloride, was heated to 80–90°C. for approximately 12 hr. At these temperatures the persulphate slowly decomposes (3) to form sulphate, which also precipitates as barium sulphate. From the specific activities of the two barium sulphate precipitates the extent of the exchange could be calculated. As a check on the amount of radioactivity present, control experiments were made in which no potassium persulphate was added.

Two preliminary experiments, in which no undue care was taken in the separation involved, were made to determine approximately the extent of exchange between sulphate and persulphate. In one of these experiments the solvent was water while in the other experiment the solvent was the acetic acid – water mixture used by Eager and Winkler (1). If, as indicated by the previous work, the exchange was found to be small or negligible, then such factors as exchange during separations could be neglected in more carefully controlled experiments. The centrifugate from the acetic acid solution was cloudy with barium sulphate, while small crystals of barium sulphate were observed in the centrifugate from the aqueous solution. A second centrifugation failed to prevent some carry-over of barium sulphate in both experiments. It is likely that the carry-over of precipitate was due to the use of 50-ml. round-bottomed centrifuge tubes and to removal of the centrifugates by decantation.

The results are given in Table I. The extent of exchange in the concentrated acetic acid solvent, Experiment 1, is 2.2 ± 0.3%, and in water, Experiment 2, it is 2.0 ± 0.2%.

While these results indicated that the possibility of Reaction 2 occurring to any appreciable extent is very unlikely, it seemed desirable to repeat the experiments with more careful separation of the sulphate from the persulphate. Fifteen-milliliter centrifuge tubes with pointed ends were used, which permitted the centrifugates to be removed with a pipette without seriously disturbing the precipitates. The centrifugates appeared perfectly clear, but as an additional precaution they were scavenged with inactive barium sulphate. To each was added an inactive sodium sulphate solution and the scavenging precipitate of barium sulphate was centrifuged off and discarded.

**Most of the earlier rate studies were made at 35°C.*

TABLE I

EXCHANGE BETWEEN PERSULPHATE AND SULPHATE

Temperature, 34.2±0.1°C. Potassium persulphate concentration, 0.000766 gm. moles per liter. Sodium sulphate concentration, 0.00153 gm. moles per liter

Expt. No.	Time, hr.*	Solvent	Source of $BaSO_4$	Specific activity** of $BaSO_4$: counts/mgm.
1	12.1	Conc. acetic acid	$SO_4^=$ $S_2O_8^=$	128±1*** 1.4±0.2
2	13.0	Water	$SO_4^=$ $S_2O_8^=$	178±2 1.8±0.1
3	Control	Water	$SO_4^=$	166±2
4	12.4	Conc. acetic acid	$SO_4^=$ $S_2O_8^=$	141±1 0.45±0.13
5	12.4	Water	$SO_4^=$ $S_2O_8^=$	169±1 0.39±0.10
6	Control	Water	$SO_4^=$	192±1

*The times for the aqueous and for the acetic acid media were taken from addition of labelled sulphate, or addition of acetic acid, respectively, until addition of barium chloride.

**Corrected for background and for thickness of sample.

***Only the statistical errors of counting were considered when calculating the standard deviations.

Since the preliminary experiments indicated a maximum exchange of only about 2% in 12 hr., the amount of back exchange from persulphate to sulphate during the short scavenging time would be negligible.

The results are also given in Table I. The extent of exchange in the concentrated acetic acid, Experiment 4, was 0.64 ± 0.19%, and in water, Experiment 5, it was 0.46 ± 0.12%.

DISCUSSION

The values found for the exchange between sulphate and persulphate may be the result of true exchange, of exchange induced by separation, of incomplete separation, or of some combination of these. In any event, the results do set, for the solvents used, an upper limit of approximately 0.5% for the extent of exchange between sulphate and persulphate in a 12 hr. period at 34.2°C.

As mentioned earlier, if Levitt's proposed mechanism is correct, the exchange between sulphate and persulphate should be essentially complete in times that are short compared with those used in the previous rate studies (1). From the data of Eager and Winkler it is estimated, for the potassium persulphate and sodium sulphate concentrations used in the present work, that the first order rate constant with respect to the persulphate concentration will be approximately 0.2 $hr.^{-1}$, if excess mercaptan were present. This means that two thirds of the persulphate would have reacted in a 5.5 hr. period. In many of the rate experiments the reactions were allowed to proceed to this extent. Since the value of 0.2 $hr.^{-1}$ for the value of the observed rate constant is that found when excess mercaptan is present, then on the basis of the proposed mechanisms this is also the value of the specific rate constant for the decomposition of persulphate into the reactive intermediates. From this value for the specific rate constant, it may be calculated that each persulphate ion has *on the average* been in the reactive intermediate form 2.5 times in the 12.4 hr. period used in the present exchange studies. Alternatively, the time for the half-life of the forward reaction may be calculated and is found to be 3.7 hr. From this value for the half-life it follows that in a 12.4 hr. period, slightly more than 91% of the persulphate was in the reactive intermediate form *at least once*. From the observed stability of potassium persulphate in the solvents used the specific rate constant for the recombination of the intermediates must be very large. Hence there has been a good opportunity for close to 90% exchange to have occurred if Levitt's mechanism is operative. Since the exchange actually found was much less than 90% it would appear from the above considerations that the equilibrium proposed by Levitt is relatively unimportant in the reactions of persulphates in aqueous or in concentrated acetic acid solutions. It is still possible that SO_4 is an intermediate in persulphate oxidations, but if so, it must occur in some reaction other than a reversible one involving sulphate and persulphate ions.

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THE SYSTEM LITHIUM SULPHATE - AMMONIUM SULPHATE - WATER[1]

By A. N. Campbell, W. J. G. McCulloch, and E. M. Kartzmark

ABSTRACT

The binary eutectics $Li_2SO_4 \cdot H_2O$ - ice and $(NH_4)_2SO_4$ - ice as well as the ternary eutectics $Li_2SO_4 \cdot H_2O - Li_2SO_4 \cdot (NH_4)_2SO_4$ - ice and $(NH_4)_2SO_4 - Li_2SO_4 \cdot (NH_4)_2SO_4$-ice have been determined as to temperature and composition. The complete solubility isotherms at 0.1°, 71.8°, and 95.2°C. have been investigated. The enthalpies of solution of lithium sulphate monohydrate, of ammonium sulphate, and of double salt have been determined (in water at room temperature), and from these data, as well as from the solubility isotherms, it has been shown that the temperature of the transition of the double salt, $Li_2SO_4 \cdot (NH_4)_2SO_4$, to its component single salts (in the presence of water) is approached by lowering the temperature, but this transition temperature is still far from reached when the system freezes completely.

INTRODUCTION

A double salt of the formula $Li_2SO_4 \cdot (NH_4)_2SO_4$ was known to form in the above system but no transition point had been established for the reaction:

$$Li_2SO_4 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Li_2SO_4 \cdot (NH_4)_2SO_4 + H_2O.$$

In the corresponding system $Na_2SO_4 - (NH_4)_2SO_4 - H_2O$, the transition temperature is well known to be 59.3° (11, 4, 5), the double salt being unstable above this temperature; there is also a lower transition temperature at -16°C., but the situation is complicated by the fact that sodium sulphate is anhydrous at the higher transition temperature but hydrated, as Glauber's salt, at the lower. We therefore decided to investigate several isotherms of the above system, as well as the ternary eutectics, with a view to predicting the transition temperature, by extrapolation in the usual manner.

The component binary systems ammonium sulphate - water and lithium sulphate - water* are well known, but there has been some controversy about the lithium sulphate - water system. In a previous paper, one of us (3) determined the complete equilibrium diagram of the system, with the exception of the critical data for water in the presence of lithium sulphate. Some of these data were again checked in the present work. The most debatable point is the composition of the eutectic ice - $Li_2SO_4 \cdot H_2O$, which Campbell was only able to obtain by extrapolation. Another point at issue was the claim of Friend (6) that at low temperatures a dihydrate of lithium sulphate exists, a claim which Campbell was unable to verify.

The double salt of ammonium and lithium sulphates is congruently soluble and is therefore readily prepared by dissolving stoichiometric quantities of the constituent salts in water and crystallizing out. Schreinemakers (17) has determined the solubility of the pure double salt in water at temperatures ranging from -10°C. to 70.0°C., and he found the solubility to be nearly

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Contribution from the Chemistry Department of the University of Manitoba, Winnipeg, Man.

The binary lithium sulphate - ammonium sulphate has only a theoretical existence, at least over the greater part of the curve, since lithium sulphate melts some seven hundred degrees above the temperature at which ammonium sulphate decomposes.

independent of temperature. Schreinemakers' results, however, cannot be quite correct, since they show an increase of solubility from 35.25% at −10°C. to 36.18% at 70°C., but our calorimetric work, described in this paper, shows that the enthalpy of solution, though small in saturated solution, is definitely negative and this, of course, is incompatible with a solubility increasing with temperature. Schreinemakers has also determined the ice-line in the pseudobinary system water – double salt, and from the intersection of this curve with the solubility curve he has determined the pseudobinary eutectic ice – double salt, to contain 35.15% double salt and to lie at a temperature of −20.7°C., a temperature which he verified by direct experiment.

Schreinemakers and Cocheret (17) have determined the complete isotherms of the ternary system at 30°C. and at 50°C., while Spielrein (18) has determined the isothermal invariant points, not very accurately, at 20°, 57°, and 97°C. At all temperatures, the solid phases occurring are ammonium sulphate, double salt, and either anhydrous lithium sulphate mixed with monohydrate or, more probably, solid solutions containing ammonium sulphate in excess of lithium sulphate. From an examination of the lithium sulphate corner of any of the isotherms, particularly that for 95°C., the uncertainty involved in defining the nature of the lithium sulphate solid phase is evident. The tie lines to the first branch of the isotherm shift progressively, without crossing, from the composition of the pure monohydrate to a point on the lithium sulphate – ammonium sulphate base corresponding to a solid phase containing about 10% by weight ammonium sulphate (at invariance). It is impossible to account for this as due to analytical error; it must represent solid solution; the same observation was made by Schreinemakers. On the other hand dehydration of monohydrate to anhydrous lithium sulphate is unlikely because of the very high transition temperature (3) of monohydrate to anhydrous form.

EXPERIMENTAL WORK

The main purpose of this work was the complete investigation of the isotherms at 0.1°, 71.8°, and 95.2°C. by the familiar "wetrest" method of Schreinemakers, with a view to the prediction of the transition temperature of the double salt. In order to complete the study of the system in a downwards temperature direction, the two ternary eutectics were determined by the method of thermal analysis. Other points arose in the course of the investigation, viz.:

The checking of the two binary eutectic temperatures and compositions by thermal analysis.

The investigation of Friend's contention (6) that a higher hydrate than the monohydrate exists at low temperatures; the dilatometer was used for this.

Finally, since the forms of our isotherms indicated that the transition temperature from double salt to constituent single salts was approached by lowering the temperature (of course, it cannot be realized because the system freezes), it was decided to confirm this thermodynamically by determining the enthalpies of solution of single salts and of double salt and hence obtaining the enthalpy of formation of double salt from single salts:

$$Li_2SO_4 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Li_2SO_4 \cdot (NH_4)_2SO_4 + H_2O.$$

Le Chatelier's principle then confirms our deduction.

Preparation and Purification of Materials

B.D.H. Analar lithium sulphate, containing only negligible impurities, was used without recrystallization. Baker's C.P. Analyzed ammonium sulphate, free from pyridine, was recrystallized once. The double salt was prepared by adding the two sulphates in equimolecular proportion to water until the hot solution was saturated. Nicol's "Mercury Metal" and Analar grade chloroform were used for the calibration of the thermocouple and were redistilled before use.

Method of Analysis

Total sulphate and ammonia were determined and the lithium obtained by difference. Despite extensive criticism of the method (1, 8) sulphate was determined by the time-honored gravimetric method of precipitation as barium sulphate. Following the procedure of Kolthoff and Sandell (9) an accuracy of better than 0.5% was consistently obtained and this was sufficient for our purposes.

The determination of the ammonia content was made by steam distillation of a basic solution. The distillate was absorbed in a boric acid solution of approximately 4% strength, following the method outlined in Pierce and Haenisch (12) and originally proposed by Winkler (19).

Calibration of Thermocouple

For the thermal analysis work at low temperature, an iron constantan thermocouple was used, the e.m.f. being determined on a sensitive potentiometer. The method of calibration was that of Rosser and Dahl (14). The fixed points used were: freezing point of mercury (−38.9°C.), freezing point of chloroform (−63.5°C.), sublimation point of carbon dioxide (−78.5°C.), and the melting point of ice; the hot junction was kept in melting ice.

Calorimetric Measurements

Determinations of enthalpies of solution were made in order to find the enthalpy of formation of the double salt. An electrical calorimeter was used with ordinary precautions; for example, the power input was determined as the fall of potential over a standard resistance and voltage determinations were made on a potentiometer; radiation corrections were applied. The accuracy of the results is sufficient for our purpose, which was merely to demonstrate that the formation of the double salt from the constituent salts is an endothermal process, but is not to be compared with the accuracy required in modern thermochemical work.

RESULTS

The Binary Eutectic Ammonium Sulphate – Ice

Previous workers (7, 13, 16, 15, 2, 10) give the eutectic conditions as:—composition, 38.40 – 39.90% $(NH_4)_2SO_4$, temperature −18.34°C. to −19.5°C.

We redetermined these values by thermal analysis. A solution of approximately eutectic composition was cooled in dry ice, two air jackets being used to decrease the rate of cooling. The solution was stirred mechanically throughout. When the thermocouple potential became constant, a sample of solution was removed through a (previously chilled) fritted glass filter, for analysis. As the mean of two experiments, we find eutectic temperature −19.5°C., eutectic composition 39.2% $(NH_4)_2SO_4$.

Binary Eutectic Lithium Sulphate Monohydrate – Water

According to Campbell (3) the eutectic temperature for this is −23.0°C. and the eutectic composition 27.9% anhydrous lithium sulphate. The eutectic composition was obtained by extrapolation of Friend's (6) solubility curve and Campbell's ice-line. We attempted to check these data in the same manner that we used to check the eutectic of the ammonium sulphate – water system. A mixture of 27.9 gm. anhydrous lithium sulphate and 72.1 gm. of water was prepared. With steady cooling, a constant e.m.f. value was, however, never obtained. Since it was possible that the rate of cooling might have been too rapid, this rate was lessened in a repeat experiment, but again no constant e.m.f. value was obtained. In a second repeat of the experiment, excess of lithium sulphate was added to the initial solution and a better system of stirring devised, but no e.m.f. value was obtained which could be interpreted as being the eutectic temperature. Samples of clear solution which were withdrawn at −23.0°C. were found upon analysis to contain 26.1% lithium sulphate and this is in fair agreement with Campbell's result. We are unable to state why a direct experimental determination of the eutectic seems to be impossible, unless it be connected with the peculiar re-entrant form of the solubility curve, just above the eutectic temperature.

Hydrates of Lithium Sulphate

To investigate further Friend's (6) statement that a higher hydrate of lithium sulphate than monohydrate exists at low temperatures and Campbell's (3) contrary conclusions that no such higher hydrate exists, a dilatometer was used. The bulb of the dilatometer was charged with wet monohydrate and toluene was the indicator fluid. The temperature of the dilatometer was lowered progressively from −0.5°C. to −17.9°C. The plot of toluene level against temperature was a perfectly straight line, indicating the absence of any transition. Since it was possible that time had not been allowed for the conversion to take place, the bulb of the dilatometer was now immersed in a large quantity of ice and sodium chloride mixture and cathetometer readings of the toluene level taken until a constant reading was obtained. The temperature was noted (−21°C.) and the assemblage allowed to stand for 24 hr. No change was observed in the toluene level at the expiration of the period. Hence a higher hydrate did not form under these experimental conditions. Finally, samples of moistened lithium sulphate monohydrate were sealed in glass containers and preserved in ice – sodium chloride mixtures for periods ranging from 24 to 72 hr. No visible change in crystal structure could be observed and the samples still appeared wet.

The Ternary Eutectics

In a ternary system consisting of two salts and water and forming one double salt (congruently saturating), there are two eutectics involving ice as one phase. These ternary eutectics represent completely invariant systems (F = O), since five phases, three of them solid, are in equilibrium. The solid phases in equilibrium at the two eutectics are, respectively: (1) ammonium sulphate, double salt, ice and (2) lithium sulphate monohydrate, double salt, ice.

The temperatures and compositions of these two eutectics were determined by thermal analysis. The procedure was similar to that employed in investigating the two binary eutectics. Starting from weighed amounts of the respective binary eutectic solutions, weighed quantities of the second salt were added and the mixture submitted to thermal analysis. Provided the original mixture lay exactly in the eutectic trough, the first point of inflection on the cooling curve represented the so-called freezing point, that is, the temperature at which simultaneous deposition of ice and one salt occurred. If the composition were slightly off the trough composition, a preliminary point of inflection would indicate prior separation of either ice or salt singly, followed by simultaneous crystallization, but such points on the cooling curve are easily interpreted. The composition of the first (ternary eutectic) solution was determined by withdrawing a sample for analysis. Theoretically, any initial solution containing the three components should, on continued cooling, give a final solution corresponding to one or other of the (ternary) eutectic compositions. In practice, however, it was found that it was necessary to have initial solutions whose compositions were rather close to the eutectic composition, in order to obtain the true eutectic composition on cooling. In addition to the two binary eutectic troughs, the two ternary eutectics are joined by a section of a surface, having a temperature maximum representing the pseudobinary eutectic ice – double salt. Three points on this curve were obtained by cooling a solution of double salt, with or without slight excess of lithium sulphate or of ammonium sulphate. The data obtained are reproduced in Table I.

TABLE I

THE TERNARY EUTECTIC CURVES

Temperature	%$(NH_4)_2SO_4$	%Li_2SO_4
−19.5	39.2	0.0
−22.5	37.0	5.1
−27.0	33.2	10.5*
−26.0	23.3	16.2
−26.0	20.4	18.8
−23.0	18.3	20.8
−30.0	10.6	27.4*
−24.0	6.0	26.8
−23.0	0.0	27.9

**These determinations represent the two eutectic temperatures and compositions. They are mean values.*

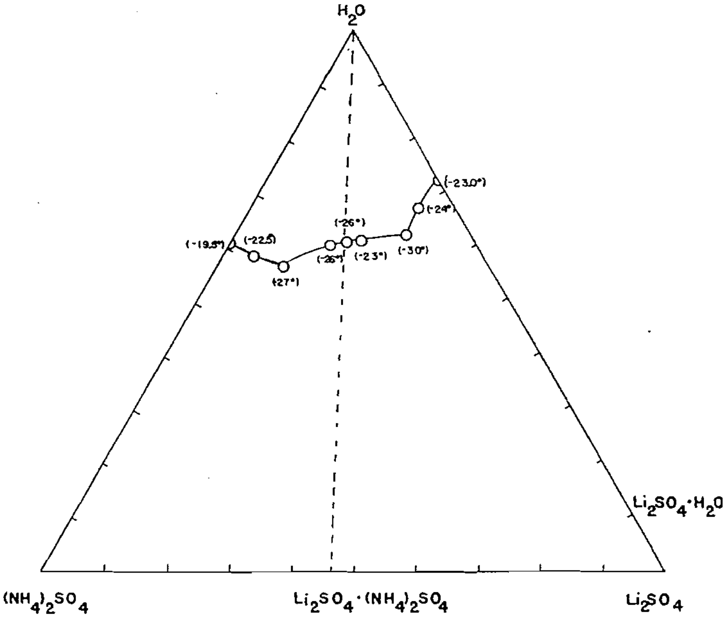

FIG. 1. The ternary eutectic curves.

The above data are plotted in Fig. 1. From an examination of Table I and Fig. 1, the eutectics are to be deduced as follows: Eutectic 1. Solid phases: ammonium sulphate, double salt, ice; temperature − 27°C.; composition: 33.2% $(NH_4)_2SO_4$, 10.5% Li_2SO_4. Eutectic 2. Solid phases: lithium sulphate monohydrate, double salt, ice; temperature − 30.0°C.; composition: 10.6% $(NH_4)_2SO_4$, 27.4% Li_2SO_4.

TABLE II
ISOTHERM FOR 0.10° (± 0.05°)

No.	Solution		Wet residue		Nature of the solid phase
	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	
1	0.0	26.5	....	....	$Li_2SO_4 \cdot H_2O$
2	6.4	25.4	2.3	64.4	"
3	6.2	25.2	1.0	78.8	"
4	9.7	24.4	14.1	51.0	$Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot (NH_4)_2SO_4$
5	9.8	24.3	25.3	35.7	"
6	14.1	20.9	38.0	36.1	$Li_2SO_4 \cdot (NH_4)_2SO_4$
7	18.4	17.4	38.1	33.9	"
8	18.5	17.3	40.0	34.0	"
9	20.5	16.0	40.6	34.4	"
10	24.8	13.8	41.6	32.2	"
11	36.1	8.4	78.6	7.6	$Li_2SO_4 \cdot (NH_4)_2SO_4$ and $(NH_4)_2SO_4$
12	36.2	8.1	82.1	4.1	"
13	37.7	5.3	84.5	2.1	$(NH_4)_2SO_4$
14	38.7	3.5	82.4	1.4	"
15	41.8	0.0	....	....	"

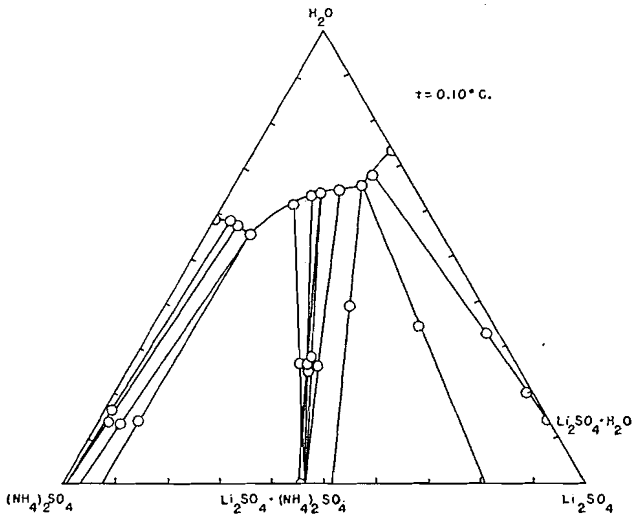

FIG. 2. The 0.1°C. isotherm.

The 0.1°, 71.8°, and 95.2°C. Isotherms of the Ternary System

The technique of this kind of work has been too frequently described to require discussion here. For 0.1°C., the thermostat, containing kerosene, consisted of a large glass cylinder placed in an outer tank which also contained kerosene. The outer bath was cooled by a thermostatically controlled refrigerating coil. The inner thermostat, which was electrically controlled, was heated by a light bulb. For the other temperatures, the thermostat was of the usual type. The results in weight per cent are given in Tables II, III, and IV. The corresponding equilibrium diagrams are represented in Figs. 2, 3, and 4.

TABLE III

ISOTHERM FOR 71.8° ± 0.10°C.

No.	Solution		Wet residue		Nature of the solid phase
	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	
1	0.0	24.2	....	....	$Li_2SO_4 \cdot H_2O$
2	2.4	23.5	1.2	66.3	"
3	5.6	23.1	2.1	62.5	"
4	12.1	21.8	8.5	59.6	$Li_2SO_4 \cdot H_2O$ and $Li_2SO_4 \cdot (NH_4)_2SO_4$
5	20.1	17.1	48.2	40.0	$Li_2SO_4 \cdot (NH_4)_2SO_4$
6	20.4	17.2	42.4	35.2	"
7	25.6	14.2	44.9	35.0	"
8	32.1	10.5	46.8	35.4	"
9	44.9	5.2	66.2	19.3	$Li_2SO_4 \cdot (NH_4)_2SO_4$ and $(NH_4)_2SO_4$
10	45.1	5.5	76.8	2.7	$(NH_4)_2SO_4$
11	47.9	0.0	....	....	"

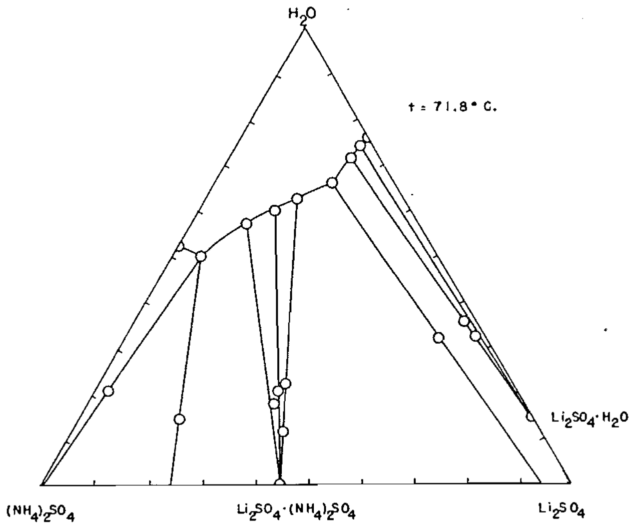

FIG. 3. The 71.8°C. isotherm.

TABLE IV
ISOTHERM FOR 95.2°C.

No.	Solution		Wet residue		Nature of solid phase
	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	Wt. %$(NH_4)_2SO_4$	Wt. %Li_2SO_4	
1	0.0	24.12	....	....	$Li_2SO_4 \cdot H_2O$
2	0.69	24.70	0.36	78.90	Solid solution in $Li_2SO_4 \cdot H_2O$
3	4.65	23.09	3.35	66.60	"
4	9.34	21.72	9.13	58.76	"
5	15.89	20.46	34.36	38.99	Sat'd. solid sol'n. in $Li_2SO_4 \cdot H_2O$ + $Li_2SO_4(NH_4)_2SO_4$
5*a*	15.91	20.62	22.96	50.65	"
6	21.11	16.37	44.47	36.81	$Li_2SO_4 \cdot (NH_4)_2SO_4$
7	40.03	6.73	47.50	26.66	"
8	47.98	3.67	68.05	19.94	$Li_2SO_4 \cdot (NH_4)_2SO_4$ + $(NH_4)_2SO_4$
9	48.67	3.04	83.10	1.00	$(NH_4)_2SO_4$
10	50.87	0.0	....	....	$(NH_4)_2SO_4$

Heats of Solution

The results for the molal enthalpies of solution of ammonium sulphate, of lithium sulphate monohydrate, and of double salt, in water, at various concentrations, and of ammonium sulphate in solutions containing equivalent quantities of lithium sulphate (all at room temperature), are given in Table V. In accordance with thermodynamic notation, a positive value of ΔH means that during the process of solution the solution absorbs heat from the surroundings.

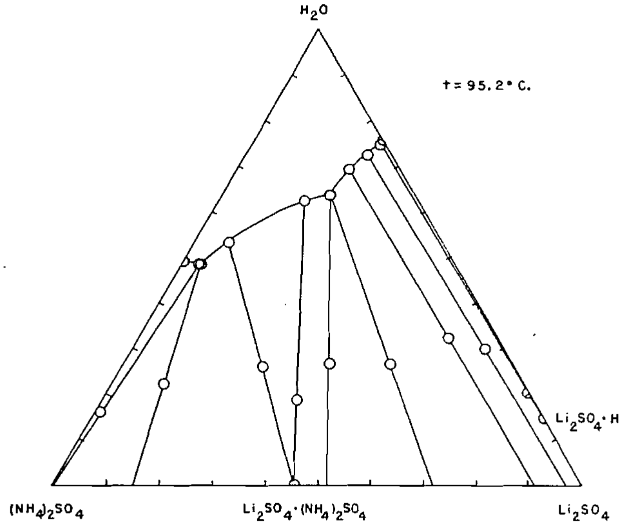

Fig. 4. The 95.2°C. isotherm.

TABLE V

ENTHALPIES OF SOLUTION AT ROOM TEMPERATURE (24°C.)

$Li_2SO_4 \cdot H_2O$ in water		$(NH_4)_2SO_4$ in water	
Molality	ΔH_1 (kcal.)	Molality	ΔH (kcal.)
0.274	−2.34	0.599	3.09
0.546	−2.40	1.16	2.83
0.796	−2.46	1.74	2.69
1.08	−2.63	2.31	2.59
1.35	−2.79	2.89	2.44
1.61	−2.88	4.41	2.33
1.86	−2.84	5.15	2.41
2.12	−2.63	6.00	2.39
2.37	−2.47		
2.63	−2.34		

$(NH_4)_2SO_4$ in equiv. Li_2SO_4		Double salt in water	
Molality	ΔH_2 (kcal.)	Molality	ΔH_4
0.341	2.91	0.165	−2.40
0.685	2.80	0.330	−2.59
1.13	2.63	0.495	−2.57
1.37	2.47	0.660	−2.41
1.71	2.46	0.825	−2.29
2.05	2.39	0.990	−2.15
2.39	2.39	1.16	−2.04
		1.32	−1.93
		1.63	−1.83
		1.81	−1.74
		1.98	−1.61
		2.17	−1.51

DISCUSSION OF RESULTS

The values of composition and of temperature for the binary eutectic ammonium sulphate – ice agree well with the literature data but the direct experimental check of the corresponding data for the eutectic lithium sulphate monohydrate – ice is somewhat uncertain. In one of the experiments, the cooling curve exhibited a change of slope at − 23°C. and a sample of solution withdrawn at this temperature contained 26.1% Li_2SO_4, in rough agreement with Campbell's interpolated value of 27.9%. The cooling curve did not, however, show a definite halt and thus the figure is at best uncertain. The ternary eutectic curves of Table I and Fig. 1 tend to substantiate Campbell's result; the right hand eutectic curve of Fig. 1 includes Campbell's value for the binary eutectic smoothly: the depression by 1° of the binary eutectic temperature seems reasonable. If reference is made to the equilibrium diagram of the system $Li_2SO_4 - H_2O$, given in Campbell's paper (3), the reason for our inability to obtain a eutectic halt may seem to lie in the peculiar form of the freezing and solubility curves in the neighborhood of this eutectic.

We have been unable to find any positive evidence for the existence of Friend's (6) higher hydrate of lithium sulphate.

Examination of the solubility isotherms, both those of Schreinemakers and our own, shows that at all temperatures from 0°C. to 95°C., the double salt is stable and congruently saturating. Only one double salt is formed, viz. $Li_2SO_4 \cdot (NH_4)_2SO_4$. All isotherms indicate a limited solid solubility of ammonium sulphate in lithium sulphate (presumably the monohydrate). There may also be a slight solubility of lithium sulphate in double salt but there is no detectable solubility of double salt in ammonium sulphate or of ammonium sulphate in double salt. This leads us to suppose that the lattices of lithium sulphate monohydrate and of the double salt are similar, but that no such similarity exists between the lattices of double salt and of ammonium sulphate. The question might merit a crystallographic and X-ray study.

The data of the isotherms (our own and Schreinemakers') were recalculated in the form: weight ammonium sulphate and weight (anhydrous) lithium sulphate per 100 gm. water. These were expressed graphically in Fig. 5. The comparative lengths of the intermediate curve, on which double salt is stable, indicate the relative regions of stability of the double salt. If these are measured as straight lines, the following figures are obtained, (on the original diagram):

0°C.	14 cm.
30°C.	15 cm.
50°C.	17 cm.
71.8°C.	19.5 cm.
95°C.	20 cm.

Such measurements are, of course, very rough but they show beyond a doubt that the (hypothetical) transition temperature of the double salt is approached by lowering the temperature. (Cf. the behavior of the corresponding sodium ammonium double salt, which is quite different.)

It therefore appears, since the stability of the lithium ammonium double salt increases with rising temperature, that it is an endothermal compound, that is, that in the process

$$Li_2SO_4 \cdot H_2O + (NH_4)_2SO_4 \rightarrow Li_2SO_4 \cdot (NH_4)_2SO_4 + H_2O$$

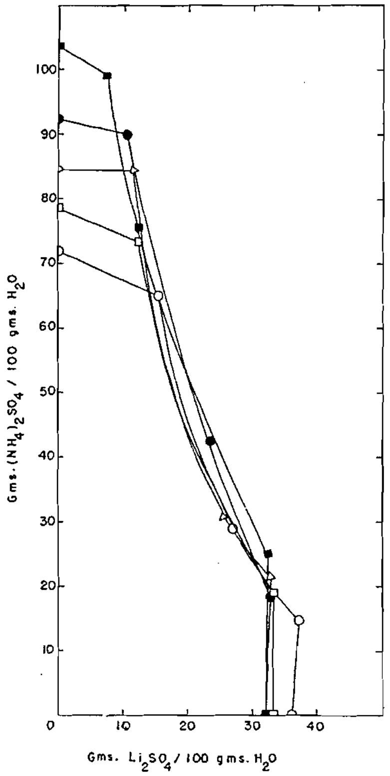

FIG. 5. The isotherms on rectangular co-ordinates.

○	0.1°C.	C. Mc. K.
□	30°	Schreinemakers
△	50°	Schreinemakers
●	71.8°	C. Mc. K.
■	95.2°	C. Mc. K.

heat is absorbed, and therefore ΔH is positive. If we give the symbol ΔH_3 to the enthalpy of the above process and indicate by ΔH_1 the enthalpy of the process

$$Li_2SO_4 \cdot H_2O + Aq \rightarrow Li_2SO_4 \cdot Aq,$$

by ΔH_2 that of the process

$$(NH_4)_2SO_4 + Aq \rightarrow (NH_4)_2SO_4 \cdot Aq,$$

and by ΔH_4 that of the process

$$(NH_4)_2SO_4 \cdot Li_2SO_4 + Aq \rightarrow (NH_4)_2SO_4 \cdot Li_2SO_4 \cdot Aq,$$

we obtain ΔH_3 as

$$\Delta H_3 = \Delta H_1 + \Delta H_2 - \Delta H_4,$$

provided that we use for ΔH_2, not the enthalpy of solution of $(NH_4)_2SO_4$ in pure water, but that in a solution containing equivalent quantities of lithium sulphate. The following figures are obtained.

Concentration of solution, molal	ΔH_3, kcal.
0.2	3.27
0.4	3.07
0.6	2.84
0.8	2.58
1.0	2.24
1.2	2.03
1.4	1.62
1.6	1.63
1.8	1.28
2.0	1.27
2.2 (saturated)	1.29

The levelling off to constancy as saturation is approached shows that the true ΔH of formation of the double salt is 1.28 ± 0.01 kcal. This positive value accounts for the double salt having a downwards transition temperature.

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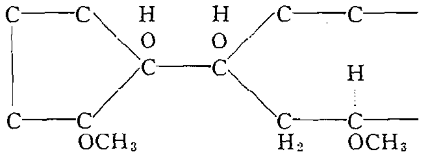
LYCOCTONINE: ACID CATALYZED REARRANGEMENTS[1]

By O. E. Edwards, Léo Marion, and R. A. McIvor[2]

ABSTRACT

The lactam derived from the alkaloid lycoctonine has been shown to undergo rearrangement when heated with mineral acids. A ketone, anhydrolycoctonam, is formed first by pinacolic dehydration. This ketone then undergoes elimination of the elements of methyl alcohol, and hydrolysis of a methoxyl to give lycoctamone, an α–β unsaturated ketone containing a new tertiary hydroxyl. Reactions of lycoctamone and its reduction products are described and discussed.

The alkaloid lycoctonine, for which the expanded formula $C_{19}H_{21}(OH)_3(OCH_3)_4NC_2H_5$ can be written, is most probably a saturated hexacyclic base. Evidence has been presented in the preceding papers (4,5) for the presence in the alkaloid of the systems



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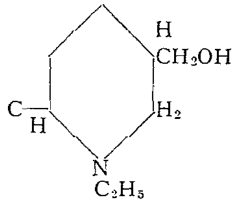
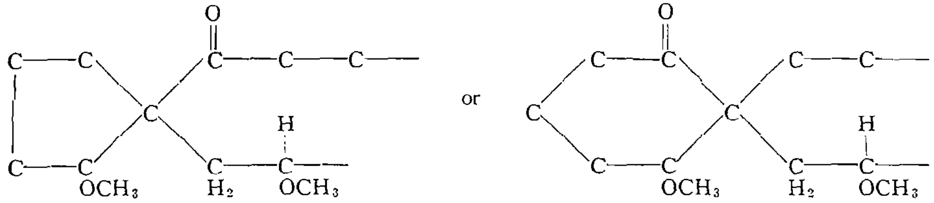


It was shown that the glycol system can undergo a ready pinacolic dehydration. For example, the lactam derived from lycoctonine, lycoctonam, gives the ketone, anhydrolycoctonam, with loss of one molecule of water. Since anhydrolycoctonam only gives a faint reaction with hot Fehling's solution, and only slowly gives a weak Tollens' test, it is unlikely that it has a methoxyl α to the carbonyl. It is stable to alkali, hence has no methoxyl β to the carbonyl which can be readily eliminated. Thus the two most probable partial structures for the 'anhydro' compounds derivable from the above structure are:



I II

Anhydro Compound

Several arguments can be advanced as to the relative likelihood of I and II. The hydroxyl on the cyclopentane ring in the glycol system, being α to a

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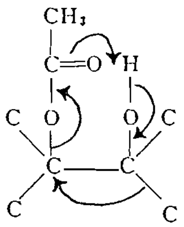
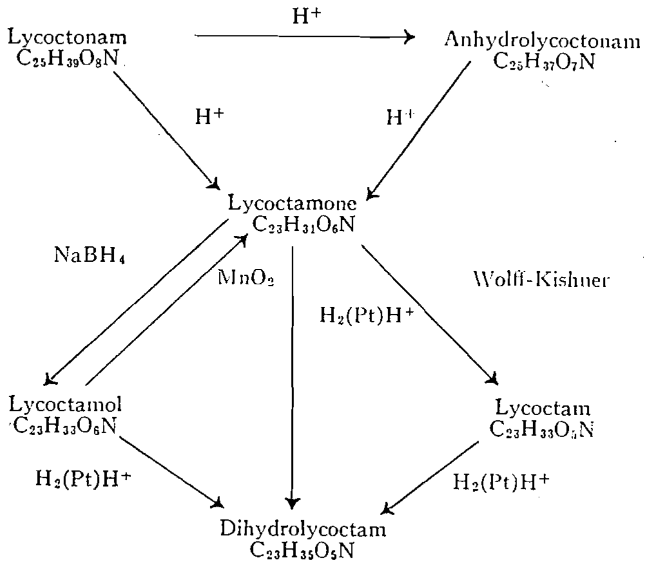
methoxyl, should be less basic than the one on the larger ring. Thus on this basis alone, the pinacolic dehydration would be expected to give II. However, on the basis of the considerations of Brown and co-workers (3) it appears likely that the hydroxyl on the five-membered ring would be more readily eliminated, giving the more stable cyclopentyl carbonium ion. This would give rise to I on rearrangement. The same conclusion is reached on consideration of the pyrolysis of des(oxymethylene)-lycoctonam monoacetate (4). Since the cyclopentanone carbonyl in the diketones derived from lycoctonine derivatives is much less hindered than that on the larger ring (5), it is reasonable to suppose that the same relative hindrance exists for the hydroxyls in the parent glycol. Hence the above acetate should involve the hydroxyl on the five-membered ring. Since the pyrolysis most likely proceeds as shown,



the product would again be I, making this seem the more likely possibility.

Anhydrolycoctonam could be recovered unchanged after attempted Wolff-Kishner reduction, hence the carbonyl is very hindered. In concordance with this, the carbonyl is only slowly reduced by sodium borohydride. The hydroxyl derived from the ketone in this reduction could be acetylated readily, however, giving an acetate which did not lose acetic acid readily at 290°. These observations, and the fact that the ketone was inert to selenium dioxide in

FLOWSHEET



refluxing acetic acid, suggest that the other carbon α to the carbonyl is tertiary or perhaps quaternary.

On more vigorous treatment with acid, lycoctonam and anhydrolycoctonam undergo extensive change. One methoxyl is hydrolyzed to a tertiary hydroxyl

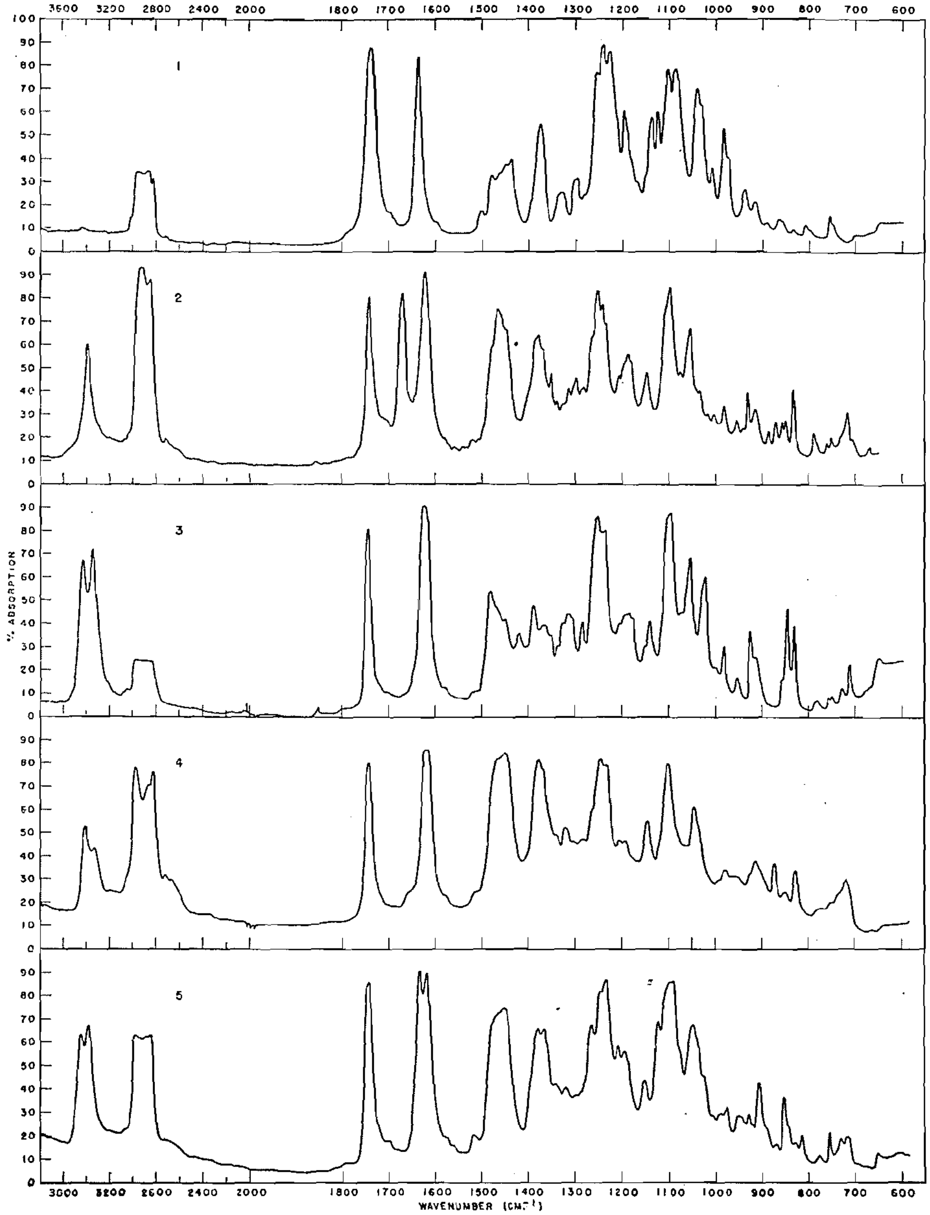


FIG. 1. Infrared spectra (nujol mulls): 1. Dihydroanhydrolycoctonam diacetate. 2. Lycoctamone monoacetate. 3. Lycoctamol monoacetate. 4. Lycoctam monoacetate. 5. Dihydrolycoctam monoacetate.

This page has been reprinted to include the correction pointed out in the Errata that appear at the end of the volume.

(highly hindered and inert to chromic acid), and a second methoxyl is eliminated as methyl alcohol. The product is an α–β unsaturated ketone ($\lambda\lambda_{max}$ 245 mμ, log ϵ 4.01 and 310 mμ, log ϵ 2.20) of formula $C_{23}H_{31}O_6N$. The name lycoctamone has been chosen to designate this important degradation product. The reactions which have been used to elucidate the changes in the formation of lycoctamone are indicated on the flowsheet.

It is evident that anhydrolycoctonam is an intermediate in the formation of lycoctamone, and that information gathered about the environment of the carbonyl in the former may be used in the interpretation of the mode of formation of the latter.

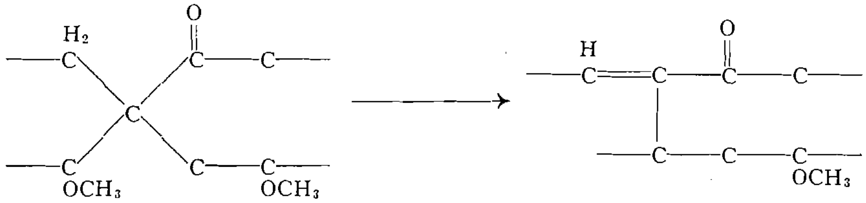
Lycoctamone and dihydrolycoctam form exceptionally stable monohydrates, and no very satisfactory analyses have been obtained for the anhydrous compounds. The acetates, however, gave good analyses.

Lycoctamone still contains a readily acetylated hydroxyl, presumably the original primary one. The position of the short wave length ultraviolet maximum indicates, if the Woodward-Fieser (6) rules are obeyed, that the α–β unsaturated ketone is trisubstituted endocyclic (calc. λ_{max}249 mμ) or disubstituted exocyclic (calc. λ_{max}242-244 mμ). The fairly rapid catalytic reduction of the double bond argues in favor of the disubstituted possibility. Additional support for this comes from the infrared spectrum. Lycoctamone, lycoctamol, and lycoctam (see flowsheet) have what is probably a CH-bending band near 830 cm.$^{-1}$ (Fig. 1) which is absent in dihydrolycoctam. A band in this position is characteristic of a trialkyl substituted double[3] bond (9).

Lycoctamone is inert to bismuth oxide in boiling acetic acid (8) and to periodic acid, hence it is not an α-ketol. In contrast to the situation in anhydrolycoctonam, the carbonyl in lycoctamone is readily reduced by sodium borohydride to the allyl alcohol lycoctamol, and by the Wolff-Kishner method to lycoctam. This suggests that some of the hindrance of the carbonyl has been removed by carbon migration.

A plausible explanation of the formation of lycoctamone is that a methoxyl β to the carbonyl in anhydrolycoctonam is eliminated with an attendant Wagner-Meerwein shift to give the α–β unsaturated ketone. Two types of situation can be envisaged which would favor such a change. Either a methoxyl separated from the carbonyl by a quaternary carbon is involved as in (*a*), or a methoxyl β to the carbonyl, having the wrong orientation for easy elimination with an α-hydrogen, is eliminated as in (*b*).

(*a*)



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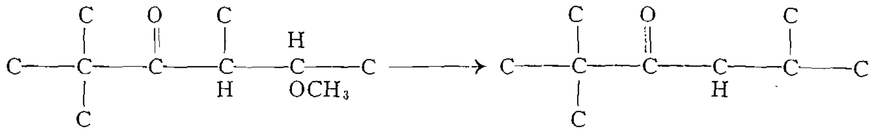
[3] *Note the difference in nomenclature. A trisubstituted double bond corresponds to a disubstituted α–β unsaturated ketone.*

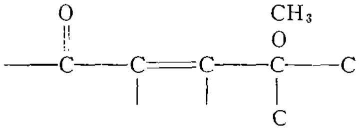
(b)



$$C\text{---}\overset{C}{\underset{C}{C}}\text{---}\overset{O}{\overset{\|}{C}}\text{---}\overset{C}{\underset{H}{C}}\text{---}\overset{H}{\underset{OCH_3}{C}}\text{---}C \longrightarrow C\text{---}\overset{C}{\underset{C}{C}}\text{---}\overset{O}{\overset{\|}{C}}\text{---}\underset{H}{C}\text{---}\overset{C}{C}\text{---}C$$

The arrangement of atoms necessary for (a) is present in partial structures I and II for anhydrolycoctonam. However, a detailed consideration of the various possibilities will be deferred until more evidence is available on the substitution near the carbonyl in lycoctamone and anhydrolycoctonam.

Since in the products of periodate cleavage of the glycol system in lycoctonam the methoxyls are resistant to hydrolysis (see experimental section and reference 5) it is clear that during the formation of lycoctamone a methoxyl becomes unusually labile. This lability would be readily explained if the methoxyl were located as shown, making it a vinylogue of an α-methoxy ketone.



$$\text{---}\overset{O}{\overset{\|}{C}}\text{---}\underset{|}{C}\text{=}\underset{|}{C}\text{---}\overset{\overset{CH_3}{O}}{\underset{\underset{C}{|}}{C}}\text{---}C$$

The hydrogenolysis of lycoctamone and lycoctamol has many parallels (7,10). Although the new tertiary hydroxyl is also in an allylic position if the above conclusions are correct, it does not readily undergo hydrogenolysis. The uptake of hydrogen by lycoctamol was consistently over two moles, but the product consisted mainly of lycoctam, in which only the secondary hydroxyl was eliminated.

Considerable information is now available about two or perhaps three of the methoxy groups of lycoctonine. The conclusions as to the degree of substitution of the double bonds in lycoctamone and the desmethanol diketones (5) will have to be checked by oxidation studies before a choice can be made among the various possible partial structures for lycoctamone.

EXPERIMENTAL

The activity of the alumina is cited using the scale proposed by Brockmann (2). Melting points are corrected to within one degree. Rotations were determined in absolute ethanol, the cited temperature being that of the room. The ultraviolet spectra were determined on solutions in 95% ethanol using a Beckman D.U. spectrophotometer. Infrared spectra were determined on a Perkin-Elmer model 21 double beam spectrophotometer.

Anhydrolycoctonam—Attempted Reactions

(a) The compound was recovered unchanged after attempted Wolff-Kishner reduction at 200° in triethylene glycol.

(b) Over 90% of the compound was recovered after 20 hr. reflux with selenium dioxide (1 mole) in acetic acid.

(*c*) Anhydrolycoctonam darkened Tollens' solution slightly in 30 min. at room temperature. It gave a tiny red precipitate with Fehling's solution at 100° in five minutes with little change after a further five minutes of heating.

Dihydroanhydrolycoctonam Diacetate

Anhydrolycoctonam (116 mgm.) was dissolved in 2 cc. of methanol and 1 cc. of 10% aqueous sodium borohydride solution added. After standing for 22 hr. at room temperature, the solution was refluxed for 35 min. The excess borohydride was decomposed with acid and the product extracted into chloroform. The 125 mgm. recovered from the chloroform could not be induced to crystallize. It was acetylated overnight with acetic anhydride – pyridine. The 145 mgm. of neutral product was dissolved in ether and petroleum ether added, giving 83 mgm. of crude crystals. After one recrystallization this melted at 167–172°. After purification by chromatography on alumina and recrystallization the diacetate was obtained as needles, m.p. 174–177°. $[\alpha]_D^{25}$ 33 ± 1° ($c = 1.8$). Found: C, 63.81; H, 7.85. Calc. for $C_{29}H_{43}O_9N$: C, 63.37; H, 7.89. Infrared spectrum (Fig. 1): Bands at 1636 and 1738 cm^{-1}.

When anhydrolycoctonam was treated with sodium borohydride solution for 15 min. at room temp. 81% of the compound was recovered in a slightly impure condition (m.p. 142°).

Desmethanolsecolycoctonam Diketone—Attempted Hydrolysis

A solution of 44 mgm. of the ketone in 2 cc. of 6 *N* sulphuric acid was refluxed vigorously for 3.5 hr. The product was extracted with methylene chloride, and the solvent removed. The residue (45 mgm.) crystallized from ether containing a little acetone, giving 34 mgm. of starting material.

Lycoctamone

(*a*) Lycoctonam hydrate (500 mgm.) in 8 cc. of 12 *N* sulphuric acid was heated at 100° for two hours. The solution was cooled, partially neutralized with sodium carbonate, and extracted with chloroform. The 440 mgm. of brown residue from the chloroform solution crystallized when water was added, giving 260 mgm. of tan crystals, m.p. 205–215°. This was best purified by adsorption from 50% benzene–chloroform on 20 times its weight of neutral alumina, activity 4, and elution with this solvent mixture and with chloroform. The eluates, crystallized from aqueous methanol, melted at 218–225° (immersed at 200°). After three recrystallizations from concentrated methanol solution the colorless prisms melted at 221–225°. After drying 24 hr. at 110° over phosphorus pentoxide *in vacuo* it had $[\alpha]_D^{20}$ 274 ± 2° ($c = 2.0$). Found: C, 63.70, 64.01; H, 7.64, 7.81; OCH_3, 15.43, 14.91. Calc. for $C_{23}H_{31}O_6N \cdot H_2O$: C, 63.43; H, 7.64; 2 OCH_3, 14.25. Ultraviolet spectrum: λ_{min}230 mμ (3.95); λ_{max} 245 mμ (4.01); λ_{min} 300 mμ (2.18); λ_{max} 310 mμ (2.20). A sample of lycoctamone hydrate was sublimed at 180° under 5×10^{-4} mm. It then melted at 217–223°, $[\alpha]_D^{22}$ 258 ± 4° ($c = 1.3$). Found: C, 65.97, 65.54; H, 8.15, 8.07; Calc. for $C_{23}H_{31}O_6N$: C, 66.16; H, 7.48. Infrared spectrum (mull): Bands at 1610 (lactam) and 1661 cm.$^{-1}$ (ketone) and 3550, 3370, and 3260 cm.$^{-1}$ (hydroxyls).

(*b*) Anhydrolycoctonam (40 mgm.) in 2 cc. of 6 *N* sulphuric acid was refluxed gently in a carbon dioxide atmosphere for five hours. The solution was cooled, neutralized with ammonia, and extracted with chloroform. The 34 mgm. of product crystallized when water was added, giving 25 mgm., m.p. 210–220°. This did not depress the melting point of the product from (*a*).

Lycoctamone gave a black precipitate with Tollens' reagent at room temperature in 20 min. It only reduced Fehling's solution slightly after 15 min. at 100°. It was recovered unchanged after 70 hr. in an aqueous-methanol solution of periodic acid (approx. 0.2 molar) and it was not oxidized by bismuth oxide in refluxing acetic acid.

Lycoctamone Monoacetate

(*a*) Pure lycoctamone (108 mgm.) left at room temperature for 72 hr. with 2 cc. of acetic anhydride and 2 cc. of pyridine gave 114 mgm. of neutral acetate. This crystallized readily from acetone, giving 72 mgm., m.p. 235–242°. The compound purified by chromatography on alumina (activity 4) and recrystallization softened at 235° and melted by 242° (immersed at 215°). $[\alpha]_D$ 192 ± 2° ($c = 2.6$). Found: C, 65.26, 65.56; H, 7.37, 7.18; N, 3.04; OCH_3, 13.22. Calc. for $C_{25}H_{33}O_7N$: C, 65.34; H, 7.24; N, 3.05; 2 OCH_3, 13.51. Ultraviolet spectrum: λ_{min} 231 mμ (3.94); λ_{max} 245 mμ (3.98). Infrared spectrum (Fig. 1): Bands at 3425, 1741, 1670, and 1623 cm^{-1}.

(*b*) Lycoctonam acetate (253 mgm.) in 20 cc. of glacial acetic acid containing 0.02 cc. of conc. sulphuric acid was heated at 105 ± 2° for 1.5 hr. Two hundred milligrams of sodium carbonate was added, then the solution taken to near dryness under reduced pressure. The residue was taken up in chloroform, washed with sodium carbonate solution, dried, and evaporated to a volume of 5 cc. Ten cubic centimeters of dry benzene was added, and the compound adsorbed from this onto 5 gm. of neutral alumina activity 3. The products were eluted rapidly with 50% benzene-chloroform. The first 84 mgm. crystallized readily from ether, giving 51 mgm. of crude anhydrolycoctonam acetate. The next 117 mgm. proved to be quite pure lycoctamone acetate, m.p. 242°. The material eluted by chloroform and methanol in chloroform did not crystallize readily.

At temperatures around 115° with similar reagent mixtures the conversion to lycoctamone acetate was more complete, yields of up to 80% on a weight basis being obtained.

Lycoctamone acetate was saponified readily at room temperature by potassium hydroxide in methanol. The recovered lycoctamone melted over a range up to 220°. A purer product was obtained by saponification at room temperature with aqueous methanol containing mineral acid (1 cc. of conc. sulphuric acid in 6 cc. of 50% aqueous methanol).

Lycoctamol

Sodium borohydride (30 mgm.) was added to a solution of 52 mgm. of lycoctamone in 2 cc. of 50% aqueous methanol. After 30 min. the excess borohydride was decomposed by addition of dilute sulphuric acid, and the solution extracted with six 4 cc. portions of chloroform. The 52 mgm. of product crystallized readily from ethyl acetate giving 37 mgm., m.p. 205°

and 9 mgm., m.p. up to 190°. After four recrystallizations from ethyl acetate the compound melted at 207–212° (immersed at 190°). It was dried at 100° over P_2O_5 *in vacuo* for 16 hr. $[\alpha]_D^{25}$ 212 ± 2° (c = 2.0). Found: C, 65.89, 66.03; H, 8.41, 8.38. Calc. for $C_{23}H_{33}O_6N$: C, 65.85; H, 7.93. The compound showed only end absorption in the ultraviolet. It appeared somewhat unstable. Freshly recrystallized samples dried at 100° for three to five hours *in vacuo* had rotation of 219 ± 3°, definitely higher than the sample heated for a longer period. Infrared spectrum (mull): Bands at 3350 and 1610 cm^{-1}.

A suspension of 0.4 gm. of active manganese dioxide (1) in a solution of 20 mgm. of lycoctamol in 3 cc. of dry benzene and 2 cc. of dry chloroform was agitated for 2.5 hr. The manganese dioxide was removed by filtration and the solid washed with chloroform. The combined filtrates contained 13 mgm. of product. This crystallized from ethyl acetate, giving 11 mgm., m.p. 224–228° which did not depress the melting point of lycoctamone.

Lycoctamol Monoacetate

Lycoctamone acetate (250 mgm.) was dissolved in 5 cc. of methanol, and 55 mgm. of sodium borohydride in 2 cc. of water was added. After five minutes the solution was acidified with dilute acid, and extracted with chloroform. The product crystallized nearly completely from acetone–ether, m.p. 170–214°. This was purified by chromatography on alumina giving 90 mgm., m.p. 214–218°. After three recrystallizations from acetone ether the compound melted at 216–218°. $[\alpha]_D^{20}$ 175 ± 2° (c = 2.7). Found: C, 65.13, 65.69; H, 7.91, 8.23. Calc. for $C_{25}H_{35}O_7N$: C, 65.05; H, 7.64. Infrared spectrum (mull) (Fig. 1): Bands at 3455, 3365, 1744, and 1623 cm^{-1}.

Lycoctamol Diacetate

When lycoctamol and lycoctamol monoacetate were acetylated overnight with acetic anhydride and pyridine they were converted to the same diacetate. This crystallized from ether – petroleum ether as fine needles, m.p. 177–180°. $[\alpha]_D^{18}$ 163 ± 2° (c = 1.84). Found: C, 63.87, 63.70; H, 7.11, 7.01; OCH_3, 12.45. Calc. for $C_{27}H_{37}O_8N$: C, 64.39; H, 7.41; 2 OCH_3, 12.32. Infrared spectrum (mull): Bands at 3435, 1743, 1625 cm^{-1}.

Lycoctam

Lycoctamone (45 mgm.), 1 cc. of triethylene glycol and 0.5 cc. of 85% hydrazine hydrate were heated in a bath at 130° for one hour. Eighty milligrams of potassium hydroxide was added, and the bath temperature raised over a period of one hour to 200°, allowing water and hydrazine to escape. The solution was then allowed to reflux at that bath temperature for four hours. It was cooled, diluted, and extracted with methylene chloride (5 cc. portions). Water was added to the 71 mgm. of oil extracted by the methylene chloride. Thirty milligrams of crystals were deposited which liquified between 100 and 105°, but did not run down in the tube until 125° was reached. On the hot stage this melted around 95°, slowly resolidified and melted at 157°. The compound after recrystallization from aqueous methanol had the form of feathery needles, m.p. 115–125°. This was dried for three hours at 100° *in vacuo* over P_2O_5, the melt cooled, pulverized, and redried for one hour $[\alpha]_D^{21}$ 160 ± 2° (c = 3.2). Found: C, 68.73; H, 8.43. Calc. for $C_{23}H_{33}O_5N$:

C, 68.46; H, 8.24. The ultraviolet spectrum showed only end absorption. Infrared spectrum (chloroform solution, 30 mgm. per ml., 0.1 mm. cell): Bands at 3575, 3400, 1615 cm^{-1}.

Lycoctam Monoacetate

Lycoctam (50 mgm.) was dissolved in 3 cc. of acetic anhydride and the solution left overnight at room temperature. The 54 mgm. of neutral acetate so obtained crystallized from ether on addition of petroleum ether. Crop 1, 16 mgm., m.p. 154–156°. Crop 2, 12 mgm., m.p. 140–158°. Crop 3, 6 mgm., softened at 100°, melted over a wide range. Products from preparations under varied conditions melted over ranges such as 151–159° and 153–162° after recrystallization. Found: C, 67.52; H, 8.16. Calc. for $C_{25}H_{35}O_6N$: C, 67.39; H, 7.92. Infrared spectrum: (Fig. 1): Bands at 3435, 3350, 1743, and 1620 cm^{-1}. Low melting material from the mother liquors from recrystallizations of the acetate (approx. 40 mgm.) was saponified readily by potassium hydroxide in methanol. The product gave crystals (29 mgm.) from aqueous methanol, m.p. 105–115°. This did not depress the m.p. of lycoctam.

Dihydrolycoctam

(*a*) Lycoctamone (27.1 mgm.) in 3 cc. of ethanol containing three drops of concentrated hydrochloric acid in the presence of platinum from 10.2 mgm. of platinum oxide (Adams') absorbed 4.43 cc. of hydrogen at 32°C. and 756 mm. pressure (mole ratio 2.84) in four hours. The catalyst was removed by filtration, the solvent evaporated under reduced pressure, and the residue taken up in 1 *N* sulphuric acid. Methylene chloride extraction of this solution yielded 27 mgm. of neutral product which crystallized from aqueous methanol giving 9 mgm., m.p. up to 170°. When recrystallized from ethyl acetate on addition of petroleum ether it melted at 179° and proved identical with the products from (*b*) and (*c*) (mixed m.p. and comparison of infrared spectra).

In similar hydrogenations varying the ratio of catalyst to compound and the concentration of hydrochloric acid, a molar uptake of hydrogen varying from 2.6 to 3 was observed. Yields of the crystalline product varied from 40 to 55% by weight of starting material.

(*b*) Lycoctamol (29 mgm.) in 3 cc. of ethanol containing three drops of concentrated hydrochloric acid in the presence of platinum from 10 mgm. of platinum oxide (Adams') absorbed 4.15 cc. of hydrogen at 26°C. under 754 mm. pressure (mole ratio 2.4). The product, isolated as in (*a*), crystallized readily from aqueous methanol giving 21 mgm., m.p. 173–178°.

(*c*) Lycoctam (16.8 mgm.) hydrogenated exactly as described in (*b*), absorbed 1.27 cc. of hydrogen at 27°C. under 763 mm. pressure (1.24 mole). The product crystallized from aqueous methanol, giving 13.5 mgm., m.p. 182°. After one recrystallization it melted at 180–185° and had an infrared spectrum identical with that of the product from (*a*).

Dihydrolycoctam, purified by chromatography on alumina of activity 4 (readily eluted by 50% chloroform–benzene) and recrystallized from aqueous methanol, had the form of needles, m.p. 182–184°. After drying seven hours at 110° over P_2O_5 *in vacuo* it had $[\alpha]_D^{21}$ 85 ± 2° ($c = 2.4$). Found: C, 67.59; H, 8.59; OCH_3, 16.39. Infrared spectrum (mull): Bands at 3525, 3420, 1616 cm^{-1}. A sample was distilled at 170°, 5×10^{-4} mm. and the glass analyzed. Found: C, 67.48; H, 8.66. Calc. for $C_{23}H_{35}O_5N$: C, 68.12; H, 8.70; two OCH_3, 15.30.

Dihydrolycoctam Acetate

A solution of 79 mgm. of dihydrolycoctam in 1 cc. of acetic anhydride and 1 cc. of pyridine was left at room temperature for 45 hr. The mixture was taken to near dryness under reduced pressure and the residue taken up in chloroform. This solution was washed with dilute acid and with sodium carbonate solution, dried, and the solvent removed. The residue crystallized readily from ether giving 75 mgm., m.p. 198–204°, and some less pure material. After three recrystallizations from acetone–ether the compound softened at 202° and melted at 206°, $[\alpha]_D^{21}$ 33 ± 2° ($c = 1.9$). Found: C, 67.15, 67.05; H, 8.29, 8.46; OCH_3, 14.75; active hydrogen, 0.217. Calc. for $C_{25}H_{37}O_6N$: C, 67.09; H, 8.33; 2 OCH_3, 13.86; one active hydrogen, 0.225. Infrared spectrum (Fig. 1): Bands at 3475, 3425, 1742 and at 1635 and 1620 (split band) cm^{-1}.

Thirty seven milligrams of the acetate in 2 cc. of glacial acetic acid reduced 3 mgm. of chromium trioxide in five hours at room temperature, and 6 mgm. more when left overnight. The 40 mgm. of neutral product was taken up in ether, filtered from 2 mgm. of green residue, and concentrated. Crop 1: 18 mgm. m.p. 192–199°; crop 2, 4 mgm., m.p. 185–199°; crop 3, 3 mgm., m.p. 180–193°. These did not give a melting point depression when mixed with dihydrolycoctam acetate. The combined crystals when recrystallized from ether – petroleum ether melted at 200–204°.

ACKNOWLEDGMENT

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THE REACTIONS OF ACTIVE NITROGEN WITH THE BUTANES[1]

By R. A. Back and C. A. Winkler

ABSTRACT

The main product of the reactions of active nitrogen with *n*- and iso-butanes at 75° C. and 250° C. was hydrogen cyanide. Small amounts of C_2 hydrocarbons, mainly ethylene and acetylene, were produced in both reactions. Second order rate constants were calculated on the assumption that the reactive species in active nitrogen is atomic nitrogen, and that the initial attack of a nitrogen atom is the rate-controlling step. The activation energies were then estimated to be 3.6 kcal. and 3.1 kcal. and the probability factors 4.5×10^{-4} and 4.4×10^{-4}, for the *n*-butane and isobutane reactions respectively.

INTRODUCTION

Previous papers from this laboratory have described the reactions of active nitrogen with methane and ethane (1), propane (9), acetylene (13), ethylene (4, 14), propylene (12), and the butenes (3).

In the present paper are discussed the reactions of active nitrogen with *n*-butane and isobutane. The active species is assumed to be atomic nitrogen, for reasons indicated elsewhere (15).

EXPERIMENTAL

The apparatus was essentially similar to that described in previous papers. Reactions were studied in a fast flow system at a pressure of 1.34 mm. Hg. Active nitrogen was produced by a condensed discharge.

Condensable reaction products were separated into three fractions in a low temperature still of the type described by LeRoy (6). Ethane and ethylene were distilled at −170° C., and acetylene, propane, and propylene at −147° C. Each fraction was analyzed for total unsaturation, using conventional absorption technique (8, 2).

The third fraction, distilled at −30° C., contained hydrogen cyanide and butane. It was condensed into a large calibrated volume, warmed to room temperature, and the pressure recorded. By keeping the trap clean to avoid traces of water, and by never exceeding a total gas pressure of 400 mm. Hg, the hydrogen cyanide could be completely vaporized without appreciable polymer formation. The hydrogen cyanide and butane were then condensed into a detachable trap on top of 10 ml. of 1 *N* potassium hydroxide solution which was previously degassed and frozen in liquid nitrogen. The trap was removed under vacuum, and the bottom immersed in boiling water. In this way the solution melted first and the hydrogen cyanide dissolved before it could melt and polymerize. The cyanide content of the solution was determined by a silver nitrate titration, and the butane determined by difference.

Samples of noncondensable gas were removed from the flow system during

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Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Quebec, with financial assistance from the National Research Council of Canada.

the reactions with a Toepler pump located beyond the liquid nitrogen traps, and were analyzed for N_2, H_2, and CH_4 with a mass spectrometer.*

Experiments were made at two temperatures with each hydrocarbon. Nitrogen atom flow was maintained constant, while butane flow was varied over a wide range.

RESULTS

Hydrogen cyanide was the main product of both the *n*-butane and the isobutane reactions. At 75° C., from 85 to 95% of the *n*-butane consumed was converted to hydrogen cyanide. At 250° C., the yield was from 80 to 90%. At 100° C., from 90 to 97% of the isobutane consumed was converted to hydrogen cyanide, while at 260° C., the yield was from 87 to 95%.

In Fig. 1, hydrogen cyanide production is shown as a function of *n*-butane flow rate. It increased to a maximum at both temperatures, then fell off at higher flow rates. The value of the maximum was higher for the reaction at the higher temperature. Several nitrogen atom – hydrocarbon reactions studied previously (3, 4, 9, 12, 13, 14) have been characterized by complete consumption of nitrogen atoms at high hydrocarbon flow rates. The curves shown in Fig. 1 are, however, incompatible with behavior of this sort.

Hydrogen cyanide production in the isobutane reaction is shown in Fig. 2. As with *n*-butane, the hydrogen cyanide produced from isobutane at 100° C.

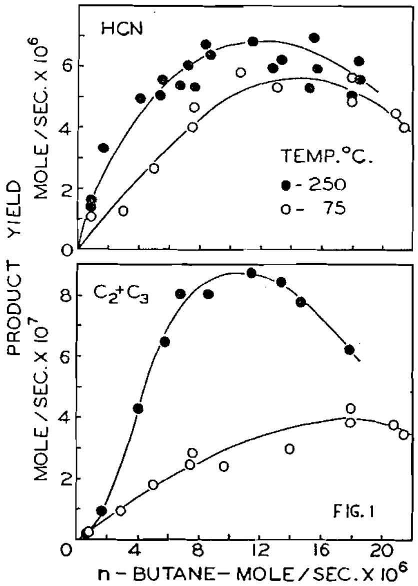


FIG. 1

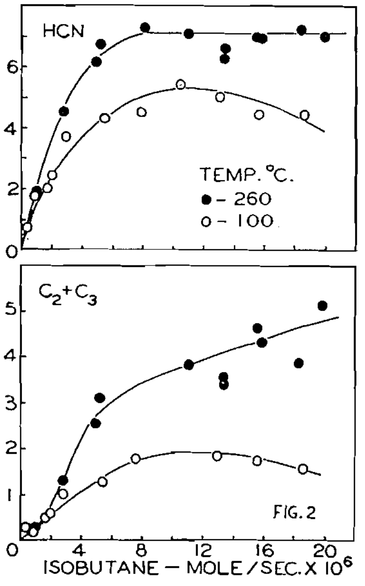


FIG. 2

FIG. 1. Rate of formation of products in the nitrogen atom – *n*-butane reaction, as a function of *n*-butane flow rate.

FIG. 2. Rate of formation of products in the nitrogen atom – isobutane reaction, as a function of isobutane flow rate.

**We are grateful to Dr. H. I. Schiff of this department for making the mass spectrometer analyses reported in this paper.*

passed through a maximum, apparently without complete consumption of nitrogen atoms. At 260° C., however, consumption of nitrogen atoms appeared to be complete, since hydrogen cyanide production increased to a value of about 7.5×10^{-6} mole/sec., and remained constant, within experimental error, with increasing isobutane flow. Further evidence that the value of hydrogen cyanide production represented complete consumption of nitrogen atoms was obtained by making several experiments with ethylene at 250° C. Previous studies (13) have indicated rather clearly that, beyond a fairly well defined flow rate, this reaction occurs with complete consumption of nitrogen atoms. The maximum hydrogen cyanide production was approximately the same as that from the isobutane reaction at 260° C.

Dilution effects and reduction in reaction time at high hydrocarbon flow rates might explain the incomplete consumption of nitrogen atoms at 100° C. in the butane reactions, but cannot account for the maxima in the hydrogen cyanide curves with increase in butane flow rate. However, the reaction flame at these high butane flow rates is located in the narrow neck at the top of the reaction vessel, where surface effects might become important, and surface recombination of nitrogen atoms or destruction of nitrogen–butane reaction complexes could explain the observed decrease in reaction at high butane flow rates.

The hydrocarbon fractions obtained by distillation at −170° C. and −147° C. were found by absorption analysis to be 95 to 100% unsaturated. Mass spectrometer analysis indicated incomplete separation of the unsaturates, with acetylene and ethylene occurring in both fractions. By plotting the sum of these fractions against butane flow, consistent curves were obtained, shown in Figs. 1 and 2 for *n*-butane and isobutane respectively. The shapes of these curves offer additional evidence for the incomplete consumption of nitrogen atoms in the *n*-butane reaction at both temperatures and in the isobutane reaction at 100° C. The unsaturated C_2–C_3 hydrocarbons react rapidly with nitrogen atoms; hence, if nitrogen atoms were completely consumed at high butane flow rates a sharp increase in C_2–C_3 recovered would be expected, as observed, for example, in the recovery of ethylene from the reaction of nitrogen atoms with propylene (12). In the *n*-butane reaction, however, and in the isobutane reaction at 100° C., recovery of C_2–C_3 increased to a maximum, then decreased at high butane flow rates, roughly paralleling the hydrogen chloride curves.

In the isobutane reaction at 260° C., on the other hand, the C_2–C_3 recovered shows a marked increase at high isobutane flow rates, indicating complete consumption of nitrogen atoms in this reaction.

Mass spectrometer analyses of the combined C_2–C_3 fractions are shown in Tables I and II for the *n*-butane and isobutane reaction respectively. It is seen that these fractions consist almost entirely of ethylene and acetylene, with small amounts of ethane, propane, and propylene.

Analyses of noncondensable gases showed that in the temperature range investigated, methane was produced in only small quantities (of the order of 5×10^{-8} mole/sec.) in both the *n*-butane and isobutane reactions.

TABLE I
MASS SPECTROMETER ANALYSIS OF COMBINED C_2–C_3 FRACTION OF *n*-BUTANE REACTION PRODUCTS

Temp., ° C.	Butane flow, mole/sec.	Combined C_2–C_3 $\times 10^6$			Percentage		
			C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8
75	0.875	0.028	57.6	41.6	1.2	—	—
75	7.57	0.285	35.0	64.5	Trace	—	—
75	10.64	0.244	36.0	63.5	Trace	—	—
75	12.95	0.302	30.7	68.6	0.7	—	—
250	4.04	0.428	20.5	68.0	6.0	3.5	2.0
250	8.59	0.804	16.0	67.5	9.6	4.8	2.0
250	11.42	0.877	15.0	67.0	10.0	6.0	2.0

TABLE II
MASS SPECTROMETER ANALYSIS OF COMBINED C_2–C_3 FRACTION OF ISOBUTANE REACTION PRODUCTS

Temp., ° C.	Isobutane flow, mole/sec.	Combined C_2–C_3 $\times 10^6$		Percentage		
			C_2H_2	C_2H_4	C_2H_6	C_3H_6
100	10.5	0.18	46.8	51.8	1.3	—
260	4.90	0.29	31.1	62.2	4.6	2.1
260	15.5	0.44	22.3	67.6	6.8	3.1

DISCUSSION

Since no nitrogen-containing product other than hydrogen cyanide was detectable in either of the systems under investigation, the occurrence of hydrogen abstraction reactions to a significant extent would appear to be excluded.

In the *n*-butane reaction, an initial attack at a primary carbon atom seems most probable:

$$N + C_4H_{10} \rightarrow HCN + H_2 + C_3H_7 \qquad [1]$$

Attack at a secondary carbon atom is less favorable energetically and sterically, but probably occurs to some extent.

$$N + C_4H_{10} \rightarrow HCN + H + C_2H_5 + CH_3 \qquad [2]$$

The propyl radical might be expected to react with another nitrogen atom,

$$N + C_3H_7 \rightarrow HCN + H + C_2H_5 \qquad [3]$$

followed by

$$N + C_2H_5 \rightarrow HCN + CH_3 + H \qquad [4]$$

and

$$N + CH_3 \rightarrow HCN + H_2 \qquad [5]$$

However, this reaction sequence cannot account satisfactorily for a C_2–C_3 fraction composed almost entirely of ethylene and acetylene. Some ethylene might be formed by the disproportionation and hydrogenation of ethyl radicals, but at least an equal quantity of ethane must be expected from these reactions (5). Since ethylene reacts much more rapidly than ethane with nitrogen atoms, more ethane than ethylene would be found in the C_2–C_3 fraction.

The presence of acetylene in the reaction products is even more difficult to explain. While small amounts of acetylene might be accounted for by dehydrogenation of ethylene, the quantities found (Table I) cannot be satisfactorily explained in this way. Furthermore, the ethylene – hydrogen atom reaction forms ethane rather than acetylene as the main product (7).

It would seem necessary to postulate the direct formation of ethylene and acetylene by the reaction of nitrogen atoms with *n*-butane or with *n*-propyl radicals. A number of possible reactions could be suggested, but some of these are energetically unfavorable, while others involve the improbable formation of energetically "hot" radicals by decomposition of a collision complex. The least objectionable reaction leading to the formation of ethylene as a product of nitrogen atom attack would appear to be

$$N + C_3H_7 \rightarrow HCN + H_2 + :CH—CH_3 \qquad [6]$$

followed by

$$:CH—CH_3 \rightarrow CH_2{=}CH_2$$

For acetylene formation, the reaction

$$N + C_3H_7 \rightarrow CH{\equiv}CH + HCN + 2H_2 \qquad [7]$$

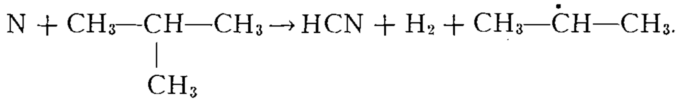
seems most probable.

Reactions of the type [6] and [7], especially the latter, are admittedly incompatible with the Rice–Teller principle of least motion. This principle has been concerned mainly with relatively simple processes, involving energies of the order of 100 kcal. or less, whereas the high energy of formation of the C≡N bond (170–200 kcal.), released within a reaction complex, might permit considerably more intracomplex rearrangement than would otherwise be expected.

Another possibility is the attack by a nitrogen atom at a secondary carbon atom of *n*-butane, with similar direct formation of ethylene or acetylene. This is less favorable, however, both energetically and sterically.

The amounts of ethylene and acetylene recovered represent a relatively small fraction of the *n*-butane consumed. However, if it is assumed that the initial attack of the nitrogen atom is rate controlling, the rate of reaction of nitrogen atoms with these unsaturates is roughly seven times faster than the reaction with *n*-butane. Since nitrogen atoms were never completely consumed in the *n*-butane reaction, ethylene, acetylene, and butane would be expected to compete for nitrogen atoms according to their relative reactivities, independently of the sequence of the reactions. Thus the ethylene and acetylene recovered represents only a fraction of the total amounts of these unsaturates formed during the reaction. Making conservative calculations on this basis, it seems probable that close to 50% of the hydrogen cyanide must have been derived from ethylene or acetylene. Thus the reaction of nitrogen atoms with butane would appear to proceed almost exclusively through reactions of the type [6] and [7] rather than [3]. These would be followed by further reactions with nitrogen atoms, as described in previous papers (13, 14).

In the isobutane reaction, the most probable initial step is the attack by a nitrogen atom at a primary carbon atom:



$$\mathrm{N + CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3 \rightarrow HCN + H_2 + CH_3{-}\dot{C}H{-}CH_3.} \qquad [8]$$

An attack at the secondary carbon atom is unlikely, both energetically and sterically. Again, it appears necessary to postulate the direct formation of ethylene and acetylene. If the unpaired electron of the isopropyl radical is considered to be localized on the secondary carbon atom, nitrogen atom attack at this point is highly probable:

$$\mathrm{N + CH_3{-}\dot{C}H{-}CH_3 \rightarrow HCN + 2CH_3.} \qquad [9]$$

Formation of ethylene or acetylene directly in this reaction would involve rather extensive intracomplex rearrangement, and seems unlikely.

There is some evidence, however, that the isopropyl radical may exhibit partial double bond characteristics (10), resonating between the three structures

$$\mathrm{\overset{-}{C}H_3{=}\overset{+}{C}H{-}CH_3,\quad CH_3{-}\dot{C}H{-}CH_3,\quad CH_3{-}\overset{+}{C}H{=}\overset{-}{C}H_3}$$

so that the free electron is shared by the three carbon atoms, making nitrogen atom attack at the terminal carbon atoms much more probable.

Thus the reaction

$$\mathrm{N + CH_3{-}\dot{C}H{-}CH_3 \rightarrow HCN + H_2 + :CH{-}CH_3} \qquad [10]$$

followed by rearrangement of the ethylidene radical, and

$$\mathrm{N + CH_3{-}\dot{C}H{-}CH_3 \rightarrow HCN + 2H_2 + C_2H_2} \qquad [11]$$

would seem to be the most probable sources of ethylene and acetylene.

The smaller amounts of ethylene and acetylene recovered from the isobutane reaction would indicate that part of the reaction proceeds through reaction [9].

The small quantities of ethane, propane, and propylene (Tables I, II) may be adequately explained by hydrogen atom and inter-radical reactions.

Second order rate constants were evaluated for both the *n*-butane and isobutane systems, assuming streamline flow (3). These decreased rather markedly at high butane flow rates beyond the maxima in Figs. 1 and 2 and values for butane flow rates above 12×10^{-6} mole/sec. were therefore not included in the average taken to obtain the following summary of the rate constants:

	Temperature, ° C.	k, liter. mole^{-1}. sec^{-1}.
n-Butane	75	9.8×10^4
	250	5.6×10^5
Isobutane	100	2.4×10^5
	260	8.5×10^5

Activation energies and collision rates, Z, were calculated in the usual way. Collision diameters of 3.0×10^{-8}, 4.8×10^{-8}, and 4.66×10^{-8} cm. were assumed for the nitrogen atom, *n*-butane and isobutane respectively (4, 11).

Probability factors and activation energies for the two reactions were estimated to be as follows:

	E, kcal.	*P**
n-Butane	3.6	4.5×10^{-4}
Isobutane	3.1	4.4×10^{-4}

* *Values of P shown are averages of those for the two temperatures.*

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NOTE

THE PHOTOLYSIS OF CYCLOHEXANONE IN PRESENCE OF OXYGEN AND OF CARBON DIOXIDE[1]

By J. R. Dunn[2] and K. O. Kutschke

This work arose from an attempted study of the reaction between oxygen and the radicals produced in the photolysis of cyclohexanone. Benson and Kistiakowsky (1) considered the initial step to involve the formation of the pentamethylene-acyl radical:

$$C_6H_{10}O + h\nu \rightarrow (CH_2)_5{\cdot}CO$$

which could break down as follows:

$$(CH_2)_5CO \rightarrow CH_2(CH_2)_3CH_2 + CO.$$

The initial studies on the photolysis in presence of oxygen were made at room temperature, since cyclohexanone is known to autoxidize at temperatures above 100° C. (3). A small amount of carbon monoxide was produced when cyclohexanone and oxygen were mixed at room temperature in the absence of light.

The cyclohexanone–oxygen mixtures were stirred by a magnetic device and illuminated in a cylindrical cell by the full arc from an S-500 Hanovia lamp. The photolysis products were condensed in liquid nitrogen and the non-condensable products (fraction (*a*)) were taken onto a Cu–CuO furnace heated to 220° C. Any residual oxygen was removed by the copper, and carbon monoxide was oxidized to carbon dioxide and measured as such. Two further fractions (*b*) and (*c*) were taken from the products condensable in liquid nitrogen with the aid of a LeRoy–Ward still. The vapor taken at $-155°$ C. contained ethylene and propane, which had been found by previous workers in the photolysis of cyclohexanone alone. It also contained some 50% of carbon dioxide which had not been found in the absence of oxygen.

During later runs in the absence of oxygen, peaks characteristic of ethane, propyne, and acetylene, as well as unidentifiable high mass peaks, occurred in the mass spectrogram of this fraction. Presumably these products arose from the photolysis of polymers which had collected on the windows of the cell. Between runs the cell was raised to a temperature of about 150° and pumped out for several hours but there was, none the less, a marked drop in the total yield of products as the work proceeded.

Fraction (*c*) was taken at $-78°$ C., and was shown mass spectrographically to contain 1-pentene and cyclopentane in the ratio 2.6:1, both in those experiments where oxygen was present and in its absence. This ratio differed both from that found by Benson and Kistiakowsky (1) and that given by Miller (2). The exact value of this ratio seems to depend upon experimental conditions.

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[1] *Issued as N.R.C. 3302.*

[2] *National Research Laboratories Postdoctorate Fellow 1953–.*

The analysis figures for typical photolyses in presence and absence of oxygen are given in Table I.

In presence of oxygen the yield of carbon monoxide is considerably greater than in its absence, while there is a 25% decrease in the yield of C_5's. In the absence of oxygen the yield of carbon monoxide is only slightly greater than that of the other volatile products. However, when oxygen is present the material balance is poor, indicating that there is some reaction giving rise to much material of high boiling point.

TABLE I
PHOTOLYSIS OF CYCLOHEXANONE (4.5 MM. CYCLOHEXANONE; 27° C.; FOUR HOURS' ILLUMINATION)

Run	CO, cc.	Fraction (*b*), cc.	Fraction (*c*), cc.
A_4 (10 mm. O_2)	1.36	0.29	0.50
A_6 (O_2 absent)	0.77	0.085	0.67

The considerable yield of C_5 fraction in presence of oxygen indicates that oxygen does not react readily either with the pentamethylene-acyl radical or the pentamethylene radical. It is possible that these radicals are formed by a slow step from excited cyclohexanone and that they give rise to 1-pentene and cyclopentane by a very rapid reaction. In such a case the oxygen may act as a quencher of the excited ketone, and this action alone could account for the 25% decrease in C_5 yield.

No previous studies could be found on the course of cyclohexanone photolysis in presence of foreign gases and, in order to test the quenching theory, a number of experiments were carried out in presence of carbon dioxide at various pressures. In Table II the yield of carbon monoxide, which, in absence of oxygen is 10–15% higher than that of C_5's, is given together with the pressures of carbon dioxide.

TABLE II
PHOTOLYSIS OF CYCLOHEXANONE IN PRESENCE OF CARBON DIOXIDE (FOUR HOURS' ILLUMINATION)

Run	Pressure, mm.		CO, cc.
	Cyclohexanone	CO_2	
	Runs at 27° C.		
A_9	5.0	0	0.13
A_{12}	5.0	0	0.137
A_{16}	5.3	0	0.096
A_{11}	5.2	10	0.090
A_{15}	4.5	20	0.073
A_{14}	4.5	30	0.058
A_{13}	5.0	50	0.053
	Runs at ~ 150° C.		
A_{18}	4.5	0	0.100
A_{19}	4.8	50	0.091

The accuracy of these figures is, undoubtedly, low owing to the decrease in light intensity as the products from subsequent runs deposited on the cell. The fact that the polymeric deposit was slightly charred by heat treatment in an attempt to dislodge it will probably account for the lowered yields in A_9,A_{12}, and A_{16}, Table II (cf. A_6, Table I). However, the trend toward low efficiencies at high carbon dioxide pressures is marked, and quenching of excited cyclohexanone by carbon dioxide would be consistent with this.

At higher temperatures (~150° C.) the quantum yield in the uninhibited reaction is almost unchanged (1, 2) but the quenching effect is far less marked.

Owing to the interference of polymeric products, and also of autoxidation at higher temperatures, it is impracticable to investigate the reaction between oxygen and the radicals from cyclohexanone photolysis more fully. However, the quenching effect of foreign gases on the photochemical decomposition of cyclohexanone is interesting and unusual, and similar studies on cyclopentanone might be profitable.

We wish to thank Dr. E. W. R. Steacie for his constant interest in this work, and we are indebted to Miss Frances Gauthier and Miss June Fuller of these laboratories for mass spectrographic analyses.

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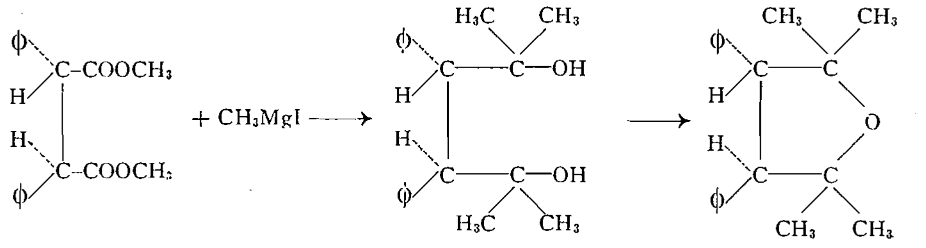
ROTAMERISM DURING DEMETHYLATION OF THE 2,5-DIMETHOXY-2,5-DIMETHYL-3,4-DIPHENYLHEXANES[1]

BY J. G. SMITH AND GEORGE F WRIGHT

ABSTRACT

The fission of methanol from the diastereomeric 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexanes leads to products which are best explained in terms of restriction about the central carbon–carbon bond. As would be expected from its stable conformation the *dd,ll* diastereomer easily forms the 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran, but the *meso* diastereomer forms a tetrahydrofuran with difficulty. On the other hand the *meso* diastereomer readily undergoes Friedel-Crafts types of condensation leading in different media to either 3,3-dimethyl-1-isopropenyl-2-phenylindane, 3,3-dimethyl-1-isopropyl-2-phenylindene or 5,5,10,10-tetramethyl-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]-indene. These indenes are the expected products from a consideration of the conformation of the *meso*-dimethoxydimethyldiphenylhexane which is most free from steric restriction.

The two possible diastereomers of 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane have been reported (1). One is a liquid (IV), very viscous, which has resisted attempts to cause it to crystallize during three years. Treatment with a variety of acidic demethylating agents forms only one product, 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran (III). This cyclic ether has been prepared by methylation of the corresponding diol II which was synthesized from dimethyl *dd,ll*-diphenylsuccinate (I) and methyl iodide Grignard reagent, and the oil (IV) therefore must have the same *dd,ll* configuration (3). The ease with which this *dd,ll*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (IV) may be converted to the tetrahydrofuran might have been predicted by consideration of the hindrance which would be imposed by the bulky sub-



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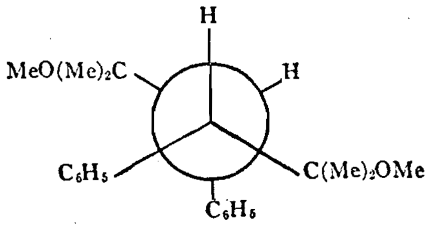
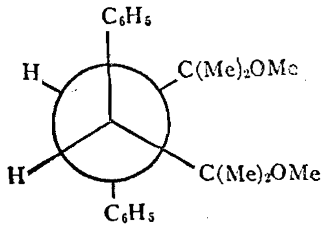
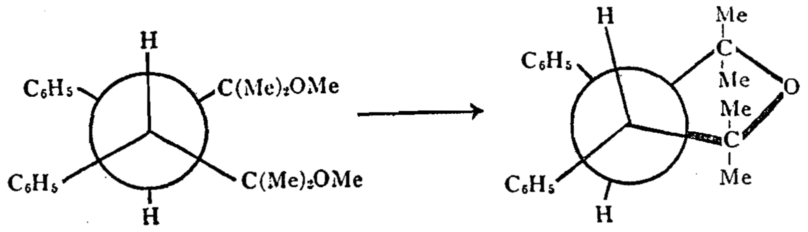
Contribution from Department of Chemistry, University of Toronto, Toronto, Ont.



IV*b*



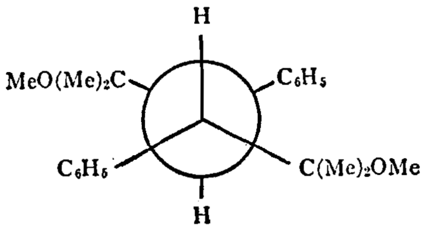
IV*c*



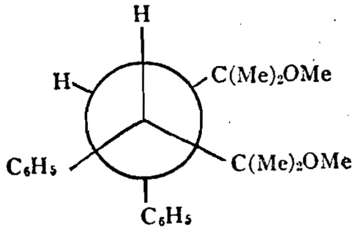
IV*a*

dd,ll-III

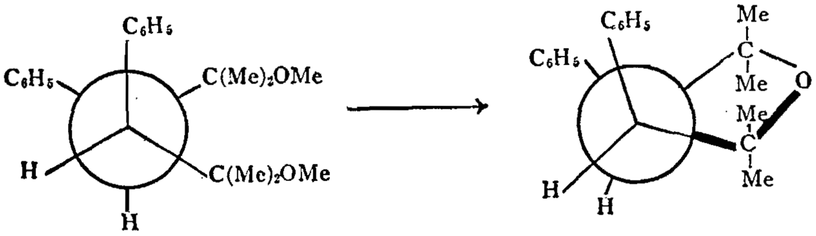
stituents. Thus of the three possible rotamers*, IV*a*, *b*, *c*, that one (IV*a*) which might be expected to be in preponderance because of symmetrical disposition and minimum in crowding of the substituent group is also the rotamer in which pivotal rotation to form *dd,ll*-III would separate the phenyl groups (compare IV*a* with *dd,ll*-III).



V*b*



V*c*



V*a*

meso-III

**The term "rotamer" (7) seems to us so much more appropriate than "restriction isomer" (11) that we have abandoned the latter term in favor of the former. However the concept of electrostriction is implicit in any discussion of these isomers.*

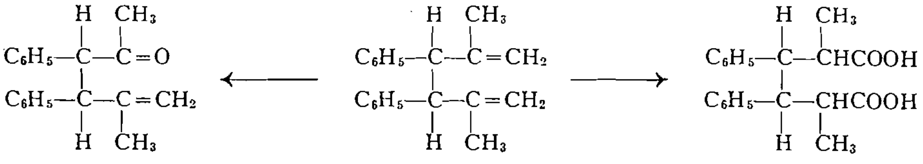
The solid 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) must necessarily be the *dl,ld* (*meso*) diastereomer. If one examines the structures corresponding to rotamers it is evident that the most symmetrical form (V*b*, which probably represents all of this diastereomer in the solid form) will have the conformation least favorable for cyclization to the diastereomeric 2,2,5,5-tetramethyl-3,4-diphenyltetrahydrofuran (*meso*-III). Furthermore conversion of either of the enantiomeric forms (V*a* or V*c*) to *meso*-III would be hindered to the extent that pivotal rotation would bring the phenyl groups closer together. In consequence it might be expected that this cyclization would occur with difficulty; this is found to be the fact. However the cyclization does occur under the unique influence of hydriodic acid in boiling dioxane. The product is evidently *meso*-III since it contains neither hydroxyl groups nor aliphatic unsaturation and its ultraviolet absorption spectrum is almost identical with that of *dd,ll*-III.

This method for preparation of *meso*-III is better than mixtures of hydrobromic and acetic acids which were used by Berman *et al.* (1) to obtain the same compound to which they did not assign a structure. But it should be noted that one of these two methods is required for the formation of *meso*-2,5-dimethyl-3,4-diphenyltetrahydrofuran (III), in contrast to formation of the *dd,ll* diastereomer which occurs in diverse reaction media.

In further contrast the formation of the *meso* (but not the *dd,ll*) diastereomer III is accompanied by at least one by-product. The isolable contaminant is 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI), the preparation of which has previously been described (1) as the treatment of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) with sodium chloride, acetic anhydride, and sulphuric acid.

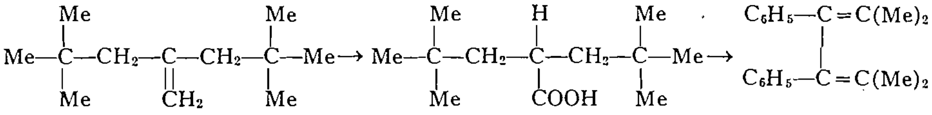
We have reinvestigated the diene VI and have improved its mode of preparation by use only of potassium bisulphate and acetic anhydride. We have also confirmed the structure of VI by ozonolysis and by catalytic reduction (with difficulty) to *meso*-2,5-dimethyl-3,4-diphenylhexane (VII) (8). This additional proof has been welcome. One might normally expect that the elimination of two molecules of methanol from V would lead to 2,5-dimethyl-3,4-diphenylhexadiene-2,4 (XII) instead of the nonconjugated 1,5-diene (VI) which actually is obtained. But such an expectation does not take into account the steric aspects of the diene XII.

However our oxidation of the isolated diene VI may explain why the conjugated diene was not obtained by demethanolation. With chromium trioxide in acetic acid four products have been isolated besides unchanged VI. In addition to benzoic acid, two diastereomeric acids have been isolated as their esters, which conform in analysis with that expected for dimethyl *ddld,lldl*- and *ddll,lldd*-2,5-dimethyl-3,4-diphenyladipates. Finally a ketone has been isolated in small amount as its dinitrophenylhydrazone; according to analysis this is 5-methyl-3,4-diphenylhexen-5-one-2 (VIII). One might expect this partial oxidation product of an ordinary nonconjugated diene. The dimethyldiphenyladipic acids (IX) are unexpected except as one considers the unusual oxidations of hindered alkenes such as 1,1-dineopentylethene (X) (4, 10). This



VIII VI IX

compound yields dineopentyl acetic acid (XI) which, like IX, contains the same number of carbon atoms as does the alkene. In view of similar evidence of hindrance in our derivatives of diphenylethane it may not be surprising that



X XI XII

no method of methanol removal from the 2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexanes (IV and V) has yet produced the conjugated diene XII.

The practical preparation of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI) by potassium bisulphate and acetic anhydride does produce, in trace yield, another hydrocarbon of the same empirical formula, but it is not XII. Instead we believe it to be 1,1-dimethyl-3-isopropenyl-2-phenylindane (XIII) which may be prepared more satisfactorily by a two-step reaction. When *meso*-dimethoxydimethyldiphenylhexane (V) is treated with the Lucas reagent (equimolar mixture of zinc chloride and concentrated hydrochloric acid) two moles of methanol are eliminated and one mole of hydrogen chloride is added. We believe the product to be 2-chloro-2-[3,3-dimethyl-2-phenylindanyl]-propane, XIV. Treatment of XIV with alcoholic sodium hydroxide or alumina leads to the dimethylisopropenylphenylindane (XIII).

The empirical formula of XIII is established as $C_{20}H_{22}$ by elemental analysis and molecular weight determinations. The presence of the terminal double bond has been established by ozonolysis, from which a 35% yield of the dimedone derivative of formaldehyde may be isolated. This yield, under the conditions of the entire ozonolysis procedure, indicates one double bond per $C_{20}H_{22}$ unit (9). Moreover indirect proof establishing the presence of the phenylindane nucleus is afforded by examination of a second product obtained during preparation of the tertiary chloride, XIV.

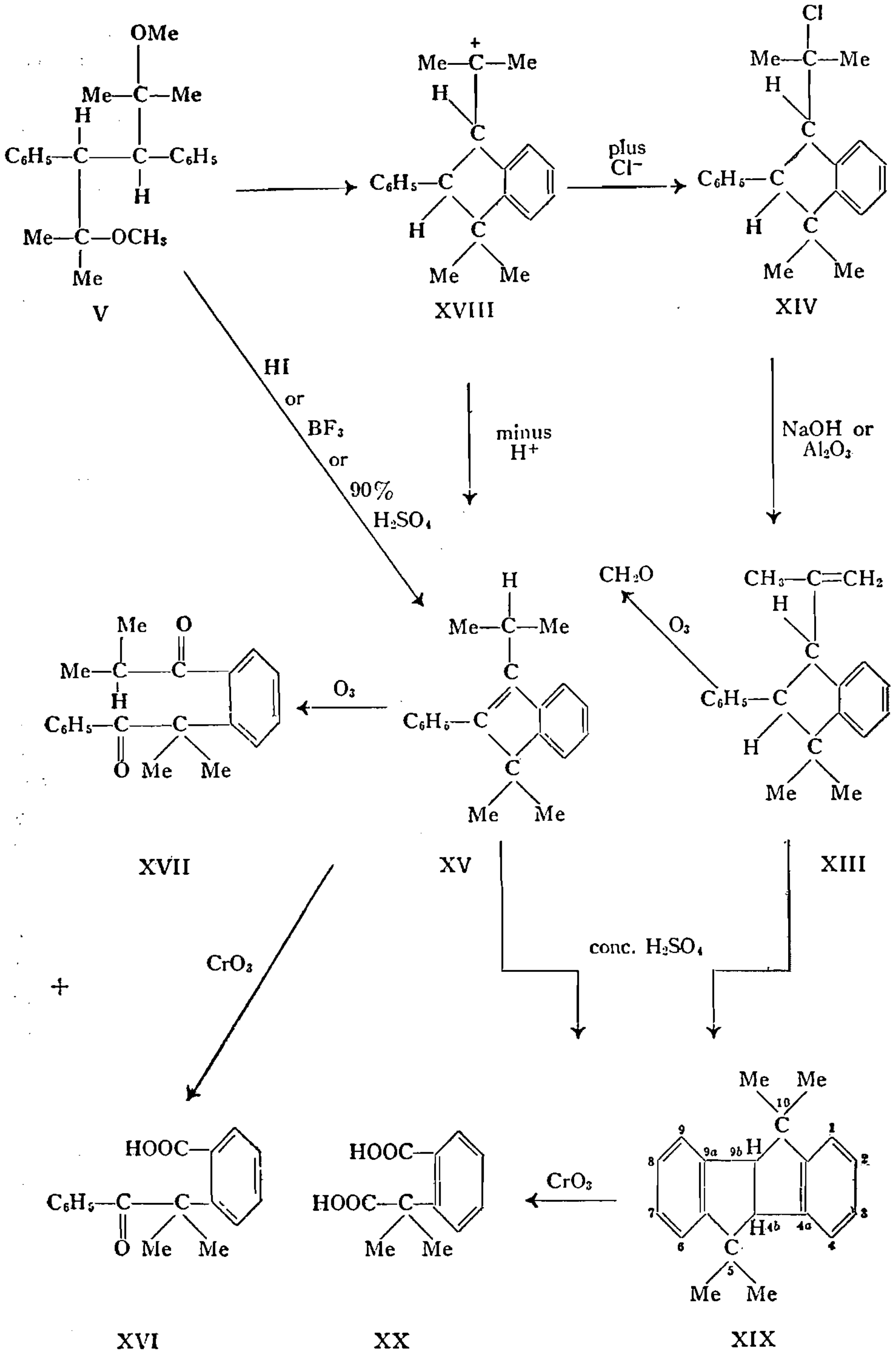
Actually this second product is the major one (40 versus 17%) and like XIII, has the empirical formula $C_{20}H_{22}$. This product, 3,3-dimethyl-2-phenyl-1-isopropylindene (XV) may also be formed from *meso*-dimethoxydimethyldiphenylhexane (V) by reflux with 50% hydriodic acid (76%) or by boron fluoride etherate in boiling petroleum ether (60%) or by 90% sulphuric acid at room temperature (50% yield). This compound has been assigned structure XV for several reasons. Firstly it resists hydrogenation at 20–50° with either platinum or nickel up to 1500 lb. gauge pressure and bromine will not add to it, although substitution seems to occur. Secondly the compound behaves as a highly-conjugated aromatic system: it imparts a deep red color to tetranitromethane, and its ultraviolet absorption resembles that of stilbene. In conformity with this similarity it reacts with sodium to form a highly-colored adduct in 1,2-dimethoxyethane (3).

The substance believed to be 3,3-dimethyl-1-isopropyl-2-phenylindene (XV) does undergo ozonization, but none of formaldehyde, acetaldehyde, or acetone can be detected among the products. However a diketone, $C_{20}H_{22}O_2$, has been isolated as its mono 2,4-dinitrophenylhydrazone. Since no carbon atoms are lost the keto linkages are evidently the result of oxidative fission of the indene double bond. In addition to this diketone the ozonization yields an acid believed to be *o*-carboxyphenylisopropiophenone (XVI) on the basis of analysis and neutralization equivalent. The keto group in this acid is nonreactive, and this property might be expected if XVI existed in ketol form. If this acid is considered to be an oxidative degradation product of the diketone then the latter may be formulated as *o*-isobutyrylphenylisopropiophenone (XVII).

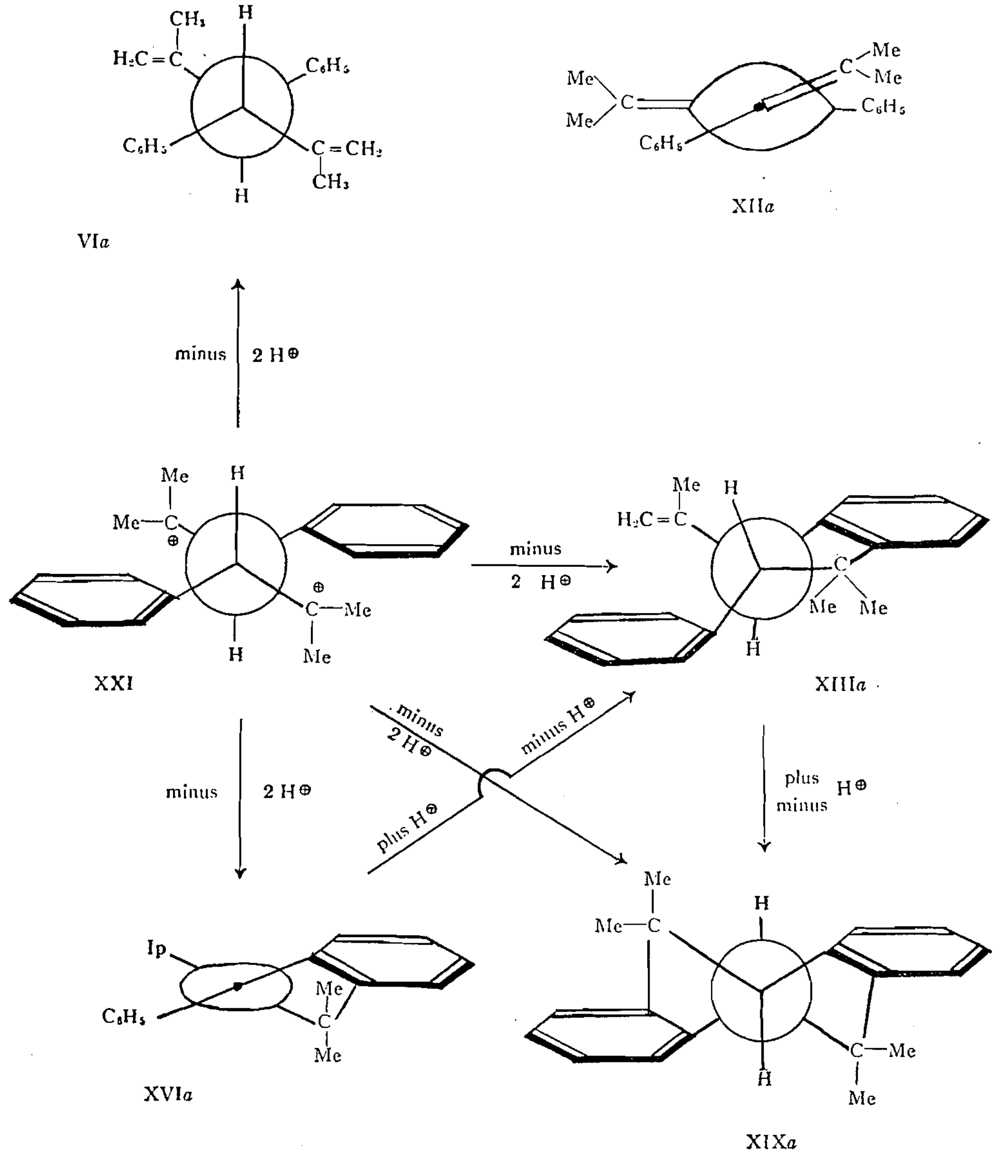
We believe that this evidence justifies the formulation of 3,3-dimethyl-1-isopropyl-2-phenylindene (XV). Since this structure is isomeric with that of 3,3-dimethyl-1-isopropenyl-2-phenylindane (XIII) the characterization of XV would tend to support that of XIII. Thus the formation of XV and (via XIV) of XIII may be presumed to proceed through an intermediate portrayed for convenience as the electropositive particle XVIII. The reaction resembles that by which 1,1-dimethyl-3-phenyl-1-propanol is converted to 1,1-dimethylindane (2) by means of 85% sulphuric acid.

According to this postulation the Friedel-Crafts type of cyclization which produces XIII and XV ought to continue further through the intermediate cation XVIII (under conditions wherein it was sufficiently stable) to form 5,5,10,10-tetramethyl-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]indene (XIX). Actually a compound conforming with this analysis and molecular weight may be formed by treatment of either XIII or XV or even V with concentrated sulphuric acid. However the tetracyclic XIX can best be prepared by treatment of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (V) with anhydrous hydrofluoric acid. We believe the tetracyclic structure XIX to be authentic because no reaction occurs with ozone, because the ultraviolet absorption spectrum closely resembles that of XIII and of indane itself, and finally because chromic acid oxidation gives the known α,α-dimethylhomophthalic acid, XX.

Earlier in this report it has been suggested that bulky substituents on the central carbon atoms in diphenylethane tend to cause restriction about the pivotal linkage. According to this postulation the most stable (symmetrical) form of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane, V*b*, would form the cyclic ether, *meso*-2,5-dimethyl-3,4-diphenyltetrahydrofuran (*meso*-III), with difficulty in contrast to the easy conversion of IV to *dd,ll*-III. On the other hand inspection of structure V*b* shows that this spatial conformation is favorable to removal of methanol by a Friedel-Crafts mechanism via intermediates which (for purposes of illustration) may be represented by the dication XXI. Loss of two protons may thus lead with conformational con-


V
XVIII
XIV
plus Cl⁻
HI or BF₃ or 90% H₂SO₄
minus H⁺
NaOH or Al₂O₃
XVII
XV
XIII
O₃
CH₂O
O₃
CrO₃
conc. H₂SO₄
XVI
XX
XIX
CrO₃

venience to the indane, XIII*a*, or the indene, XVI*a* (the latter being convertible by proton exchange to the former), while the same convenience may lead directly by proton loss from XXI to the indeno-indene (XIX*a*), also by proton exchange from XIII*a*. These Friedel-Crafts processes do not preclude



direct proton loss from XXI to the nonconjugated diene VI*a*, but it may be seen that steric hindrance prevents the coplanarity expected for conjugation in the formation of XII*a*. The series of products arising from methanol fission from *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) thus are expected ones from the aspect of steric restriction. However the specificity in respect of which the several products are formed in different reaction media shows that free-cationic structures such as XXI are probably fallacious and are certainly inadequate from the aspect of prediction. Such prediction may become possible when more is known about the co-ordination complexes of which free-ionic structures such as XXI represent a simplification.

EXPERIMENTAL*

meso-2,2,5,5-Tetramethyl-3,4-diphenyltetrahydrofuran (*meso-III*)

A solution of 0.5 gm. (0.00153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane, m.p. 137–138° C., and 0.30 ml. (0.0017 mole) of hydriodic acid (density 1.57) in 7.5 ml. of dioxane was boiled under reflux for eight hours, then poured into ice and the solid, m.p. 70–78° C. (0.37 gm., 86%), was filtered off. This crude product was extracted with 0.5 ml. of 95% ethanol leaving 2 mgm., m.p. 159–163° C., of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 (VI). Evaporation of the extract left a residue, m.p. 84–87° C., which was heated at 80° C. (10 mm.) for two days. The residue, after this sublimation of impurities, weighed 0.23 gm. (53%), m.p. 92–93° C. This compound showed neither addition nor active hydrogen in the Grignard machine and it contained no methoxyl function. The ultraviolet absorption spectrum comprised a single peak at 260 mμ with $E_{\text{molar}} = 350$. The spectrum resembled closely that of the *dd,ll* diastereomer ($E_{\text{molar}} = 325$), except that absorption was slightly greater throughout the curve.

2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (*VI*)

A solution of 5.0 gm. (0.0153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 2.1 gm. (0.0154 mole) of anhydrous po-

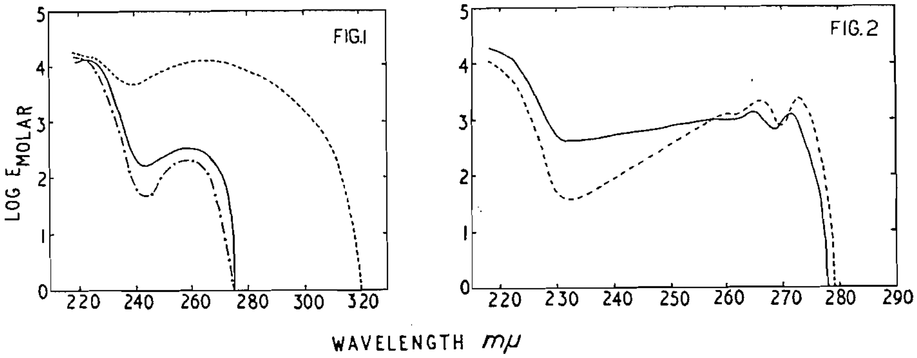


FIG. 1. ------ 3,3-Dimethyl-1-isopropyl-2-phenylindene (XV)
———— *meso*-2,5-Dimethyl-2,5-dimethoxy-3,4-diphenylhexane (V)
—·—·—2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)
FIG. 2. ------ 5,5,10,10-Tetramethyl-4*b*,5,9*b*,10-tetrahydroindeno[2,1-*a*]indene (XIX)
———— 1,1-Dimethyl-3-isopropenyl-2-phenylindane (XIII)

**Melting points have been corrected against reliable standards. X-ray diffraction patterns are recorded as relative intensities* [I/I_1] *at d spacings in Å using* CuK_α *radiation* (*Ni filtered*). *Only the strongest lines were recorded.*

tassium bisulphate in 50 ml. of acetic anhydride was boiled under reflux for four hours, then diluted with ice. The crude precipitate was water-washed, 3.15 gm., m.p. 90–143° C. It was dissolved in 30 ml. of hot absolute ethanol, filtered, and cooled, yielding 1.24 gm. (31%) of VI, m.p. 161–163° C. A mixture melting point with the substance reported previously (1) was not lowered. The ultraviolet absorption spectrum is shown in Fig. 1 for an ethanolic solution (4.21×10^{-5} moles per liter).

The ethanolic mother liquors were evaporated and the residue, m.p. 67–93° C., was sublimed at 65° C. (8 mm.), yielding 91 mgm., m.p. 71–74° C. (2%), of impure 1,1-dimethyl-3-isopropenyl-2-phenylindane (XIII).

Oxidation of meso-2,5-Dimethyl-3,4-diphenylhexadiene-1,5 (VI)

A mixture of VI (1.25 gm., 0.0048 mole) and 1.87 gm. (0.0187 mole) of dichromium trioxide, 50 ml. of acetic acid and 1.5 ml. (0.0833 mole) of water was heated at 90–100° C. with stirring for one hour, then diluted with 50 ml. of water. The insoluble phase was filtered and dissolved in 10 ml. of diethyl ether plus 10 ml. of 5% aqueous sodium hydroxide. The etherous phase, washed with water, then dried and evaporated, left 97 mgm., m.p. 137–152° C. Crystallization from 1 ml. of absolute ethanol left 53 mgm. (4%) of unchanged VI, m.p. 159–162° C. The alkaline phase was acidified with concentrated hydrochloric acid. The precipitate, 0.207 gm. (13%), m.p. 305–308° C., was crystallized from acetic acid (120 ml. per gm.), m.p. 325–326° C. Strongest lines of the X-ray powder diagram are: [10] 4.21, 4.00; [7] 5.71, 4.69, 4.48, 3.83. Neut. equiv. calc. for $C_{20}H_{22}O_4$, 163; found, 155. This diastereomer of 2,5-dimethyl-3,4-diphenyladipic acid (IX) was converted by etherous diazomethane into the methyl ester, crystallized from methanol, 100 ml. per gm., m.p. 108–109° C. Calc. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.39. Found: C, 74.8; H, 7.41.

The original drowned reaction system from which VI and one diastereomer of IX had been removed by filtration was twice-extracted with 25-ml. portions of ether. This ether was water-washed and then thrice-extracted with 5-ml. portions of 5% aqueous alkali. The etherous phase was then evaporated leaving 0.372 gm. of an oil, 50 mgm. of which was treated with 1 ml. of a methanolic solution of 2,4-dinitrophenylhydrazine containing hydrogen chloride. The dinitrophenylhydrazone of 5-methyl-3,4-diphenylhexen-5-one-2 (VIII) (30 mgm., m.p. 211–214° C.) was twice-crystallized from 1:1 ethanol – ethyl acetate (0.16 ml. per mgm.), m.p. 230–230.5° C. Calc. for $C_{25}H_{24}N_4O_4$: C, 67.6; H, 5.44; N, 12.6. Found: C, 68.2; H, 5.36; N, 12.4.

The combined alkaline extract of the etherous solution of VIII was acidified with concentrated hydrochloric acid. The gummy precipitate (0.475 gm.) was removed. The remaining aqueous phase, by ether extraction and sublimation after evaporation of the ether, yielded 11 mgm. (2%) of benzoic acid. The gummy precipitate was boiled under reflux with 2 ml. of methanol containing 10 mgm. of 96% sulphuric acid for three hours, then cooled to 0° C. This crude second diastereomer of dimethyl 2,5-dimethyl-3,4-diphenyladipate (ester of IX), 25 mgm., m.p. 130–140° C., was four times crystallized from 0.5 ml. of methanol, m.p. 163–164.5° C. Calc. for $C_{22}H_{26}O_4$: C, 74.5; H, 7.39. Found: C, 74.1; H, 7.45.

meso-2,5-Dimethyl-3,4-diphenylhexane (VII)

A solution of 80 mgm. (0.000306 mole) of 2,5-dimethyl-3,4-diphenylhexadiene-1,5 in 10 ml. of absolute ethanol containing 1 gm. of Raney nickel catalyst (W-1) was shaken 19 hr. with hydrogen at 1500 lb. pressure. The system was filtered and evaporated, leaving 63 mgm. (79%) of *meso*-dimethyldiphenylhexane, m.p. 149–150.5°. A mixture melting point with authentic material (7) was not depressed.

dl,ld-2-Chloro-2-[3,3-dimethyl-2-phenylindanyl]-propane (XIV)

A system comprising 1.00 gm. (0.00306 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 4.1 gm. (0.03 mole) of zinc chloride in 2.5 ml. (0.03 mole) of concentrated hydrochloric acid was stirred for 12 hr. The oily solid was taken up in 15 ml. of petroleum ether (b.p. 40–60° C.); the solution was washed thoroughly with water, then dried, and evaporated. The crude 3,3-dimethyl-1-isopropyl-2-phenylindene (XV, 0.861 gm.) was crystallized from 5 ml. of hot methanol, 0.322 gm. (40%), m.p. 67–68° C. A mixture melting point with the compound described later in this report was not depressed.

The methanolic filtrate was diluted to a volume of 10 ml., chilled to −80°C., and filtered to separate 0.16 gm. (18%) of the crude chloro compound XIV, m.p. 78–83° C. After two recrystallizations it melted at 89–90.5° C. and still gave a positive halide test with alcoholic silver nitrate. Calc. for $C_{20}H_{23}Cl$: C, 80.4; H, 7.76. Found: C, 79.7; H, 7.85.

3,3-Dimethyl-1-isopropenyl-2-phenylindane (XIII)

A. From XIV with Alcoholic Alkali

A solution of 0.23 gm. (0.01 atom) of metallic sodium in 3 ml. of absolute ethanol was combined with 0.076 gm. (0.000255 mole) of XIV in 1 ml. of the same solvent and boiled for two hours under reflux, then cooled, and diluted with 50 ml. of water. After slow separation the crude dimethylisopropenylphenylindane (XIII), 66 mgm. (99%), m.p. 67–73° C., was crystallized from hot methanol (1 ml. per gm.), m.p. 76–77° C. Mol. wt. (Rast) was calculated as 262; found 258. The X-ray powder pattern was: [10] 5.40, 5.18; [5] 3.80; [4] 6.32, 4.46, 4.07, 3.66. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45. Found: C, 91.7; H, 8.61.

B. From XIV with Alumina

The crude reaction product from the preparation of XIV described above (0.837 gm.) was dissolved in 5 ml. of petroleum ether (b.p. 40–60° C.). This solution, on a 1.5 × 45 cm. column of alumina, was eluted with the same solvent yielding 0.486 gm. (61%) (75 ml. eluent) of 3,3-dimethyl-1-isopropyl-2-phenylindene (XV, m.p. 67–69° C.), 0.080 gm. (25 ml. eluent) of intermediate fraction, m.p. 50–65° C., and 0.242 gm. (30%) (100 ml. eluent) of 3,3-dimethyl-1-isopropenyl-2-phenylindane (XIII, m.p. 73–75° C.). The ultraviolet absorption spectrum of XIII is shown in Fig. 2.

Ozonization of 3,3-Dimethyl-1-isopropenyl-2-phenylindane (XIII)

A solution of 0.102 gm. (3.88×10^{-4} mole) of XIII in 6 ml. of pre-ozonized and purified carbon tetrachloride was treated with 1.8 liters of 6% ozonized oxygen at 0° during 100 min. The solid ozonide was hydrolyzed with 20% acetic acid and 150 mgm. of zinc dust in the carbon tetrachloride medium at 40–50° C. with a stream of nitrogen bubbling through. No acetone could be detected in the effluent gas by acid-methanolic 2,4-dinitrophenylhydrazine. The nonaqueous layer was removed.

The aqueous layer was distilled almost completely and the distillate adjusted to pH 4.0–4.5 with acetic acid and sodium hydroxide; then 0.1 gm. of dimedone in 30 ml. of water was added. The precipitate, methylene-*bis*-dimethyldihydroresorcinol, weighed 0.386 gm., m.p. 188–189° C., mixture melting point with authentic material not lowered. Yield of formaldehyde is thus 34.6% based on one methylene group per mole of XIII.

3,3-Dimethyl-1-isopropyl-2-phenylindene (*XV*)

A system comprising 5.0 gm. (0.0153 mole) of *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III) and 70 ml. of hydriodic acid (density 1.54) was boiled under reflux for 12 hr., then poured into ice. The crude product, 4.12 gm., m.p. 55–62° C., was dissolved in 10 ml. of hot methanol and the solution was cooled to 0° C. The crystals, 3.06 gm. (76%), m.p. 68.5–69.5° C., were recrystallized from hot methanol (2 ml. per gm.), m.p. 69–70° C. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45. Found: C, 91.3; H, 8.65.

The X-ray powder pattern of XV is: [10] 4.19; [9] 4.72; [8] 7.49, 6.96, 6.15, 5.71. The ultraviolet absorption spectrum in absolute ethanol (4.32×10^{-5} moles per liter) is shown in Fig. 1. *meso*-III may also be converted to XV in 50% yield by 90% sulphuric acid at 25° C. or in 60% yield by boron fluoride etherate in boiling petroleum ether (b.p. 40–60° C.).

Disodium Adduct of XV

A solution of 0.26 gm. (0.001 mole) of dimethylisopropylphenylindene (XV) in 7 ml. of 1,2-dimethoxyethane was shaken with 0.10 gm. (0.0041 atom) of sodium under nitrogen. A deep red color appeared at once. After three days the system was treated with gaseous carbon dioxide; then the dimethoxyethane was vacuum-evaporated and replaced with 10 ml. each of diethyl ether and water. The etherous phase, water-washed, dried, and evaporated left 0.13 gm. (50%) of an oily solid which, crystallized from 2 ml. of methanol, gave 50 mgm. (19%) of unchanged XV.

The alkaline phase was acidified with concentrated hydrochloric acid to precipitate 0.13 gm., m.p. 156–175° C. From this mixture was isolated a few milligrams of pure compound by crystallization from 85: 15 petroleum ether (b.p. 60–70° C.) – benzene (30 ml. per gm.), m.p. 203–204° C. Calc. for $C_{21}H_{24}O_2$: C, 81.7; H, 7.85. Found: C, 81.8; H, 8.04. According to this analysis the compound is 3,3-dimethyl-1-isopropyl-2-phenyl-1 or 2-indanecarboxylic acid. However if the hydrogen value were slightly in error the compound could be 3,3,3′,3′-tetramethyl-1,1′-diisopropyl-2,2′-diphenylbiindanyldicarboxylic acid.

Ozonization of XV

A solution of 1.04 gm. (0.004 mole) of XV in 25 ml. of preozonized and purified carbon tetrachloride was treated with 4.1 liters of 5% ozonized oxygen during three hours. The solvent was vacuum-evaporated and the residual oily ozonide was hydrolyzed by heating it under reflux with 15 ml. of water, 300 mgm. of zinc dust, and 1 mgm. each of hydroquinone and silver nitrate. The mixture was filtered, the zinc was washed with 15 ml. of benzene, and the phases were separated. The aqueous phase was warmed to 40–50° and a stream of nitrogen was bubbled through it. No acetone in the effluent could be detected by dinitrophenylhydrazine reagent. The aqueous layer was then distilled, but dimedone showed the absence of any formaldehyde in the distillate.

The benzene phase was extracted once with 10 ml. of 10% aqueous sodium hydroxide and twice with 5-ml. portions of water. The combined extracts were acidified with concentrated hydrochloric acid, precipitating 0.130 gm., m.p. 173–190° C. This crude *o*-carboxyphenylisopropiophenone (XVI) was crystallized from 2 ml. of benzene, 0.115 gm. (11%), m.p. 208.5–209.5° C. Potentiometric titration showed $K_A = 4.5 \times 10^{-7}$. Calc. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.01; neut. equiv., 268. Found: C, 75.8; H, 6.04; neut. equiv., 256. The mother liquor from the crystallization yielded 1% of benzoic acid.

The benzene phase from which XVI was alkali-extracted was dried and then evaporated. When the oily residue (0.956 gm.) was treated with excess acid-methanolic 2,4-dinitrophenylhydrazine a derivative (0.446 gm.) was obtained, m.p. 201–203° C. This dinitrophenylhydrazone of *o*-isobutyrophenylisopropiophenone (XVII) was crystallized from acetic acid (20 ml. per gm.), m.p. 206–207° C. Calc. for $C_{26}H_{26}N_4O_5$: C, 65.8; H, 5.52; N, 11.8. Found: C, 65.3; H, 5.51; N, 11.9.

When the ozonide of XV was heated in water alone (oxidative hydrolysis) a 28% yield of benzoic acid and a 13% yield of XVI was isolated, but none of the carbonyl-containing XVII was found. If, instead of ozonization, XV was oxidized with sodium dichromate – sulphuric acid in acetic acid the only isolable product was XVI.

5,5,10,10-Tetramethyl-4b,5,9b,10-tetrahydroindeno[2,1-a]indene (XIX)

A. From meso-III and Concentrated Sulphuric Acid

The *meso*-2,5-dimethoxy-2,5-dimethyl-3,4-diphenylhexane (*meso*-III, 0.50 gm., 0.00153 mole) was added to 5.0 ml. of concentrated sulphuric acid at 25° C. A bright red color appeared and an oil separated which crystallized after seven hours. The system was drowned with ice and the crude solid (88 mgm., 22%, m.p. 78–79° C.) was crystallized from 0.5 ml. of hot methanol, 51 mgm. of XIX, m.p. 82–83° C. Variation in time, temperature, or amount of sulphuric acid did not alter the yield. Calc. for $C_{20}H_{22}$: C, 91.5; H, 8.45; Mol. wt. (Rast), 262. Found: C, 91.5; H, 8.62; mol. wt. (Rast), 270.

B. From meso-III and Hydrogen Fluoride

The *meso*-III (2.50 gm., 0.077 mole) was added to 160 gm. of liquid hydrogen fluoride at −80° C. in a polythene bottle. A bright orange color developed.

The mixture was stirred for three to five hours at 0° C. and then was poured into ice. The aqueous mixture was extracted with 100 ml. of diethyl ether. This extract was washed with 10% aqueous alkali, then with water, and dried. The residue left by ether evaporation (1.93 gm., m.p. 70–77° C.) was crystallized from 7 ml. of hot methanol, 1.47 gm. (73%), m.p. 82–83° C. No reduction was apparent when the product was boiled for three hours with an excess of sodium in ethanol. XIX was also recovered after treatment with ozone. The ultraviolet absorption spectrum of XIX, Fig. 2, resembles that of indane when determined in absolute ethanol (5.30×10^{-5} moles per liter).

C. From Dimethylisopropenylphenylindane (XIII) and Sulphuric Acid

When 31.1 mgm. (1.19×10^{-5} mole) of XIII was added to 3.0 ml. of 96% sulphuric acid at 0° C. it liquefied and a yellow color appeared. After six hours the oil solidified. The solid obtained after drowning with ice weighed 10.6 mgm. (34%), m.p. 81–82° C., mixture melting point with material from *A* and *B* not lowered.

D. From Dimethylisopropylphenylindene (XV) and Sulphuric Acid

The hydrocarbon (XV, 10 mgm., 3.9×10^{-3} mole) was added to 0.10 ml. of 96% sulphuric acid at 20° C. A yellow color appeared but the solid did not liquefy rapidly. After five hours ice was added and the solid filtered, 2 mgm., m.p. 79–80° C. A mixture melting point with material prepared according to *A*, *B*, or *C* was not lowered. The product was recovered: 99% after one day at 15 lb. hydrogen pressure with Adams' platinum catalyst, 75% after shaking with Raney nickel catalyst (W-2) at 1500 lb. hydrogen pressure either at 25° C., 55° C., or 80° C.

Bromination of Tetramethyltetrahydroindenoindene (XIX)

A solution of 0.52 gm. (0.002 mole) of XIX in 20 ml. of carbon tetrachloride with 0.64 gm. (0.008 mole) of bromine became colorless after eight hours and 0.64 gm. (0.0051 mole) of hydrogen bromide was evolved. Evaporation of the system left 0.801 gm. which was crystallized from benzene (20 ml. per gm.) finally to melt at 313–314° C. Elemental analysis showed the compound to contain bromine although it would not react with alcoholic silver nitrate. The X-ray diffraction powder diagram was: [10] 5.68, 5.52; [9] 3.33; [6] 6.25, 6.00, 3.85, 3.75. Calc. for $C_{20}H_{18}Br_2$: C, 57.4; H, 4.34. Found: C, 58.0; H, 4.46.

The first mother liquor from the benzene crystallization was evaporated and treated to get a steam distillate, 0.22 gm., m.p. 75–105° C. Repeated crystallization from petroleum ether (b.p. 60–70° C., 15 ml. per gm.) and from absolute ethanol (15 ml. per gm.) left 10 mgm., m.p. 206–207° C. Calc. for $C_{20}H_{19}Br$: C, 70.8; H, 5.64. Found: C, 70.7; H, 5.78.

Oxidation of Tetramethyltetrahydroindenoindene (XIX)

Either hot aqueous nitric acid or potassium permanganate seems to be inadequate as an oxidizing agent for XIX, but chromic acid is effective. A mixture of 12.0 gm. (0.04 mole) of sodium dichromate dihydrate in 43 ml. of 50 volume per cent aqueous sulphuric acid and 30 ml. of acetic acid was stirred for 20 hr. with 2.08 gm. (0.008 mole) of XIX.

The system was then diluted with 50 ml. of water and extracted with 70 and then 20 ml. of diethyl ether. The etherous phase was washed with water, then extracted with alkali followed by water. The etherous phase was then dried and evaporated, leaving 1.05 gm. of gum which was crystallized from 5 ml. of hot absolute ethanol, 0.32 gm. (13%), m.p. 203–205° C. (after recrystallization, 205–205.5° C.). Calc. for $C_{20}H_{20}O_3$: C, 77.9; H, 6.53. Found: C, 78.3; H, 6.65. This product of unknown structure was recovered unchanged after long heating with hot 15% alkali in which it was insoluble. It reacted neither with hot hydrogen bromide in acetic acid nor with hydrogen in presence of Adams' platinum catalyst. It was also inert toward chromic acid and permanganate (in acetone) oxidation.

Evaporation of the mother liquor from the ethanolic crystallization of the 1.05 gm. of gum left a residue, m.p. 60–70° C., which was extracted with 10 ml. of hot petroleum ether (b.p. 40–60° C.). When cool the insoluble portion (0.288 gm.) melted at 180–206° C. while the solution, evaporated, left 0.508 gm., m.p. 65–75° C. The latter was crystallized from 2 ml. of hot methanol, 0.354 gm. (17%) of unchanged XIX, m.p. 82–83.5° C., mixture melting point not depressed. The 0.288 gm. portion was crystallized from 2 ml. of benzene, 0.035 gm., m.p. 236–240° C. For analysis this was crystallized from 1 ml. of methanol, m.p. 237–238.5° C. Calc. for $C_{20}H_{22}O_3$: C, 77.4; H, 7.14. Found: C, 77.4; H, 7.26.

The alkaline extract of the original ether solution was acidified with concentrated hydrochloric acid and then extracted with diethyl ether. This extract, dried, was evaporated, leaving 0.16 gm. which was sublimed at 100° C. (8 mm.) for 40 hr. The sublimate, 0.0983 gm., m.p. 65–72° C., was fractionally resublimed at 80° C. (10 mm.) to obtain an intermediate fraction, 52 mgm. (3%), m.p. 75–78° C. Crystallization of this crude dimethylhomophthalic anhydride from petroleum ether (b.p. 40–60° C., 10 ml. per gm.) raised the melting point to 80–81° C. Calc. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.30. Found: C, 69.5; H, 5.30. This anhydride (5 mgm.) was dissolved in 0.5 ml. of 3% aqueous sodium hydroxide, then acidified with 0.05 ml. of concentrated hydrochloric acid, yielding the dimethylhomophthalic acid (XX, m.p. 126–127.5° C.). Vacuum resublimation converted XX to the anhydride. The alkaline solution of the anhydride was potentiometrically titrated with hydrochloric acid, equivalent weight, 94.6 (calc., 95.1), approximately $K_{A_1} = 2.5 \times 10^{-4}$, $K_{A_2} = 5.6 \times 10^{-6}$. When the anhydride (5 mgm.) was dissolved in 1 ml. of 10% aqua ammonia and the solution was evaporated to dryness, either the acid-amide or the diamide must have been formed (m.p. 165–173° C.); it was sublimed at 200° C. (8 mm.), m.p. 105–109° C. This crude homophthalimide, after two crystallizations from 0.25 ml. of water, melted at 118–119° C. The melting point reported previously (5, 6) is 119–120° C.

When the ratio of XIX to oxidizing agent was decreased the amount of $C_{20}H_{20}O_3$ was increased to 14% while none of the dimethylhomophthalic anhydride could be isolated. In contrast, increase of the ratio increased the yield of the anhydride to 7%.

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DIELECTRIC RELAXATION IN CELLULOSE CONTAINING SORBED VAPORS[1]

BY R. SEIDMAN[2] AND S. G. MASON

ABSTRACT

The dielectric constant and dielectric loss factor were measured in a dispersion region for a paper of high cellulose content. The complex arrangement of the paper in the measuring condenser did not effectively alter the position of the dispersion region of the paper itself, as shown by electrical analysis. From this analysis equations were derived from which the dielectric constant and maximum dielectric loss factor of the cellulose fiber were evaluated for varying amounts of sorbed water, methanol, and ethanol. The effect of each of these vapors on the position of the dispersion region was studied, measurements being performed over a range of frequency of 10 to 1000 kc.p.s., and a range of temperature of −58 to 26°C. A typical plasticizing action was observed in all three cases. This was confirmed from an analysis of the data using the theory of absolute reaction rates.

INTRODUCTION

The effect of sorbed vapors of polar compounds, particularly water, on various properties of cellulose has been extensively investigated. This communication describes a study of the influence of sorbed water, methanol, and ethanol on the dielectric properties. By analogy with other polymer systems, it was considered that the pronounced swelling action of these vapors would be reflected by definite changes in the dielectric relaxation times and related properties.

It is convenient to characterize the effective dielectric constant ϵ in terms of its vector components by the relation:

$$\epsilon = \epsilon' - i\epsilon''$$

where ϵ' is the usual dielectric constant and ϵ'' is the loss factor. The angular frequency $\omega_{\max}$ at which ϵ'' at a given temperature is at a maximum may be used to define a temperature-dependent relaxation time T defined by:

$$\mathrm{T} = \frac{1}{\omega_{\max}}$$

a measure of the ease of oscillation of the dipoles involved. This may be measured as well by the temperature T_m at which ϵ'' at a given frequency is at a maximum.

In general, log T is an approximately linear function of the reciprocal of the absolute temperature. This suggests an energy term which Eyring (16) expresses in the form:

$$\frac{1}{\mathrm{T}} = \frac{kT}{h} e^{-\Delta F^*/RT}$$

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[2] *Holder of a Fellowship from the National Research Council of Canada.*

where k and h are Boltzmann's and Planck's constants, respectively, and ΔF^* is the free energy of activation for dielectric relaxation. This can be rewritten as:

$$\frac{1}{\mathrm{T}} = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

where ΔS^* and ΔH^* are the corresponding entropy and enthalpy for dielectric relaxation.

Investigations have been made on rubber swollen in both polar and nonpolar solvents (24). From measurements at constant frequency, it was found that T_m was shifted in varying degree to lower temperatures by increases in concentration of swelling agent; at the same time there was a decrease in ΔH^*. Similar effects were produced in polyvinyl chloride by tetralin (15), diphenyl (14), and tricresyl phosphate (7), in polycaproamide by water and methanol (12), and in starch by water (20). On the other hand, the vulcanization of rubber with increasing amounts of sulphur is accompanied by regularly increasing values of ΔH^* and ΔS^* (19, 25). Stoops (26) measured the dielectric relaxation in dry cellophane. An analysis of his data shows no significant difference in the values of T whether calculated from data obtained at constant temperature or at constant frequency. There is no reason why this should not also be the case for other forms of cellulose.

Because of the softening action of water on cellulose, it was reasonable to assume that sorbed moisture facilitates dipole rotation and thus appropriately shifts the position of maximum absorption. Limited data on this effect has been reported, but the results appear to be contradictory.

Dakin and Auxier (6) measured the dielectric constant and dissipation factor of commercial papers as a function of frequency at 28°C. When observable, the frequency of maximum absorption was unaffected by the moisture content. Similar measurements by Henniger (17) at −5°C. for paper with moisture contents of 0 and 5.6% gave the same general results.

On the other hand Veith (28) measured the dissipation factor of paper at different moisture contents as a function of temperature over the range 0 to 40°C. at fixed frequencies. The temperature of maximum loss, observed only at the highest experimental frequency, 100 kc.p.s., appeared to decrease with increasing moisture content.

In view of this conflicting evidence further investigation appeared desirable. It was decided to work with a purified form of cellulose in order to eliminate effects due to high loss impurities. The working frequencies chosen were such that absorption regions appeared in the temperature range −60 to 25°C.

EXPERIMENTAL

Dielectric Cell

The cell in which the dielectric measurements were made was designed so that the amount of vapor sorbed by the cellulose could be systematically varied. It consisted of two concentric pyrex cylinders connected at a standard-taper ground-glass joint A (Fig. 1). Platinum electrodes were deposited on the

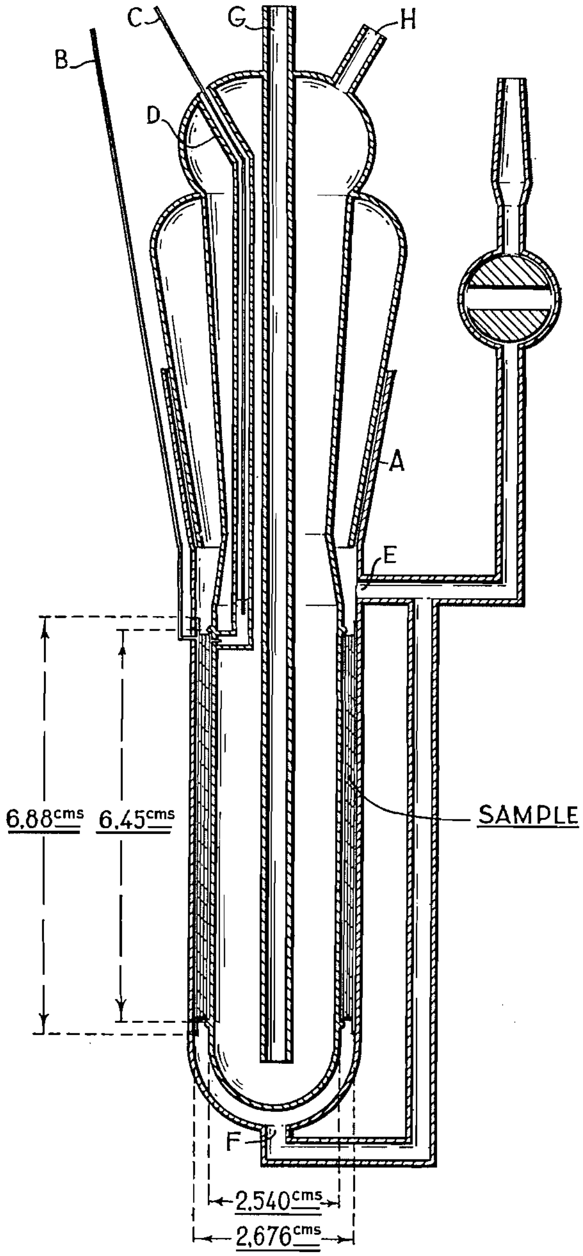


FIG. 1. Dielectric cell.

glass wall on each side of the annular space and were connected to the lead wires *B* and *C* through platinum seals. Four buttons of glass sealed both above and below the electrode on the inner cylinder served as spacers for the sample. The cell could be connected via the standard joint on the side arm to a vapor conditioning system, access of the vapor to the sample being through E and F to both ends of the annular sample space.

The cell was calibrated with dry benzene at 25.0°C. Assuming the dielectric constant of benzene at this temperature (3) to be 2.274, the geometric capacitance, C_g, was found to be 68.0 μμf., while the extraneous capacitance, C_0, including leads, was 9.0 μμf.

The cell was connected to the measuring circuits using a system of leads having a minimum length and a fixed geometry.

Electrical Apparatus

Measurements of capacitance and equivalent a-c. conductance at 1 and 0.55 Mc.p.s. were made using a General Radio Type 821-A Twin-T Impedance measuring circuit, necessary corrections being made for residual impedances, as described elsewhere (13). A General Radio Type 716-C Schering bridge was employed for measurements at lower frequencies. D-c. resistance measurements were made with a General Radio Type 1861-A Megohmmeter; the contribution of the d-c. conductance to the a-c. loss was negligible and no correction for this effect was found necessary.

Materials

The cellulose investigated was a sample from Schleicher and Schuell No. 589 Red Ribbon quantitative filter paper having an ash content of 0.007%. Microscopic examination of the paper indicated it to be a rag furnish containing 75% linen fiber and 25% cotton. The analysis was as follows:

α-cellulose	98.4%
pentosan	1.1%
cupriethylene diamine viscosity	15.7 centipoises

Saturated aqueous solutions of potassium acetate, magnesium chloride, and potassium carbonate were used for conditioning the sample to different water contents.

Absolute ethanol and absolute methanol were dried according to the method of Lund and Bjerrum (21).

Method

The vapor content was determined on a separate sample of paper to within 0.1% using a quartz spiral mounted in a sorption cell which could be connected to the dielectric cell and/or the tube containing the vapor source, all three being maintained at 25.00 ± 0.05°C. in a water bath. In this way the paper suspended from the spiral could be subjected to the same experimental conditions of temperature and relative humidity as the paper in the dielectric cell.

Throughout this work the amount of sorbed vapor was always taken up in the direction of increasing vapor contents.

A strip of paper was tightly wrapped around the inner cylinder of the dielectric cell between the spacers and held in place by means of a spot of Glyptal cement. The cell with the paper fitting snugly into the annular space was assembled and evacuated at 25.00 ± 0.05°C. for a period of 20 hr. Paper conditioned in this way is considered to be dry, although it is pointed out that a small quantity of water probably remained, amounting to as much as 0.4% (29, 30) which would require more drastic methods for removal (18).

A series of dielectric measurements (described below) was carried out.

The cell was then exposed to the potassium acetate solution for 48 hr. to establish equilibrium, disconnected, and dielectric measurements carried out as before. This procedure was repeated for each of the other salt solutions.

The dielectric runs were carried out at fixed frequencies. A dewar flask filled with toluene and fitted with a small variac-controlled heater served as bath for the cell. Some of the runs were performed by going up the temperature scale, others by going down, cooling being accomplished by means of dry ice. By determining a complete cycle at a single frequency, it was shown that there was no temperature hysteresis. Some slight exception to this was found in the work with methanol and ethanol, and will be described later.

With dry paper, *in vacuo*, a marked temperature hysteresis was observed. This resulted from the low thermal conductivity in the evacuated cell. The effect was eliminated by introducing a small amount of dry nitrogen gas, which served as a heat conductor.

In the experiments with methanol and ethanol it was necessary to avoid continuous exposure of the stopcocks in the conditioning system to alcohol vapors over the long periods (several weeks) necessary for a complete series of measurements with a given vapor. Furthermore, since methanol (23), and presumably ethanol, cannot be completely removed from cellulose by evacuation at room temperature, it appeared desirable to use as reference for the measurements not only the paper in a dry condition but paper containing these tightly held portions of alcohol as well. The following modifications of the above procedure were accordingly adopted.

Methanol vapor admitted to the conditioning system at a pressure of 60 mm. was allowed to remain in contact with the previously dried paper for two hours and the system was then evacuated over a second period of two hours. This process was repeated twice, the final evacuation being extended over a period of 12 hr., when the methanol content was 1.7%. After a series of dielectric measurements was performed, the paper was conditioned to a methanol content of 2.5% and a further series of dielectric measurements was made. The paper was then subjected to a further process of alternate methanol conditionings up to a methanol content of 7.0%. Before each conditioning, air was admitted to the system to permit regreasing of stopcocks, after which evacuation was carried out over a period of 12 hr., as before. With one exception, the amount of tightly bound methanol determined after the evacuation was always reproducible within experimental error.

After the experiments on methanol were completed, the residual alcohol was removed following the method of Russell, Maass, and Campbell (23). Water vapor was admitted to the system at 100% *R.H.* and was allowed to remain in contact with the paper for several hours. The system was then evacuated over a period of 15 hr., water vapor was readmitted, and the evacuation was repeated.

The net amount of sorbed vapor after this treatment was 0.2%; assuming this to be methanol 85% of the residue was therefore removed.

The paper was next conditioned to an ethanol content of 8.5% and the dielectric measurements were made. Evacuation of the system for six hours left 2.3% residual ethanol, none of which was removed after a subsequent evacuation lasting 14 hr. Dielectric measurements were performed at this ethanol content as well as at 4.6 and 6.9%. For reasons to be mentioned later these runs were all performed over a complete temperature cycle.

Two samples of paper were employed for dielectric measurements in the course of this work. Sample No. 1 was used for the work on water and No. 2 for the work on methanol and ethanol. The dimensions of the samples as well as the appropriate volume fractions are presented in Table I.

TABLE I
SAMPLE DIMENSIONS AND VOLUME FRACTIONS IN DIELECTRIC CELL

Sample No.	Length (in.)	Width (in.)	Paper thickness (in.)	Volume (cc.)	Dry weight (gm.)	Paper density (gm./cc.)	Vol. fraction in cell (c)
1	8.91	2.59	.0063	2.38	1.182	.496	.625
2	8.88	2.64	.0063	2.42	1.202	.496	.635

Volume of interlectrode space = 3.81 cc.

RESULTS

Water–Cellulose

The measured electrical values are expressed in terms of the dielectric constant and loss, ϵ'_2 and ϵ''_2, of the composite of multiple layers of paper as arranged in the dielectric cell. ϵ'_2 is equivalent to the term "dielectric value" employed by Tausz and Rumm (27) and Brown (4).

Results were obtained for water contents over the range 0 to 5.3% at frequencies between 30 and 1000 kc.p.s. These are presented as a function of temperature in Figs. 2*a* and 2*b*. Upon examination of the data certain salient trends are observed at once.

The temperature coefficient of ϵ'_2 is always positive. At the same time absorption regions occur at the temperature T_m where ϵ''_2 passes through a maximum value. At a fixed moisture content a decrease in frequency causes a shift of T_m to lower temperatures and an increase in ϵ'_2 at a particular temperature. Similar effects are shown for dry paper in Fig. 3, and are qualitative indications of dielectric relaxation due to dipole orientation according to the Debye theory (8).

Sorbed water produces interesting variations in the data. ϵ'_2 increases as has been observed previously (2, 4, 9, 27, 28). This follows logically from the high static dielectric constant of water, 80, compared with 6 for cellulose. In agreement with Veith (28) the effect is more pronounced at the higher temperatures. At the same time moisture causes a distinct increase in $(\epsilon''_2)_{\max}$ (see below).

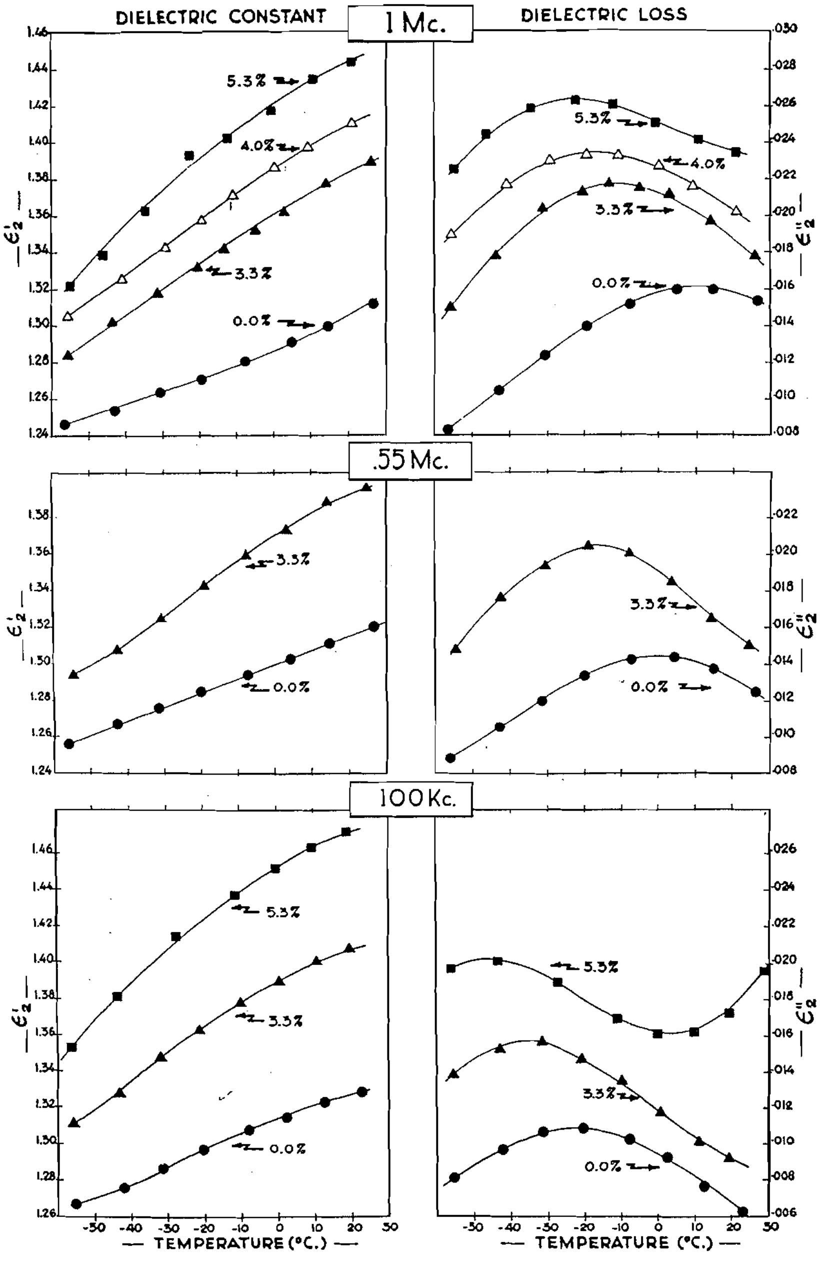


FIG. 2*a*. Dielectric dispersion at 1 Mc., 0.55 Mc., and 100 kc. of paper containing sorbed water at the inscribed percentages.

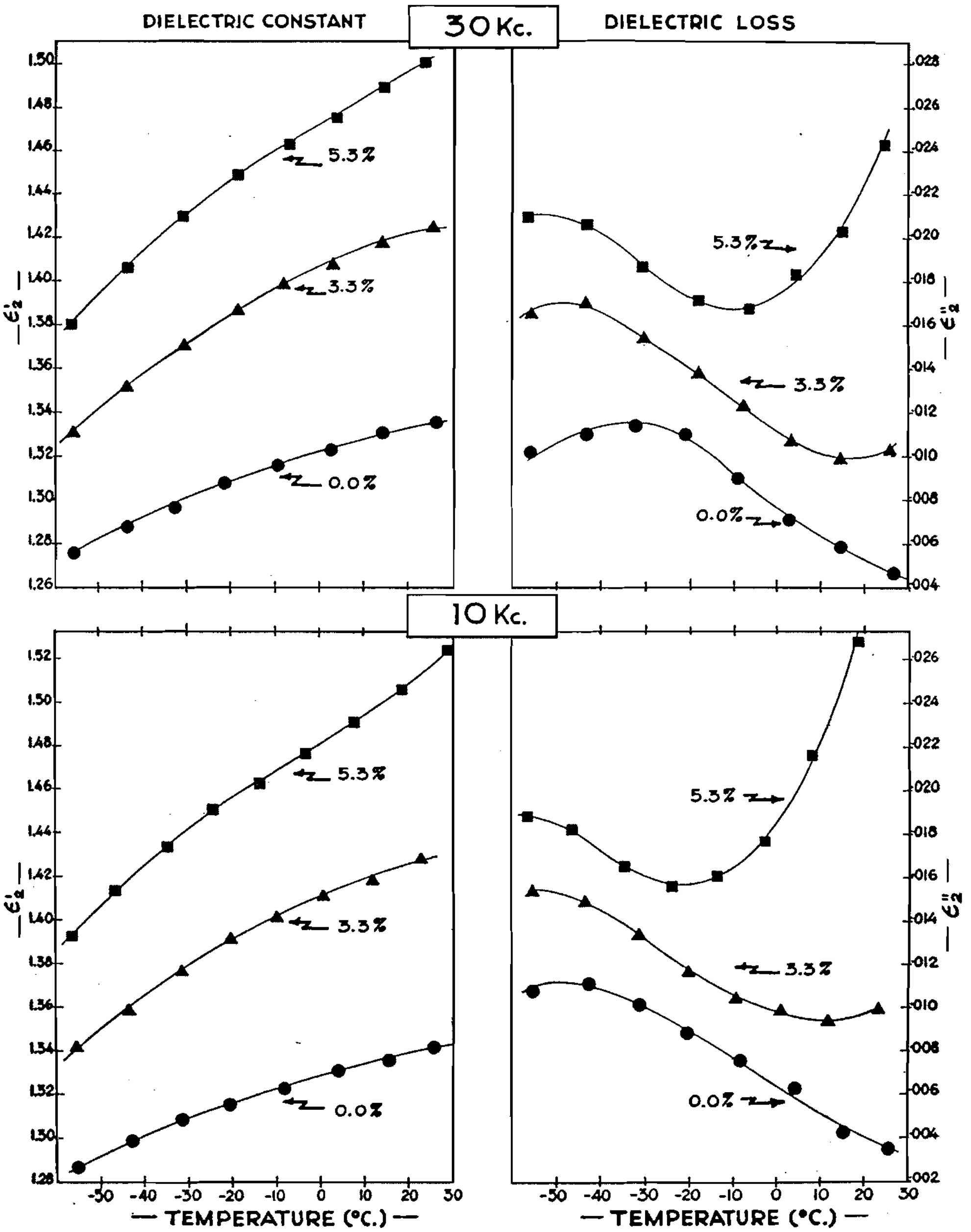


FIG. 2*b*. Dielectric dispersion at 30 and 10 kc. of paper containing sorbed water at the inscribed percentages.

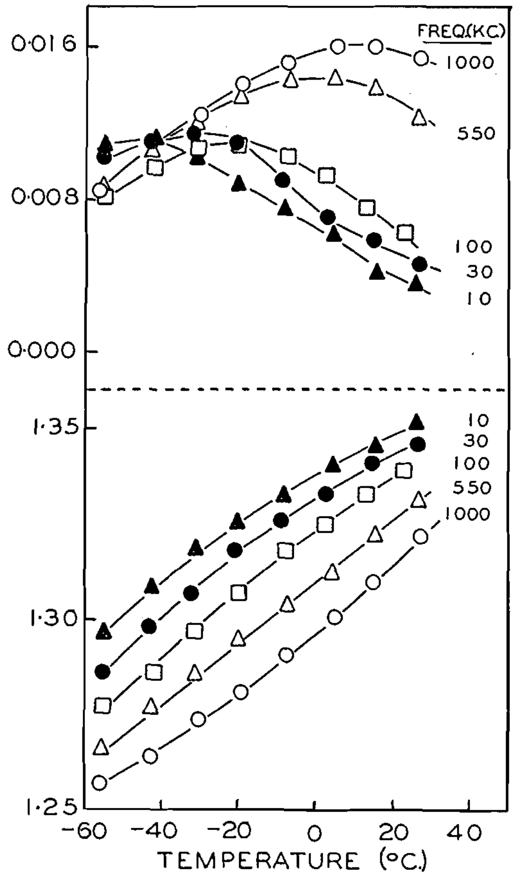


FIG. 3. Dielectric dispersion of dry paper at the inscribed frequencies.

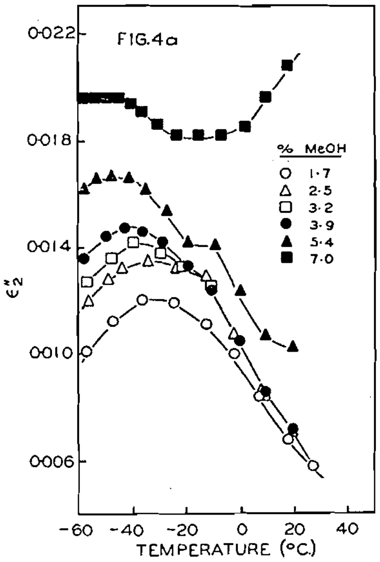
The most significant feature of the results is the shift of T_m toward lower temperatures by an increase in moisture content. This effect, similar to that produced by a lowering in the frequency at constant moisture content, signifies a decrease in the restriction to rotation, as observed previously in several other systems (7, 14, 20, 24). T_m for dry paper at 1 Mc. was 10°C., compared with 16°C. determined from Stoops' data (26) for dry cellophane at the same frequency. The difference may be due to the residual moisture in the dry paper as defined above, Stoops having dried his sample by heating at 105°C.

A high temperature increase in ϵ''_2 is observed at the lower frequencies and the higher moisture contents. Assuming that the fractional d-c. loss is the same for paper as for the compound dielectric studied here, it is impossible to explain the high temperature rise in the loss curve in terms of ionic conductance, since there is no appreciable contribution of d-c. conductance to the measured a-c. losses. At the same time it was not experimentally feasible to establish whether a second dispersion region at a higher temperature exists such as has been observed with terylene (22).

Methanol–Cellulose

Results were obtained for methanol contents of 0.0 to 7.0% at 100, 200, 550, and 1000 kc.p.s. The results are not reported in detail since the general effect of methanol on the dispersion region was similar to that of water. There were, however, several significant differences in degree. For example, the rate of increase of $(\epsilon''_2)_{\max}$ with vapor content was significantly smaller for methanol than for water, a result to be expected if the dispersion region is due to hydroxyl groups, of which there are fewer per gram of methanol than per gram of water. This point is discussed below. The more pronounced effect due to water was observed as well for the rate of increase of ϵ'_2 with vapor content at a particular temperature and frequency and for the high temperature rise in ϵ''_2. The latter is apparent in the loss curves at 100 kc. for the two cases (Figs. 2*a* and 4*a*).

In addition a characteristic break appears in the loss curves for methanol between −20 and −10°C. The effect becomes more marked at increased methanol contents as shown in Fig. 4*a*. There is no corresponding break in the dielectric constant curves (Fig. 4*b*). Furthermore, the effect appears only in the cases where the runs were performed by cooling. It is not observed where T_m occurs in or near the temperature range of break, as in the runs at 550 and 1000 kc.p.s.



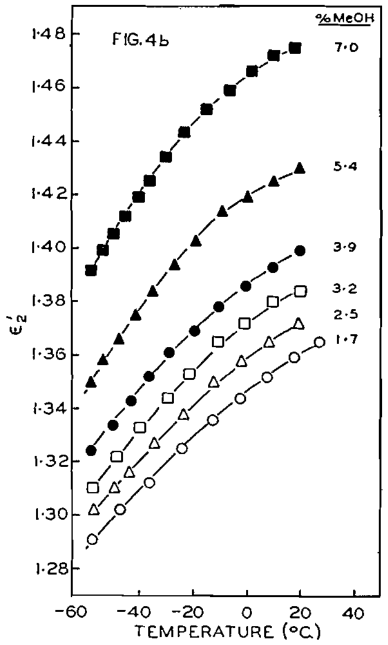


FIG. 4*a*. Dielectric loss at 100 kc. of paper containing sorbed methanol at the inscribed percentages.

FIG. 4*b*. Dielectric constant at 100 kc. of paper containing sorbed methanol at the inscribed percentages.

Ethanol–Cellulose

Measurements were made at ethanol contents of 0.0 to 8.5% at 100, 200, 550, and 1000 kc.p.s. After completion of the runs on paper containing 8.5% ethanol, it was decided that each subsequent run be performed over a complete temperature cycle in order to determine the existence and the nature of the effect described above for methanol. The results at 100 kc. for paper containing 4.6% ethanol are shown in Fig. 5 and represent this effect in a typical fashion.

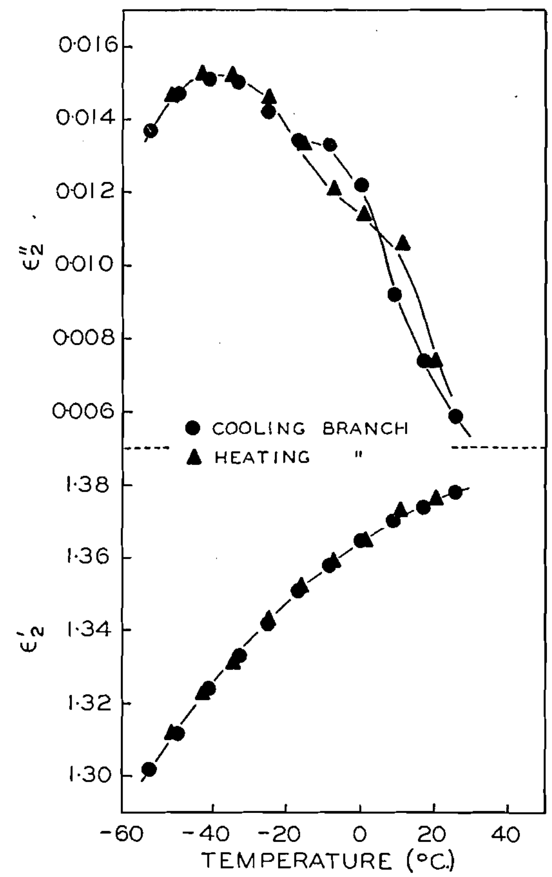


FIG. 5. Dielectric dispersion at 100 kc. of paper containing 4.6% ethanol.

It appears to be a hysteresis of some kind occurring over the temperature range −20 to 20°C. As in the case of methanol the break in the curve obtained by cooling occurs in the range −20 to −10°C., and there is no corresponding irregularity in the ϵ'_2 curves. In other respects, the results for ethanol stood in the same relation to those for methanol as the latter did to those for water. No high temperature increase in ϵ''_2 was observed in any of the ethanol curves. It was found that when $(\epsilon''_2)_{max}$ was plotted against vapor content the plots were linear within experimental error; furthermore, there was a characteristic slope for each vapor, the same value being obtained at each of the frequencies used. The slope signifies the increase in loss due to one gram of vapor per 100 gm. dry cellulose.

In Table II the increase in loss due to 1 gm. of hydroxyl in water, methanol, and ethanol is shown. The agreement among the three values is surprisingly good when one considers that the logical basis for comparison should be the area under the ϵ''_2 curves rather than $(\epsilon''_2)_{\text{max}}$. According to Reddish (22), the area under the ϵ'' vs. $\ln f$ curves is a function of the dipole moment density independent of the distribution function of T. In the ideal case of a single T, this area is $\pi\epsilon''_{\text{max}}$ so that ϵ''_{max} can be taken as a direct measure of the number of dipoles. However, when there is a distribution of T, this no longer applies, and one must then resort to the measurement of areas.

TABLE II

INCREASE IN $(\epsilon''_2)_{\text{max}}$ FOR CELLULOSE DUE TO THE HYDROXYL GROUPS OF THE SORBED VAPOR

Vapor sorbed	Loss per gm. vapor	Deviation from mean, %	Molecular weight of vapor	Loss per gm. OH	Deviation from mean, %
Water	0.00188	48	18	0.0020	0
Methanol	0.00140	10	32	0.0026	30
Ethanol	0.00052	59	46	0.0014	30
	Mean = 0.00127			Mean = 0.0020	

DISCUSSION

The arrangement in the experimental condenser was that of layers of paper alternating with layers of vapor, the layers being parallel to one another and to the electrodes. The dielectric constant and loss of this compound dielectric are referred to as ϵ'_2 and ϵ''_2, respectively. Designating the corresponding values for the paper itself as ϵ'_1, and ϵ''_1 and assuming that $(\epsilon''_1)^2 \ll (\epsilon'_1)^2$ and that the vapor layer is a pure capacitance, the following equations can be readily derived:

$$\epsilon'_2 = \epsilon'_1 \left[\frac{1}{c + \epsilon'_1(1-c)}\right] \tag{1}$$

$$\epsilon''_2 = \epsilon''_1 c^{\frac{1}{2}} \left(\frac{\epsilon'_2}{\epsilon'_1}\right)^{3/2} \tag{2}$$

where c represents the volume fraction of paper in the cell (Table I). Equation [1] is the same as that obtained by Argue and Maass for a similar model (1). Unless otherwise stated ϵ' and ϵ'' represent the dielectric constant and loss of the cellulose fiber itself, as distinguished from ϵ'_2 and ϵ''_2, and ϵ'_1 and ϵ''_1.

In Fig. 6 are shown the loss curves at 1 Mc.p.s. for paper containing 0 and 5.3% water. Within experimental error the value of T_m appears to be the same for corresponding ϵ''_2 and ϵ''_1 curves. For 5.3% water the value of c was deter-

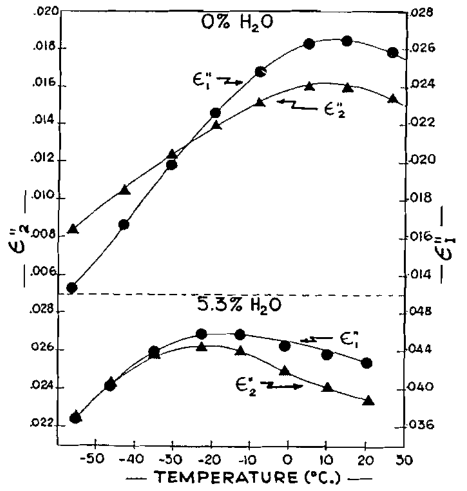


FIG. 6. Effect of the transformation of ϵ''_2 to ϵ''_1 on dielectric dispersion at 1 Mc. of paper containing 0.0 and 5.3% water.

mined as 0.635, on the assumption that the volumes of cellulose and water are additive (2), and further that the changes in volume of the fibers were duplicated in similar changes for the paper. All subsequent values of c reported were calculated on the basis of these assumptions. Because of the low coefficients of thermal expansion of cellulose (11), c varied over the temperature range covered by only about 0.2%, which is well within the experimental error.

Delevanti and Hansen (10) showed that the relationship between the density and dielectric constant of paper is expressed by a Clausius–Mosotti type of equation:

$$[3] \qquad \frac{1}{d}\frac{\epsilon' - 1}{\epsilon' + 2} = K$$

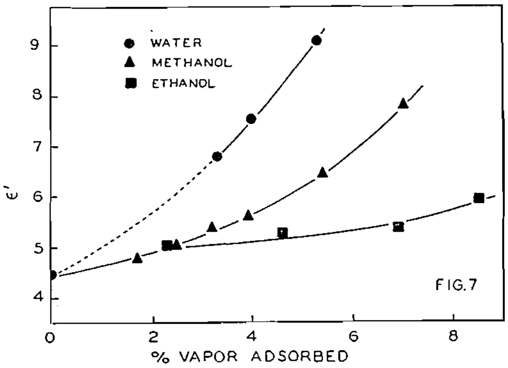
where ϵ' is the dielectric constant, d is the density, and K is a constant for a particular fiber. These results were confirmed by Calkins with an improved apparatus (5).

In Table III is presented, for dry cellulose at 25°C., a comparison of the results of Brown (4), Calkins (5), and the present authors, equations [1] to [3] having been employed where necessary. If it is assumed that the fibers in the samples employed were in a plane perpendicular to the electrical field, then the differences in the results of the various workers may be partly attributed to the dielectric anisotropy of cellulose. The transverse and axial dielectric constants of the cellulose crystallite have been found to be 5.27 and 7.19, respectively, at a frequency of 300 kc.p.s. (4). In cotton the fibrils are arranged spirally about the fiber axis whereas in linen they are nearly parallel to the fiber axis. Thus, when dielectric constants are measured transverse to the fiber axis, the values should increase in the order linen, linen + cotton, and cotton; the results given in Table III fall into this order.

TABLE III
DIELECTRIC CONSTANT OF DRY CELLULOSE AT 25°C.
COMPARISON OF RESULTS OF VARIOUS WORKERS

Data	Material	Freq. (kc.p.s.)	Reported values			Recalculated values		
			c	Density (gm./cc.)	Dielectric constant		ϵ'_2	ϵ'
Brown	Linen paper	300	0.648	0.610	$\epsilon'_2 = 1.363$	$c = 0.625$	1.282	3.8
Calkins	Cotton paper	1	1.000	0.8	$\epsilon'_1 = 2.42$	Density = 0.496	1.364	5.9
Present	75% linen + 25% cotton paper	300	0.625	0.496	$\epsilon'_2 = 1.334$*		1.334	5.0
		10			1.351		1.351	5.5
		1			1.357*		1.357	5.7

Estimated from the results at other frequencies.



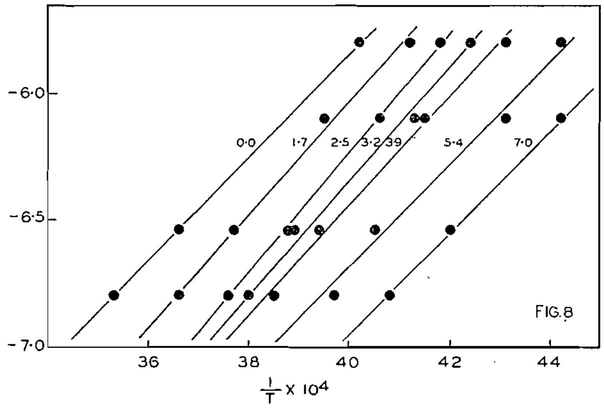


FIG. 7. Dielectric constant of cellulose at 1 Mc. and 20°C.: its variation with amount of vapor sorbed.

FIG. 8. Log τ versus $1/T$ for paper containing sorbed methanol at the inscribed percentages.

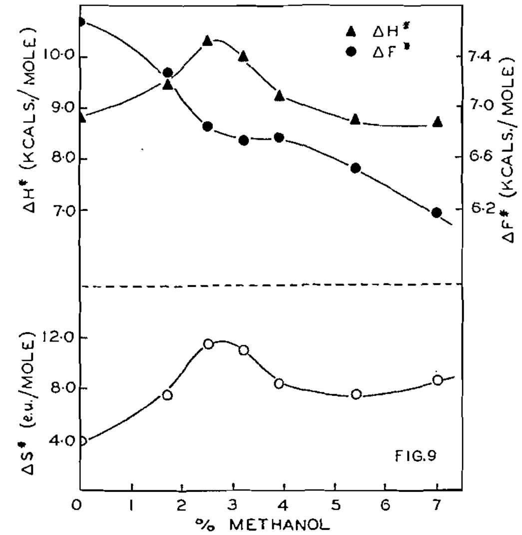
Plots of ϵ' vs. vapor content at 1 Mc.p.s. and 20°C. are shown in Fig. 7. For the calculations of ϵ' the variation of fiber density with water content was obtained from Hermans (18). This effect was slight, thus justifying the assumption that methanol and ethanol had no effect on fiber density over the range of alcohol contents covered. The rate of increase of ϵ' increases in the order ethanol, methanol, and water. At 5.3% vapor content, ethanol has produced a change in ϵ' of only 18%, while the corresponding change due to water is as high as 100%. The values of ϵ' for dry paper in the curves for water, and for methanol and ethanol, correspond to the values for paper samples No. 1 and No. 2. The difference is only 2%, which is a good check on the reproducibility of the results.

Plots of log T vs. $1/T$ were found to be straight lines, as illustrated for the methanol series in Fig. 8. From such plots it was possible to analyze the data in terms of the theory of absolute reaction rates, as briefly outlined in the introduction. From them τ was determined in each case at 298°K. These values of τ, as well as corresponding values of σ, ΔH^*, ΔF^*, and ΔS^* are presented in Table IV, σ being $\Delta \log \tau/\Delta(1/T)$.

TABLE IV
EVALUATION OF FREE ENERGY, ENTHALPY, AND ENTROPY OF ACTIVATION FOR RELAXATION FOR PAPER AT 298°K.

Vapor content	$\tau \times 10^9$ (sec.)	σ (°K.)	ΔH^* (kcal./mole)	ΔF^* (kcal./mole)	ΔS^* (e.s.u.)
% Water (gm./100 gm. dry paper)					
0.0	69.2	2060	8.84	7.68	3.9
3.3	8.2	2700	11.76	6.42	17.9
5.3	7.0	2200	9.48	6.33	10.6
% Methanol					
0.0	69.2	2060	8.84	7.68	3.9
1.7	35.5	2210	9.50	7.28	7.5
2.5	17.4	2380	10.30	6.86	11.5
3.2	14.4	2320	10.00	6.75	11.0
3.9	15.0	2160	9.27	6.77	8.4
5.4	9.9	2040	8.76	6.53	7.5
7.0	5.4	2040	8.72	6.17	8.6
% Ethanol					
0.0	69.2	2060	8.84	7.68	3.9
2.3	20.4	2350	10.16	6.95	10.8
4.6	14.6	2220	9.57	6.76	9.4
6.9	15.1	2020	8.65	6.78	6.3
8.5	5.5	2320	10.02	6.18	12.9

Considering these quantities as a function of methanol content, it appears that ΔF^* decreases continuously, passing through a plateau in the range 3 to 4%, while both ΔH^* and ΔS^* go through a pronounced maximum at 2.7% (Fig. 9). Table IV indicates that the data for water in all probability shows similar trends which are observed as well for ethanol (Fig. 10), ΔH^* and ΔS^* passing through maxima quite close to 2.7%. The minima observed, especially prominent in the case of ethanol, may possibly be a consequence of the failure of the model used at the high vapor contents at which they occur.



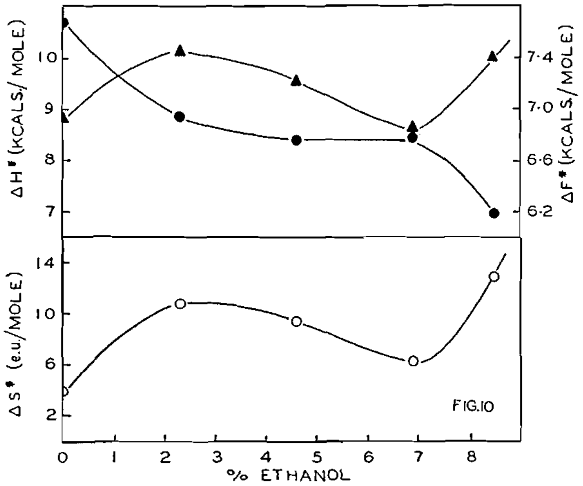


FIG. 9. Variation with % methanol of ΔH^*, ΔF^*, and ΔS^* for dielectric relaxation for paper at 298°K.

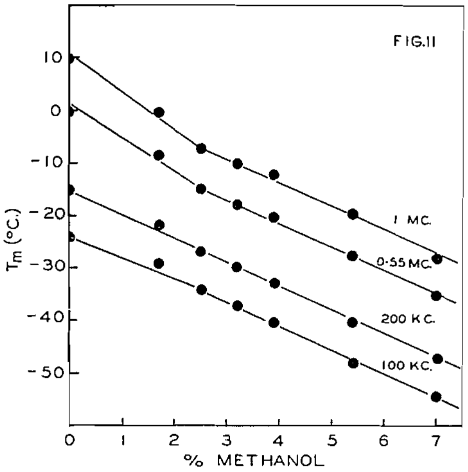
FIG. 10. Variation with % ethanol of ΔH^*, ΔF^*, and ΔS^* for dielectric relaxation for paper at 298°K.

In the neighborhood of 2.7% regain, the restriction to dipole rotation is at a maximum in all three cases. It is interesting that at this water content the density and both refractive indices of native fibers have a maximum value (18). One might expect the same to be the case for methanol and ethanol. Possibly the decrease in height of the ΔH^* and ΔS^* curves as one proceeds from water to methanol to ethanol reflects a corresponding decrease in the density effect.

In the above sense then, water as well as methanol and ethanol may be considered as having in cellulose a plasticizing action similar to that observed in other polymer systems (7, 14, 15, 24) (see Introduction).

Dielectric relaxation in starch, as in cellulose, has been attributed to the rotation of hydroxyl groups (20). It is not surprising then, in view of the similarity in structure, that the values of τ, ΔF^*, ΔH^*, and ΔS^* for starch are close to those obtained for cellulose, for example, $\Delta H^* = 7$ kcal./mole for dry starch, and 9 kcal./mole for dry cellulose. These can be compared with the value of 12.4 for a similar relaxation process in terylene (22).

The distinctness of the vapor content of 2.7% is manifested in yet another fashion. When T_m is plotted versus % methanol for each of the four experimental frequencies, one obtains the plots of Fig. 11. These plots are linear with a discontinuity at 2.5%. Above this point the slope is the same for all the frequencies, the deviation from the average being less than 1%. Below 2.5% on the other hand, the slope undergoes a marked increase with decrease in frequency.



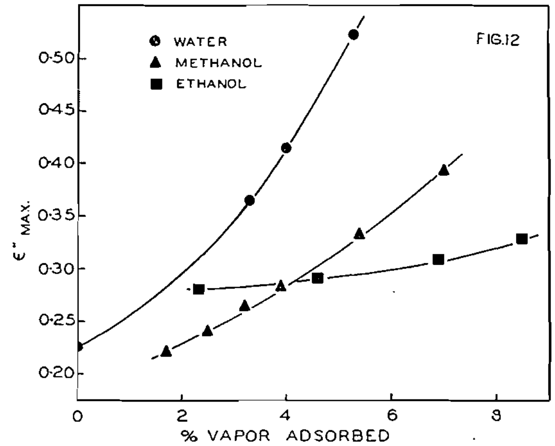


FIG. 11. Variation of T_m with % methanol at the inscribed frequencies.
FIG. 12. $\epsilon''_{\max}$ for the cellulose fiber: its variation with vapor content.

According to Reddish (22), the maximum value of ϵ'' for a single relaxation time T is given by:

$$\epsilon''_{\max} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2\mu^2 n$$

where k is the Boltzmann constant, T is the absolute temperature, ϵ_0 is the static dielectric constant, and n is the number of dipoles per cc. μ is the dipole moment, assumed to be 1.7×10^{-18} e.s.u. for the hydroxyl group (22). $d\epsilon''_{\max}/dn$ is then given by:

$$\frac{d\epsilon''_{\max}}{dn} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2\mu^2$$

assuming no change in T or ϵ_0. In this way a loss value is assigned to a single added dipole in 1 cc. of material. In order to be consistent with the convention of expressing the amount of added vapor in terms of grams per 100 gm. of dry material, a loss value is assigned to 1 gm. of added dipole in 100 gm. dry material as follows:

$$[4] \qquad \frac{d\epsilon''_{\max}}{dn_c} = \frac{2\pi}{27kT}(\epsilon_0 + 2)^2\mu^2 \frac{Nd}{M(100 + P)}$$

where N is Avogadro's number, M is the weight of N dipoles, P is the percentage vapor content, and d is the density of the material.

$d\,\epsilon''_{\max}/dn_c$ may also be obtained experimentally. The requisite ϵ''_2 data was transformed to ϵ''_1, using equations [1] and [2]. It has been shown that the dissipation factor of a paper sheet is roughly directly proportional to its density (5, 10). Using this relation, ϵ''_1 was transformed to ϵ'' for the cellulose fiber itself, using the density values employed in obtaining the plots of Fig. 7. Plots of $\epsilon''_{\max}$ versus % vapor content are shown in Fig. 12. They are slightly curved, the curvature being greatest in the case of water. Doubtless this is a

TABLE V
CONTRIBUTION OF 1 GM. ADDED HYDROXYL GROUPS TO $\epsilon''_{\max}$ IN CELLULOSE AND TERYLENE

Material	$d\,\epsilon''_{\max}/dn_c$ (loss/gm. OH/100 gm. dry cellulose) Calculated	Observed	Calculated/Observed
Terylene (amorphous)	0.233	0.0488	4.77
Terylene (crystalline)	0.220	0.0433	5.08
Cellulose + water	0.642	0.0834	7.70
Cellulose + methanol	0.642	0.0638	10.1
Cellulose + ethanol	0.642	0.0206	31.2

consequence of the decrease in T and the increase in ϵ_0 with increasing vapor content, the combined effect being greatest for water, presumably. From the slopes of these curves at 5.3% vapor content values of $d\,\epsilon''_{\max}/dn_c$ were computed; these are presented in Table V together with those obtained from Equation [4], and the corresponding values for crystalline and amorphous terylene (22). ϵ_0 for dry cellulose was taken as 6.

It will be noticed that in this table the experimental value of $d\,\epsilon''_{\max}/dn_c$ is much smaller than the theoretical value. This can be attributed to a spread of relaxation times which yields values of $\epsilon''_{\max}$ considerably lower than the theoretical value (19). Even so, the reported experimental values for cellulose are probably a little high as a result of the slight magnifying effect on $\epsilon''_{\max}$ of a decrease in temperature. Theoretically, one would expect $d\,\epsilon''_{\max}/dn_c$ to be considerably less for terylene–water than for cellulose–water because of smaller values for ϵ_0 and d. That this is so experimentally is evidence in favor of the correctness of the model used in calculating $\epsilon''_{\max}$. The effect of changes in ϵ_0 and d is manifested as well in the smaller value of $d\,\epsilon''_{\max}/dn_c$ for crystalline terylene than for the amorphous modification.

ACKNOWLEDGMENTS

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THE VISCOSITY OF SUSPENSIONS OF SPHERES: A NOTE ON THE PARTICLE INTERACTION COEFFICIENT[1]

BY R. ST. J. MANLEY[2] AND S. G. MASON

ABSTRACT

Measurements of the reduced viscosity of suspensions of glass spheres 5 μ diameter have been made up to concentrations of 18% by volume. The experimental results yield the empirical equation $\eta_{sp}/c = 2.50 + 12.7c + \ldots$ The coefficient of c, due to interactions, is in fair agreement with a value of 10.05 based upon a modification of Vand's theory which takes into account the experimentally established mechanism of two-body collisions of spheres in a velocity gradient. Several reasons for the discrepancy are suggested.

INTRODUCTION

A rigorous theoretical treatment of the viscosity of a suspension of neutral rigid spheres, without Brownian motion, in a viscous fluid has been given by Vand (5) as an extension to finite concentrations of the well-known Einstein analysis at infinite dilution. Allowance is made in the theory for the increments in viscosity due to hydrodynamic interaction between the particles and to doublets formed by shear-induced two-body collisions, and the following equation, expressed as a two-term power series, is derived:

$$[1] \quad \frac{\eta_{sp}}{c} = \frac{\eta_r - 1}{c} = \frac{\eta - \eta_0}{\eta_0 c} = \alpha_0 + \alpha_1 c + \ldots$$

Here c is the solid fraction of spheres in the suspension, η_0 is the viscosity of the medium, and η, η_r, and η_{sp} respectively are the viscosity, the relative viscosity, and the specific viscosity of the suspensions; α_0 is the Einstein coefficient $(=5/2)$ and α_1 is the interaction coefficient, calculated by Vand to be 7.35.

In computing the contribution of the doublets to α_1, Vand assumed that, in a two-body collision in a velocity gradient, the participating spheres roll over one another along an arc of a great circle on each sphere and separate when the line joining their centers is perpendicular to the direction of flow. From this assumed mechanism, it was possible to calculate the collision frequency, the mean life of a doublet, and hence the steady-state concentration of doublets.

The authors (2) have made experimental observations of doublet behavior in velocity gradients and have found these assumptions invalid. It was found that the doublets rotate at constant angular velocity about an axis normal to the direction of flow and in the direction of the gradient, with no relative

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[2] *Holder of a Fellowship from the National Research Council of Canada.*

motion between the apparent points of contact, i.e. without rolling, and that the two spheres of the doublet separate at a point which is a mirror image of the initial point of contact. While the collision frequencies were shown to be correct, the mean doublet life and, hence, the doublet concentration were found to be *exactly* twice that calculated by Vand.

If the experimentally established doublet concentration is used in the viscosity theory, the "collision time constant" r_2 (5) is doubled, and the interaction coefficient α_1 of Equation [1] becomes 10.05.

Vand made a series of viscosity measurements (6) on 130 μ diameter glass spheres suspended in zinc iodide–glycerol solutions of approximately equal density, using two Ostwald viscometers for values of c up to 50%, and a Couette viscometer for c between 35 and 55%. His experimental results yielded $\alpha_1 = 7.17$, which is in good agreement with the original theory. However, it was necessary to make large corrections for wall effects and for concentration changes due to particle crowding in the capillaries of the Ostwald viscometer. Analysis of the data shows that there is considerable scatter.

Since the corrections decrease with decreasing particle size, it was considered to be of interest to repeat the measurements using smaller spheres. This has been done with 5 μ diameter glass spheres. The precision of the measurements has been improved, and the results agree more closely with the modified theory.

EXPERIMENTAL

The spheres were made of Pyrex glass by a method due to Sollner (4). They were prepared by blowing glass, previously powdered in a ball mill, through the oxygen line feeding an ignited blow torch and collecting the particles in a tray of water. The spheres were fractionated by sedimentation in water and the fraction 1–10 μ in diameter (by microscopic measurement) was used to prepare the suspensions. When the spheres were dried by evaporating the water, aggregates formed which could not be broken up. The bonding of the spheres is believed to result from surface hydration and from the effect of the high surface tension of the water which, during the drying process, pulls the spheres into firm contact with one another. Aggregation was eliminated by replacing the water with ether by solvent exchange through acetone and ethanol, and by removing the ether under vacuum.

Homogeneous suspensions of glass spheres in zinc iodide–glycerol mixtures were prepared by dispersing measured weights of glass into measured weights of medium. Two stock solutions of zinc iodide in glycerol having densities of 2.215 and 2.342 gm./cc. at 20°C. were used. The density of the spheres (by liquid displacement) was 2.210 gm./cc.

Viscosities were measured at 20.00 ± .01 °C. in Ostwald–Fenske viscometers with capillaries 0.22 cm. in diameter. Since the solutions were hygroscopic, the viscometers were fitted with calcium chloride drying tubes.

The measured efflux times were corrected for the calculated mean density of the suspensions. The kinetic energy correction was negligible.

RESULTS

The measured relative viscosities η'_r for suspensions up to 18% by volume (the highest attempted) are listed in Table I. These have been corrected for hydrodynamic interaction between the spheres and the wall, the effect of which has been shown in Vand's theoretical analysis (5, 6) to be equivalent to interposing a layer of pure medium between the suspension and the wall of thickness $D = 0.650\ a$, a being the diameter of the spheres. This interaction gives a pseudo-slip at the wall, and for flow through a capillary of radius R the true relative viscosity η_r is given by

TABLE I

Viscosity measurements

Volume fraction c	η'_r observed	η_r corrected for wall effect	η_{sp}	η_{sp}/c
Solution No. 1 (2.342 gm./cc.)				
0	1.000	1.000	0	—
0.06375	1.206	1.209	0.209	3.278
0.0878	1.314	1.318	0.318	3.622
0.1176	1.463	1.470	0.470	3.997
0.1634	1.736	1.749	0.749	4.584
0.1838	1.863	1.879	0.879	4.782
Solution No. 2 (2.215 gm./cc.)				
0	1.000	1.000	0	—
0.04977	1.153	1.154	0.154	3.094
0.08880	1.320	1.324	0.324	3.649
0.1115	1.433	1.439	0.439	3.937
0.1401	1.583	1.592	0.592	4.226
0.1798	1.844	1.864	0.864	4.805

[2] $$\left(\frac{1}{\eta_r} - 1\right) = H\left(\frac{1}{\eta'_r} - 1\right)$$

where the correction factor

[3] $$H = (1 - D/R)^{-4}$$

Taking the mean diameter of the spheres used in the present experiments to be 5 μ, the correction factor H was only 1.012 as compared with values of 1.178 and 1.294 in Vand's experiments (6).

Corrections for the increase in concentration due to particle crowding in the viscometer, which amounted to as much as 0.12 c in Vand's experiments (6), were less than 0.005 c in the present experiments and were ignored.

Fig. 1 shows a plot of values of η_{sp}/c vs. c. The points fall on a smooth straight line which, when fitted by the method of least squares, yields the equation

[4] $$(\eta_{sp}/c) = (2.487 \pm 0.074) + (12.7 \pm 0.53)c$$

where the precision is expressed as the 95% confidence limits calculated from the residual variations around the regression line.

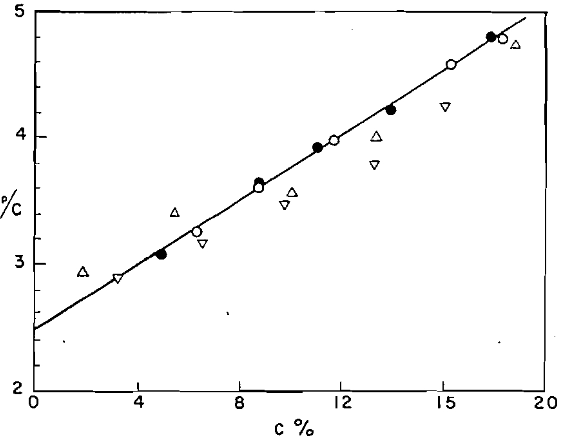

FIG. 1. Reduced viscosity – concentration plot. Vand's (5) experimental values are plotted as triangles.

The data show less scatter than those of Vand, which have been included for comparison in Fig. 1.

The first term agrees within the limit of error with the Einstein value of 5/2.

DISCUSSION

It is considered that these results provide a better experimental confirmation of Vand's theory, when modified by the experimentally established collision mechanism, than his own measurements (6). The experimental value of 12.7 for α_1 is higher than the theoretical value of 10.05.

There are several possible reasons for this discrepancy, apart from experimental error, of which the following may be cited:

(1) The collision doublets behave as rigid ellipsoids of axis ratio 2. Since the doublets are neither ellipsoidal nor rigid (2) Vand's shape factor (5) may be in error.

(2) The particles are assumed to be monodisperse, whereas spheres having a range of sizes were used. It has been shown (3) that the collision frequency is increased by polydispersity, with a possible increase in the steady state concentration of doublets and hence the collision time constant r_2. The magnitude of this effect is not known since there is no information on the mean life of polydisperse doublets. It is pointed out, however, that since the axis ratio of a doublet of spheres of unequal sizes is less than that of one of equal-sized spheres, the increase in viscosity from the increased double concentration would be offset to some extent by the decrease in the contribution per doublet.

(3) The theory assumes the particles to be neutral, i.e., the only particle interactions are due to fluid motion. However, coulombic and/or Van der Waals interactions may be appreciable for the particles used here. Calculation of the electroviscous effect for reasonable values of the ζ-potential from Booth's theoretical equations (1) show a negligible effect on α_0 for 5 μ diameter par-

ticles. It is possible, however, that the interaction term α_1 would be appreciably changed although the theory has not been sufficiently developed to estimate this effect.

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THE THERMAL DECOMPOSITION OF DIMETHYL DISULPHIDE[1]

By John A. R. Coope[2] and W. A. Bryce[3]

ABSTRACT

The thermal decomposition of dimethyl disulphide has been studied in the gaseous state by a static method. The primary reaction, which follows a reproducible induction period, produces one mole of methyl mercaptan per mole of disulphide, together with a product of low volatility believed to be a thioformaldehyde polymer:

$$CH_3SSCH_3 \longrightarrow CH_3SH + 1/n\ (CH_2S)_n.$$

There is also a competing reaction producing a large quantity of hydrogen sulphide. The remaining volatile products, hydrocarbons of two or more carbon atoms (believed to be chiefly ethylene), free sulphur, polysulphides, and carbon disulphide are formed either by the latter reaction or by the extensive decomposition of products. The decomposition is catalyzed by hydrogen sulphide, and more strongly by the complete reaction mixture. A mechanism is proposed for the main reaction.

The present investigation was undertaken as a contribution to our fragmentary understanding of the mechanisms of reactions involving the carbon–sulphur bond system in organic sulphur compounds. The C–S–S–C bond system of dimethyl disulphide was of special interest. Little is known about the thermal decomposition of the alkyl disulphides, although the thermal decomposition of aryl disulphides has received some study. The work of Schonberg, Mustafa, and Askar (10) suggests that diphenyl disulphide dissociates at the S–S bond into two free aryl thial radicals. In an early investigation Otto and Rossing (8) found that on distillation at atmospheric pressure diamyl disulphide (b.p. 248° C.) gradually decomposes into sulphur or sulphur-rich substances and a tarry residue. Bezzi (3) reported that dioctyl disulphide decomposes at its boiling point of 190° C. at 15 mm. Faragher, Morrell, and Comay (7) found that decomposition of vaporized naphtha solutions of various alkyl disulphides at 496° C. produces the corresponding alkyl mercaptan, hydrogen sulphide, free sulphur, alkyl sulphides, thiophenes, and saturated and unsaturated hydrocarbons.

In some preliminary experiments in this laboratory it was found by Patrick (9) that dimethyl and diethyl disulphides decompose above 300° C. yielding complex pressure–time curves. The homogeneous decomposition of dimethyl disulphide was found to produce large amounts of mercaptan and hydrogen sulphide.

EXPERIMENTAL

Reagents

The dimethyl disulphide, obtained from Eastman Kodak Co., Rochester, New York, gave negative tests for mercaptans, hydrogen sulphide, free

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[1] *Manuscript received December 1, 1953.*

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada. From a thesis presented by J.A.R.C. to the University of British Columbia in partial fulfilment of the requirements for the degree of Master of Science.

[2] *Present address: Wadham College, Oxford, England.*

[3] *Assistant Professor.*

sulphur, and carbon disulphide. Its refractive index of $n_D^{20} = 1.5261 \pm 0.0002$ agreed well with Vogel and Cowan's (12) value of 1.5260. It was fractionated in a vacuum apparatus before use. The pure hydrogen sulphide was prepared by the method of Bickford and Wilkinson (4). The other sulphur compounds were fractionated Eastman Kodak products.

Apparatus

The apparatus was an all-glass static system consisting essentially of a heated 250 ml. pyrex reaction vessel connected to an evacuating system, a sampling system, and to storage vessels for the reactants. To avoid difficulties of corrosion and condensation, a glass spoon-type Bourdon gauge was used for pressure measurement. The gauge was used both as a direct measuring instrument and as a null indicator.

The volatile constituents of the reaction mixture were sampled in gas pipettes which were attached to the capillary connections of the reaction vessel. From the results of the analyses of the contents of these pipettes the partial pressures of various substances in the reaction vessel during decomposition were calculated. The less volatile constituents were collected in a dry ice trap and analyzed qualitatively.

Analytical Methods

Carbon disulphide was estimated colorimetrically by means of its reaction with cupric acetate and piperidine (5). Thiophenes were tested for with isatin solution (1). Free sulphur was determined in an AnalaR petroleum ether solution of the sample by the method of Ball (2) using dilute reagents.

Hydrocarbons were estimated approximately by a crude gas fractionation method: hydrogen and methane could be separated off at liquid nitrogen temperature. The remaining hydrocarbons were separated off at the freezing point of *n*-pentane, −130° C., and their pressure was corrected slightly for hydrogen sulphide.

The methods of analysis for mixtures of hydrogen sulphide, methyl mercaptan, and disulphide were developed in this laboratory, and are being reported elsewhere in more detail (6). Hydrogen sulphide was absorbed in dilute base, precipitated as cadmium sulphide, and separated from mercaptan by filtration through asbestos in 0.005 *M* acid. The cadmium sulphide precipitate was oxidized directly with excess acidified standard iodine and determined by back titration with thiosulphate. This method was sensitive to less than 2.5×10^{-6} moles of hydrogen sulphide (0.5 mm. pressure in the reaction vessel) and was accurate in the presence of mercaptan to within 3%. The direct determination for hydrogen sulphide made it possible to determine mercaptan indirectly from the total sulphydryl content of the reaction mixture as determined by absorption in excess standard iodine and back titration with thiosulphate.

In Ball's method (2) for the determination of disulphides the disulphides are reduced to mercaptans by refluxing with zinc and glacial acetic acid. In the present work AnalaR petroleum ether was used as the solvent. By using a slightly stronger acid (94%), a lower temperature (water bath), and by heating long enough to transfer the entire methyl mercaptan formed to a trap, it was possible to obtain results with a reproducible error in the range $110\frac{1}{2} \pm 1\frac{1}{2}\%$ reduction. The analyses were corrected appropriately. Unfortunately some of the actual analyses were invalidated by the interference of alkyl polysulphides, compounds of the type $R\text{–}S_x\text{–}R$, which reduce to mercaptan and hydrogen sulphide.

The presence of alkyl polysulphides was inferred from an interference with the disulphide determinations and by a reaction with mercury. It was observed that a solution of the volatile products in petroleum ether, although free of elementary sulphur, reacted with metallic mercury to produce a black crystalline compound. This was attributed to a reaction of the type quoted by Sidgwick (11):

$$2\,Hg + CH_3S_4CH_3 \rightarrow 2\,HgS + CH_3SSCH_3.$$

RESULTS

A typical family of pressure–time curves for the decomposition of dimethyl disulphide is presented in Fig. 1. There is an initial rapid pressure decrease, followed by a period of constant pressure, after which the rate rises slowly to a maximum. The induction period was reproducible: in a series of 16 runs at 316° C. it had a mean length of 11.6 min. with standard deviation only 0.7 min.

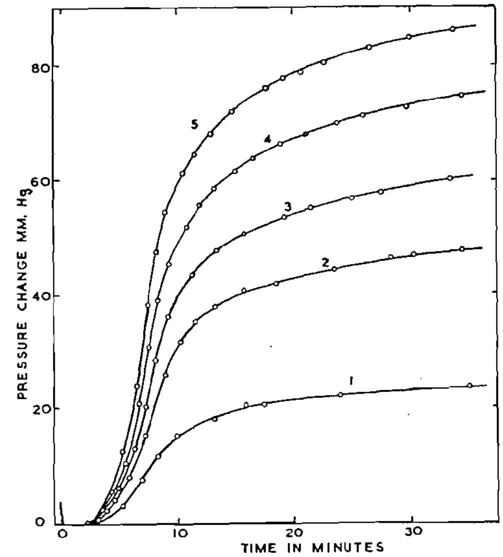


FIG. 1. Pressure–time curves for the decomposition of dimethyl disulphide at 341° C. Initial pressure of disulphide respectively (1) 24.0, (2) 57.5, (3) 73.0, (4) 92.5, (5) 108.0 mm.

The results of extended experiments showed that, after the rate had decreased quite sharply from the maximum to a low value, there remained a slow residual reaction which continued for some time. This behavior suggests the decomposition of products. Both at 341° C. and at 373° C. the final pressure increase is greater than 105% of the minimum pressure.

Effect of Packing the Reaction Vessel

A sixfold increase in the surface to volume ratio was achieved by packing the vessel with short lengths of pyrex glass tubing. The induction period and maximum rate of reaction were unaffected, indicating that the decomposition is a homogeneous process. The only effect was a slight reduction of the final pressure, attributable to increased adsorption of the products on the vessel surface.

The Initial Pressure Decrease

By using the Bourdon gauge as a direct reading instrument and by using relatively low pressures, it was possible to fill the reaction vessel in times as short as two seconds. It was possible, therefore, to observe the greater part of the initial pressure decrease. With 95 mm. of disulphide at 316° C. the pressure decrease was about 15 mm., the initial rate of the decrease was of the order of 2 mm. per second, and the process was approximately 90% complete in 15 sec. The magnitude of the decrease was greater at higher initial pressures and at lower temperatures; it was only slightly increased by packing the reaction vessel.

Analysis showed that during the induction period the reaction mixture consists almost entirely of unreacted disulphide. This fact suggested strongly that the pressure decrease is due to adsorption of the reactant disulphide on the walls of the pyrex reaction vessel. Further observations supported this view: (1) A few millimeters pressure of hydrogen sulphide in the reaction vessel reduced the extent of the decrease by 80%. Hydrogen sulphide is known to adsorb on glass. (2) If a part of the reactant were removed from the vessel during the induction period, a short, rapid pressure increase occurred, indicating desorption of the disulphide.

An estimation of the activation energy of the initial rate of the pressure decrease gave a value of 16 kcal. per mole. Whereas this is much less than the usual energies of pyrolytic reactions, it is of the order of magnitude of energies of adsorption. It leads to a frequency factor of 10^4 sec^{-1}. If a simple collision theory of adsorption is accepted, this frequency factor should be equal to the number of times a molecule strikes the wall per second. The latter was calculated from kinetic theory as 1×10^4 sec.^{-1} at 316° C.[4] This excellent agreement is considered additional proof that the initial pressure decrease is due to adsorption.

Dependence of the Rate on Initial Disulphide Pressure

The minimum pressure of the induction period was found to be a suitable 'initial' pressure for correlating the results of different experiments. There is little doubt that it represents the true initial disulphide pressure at the start of the main reaction.

The initial pressure was varied from 24 mm. to 230 mm. at 341° C. The dependence of extent of reaction on the initial pressure is given in Table I. Per cent pressure increases are listed for several reaction times. The results

[4] *From kinetic theory the "collision number" is* $\frac{1}{4}S(8RT/M)^{\frac{1}{2}}$*, where* S *is the surface to volume ratio of the reaction vessel and* M *is the molecular weight.* $S = 1$, $M = 94$, $T = 589°$ *K.*

TABLE I
DEPENDENCE OF THE EXTENT OF REACTION ON THE INITIAL PRESSURE. $T = 341°$ C.

Initial pressure, mm.	% pressure increase after: 8 min.	10 min.	15 min.	20 min.
24.0	45	62	76	85
57.5	36	53	68	74
73.0	38	54	68	74
92.5	38	53	66	73
108.0	43	54	68	73
141.8	35	48	63	68
166.5	42	53	68	74
229.5	42	54	68	73

show a first order dependence. The rate constants calculated from these data had a mean value of 20.8×10^{-4} sec.$^{-1}$ at 341° C. with a standard deviation of 0.7×10^{-4} sec^{-1}.

At pressures below 150 mm. (temperature 341° C.) the induction period is independent of the initial pressure, but at higher pressures its length is reduced. The time at which the maximum rate occurs varies in the same way.

Dependence of the Rate on Temperature

The significant results are shown in Table II. A plot of $\ln k$ vs. $1/T$ gave a straight line from which an over-all activation energy of 45 ± 4 kcal. per mole was calculated. The frequency factor was estimated to be 2×10^{13} sec^{-1}.

TABLE II
DEPENDENCE OF THE REACTION ON TEMPERATURE

Temperature, ° C.	Induction period, sec.	Time of max. rate, sec.	Rate constant, sec.$^{-1}$
316	690	1860	0.00042
314	120	420	0.00208
360	35	157	0.0067
373	19	65	0.0116

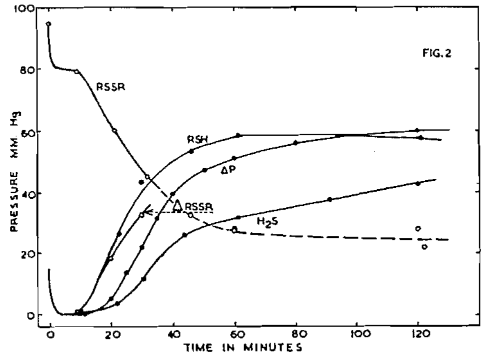
Analytical Results

A temperature of 316° C. and an initial pressure of 80 mm. were the standard conditions used for experiments in which analyses were done for the components of the reaction mixture.

Qualitative analyses of the reaction mixture showed that thiophenes are formed in traces only. The principal volatile products were hydrogen sulphide, mercaptan, carbon disulphide, alkyl polysulphides, and low boiling hydrocarbons of two or more carbon atoms. Hydrogen and methane were not detected; if present at all they appear to total less than 5% of the hydrocarbon. The mercaptan was identified as chiefly or entirely methyl mercaptan by the yellowish-green color of its silver mercaptide; the higher silver mercaptides are white. Of the products which were not sampled by the gas pipettes, free sulphur was identified amongst the accumulated products in the cold trap. An involatile tar was formed in considerable quantity; it appeared black by reflected light and reddish-brown by transmitted light.

The two volatile products formed in largest quantity were methyl mercaptan and hydrogen sulphide. The results of quantitative analyses were used to construct partial pressure-versus-time curves for these two products and for the reactant disulphide. These curves, with other results, are shown in Fig. 2. During the early stages of the reaction the rate of hydrogen sulphide formation is equal to one half the rate of increase in pressure. The rates become nearly equal in the later stages.

The alkyl polysulphides in the reaction mixture interfered so seriously with the determination of disulphide that the only accurate determinations were those which were made in the initial stages of the decomposition. A curve labelled *RSSR*, showing the disappearance of disulphide is given in Fig. 2. The values for the dotted part of the curve are believed to be much too high owing to interference by polysulphides. The estimated pressure of disulphide during this part of the reaction is approximately zero since the main reactions appear to be over at 60 min. A curve representing the amount of disulphide decomposed in the early stages of the reaction is also plotted. It was constructed by subtracting the disulphide present from the initial pressure.



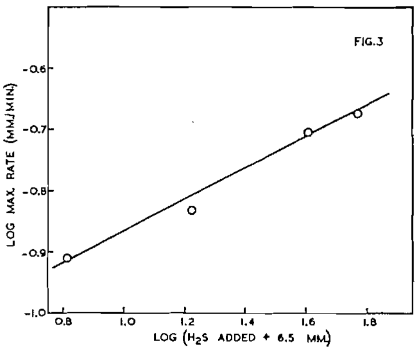


FIG. 2. Analytical results for the "standard" reaction, $T = 316°$ C., $P_{\text{min}} = 80.0$ mm. *RSSR* shows analytical results for disappearance of disulphide. Δ*RSSR* shows measured amount of disulphide decomposed.

FIG. 3. Dependence of the maximum rate on added hydrogen sulphide. Constant disulphide pressure, 52.2 mm. Temperature, 316° C.

Fig. 2 shows that the reaction producing mercaptan is distinct from that producing hydrogen sulphide. The former appears to reach its maximum rate before 20 min., whereas the latter reaches its maximum rate only after 30 min. The end of the induction period appears to be the same for both reactions. Since the pressure increase does not appear to occur until H_2S is formed, the formation of mercaptan must involve little or no pressure change. This is well illustrated by the fact that at 15 min. with a mercaptan pressure of 10 mm. the total pressure change by all processes is only $1\frac{1}{2}$ mm. Moreover, the reaction producing hydrogen sulphide must account also for much of the remaining volatile products. The reactions which occur after 60 min., the slow formation of H_2S for example, appear to be reactions amongst the decomposition products. Probably a number of complex processes occur simultaneously.

The partial pressures of all the volatile constituents of the reaction mixture were measured at 120 min., after the completion of the main reactions. The results of analyses are listed in the first column of Table III. The values for carbon disulphide and for hydrocarbons are significant to the order of magnitude only. Estimates of the remaining constituents are recorded in the second column of Table III. The order of magnitude figure for polysulphides was estimated by assuming an apparent 25 mm. of disulphide, shown by the disulphide test, to be due in reality to tetrasulphide. Elemental sulphur could not be determined quantitatively, but it appeared to be present in small amounts only. Since it exists at 317° C. almost entirely as S_8, its necessarily small pressure has been listed as zero.

TABLE III
VOLATILE CONSTITUENTS OF THE REACTION MIXTURE AFTER 120 MIN. OF REACTION AT 316° C. (P_{min} = 80 MM.)

Analytical pressures, mm.		Estimated pressures,[a] mm.	
CH_3SH	59	CH_3SSCH_3	0
H_2S	42	$CH_3S_xCH_3$	8
CS_2	15	S_8	0
Hydrocarbons (C_2)	25		
$H_2 + CH_4$	0		
Thiophene	1		

Measured total pressure 140 mm.

[a] See text.

Effect of Added Hydrogen Sulphide

The addition of hydrogen sulphide to the reaction mixture had a marked effect on the rate of reaction. The induction period and the period of autoacceleration were shortened, and the maximum rate was increased. The significant results are listed in Table IV. In each case the maximum rate of pressure rise (also of hydrogen sulphide formation) occurred after a total pressure increase of 13.7 mm., corresponding in a normal decomposition to the formation of 6.5 mm. of hydrogen sulphide. The logarithm of 'the added

TABLE IV
EFFECT OF HYDROGEN SULPHIDE ON THE DECOMPOSITION OF 52.3 MM. OF DISULPHIDE AT 316° C.

Added H_2S, mm.	Induction period, min.	Time of max. rate, min.	Maximum rate, mm./min.
0.0	13	34.0	0.123
10.2	4½	20.5	0.147
34.0	2½	12.0	0.198
52.0	1¼	9.7	0.213

hydrogen sulphide plus 6.5 mm.' is plotted in Fig. 3 against the logarithm of the maximum rate. The graph is roughly linear, suggesting that the amount of hydrogen sulphide present at the maximum rate is, in fact, the normal amount, plus the amount added. The slope of 0.25 indicates approximately a rate dependence to the one quarter power, at least at the time of the maximum rate: i.e., with disulphide constant,

$$d\,H_2S/dt = k\,[H_2S]^{\frac{1}{4}}.$$

The total pressure increase was independent of the amount of added hydrogen sulphide. This suggests that the final ratio of hydrogen sulphide formed to mercaptan is unchanged by the addition of hydrogen sulphide. The general character of the decomposition appears entirely unaffected. If this is so the hydrogen sulphide must also accelerate the reaction producing mercaptan.

Effect of Added Mercaptan

A decomposition in the presence of methyl mercaptan at a pressure equal to 30% of the disulphide, did not differ significantly from the normal. Hence, mercaptan is simply an end product of the decomposition.

Effect of the Complete Reaction Mixture

The effect of the complete decomposition products on the reaction was investigated by admitting a second sample of disulphide to the reaction vessel after the completion of a previous experiment. The induction period was reduced to a much greater extent than can be attributed to hydrogen sulphide alone. Indeed, the true induction period of the mercaptan reaction may have been removed entirely. In contrast to the effect of hydrogen sulphide alone the complete reaction mixture did not accelerate the maximum rate of pressure rise. The final pressure increase was slightly less than for the normal reaction.

Effect of Nitric Oxide

In the presence of 0.6, 2, and 7% nitric oxide, the induction period was no longer reproducible but the maximum rate was normal and occurred at the usual time.

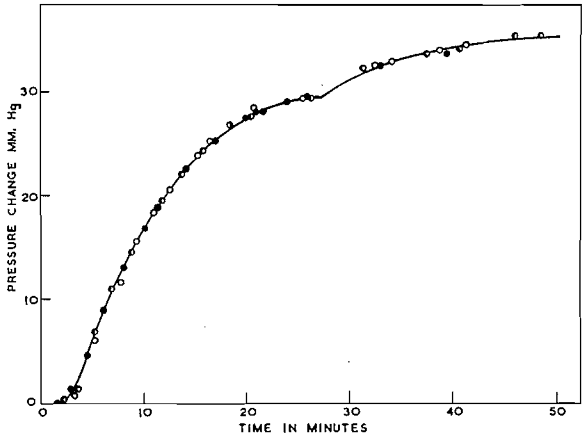


FIG. 4. Decomposition of diethyl disulphide at 318° C. Initial pressure, 28.0 mm. Results of three experiments are superimposed.

Comparison with the Decomposition of Diethyl Disulphide

The decomposition of diethyl disulphide appeared to be considerably different from the decomposition of dimethyl disulphide. Three superimposed pressure–time curves are presented in Fig. 4. Although similar in form to those of dimethyl disulphide they show a much greater total pressure increase. The maximum rate is first order with respect to the initial pressure, except at low pressures. The main rate constant of $19.7(\pm 1.1) \times 10^{-4}$ sec.$^{-1}$ at 318° C., obtained from runs at 28 mm., 33 mm., and 40 mm., falls off between 28 and 18 mm. This rate is of the same order as that for dimethyl disulphide at the much higher temperature of 341° C. The decomposition of diethyl disulphide produces an involatile tar similar in appearance to that produced by dimethyl disulphide. Unlike the decomposition of dimethyl disulphide, it produces a considerable quantity of a fine yellow solid, presumed to be elemental sulphur.

One feature of Fig. 4 is the "break" in the curve near the 30-min. mark. This suggests that the reaction may involve a second stage which is largely responsible for the pressure increase after 30 min.

DISCUSSION

The over-all reaction for the decomposition of dimethyl disulphide is complex. Two main reactions appear to occur. The first is decomposition of the disulphide with the formation of mercaptan, and the second is the formation of hydrogen sulphide and allied products. Both reactions exhibit an induction period. Extensive decomposition of the products of these reactions also takes place.

The rate curves for the formation of mercaptan and H_2S show that the decomposition of the disulphide comes to an end after about 60 min. for the 'standard reaction', i.e., the reaction illustrated in Fig. 2. This behavior cannot be due to an equilibrium as neither the addition of mercaptan nor the addition of hydrogen sulphide to the reaction mixture has any effect on the final pressure. Nor can it be due to inhibition by the products. It must be concluded that the pressure of the reactant disulphide falls to zero after about 60 min. Accordingly, the disulphide pressure at 120 min. has been listed in Table III as zero.

Hydrogen sulphide and mercaptan, the two products formed in greatest quantity, are both reduced relative to the disulphide. To balance the hydrogen, the hydrocarbon products must be either unsaturated or polymeric (Table III). Since the formation of hydrocarbons of more than two carbon atoms appears unlikely, and, indeed, could not account for the magnitude of the pressure increase, it is suggested that the hydrocarbons may be chiefly or entirely ethylene.

From Table III the estimated pressures of the components of the reaction mixture at 120 min. total 148 mm. This value agrees satisfactorily with the measured total pressure of 140 mm., and suggests that no other volatile products are formed in quantity. It supports the conclusion that the disulphide pressure is zero.

The primary reaction is believed to be the decomposition of one mole of disulphide to form one mole of methyl mercaptan. Since there is no accompanying pressure change the remaining fragment "CH_2S" of the dimethyl disulphide molecule must be removed from the system in some way. The thioaldehydes are well known for their remarkable tendency to polymerize; they are scarcely known in the monomeric state (11). The normal polymerization to cyclic trithioformaldehyde would result in a small pressure increase, but in the presence of foreign free radicals the polymerization would presumably be to higher polymers which are involatile. The following process, for example, would not allow ring closure:

$$R \xrightarrow{CH_2{=}S} RSCH_2 \xrightarrow{CH_2{=}S} RSCH_2SCH_2$$

The presence of an involatile tar in the reaction products lends support to this view. If this polymerization mechanism occurs, the primary decomposition may be represented by the following over-all reactions:

$$\left.\begin{array}{l} CH_3SSCH_3 \longrightarrow CH_3SH + CH_2{=}S \\ n\ CH_2{=}S \longrightarrow (CH_3S)_n \end{array}\right. \qquad [I]$$

Hydrogen sulphide appears to be produced by two reactions. The main reaction occurred under the conditions of these experiments between 10 and 60 min.; the total hydrogen sulphide produced by it is approximately 27 mm.; clearly its rate depends on the disulphide present. The second reaction became evident after the disulphide had disappeared. In the experiments discussed here it produces 10 mm. of hydrogen sulphide between 60 and 120 min. at a nearly constant rate, and would appear, therefore, to account for at least 5 mm. (15%) of the hydrogen sulphide produced before 60 min. This reaction must be due to the decomposition of products of the two main reactions, perhaps polythioaldehyde or alkyl polysulphides.

The disulphide available for the main reaction producing hydrogen sulphide appears to be equal to the hydrogen sulphide produced by it. This disulphide can be estimated by subtracting from the initial disulphide pressure the amount used up in producing mercaptan and polysulphide, 59 mm. and approximately 8 mm., respectively. The reaction producing mercaptan seems well established and the mercaptan analysis appears reliable. The polysulphide is in any case only a small correction and therefore the result of 28 mm. of disulphide available for hydrogen sulphide formation should not be greatly in error. It is roughly equal to the hydrogen sulphide produced. Thus one mole of disulphide appears to produce one mole of hydrogen sulphide in the main reaction. This suggestion appears consistent with the observed pressure change, whatever the complete reaction may be. There are, however, many factors affecting the pressure change and a certain deduction is difficult.

The alkyl polysulphides may be formed by addition reactions of the following type:

$$CH_3SSCH_3 + S_x \longrightarrow CH_3S_{x+2}CH_3 \qquad [II]$$

The labile character of polysulphide chains is well known.

The 25 mm. of hydrocarbons found by analysis from the standard experiment appear to be almost entirely ethylene. The ethylene could be formed by a second decomposition reaction along with the H_2S, as follows:

$$CH_3SSCH_3 \longrightarrow H_2S + CH_2{=}CH_2 + S \qquad [III]$$

This equation, though speculative, is consistent with the data available. The estimate for ethylene is in the ratio one-to-one with those for hydrogen sulphide and disulphide. When taken together, the three reactions postulated would account reasonably for all the substances observed in the decomposition. The reactant disulphide and the products hydrogen sulphide, mercaptan, and hydrogen, would be accounted for completely. The elemental sulphur of reaction [III] would produce the polysulphides of reaction [II] together with traces of S_8. Carbon disulphide, the only other volatile product could well be attributed to the secondary reactions, to the decomposition of the tar, for example. It is difficult to see how it could be produced from the disulphide directly. Finally, the amount of monomeric thioaldehyde necessary to balance reaction [I] would account quite well for the quantity and composition of the involatile products at 120 min., together with the carbon disulphide and small amounts of secondary hydrogen sulphide.

Although no direct evidence was obtained of the occurrence of free radical chains in the decomposition of dimethyl disulphide, it seems unlikely that the entire decomposition could take place by simple molecular reactions. The complexity of the reactant, the variety of the products, and the peculiar rate laws, all suggest free radical mechanisms.

For the primary reaction a straightforward unimolecular decomposition into methyl mercaptan and thioformaldehyde can be conceived. However, this reaction, being unimolecular, could not be catalyzed by the products, and therefore an explanation of the induction period on this basis would be difficult. On the other hand, a free radical chain mechanism is plausible.

The initiating radical might be CH_3S arising from the dissociation of disulphide at the S–S bond:

$$CH_3SSCH_3 \longrightarrow 2\ CH_3S \qquad [1]$$

The following sequence could result:

$$CH_3S + CH_3SSCH_3 \longrightarrow CH_3SH + CH_3SSCH_2 \qquad [2]$$

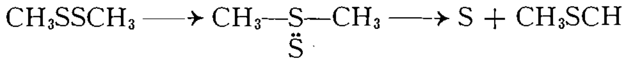
$$CH_3SSCH_2 \longrightarrow CH_2{=}S + CH_3S \qquad [3]$$

In addition to producing mercaptan to the required extent this mechanism also produces the postulated thioformaldehyde. Polymerization of the latter could arise through:

$$n\ CH_2{=}S \longrightarrow (CH_2S)_n \qquad [4]$$

$$\text{or } CH_3SSCH_2 + CH_2{=}S \longrightarrow CH_3SSCH_2SCH_2 \qquad [5]$$

A second possibility for the initiating radical of equation [1] is the production of a sulphur atom through an intermediate rearrangement of the type:



$$CH_3SSCH_3 \longrightarrow CH_3\text{—}\underset{\ddot{S}}{S}\text{—}CH_3 \longrightarrow S + CH_3SCH_3 \qquad [6]$$

through the decomposition of polysulphides:

$$CH_3S_xCH_3 \longrightarrow S + CH_3SS_{x-1}CH_3 \qquad [7]$$

or through the reaction [III] postulated for the production of hydrogen sulphide. The observed catalysis by hydrogen sulphide may be due to the production of sulphur atoms by a reduction process:

$$H_2S + CH_3SSCH_3 \longrightarrow S + 2CH_3SH \quad [8]$$

The more marked catalyses by the complete reaction mixture could be attributed to reaction [7]. The autoacceleration and approximate coincidence of the induction periods of the mercaptan and hydrogen sulphide reaction could also be dependent on the production of sulphur atoms.

More experimental work must be done before the details of the over-all reaction can be understood.

ACKNOWLEDGMENTS

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THE CHARACTERIZATION OF DELCOSINE AND SOME OF ITS DERIVATIVES[1]

By W. I. Taylor,[2] W. E. Walles,[3] and Léo Marion

ABSTRACT

Reanalysis of delcosine and several of its derivatives shows that the most likely empirical formula is $C_{24}H_{39}O_7N$. Delcosine has been shown to be identical with Goodson's base C. Acetylation produces monoacetyldelcosine, identical with Goodson's naturally occurring base B. It has been possible to prepare two isomeric diacetyl derivatives, one of which has been reported previously, and a further acetylated compound also reported previously which seems to have lost the elements of water. A dipropionyldelcosine is also described. The base contains three methoxyls and four hydroxyls, only two of which are acetylated readily.

Delcosine, one of the alkaloids of *Delphinium consolida* L., has been assigned several empirical formulae by various authors, i.e., $C_{21}H_{33}O_6N$ (5), $C_{25}H_{40}O_7N$ (*sic*) (1), and $C_{22}H_{37}O_6N$ (4). In order to arrive at a more definite formula, the alkaloid was purified and reanalyzed together with some salts and a number of its derivatives. The empirical formula which appears to agree best with all the results is $C_{24}H_{39}O_7N$. On this basis the base, which is tertiary, contains three methoxyls and four active hydrogens (Zerewitinow) corresponding to four hydroxyl groups, thus accounting for all the oxygen. Delcosine further contains an N-alkyl which is probably an ethyl (3). The pK_A of the alkaloid is 6.49. The formula can be expanded to $C_{19}H_{21}(NC_2H_5)(OCH_3)_3(OH)_4$ containing a C_{19} nucleus in agreement with that of a number of aconite and delphinium bases (2).

From *Delphinium ajacis* Goodson (3) had isolated in small quantity a base which he designated "alkaloid C" for which he proposed the empirical formula $C_{24}H_{37}O_7N$. This base contained an N-ethyl group and resembled delcosine in its properties. A sample of "alkaloid C" kindly supplied by Dr. T. M. Sharp has now been shown by direct comparison to be identical with delcosine. The melting points of the bases and that of the mixture were identical and the infrared absorption spectra were superimposable.

Two of the four hydroxyls of delcosine underwent acetylation more readily than the other two. It has been possible to prepare a monoacetyldelcosine, a diacetyldelcosine, a monotrichloroacetyldelcosine, and a dipropionyldelcosine. Diacetyldelcosine is quite distinct from the "triacetyldelcosine" already reported (4) which, on the basis of the new formula, is also a diacetyldelcosine. The infrared spectra of these two isomers show marked differences.

Among the alkaloids of *D. ajacis* Goodson (3) had reported the presence of a minor base, "alkaloid B", which gave rise to "alkaloid C" on hydrolysis and

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was considered as an acetyl derivative. A sample of "alkaloid B" kindly supplied to us by Dr. T. M. Sharp indeed proved by melting point, mixed melting point, and comparison of the infrared absorption spectra to be identical with monoacetyldelcosine.

The alkaloid delphamine isolated by Rabinovich and Konowalowa (6) from an unidentified *Delphinium* species may possibly be identical with delcosine. It is not possible to conclude this definitely without a direct comparison, but the recorded melting points of the two bases, of their hydriodides, bitartrates, chloroplatinates, and the diacetyl derivatives are remarkably similar.

The acetyl derivative of melting point 159–161° reported by Marion and Edwards (4) has again been prepared. The infrared absorption spectrum of this derivative contained no absorption bands in the hydroxyl region, and the absence of hydroxyl groups thus indicated was confirmed by an active hydrogen determination which gave negative results. The analytical figures did not agree with the requirements of a tetraacetyl derivative, but were in best agreement with a diacetyldelcosine having lost the elements of water. Since no hydroxyl was present the fourth hydroxyl oxygen must have become involved in a cyclic ether or converted to a carbonyl.

A derivative was also obtained in one experiment which appeared to be tetraacetyldelcosine, but will require further characterization before its identity is established.

EXPERIMENTAL[4]

Delcosine was purified by repeated crystallization from dioxane – petroleum ether (1:1), m.p. 203–204°. Found: C, 63.76, 64.04, 63.83; H, 9.07, 8.93, 9.01; N, 3.09, 3.18; OCH_3, 20.14, 20.75; N-alk., 7.85, 7.83; act. H (Zerewitinow), 0.75, 0.85%; mol. wt. (by titration), 455. Calc. for $C_{24}H_{39}O_7N$: C, 63.55; H, 8.67; N, 3.09; 3 OCH_3, 20.53; 4 act. H, 0.88; $N.C_2H_5$, 6.39%; mol. wt. 453.6. pK, 6.49 (value of pH at half titration in 50% methanol with 0.0333 *N* hydrochloric acid). In admixture with Goodson's "alkaloid C" (3) the melting point was unchanged. The infrared absorption spectra of delcosine and "alkaloid C" were superimposable. The spectrum of delcosine contained the following peaks:[5] 3518 (43), 3476 (57), 3362 (73), 1355 (58), 1325 (48), 1305 (67), 1275 (48), 1225 (64), 1192 (69), 1170 (64), 1140 (70), 1115 (89), 1095 (85), 1085 (88), 1050 (68), 1040 (72), 1015 (62), 1000 (47), 980 (45), 970 (56), 950 (81), 915 (27), 875 (37), 860 (41), 815 (25), 800S (22), 760 (45), 740 (34), 710 (34), 710 (29), 675 (45).

Delcosine Perchlorate

The salt was recrystallized, m.p. 217–218°, and reanalyzed. Found: C, 51.90, 52.10; H, 6.94, 7.16; N, 2.45. Calc. for $C_{24}H_{39}O_7N \cdot HClO_4$: C, 52.04; H, 7.28; N, 2.53%.

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[4] *All melting points are corrected.*

[5] *The infrared spectra were determined on a Perkin–Elmer double beam spectrophotometer model 21. The peaks are indicated by a wave number and the percentage absorption is given by the number in parentheses. Shoulders are indicated by an S after the wave number. Unless otherwise indicated the compounds were suspended in nujol as mulls for the determination.*

Delcosine Hydriodide

Delcosine was neutralized with hydriodic acid and the solution evaporated to dryness. The residue was crystallized twice from methanol. Delcosine hydriodide melted at 196–197°. Found: C, 49.39; H, 6.84; N, 2.27; I, 21.64. Calc. for $C_{24}H_{39}O_7N \cdot HI$: C, 49.61; H, 6.94; N, 2.41; I, 21.83%. All attempts to prepare delcosine methiodide failed and invariably gave rise to the hydriodide.

Delcosine Bitartrate

The salt was prepared by mixing equivalent quantities of the base and tartaric acid. After recrystallization it melted at 165–166°. Found: C, 55.55, 55.80; H, 7.03, 7.26; N, 2.47. Calc. for $C_{24}H_{39}O_7N \cdot C_4H_6O_6$: C, 55.71; H, 7.51; N, 2.32%.

Monoacetyldelcosine

Delcosine (260 mgm.) was heated for three hours at 80–90° with acetic acid (3.0 ml.) and trifluoroacetic acid (0.10 ml.). Ethanol (2 ml.) was then added and the solution alkalized with 4% aqueous sodium carbonate. The resulting solution was extracted with chloroform and the combined extract dried and evaporated under reduced pressure. The residue (288 mgm.) was dissolved in ether (5 ml.) containing ethanol (0.5 ml.) and the solution diluted with petroleum ether. The monoacetyldelcosine which crystallized out was sublimed at 182° at 10^{-5} mm., and recrystallized twice from ether – petroleum ether from which it separated as colorless prisms, m.p. 191–193°, wt. 225 mgm. $[\alpha]_D^{28} + 32$ (*c*, 3.17 in chloroform). Found: C, 63.09, 63.44; H, 8.27, 8.49; N, 2.82, 2.70; OCH_3, 18.75; act. H (Zerewitinow), 0.51; mol. wt. (titration) 495.5. Calc. for $C_{24}H_{38}O_7N \cdot COCH_3$: C, 63.01; H, 8.34; N, 2.83; 3 OCH_3, 18.79; 3 act. H, 0.61%; mol. wt. 495.6. The pK value was 6.25 (value of pH at half titration in 50% methanol with 0.0333 *N* hydrochloric acid).

In admixture with Goodson's "alkaloid B" (m.p. 193–195°, $[\alpha]_D + 34°$), the melting point of monoacetyldelcosine was unchanged. The infrared absorption spectra of the two bases taken in carbon disulphide solution were superimposable. They contained the following peaks: 3520 (45), 3475 (76), 3210 (35), 2940 (88), 2880 (81), 1735 (95), 1385 (76), 1365 (77), 1337S (50), 1325 (65), 1300 (65), 1245 (98), 1225 (88), 1215S (84), 1190 (75), 1170 (69), 1135S (78), 1120 (92), 1100 (98), 1087 (99), 1050 (82), 1040 (78), 1030 (64), 1015 (59), 1000 (58), 985 (43), 970 (47), 955 (53), 940 (48), 910 (37), 810 (16), 760 (32), 740 (34), 720 (29), 685 (39), 660 (47), 635 (36).

Monoacetyldelcosine was also obtained by the action of acetyl chloride on delcosine at room temperature for five minutes.

Mono-(trichloroacetyl)-delcosine

Delcosine (191 mgm.) was kept at 75° for five hours with trichloroacetic acid (3.2 gm.) and trifluoroacetic acid (0.1 ml.). The product was worked up as described for monoacetyldelcosine except that it could not be sublimed. After several recrystallizations from alcohol–water, mono-(trichloroacetyl)-delcosine melted at 172.5–173.5° (wt. 125 mgm.). Found: C, 53.50, 53.41;

H, 6.47, 6.42; N, 2.56%. Calc. for $C_{24}H_{38}O_7N \cdot COCCl_3$: C, 52.13; H, 6.40; N, 2.34%.

Diacetyldelcosine

Delcosine (338 mgm.) was dissolved in dry pyridine (3.0 ml.) and freshly distilled acetic anhydride (2.0 ml.) added to the solution which was kept at 87° for eight hours. The colorless reaction mixture was concentrated under reduced pressure to a thick oil to which ethanol (1.5 ml.) and water (3.0 ml.) were added. The basicity of the solution was adjusted to pH 9 to 10 by the addition of 4% aqueous sodium carbonate. A white amorphous precipitate separated and the mixture was extracted with chloroform. The combined extract was evaporated to dryness under reduced pressure and the residual colorless oil (wt. 351 mgm.) dissolved in ethanol. Addition of water to the solution caused the separation of an oil which crystallized on standing overnight, wt. 320 mgm. After two recrystallizations from dilute ethanol diacetyldelcosine consisted of colorless needles, m.p. 127–128°. It was sublimed (140° at 10^{-4} mm.) without decomposition. pK, 5.33 (pH at half titration in 50% methanol). Found: C, 62.49, 62.76; H, 7.99, 8.08; N, 2.89, 2.76; OCH_3, 17.14, 17.11; act. H (Zerewitinow), 0.36%; mol. wt. (titration), 536. Calc. for $C_{24}H_{37}O_7N \cdot (COCH_3)_2$: C, 62.55; H, 8.06; N, 2.61; 3 OCH_3, 17.32; 2 act. H, 0.37%; mol. wt. 537.6. The infrared absorption spectrum contained two absorption bands at 3459 $cm.^{-1}$ and 3392 $cm.^{-1}$ indicative of two unreacted hydroxyl groups. It also contained a strong carbonyl band at 1730 $cm.^{-1}$ and an ester band at 1246 cm^{-1}.

Dipropionyldelcosine

Delcosine (186 mgm.) was added to dry pyridine (4.0 ml.) and propionic anhydride (1.0 ml.), and the mixture heated for three hours at 100°. The dipropionyldelcosine was isolated exactly as described for diacetyldelcosine, and after several recrystallizations dilute ethanol melted at 119–120°. It could be sublimed (147° at 10^{-5}mm.) without decomposition. Found: C, 63.88; H, 8.46; N, 2.58. Calc. for $C_{24}H_{37}O_7N \cdot (COC_2H_5)_2$: C, 63.69; H, 8.37, N, 2.48%. The infrared spectrum of this derivative contained two absorption bands at 3480 $cm.^{-1}$ and 3418 $cm.^{-1}$ in the OH region, a carbonyl band at 1732 $cm.^{-1}$ and a strong absorption peak at 1190 $cm.^{-1}$ attributable to the ester groups.

Further Acetylation Experiments

A mixture of delcosine (427 mgm.) and purified acetyl chloride (5 ml.) was kept at room temperature for 72 hr. The excess reagent was distilled off under reduced pressure and the oily residue dissolved in dilute ethanol. The solution was alkalized to pH 10 with 4% aqueous sodium carbonate and extracted with chloroform. Addition of ether to the chloroform brought down a crystalline precipitate which was filtered, m.p. 264–266°. Further additions of ether caused the precipitation of a second substance, which after two crystallizations from alcohol–ether proved to be monoacetyldelcosine, m.p. 186–189°, wt. 220 mgm. The higher melting product was recrystallized from alcohol–ether from which it was obtained as colorless needles, m.p. 268.5–269.5°. The infrared absorption spectrum showed no absorption in the OH region. Found: C, 61.33, 61.39; H, 7.38, 7.11; N, 2.51; OCH_3, 16.01. Calc. for $C_{24}H_{35}O_7N \cdot (COCH_3)_4$: C, 61.82; H, 7.62; N, 2.25; 3 OCH_3, 14.98%.

Delcosine (825 mgm.) and excess acetyl chloride (5 ml.) were maintained at 60° for four hours. The excess acetyl chloride was evaporated under diminished pressure, the residue dissolved in water, the solution alkalized with sodium carbonate, and extracted with chloroform. The residue left after evaporation of the chloroform was crystallized from methanol from which it separated in colorless needles, m.p. 159–161°, either alone or in admixture with the derivative of similar melting point reported by Marion and Edwards (4), $[\alpha]_D^{28}+31°$ (*c*, 2.92 in chloroform), yield 310 mgm. The mother liquors yielded a further 100 mgm. of the same derivative. A sample for analysis was dried for 12 hr. at 92° at 0.1 mm. Found: C, 64.82, 64.73; H, 7.85, 7.87; act. H, nil. Calc. for $C_{28}H_{41}O_8N$: C, 64.72; H, 7.95%. The infrared absorption spectrum of the substances showed no absorption in the OH region.

From some preparations of the foregoing derivative, small quantities of a crystalline substance could be obtained which was characterized by its relative insolubility in methanol. Through this property it could be purified readily and crystallized as needles, m.p. 204°, either alone or in admixture with the "triacetyldelcosine" of Marion and Edwards (4). On the basis of the new formula this corresponds to a diacetyldelcosine, $[\alpha]_D^{28}+7.5°$ (*c*, 1.6 in chloroform). For analysis a sample was dried for 36 hr. at 100° at 0.1 mm. Found: C, 62.62, 62.42; H, 7.66, 7.99; OCH_3, 17.7; act. H (Zerewitinow), 0.41, 0.39%. Calc. for $C_{24}H_{37}O_7N(COCH_3)_2$: C, 62.55; H, 8.06; 3 OCH_3, 17.32; 2 act. H, 0.37%. This diacetyldelcosine was not identical with that described above (m.p. 127–128°) and the infrared absorption spectra of both compounds show quite pronounced differences.

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SOME REACTIONS OF ETHYL 2-PYRIDINEACETATE 1,2-DICARBETHOXY-3-OXO-OCTAHYDROPYRROCOLINE[1]

By O. E. Edwards, M. Chaput[2], F. H. Clarke[3], and Tara Singh[4]

ABSTRACT

Ethyl α-acetoxy-2-pyridineacetate and ethyl α-bromo-2-pyridineacetate have been prepared, and the latter converted in three steps to 1,2-dicarbethoxy-3-oxo-octahydropyrrocoline. The main carbonyl band of simple saturated five membered lactams in the infrared is observed to lie close to 1700 cm^{-1}.

The methylene group of ethyl 2-pyridineacetate is of comparable activity to that of ethyl acetoacetate. For example, a useful anion can be obtained by reaction with sodium or potassium (1, 4). Further parallel between the reactivities of the two compounds has now been found in the ease of bromination and acetoxylation. Like acetoacetic ester (6), 2-pyridineacetic esters react rapidly with a molar equivalent of bromine at 5°C. in carbon disulphide solution to give α-bromo esters, and react at room temperature with lead tetraacetate in benzene to give the α-acetoxy compound. In contrast, the methylene group of malonic esters does not react at a useful rate with lead tetraacetate in benzene until the solution is heated to around 100° (6).

The synthesis of octahydropyrrocolines with reactive substituents has been achieved by Clemo and co-workers (2, 3, 4) and by Lions and Willison (10). The work of Diels and co-workers (5, and earlier papers) has led to pyrrocolines substituted with carboxyls, which presumably could be reduced to the corresponding octahydro derivatives. By reaction of ethyl α-bromo-2-pyridineacetate with the anion from ethyl malonate, reduction of the product, and cyclization, 1,2-dicarbethoxy-3-oxo-octahydropyrrocoline III has now been obtained. The malonic hydrogen and carboxyl groups in this compound are of potential value for building additional rings on the five membered ring.

The reactions used in preparing and characterizing the various products are shown in the flowsheet. The mixture obtained when the bromo compound reacted with the malonic anion contained some ethyl 1,1,2,2-ethanetetracarboxylate, probably arising from ethyl bromomalonate formed by bromine exchange. This could be partly removed by distillation under high vacuum, but the desired product I could not be distilled without considerable decomposition. By chromatography on neutral alumina, however, I could be freed from the ethanetetracarboxylic ester, unchanged malonic ester, and colored impurities.

I proved to be a very weak base (pK_A around 2.4 in 50% aqueous methanol). A somewhat low basicity (pK 3.6) has been observed for α,α-di-(2-pyridyl)-

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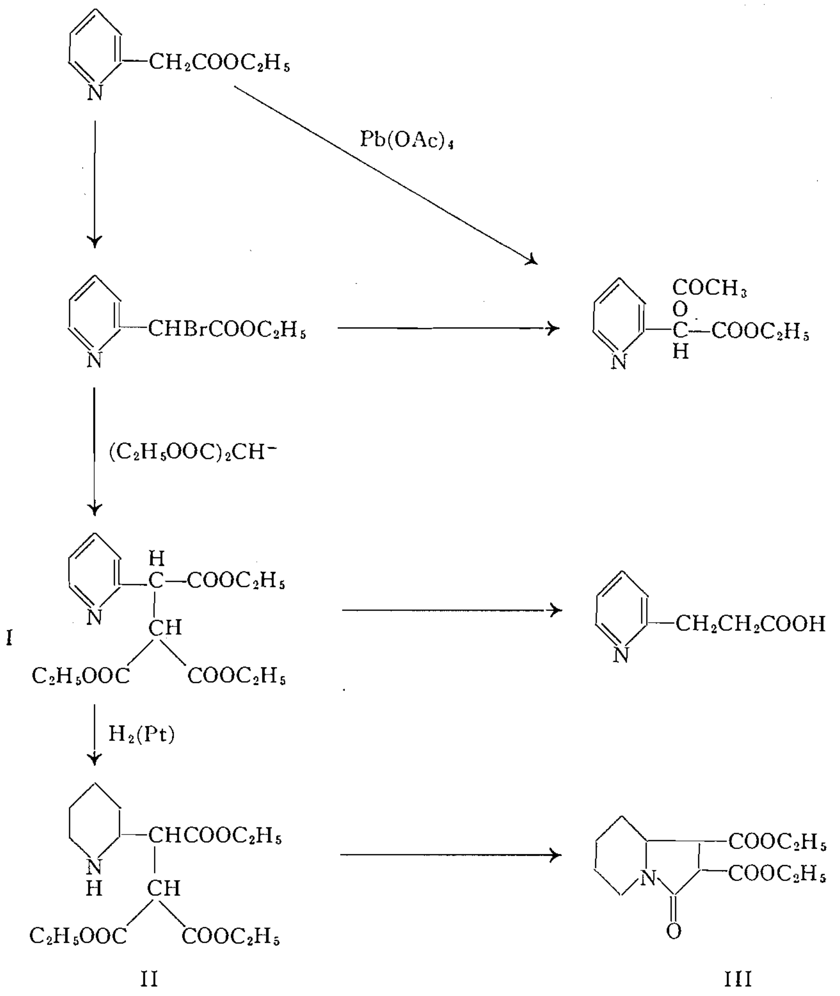
FLOWSHEET



γ,γ-dicarbethoxypropane (9). This may in part be due to interaction across space between the nitrogen and the ester carbonyls. In the case of I, however, the inductive effect of the three carbethoxy groups must be the main cause of the low basicity. The ultraviolet spectrum of I (λ_{max} 261mμ, log ϵ 3.54) was very similar to that of α-picoline, hence no rearrangement of the double bonds had taken place.

Attempts to prepare ethyl α–β-di(2-pyridyl)-succinate by reaction of ethyl α-bromo-2-pyridineacetate and the anion from ethyl pyridineacetate gave intractable highly colored products. Similar results were obtained in an attempt to obtain this compound by coupling two molecules of the anion using iodine.

When the crude I was hydrolyzed and decarboxylated, considerable tar was produced, but a 27% yield of β-(2-pyridyl)-propionic acid was obtained.

The piperidine triester II underwent smooth cyclization when distillation was attempted and only the lactam III was obtained. When III was hydrolyzed, the mixture of stereoisomeric acids proved reluctant to crystallize. On long standing, however, two diastereoisomers melting with decomposition near 170° were obtained in poor yield.

The C = O stretching vibration in saturated N-alkyl six membered lactams gives rise to an absorption band near 1640 cm.$^{-1}$ (8). The position of this band for four pyrrolidones is indicated in Table I. From these observations it appears that in simple saturated systems the position of this band can be used to assign ring size to a lactam. The spectrum of the 3-oxo-octahydropyrrocolinedicarboxylic acid, however, had unusual absorption in the 6 μ region, and the bands cannot be assigned to any individual vibration.

TABLE I

Compound	Wave number, cm.$^{-1}$	State
Lactam III	1705 1690	Liquid film Chloroform solution
N-methyl-2-pyrrolidone	1690 1680	Liquid film Chloroform solution
Octahydrogelsemine*	1693	Nujol mull
2-Pyrrolidone	1695	Film from melt

The authors wish to thank Dr. L. Marion for permission to use this value.

It is interesting to note that the relatively intense band in the OH, NH stretching region (around 3450 cm.$^{-1}$) which has been observed for N-alkyl six membered lactams (8) also appears in the spectra of the N-substituted five membered lactams. In a recent paper (11) this band has been attributed to water in the samples. We consider this unlikely in our own cases in view of the high distillation temperatures (center cuts were taken), the good carbon, hydrogen analyses of the compounds, and the complete disappearance of the bands in chloroform solution. Hence, unless some very unusual spectral effect gives rise to this band, it seems likely that it is due to the presence of considerable enol in the liquid state.

EXPERIMENTAL

The infrared spectra were taken on a Perkin-Elmer model 21 double beam spectrophotometer with a sodium chloride prism. The location of the bands is given in cm.$^{-1}$ followed in brackets by the percentage absorption. The ultraviolet spectra were taken using a Beckmann D.U. spectrophotometer.

Methyl α-Bromo-2-pyridineacetate

Methyl 2-pyridineacetate (2.0 gm., b.p. 90°, 2 mm.) was dissolved in carbon disulphide in a flask surrounded by cracked ice. A solution of 2.2 gm. of bromine in 10 ml. of carbon disulphide was added slowly while the reaction mixture was stirred. After the addition the reaction mixture was allowed to stand at room temperature for one hour. The carbon disulphide was boiled off and the residue covered with a layer of ether. Excess saturated potassium carbonate solution was added, the ether layer separated, and the aqueous layer extracted three times with ether. The yellow oil recovered from the dried ether solution was distilled over a short path at a bath temperature of 90°, 0.2 mm. Yield, 2.3 gm. Found: C, 41.78; H, 3.32; N, 5.69. Calc. for $C_8H_8O_2NBr$: C, 41.76; H, 3.51; N, 6.09.

Ethyl α-Bromo-2-pyridineacetate

Prepared as described for the methyl ester in 77% yield. Distilled over a short path at a bath temperature of 90°, 0.2 mm. Found: Br, 31.76, 31.12. Calc. for $C_9H_{10}O_2NBr$: Br, 32.74. The compound is sensitive, and develops color on heating or keeping, hence the somewhat low bromine values.

Ethyl α-(Dicarbethoxymethyl)-2-pyridineacetate (I)

To ethyl α-bromo-2-pyridineacetate (2.75 gm.) in 10 ml. of absolute ethanol was added dropwise a solution of sodio–malonic ester (from 0.265 gm. of sodium and 1.80 gm. of ethyl malonate) in 5 cc. of ethanol. After the addition the mixture was allowed to sit for 0.5 hr. at room temperature. The ethanol was then removed under reduced pressure. The residue was taken up in methylene chloride, and this solution extracted three times with 3 *N* hydrochloric acid (40 cc.). The methylene chloride solution contained 2.8 gm. of oil. The aqueous solution was made alkaline with ammonia and extracted with methylene chloride giving 0.91 gm. of base.

The neutral oil was chromatographed on 56 gm. of neutral alumina (activity 2–3, Brockmann scale). Three hundred cubic centimeters of benzene eluted 2.38 gm. of pale reddish oil. The remaining esters were eluted with chloroform and ethanol in chloroform (304 mgm.). The benzene eluates were rechromatographed on 51 gm. of neutral alumina activity 1–2. The first three groups of eluates were colorless oils. Fraction 1 contained some ethyl malonate, and ethyl 1,1,2,2-ethanetetracarboxylate in addition to the desired product. The first two esters could be separated by distillation under high vacuum. The distillate crystallized. After recrystallization from ether petroleum ether it

Solvent	Volume, cc.	Weight eluted, mgm.	λ_{max} in mμ	ϵ_{max}
1. 50% Petroleum ether – benzene	400	876	260.5	1690
2. Benzene	250	489	260.5	3420
3. 50% Chloroform benzene	200	276	260.5	3470
4. Chloroform and ethanol in chloroform	400	490	Not determined	

melted at 76° (1,1,2,2-ethanetetracarboxylate melts at 76°). Found: C, 52.84; H, 6.93. Calc. for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97.

Fraction 3 in 0.01 *N* hydrochloric acid in ethanol had λ_{max} 262 mμ, log ϵ 3.78. It had a pK_A of 2.4 in 50% aqueous methanol.

Distillation of a sample of fraction 3 under 5×10^{-5} mm. and a bath temperature of 110° gave an orange oil, and left a tarry residue. The distillate was analyzed. Found: C, 58.00; H, 6.71. Calc. for $C_{16}H_{21}O_6N$: C, 59.43; H, 6.55.

Hydrolysis and Decarboxylation of I

Four grams of crude I was hydrolyzed with hot dilute sodium hydroxide solution. The solution was made just acid to Congo red paper with hydrochloric acid. The water was removed under reduced pressure and the residue extracted with ethanol. This was transferred to a bulb and heated under 0.2 mm. pressure. At 120° brisk decomposition took place. The product was then sublimed under 3×10^{-3} mm. pressure, giving 520 mgm. of crystalline solid. This was suspended in hot benzene and filtered. The crystals melted at 141° (β-(2-pyridyl)-propionic acid is reported to melt at 141° (7)). Found: C, 63.38; H, 5.79. Calc. for $C_8H_9O_2N$: C, 63.56; H, 6.00.

1,2-Dicarbethoxy-3-oxo-octahydropyrrocoline

A sample of I, calculated from the ultraviolet spectrum to contain 1.2 gm. of the triester, was dissolved in 15 ml. of ethanol containing 0.5 ml. of concentrated hydrochloric acid. In the presence of platinum from 0.16 gm. of platinum oxide this absorbed 260 ml. of hydrogen at 25°C. in 35 min. (2.9 moles per mole). After removal of the catalyst and ethanol, the product was dissolved in dilute acid and the neutral impurity extracted with ether. The acid solution was made basic with sodium carbonate and the base extracted with methylene chloride giving 960 mgm. of colorless oil. No crystalline picrate of this base could be obtained. On treatment with acetic anhydride at room temperature a sample of the base gave a neutral oil. When the base was distilled under 10^{-3} mm. at a bath temperature of 120°, a neutral oil resulted which analyzed correctly for the pyrrocolone. Found: C, 59.75; H, 7.56. The distillate was dissolved in methylene chloride, washed with acid and alkali, dried, and the oil redistilled. Found: C, 59.78, 59.20; H, 7.50, 7.31. Calc. for $C_{14}H_{21}O_5N$: C, 59.33; H, 7.49. Infrared spectrum (liquid film): 3450 (12), 2960 (56), 2880 (35), 1740 (93), 1705 (94), 1452 (67), 1435 (62), 1404 (49), 1375 (63), 1315 (58), 1263 (83), 1237 (79), 1215 (80), 1180 (78), 1117 (38), 1097 (40), 1030 (66), 972 (27), 949 (21), 915 (11), 885 (18), 855 (32), 700 (27).

1,2-Dicarboxy-3-oxo-octahydropyrrocoline

A solution of 0.98 gm. of base from the hydrogenation of I was saponified overnight with sodium hydroxide in aqueous ethanol. The solution was made just acid to Congo red paper with hydrochloric acid, then evaporated to dryness under reduced pressure. No amino acid could be extracted from this residue by boiling chloroform. The salts were dissolved in 6 *N* hydrochloric acid, then the solution taken to dryness. The residue was taken up in water and again taken to dryness under reduced pressure. The solid was extracted with cold dry ethanol, giving 0.73 gm. of viscous oil. This was readily soluble in chloroform. When a concentrated chloroform–ether solution of this acid stood for several weeks a crystalline compound (40 mgm.) separated. After two recrystallizations from acetone ether this gave 10 mgm. m.p. 175° dec. neutral equivalent: 107. Calc. for $C_{10}H_{13}O_5N$, neutral equivalent 113.6. On long standing the main mother liquor deposited a second crop of crystals. After recrystallization 60 mgm. was obtained, m.p. 171° dec. When mixed with the first crop this melted at 165° dec. Found: neutral equivalent, 126; C, 53.18; H, 5.69; N, 6.38. Calc. for $C_{10}H_{13}O_5N$: C, 52.86; H, 5.77; N, 6.17, neutral equivalent, 113.6. The pK_A's of the two carboxyl groups were approximately 4.1 and 5.7 in 50% aqueous methanol.

Ethyl α-Acetoxy-2-pyridineacetate

(*a*) Ethyl α-bromo-2-pyridineacetate (1.13 gm.) was added to a solution of 4.0 gm. of sodium acetate in 20 cc. of ethanol and 1 cc. of water. The mixture was refluxed for six hours, the solvent then removed under reduced pressure, and the residue extracted with ether. The 715 mgm. of oil recovered from the ether was distilled at a bath temperature of 97° under 0.2 mm. pressure giving 490 mgm. of nearly colorless oil. Found: C, 59.20; H, 5.63. Calc. for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87. Infrared spectrum (liquid film) 3480 (6), 3080 (16), 3000 (37), 1750 (93), 1600 (65), 1580 (45), 1479 (56), 1443 (65), 1376 (75), 1342 (46), 1235 (83), 1216 (91), 1187 (80), 1099 (53), 957 (27), 925 (26), 830 (18), 754 (57), 699 (29), 649 (25).

The base, probably because of its low basicity, formed a picrate which had more of the character of a molecular complex than that of a salt. It was quite soluble in ether, and it had to be crystallized from a concentrated solution in this solvent. It melted at 100°. Found: C, 45.22, 45.53; H, 3.55, 3.65. Calc. for $C_{17}H_{16}N_4O_{11}$, C, 45.14; H, 3.57.

(*b*) Ethyl 2-pyridineacetate (2.0 gm.) was added to a solution of 4 gm. of lead tetraacetate in 30 cc. of benzene. Some heat was evolved, the solution turned brown, and a crystalline precipitate settled. After one hour at room temperature the mixture was filtered and the solid washed with benzene. The benzene solution was washed with sodium bicarbonate solution, dried, and distilled. A residue of 1.6 gm. of dark liquid remained. This was distilled over a short path at a bath temperature of 85–120° under 0.3 mm. pressure. The 600 mgm. of brown distillate was redistilled, giving 450 mgm. of faintly colored oil. The infrared spectrum of this was identical to that of the product from (*a*).

1-Methyl-2-pyrrolidone[5]

This was distilled under one atmosphere pressure (b.p. 200°), a center cut being taken for the spectra. Calc. for C_5H_9ON: C, 60.58; H, 9.15. Found: C, 60.90; H, 9.24. Infrared spectrum: (*a*) Liquid film, 3480 (34), 2950 (39), 2900 (38), 1690 (92), 1508 (48), 1479 (40), 1465 (42), 1442 (45), 1432 (48), 1407 (55), 1303 (67), 1267 (45), 1230 (18), 1173 (13), 1114 (36), 1025 (10), 985 (25), 925 (11), 847 (11), 740 (13), 650 (34). (*b*) Chloroform solution 31 mgm. per ml.; 3020 (66), 2900 (33), 1680 (97), 1508 (51), 1479 (37), 1465 (36), 1446 (40), 1432 (44), 1410 (59), 1305 (67), 1266 (43), 1210 (67), 1175 (14), 1115 (33), 1025 (9), 985 (22).

2-Pyrrolidone[5]

Melting point 25°. For the spectrum, a crystal was melted between rock salt plates. Infrared spectrum: 3260 (49), 2980 (29), 2910 (30), 1695 (89), 1500 (20), 1470 (31), 1445 (27), 1431 (30), 1385 (18), 1290 (50), 1272 (40), 1230 (12), 1170 (10), 1070 (21), 996 (22), 916 (7), 885 (9), 680 (32).

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[5] *The authors wish to thank the General Aniline and Film Corporation for generous gifts of these compounds.*

THE C^{14} ISOTOPE EFFECT IN THE CONDENSATION OF BENZOYLBENZOIC ACID-CARBOXYL-C^{14} TO ANTHRAQUINONE-9-C^{14} [1]

By W. H. Stevens and D. A. Crowder

ABSTRACT

Benzoylbenzoic acid-carboxyl-C^{14} has been synthesized. The C^{14} isotope effect in the condensation of this acid to anthraquinone-9-C^{14} in concentrated sulphuric acid has been measured and the ratio of the reaction rates, $k(14)/k(12)$, found to be 1.074 ± 0.003. It is suggested that this result supports the mechanism for this reaction proposed by Newman.

INTRODUCTION

A simplified theoretical treatment of isotope effects on reaction rates has been given by Bigeleisen (3). He predicts that substitution of a heavier isotopic atom in a given molecular species will generally cause the reaction rate constant for that species to decrease. This might be termed the "normal" isotope effect. The Bigeleisen treatment also gives the theoretical conditions which must obtain in a reaction for a "reverse"[2] isotope effect to occur. It appears that these conditions are most likely to be satisfied in reactions where bond formation is the rate controlling step.

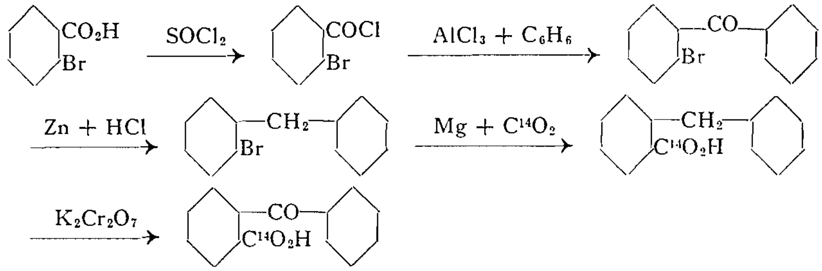
In almost all of the reactions in which carbon isotope effects have been found to occur thus far, bond cleavage is the rate controlling step. In these reactions the isotope effect is "normal", with the exception of the iodination of acetone (12). An explanation of the reverse isotope effect found in this reaction has been given by Yankwich (18). A reverse nitrogen isotope effect has been observed in the deammonation of phthalamide (15).

We were led to investigate the C^{14} isotope effect in the condensation of *o*-benzoylbenzoic acid-carboxyl-C^{14} to anthraquinone-9-C^{14} because it appeared that carbon to carbon bond formation could be the rate controlling step in the reaction. This paper reports a "reverse" isotope effect in this reaction and discusses how this result supports the mechanism proposed for the reaction by Newman (10).

EXPERIMENTAL

A. *Preparation of o-Benzoylbenzoic Acid-carboxyl-C^{14}*

o-Benzoylbenzoic acid-carboxyl-C^{14} was synthesized using the following sequence of reactions:



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Contribution from: Chemistry Branch, Atomic Energy of Canada Limited, Chalk River, Ontario. Issued as A.E.C.L. No. 118.

[2] *I.e. for the heavier isotopic molecule to have the greater rate constant.*

o-Bromobenzophenone was prepared according to the method given by Bergman (2). *o*-Bromodiphenyl methane was obtained by a Clemmenson reduction of this ketone following the method of Clarkson and Gomberg (6). Benzylbenzoic acid-carboxyl-C^{14} was prepared by carbonating the Grignard made from the *o*-bromodiphenylmethane on a 5 mM. scale using a vacuum line technique which has been described earlier (16). The benzylbenzoic acid-carboxyl-C^{14} was oxidized to benzoylbenzoic acid-carboxyl-C^{14} using potassium dichromate in acetic acid. This acid was diluted with several times its weight of inactive *o*-benzoylbenzoic acid and recrystallized from 15% aqueous alcohol, m.p. 127°C.

B. *The Condensation Reaction*

The condensation of *o*-benzoylbenzoic acid to anthraquinone in concentrated sulphuric acid was found to be a first order reaction by Gleason and Dougherty (8).

The experimental procedure used for our work was as follows: A sample of *o*-benzoylbenzoic acid-carboxyl-C^{14}, approximately 3.5 gm., was accurately weighed into a dry 50 ml. glass stoppered erlenmeyer flask. Concentrated sulphuric acid (25 ml.) was added and the flask reweighed. After the organic acid was completely dissolved, a 10 ml. sample of the homogeneous solution was withdrawn and run into a dry weighed glass stoppered tube. The tube and contents were weighed and placed in a thermostated water bath at 80 ± 0.5°C. for 15 min. This temperature and time of reaction were known to give about 10% reaction. The sulphuric acid solution was then poured onto approximately 50 gm. of crushed ice, and the tube was thoroughly rinsed out with cold water. The mixture was digested on a hot water bath for a half hour, and the precipitated anthraquinone filtered into a weighed sintered glass gooch crucible and washed with dilute ammonia solution and water. The crucible and contents were dried in a vacuum desiccator over concentrated sulphuric acid and then weighed. The extent of the reaction was calculated from the known weights.

A second 10 ml. sample of the sulphuric acid solution of *o*-benzoylbenzoic acid-carboxyl-C^{14} was withdrawn, heated, and treated in the same manner to give a second sample of anthraquinone-9-C^{14}.

The flask with the residual sulphuric acid solution (approximately 5 ml.) was heated at 100°C. for three hours, which converted the remaining *o*-benzoylbenzoic acid-carboxyl-C^{14} practically quantitatively into anthraquinone-9-C^{14}.

The entire procedure was repeated to give three more samples of anthraquinone-9-C^{14}, two from partially reacted *o*-benzoylbenzoic acid-carboxyl-C^{14} and one from completely reacted *o*-benzoylbenzoic acid-carboxyl-C^{14}.

The remaining *o*-benzoylbenzoic acid-carboxyl-C^{14}, about 0.5 gm., was heated in 5 ml. of concentrated sulphuric acid for five hours and the anthraquinone-9-C^{14} isolated in the usual manner to give a third sample of anthraquinone-9-C^{14} from completely reacted *o*-benzoylbenzoic acid-carboxyl-C^{14}.

All samples of anthraquinone-9-C^{14} were recrystallized from absolute ethanol and vacuum dried before radioactivity measurements were made.

In most previous work on C^{14} isotope effects in this laboratory (5, 16, 17) relative specific activities have been determined by comparing the counting rates of uniform, extremely thin samples of labeled compounds prepared by evaporation of known amounts of appropriate solutions on stainless steel trays. This technique did not give the desired reproducibility with anthraquinone-9-C^{14}. An adaptation of a method recently described by Schwebel, Isbell, and Karabinos (14) was then used with very satisfactory results. Briefly, the method consists of dissolving a labeled compound in a suitable, relatively nonvolatile solvent and using a thick layer of solution, i.e. a layer thicker than 25 mgm./cm.^{2}, as a sample for counting in a gas-flow proportional counter.

The technique we adopted was as follows: an approximately 20.0 mgm. sample of an anthraquinone-9-C^{14} sample was accurately weighed (± 0.02 mgm.) into a 2 ml. glass-stoppered volumetric tube. Concentrated sulphuric acid was added to give 2 ml. of solution. A 200 λ sample of this sulphuric acid solution was pipetted into a stainless steel dish and the dish rapidly transferred to a methane-flow proportional counter shown in Fig. 1. Five such samples were counted for each solution and two different sulphuric acid solutions were made up from each original anthraquinone-9-C^{14} sample.

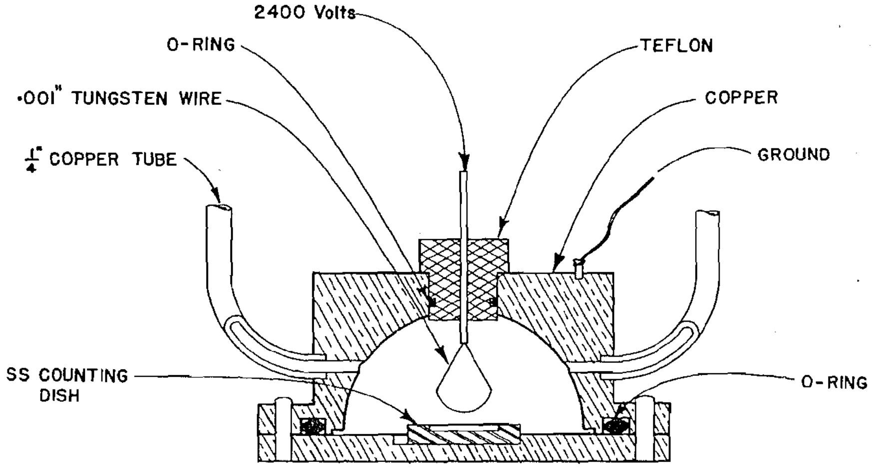

FIG. 1. Sectional view of methane-flow proportional counter and sample dish assembly.

Initially, it was found that a sample counting rate gradually decreased as a sample was counted over a period of an hour. This was found to be caused by some component of the commercial methane (96% methane) dissolving in the concentrated sulphuric acid solution. The difficulty was overcome by scrubbing the methane with concentrated sulphuric acid before it entered the counter.

This thick layer solution counting technique has the advantage, compared with either thick or thin solid sample counting, that counting samples are more reproducible. This is because a uniformly smooth layer, the entire area of which is "infinitely thick"[3] for C^{14} β particles, is presented to the counter. For a given area of sample, the measured C^{14} activity for any solution is volume independent, i.e. is independent of the thickness, provided the thickness is greater than 25 mgm./cm.^{2}, and is directly proportional to the concentration of dissolved labeled compound within comparatively wide limits.

RESULTS

Stevens and Attree (17) derived the equation

$$k(14)/k(12) = \ln (1 - rf)/(1 - f)$$

to express the C^{14} isotope effect in a given reaction, quantitatively. In this equation, $k(14)/k(12)$ is the ratio of the reaction rate constant of the C^{14} labeled compound to the reaction rate constant of the unlabeled compound, f is the fraction of initial compound reacted, and r is the ratio of the specific activity of the accumulated product, after fraction f has reacted, to the specific activity of the product after complete reaction. This equation has been used to calculate the C^{14} isotope effect in the present reaction.

The experimental results and calculated isotope effect are summarized in Table I. The "relative specific activities" given are the activities of the concentrated sulphuric acid solutions, measured under our standard conditions, normalized to a standard concentration of 10 mgm. of anthraquinone-9-C^{14} per ml. of solution. Each value is the average for ten separate counting samples, five from each of two separate sulphuric acid solutions. The standard deviation in the counting rate is shown in each case.

TABLE I
EXPERIMENTAL RESULTS

Anthraquinone-9-C^{14} sample No.	Fraction reacted (f)	Relative specific activities (counts/min.)	Specific activity ratio (r)	$k(14)/k(12)$ $\ln(1-rf)/\ln(r-f)$
1 T	Reaction taken to completion	4716 ± 43		
2 T		4700 ± 42		
3 T		4766 ± 49		
Average		4727 ± 28		
1 P–1	0.123	5058 ± 33	1.070	1.076
1 P–2	0.119	5048 ± 34	1.067	1.072
2 P–1	0.124	5090 ± 51	1.076	1.073
2 P–2	0.111	5054 ± 22	1.069	1.074
Average				1.074 ± .003

The specific activity ratios were calculated using the average specific activity value for the three complete reaction samples as denominator.

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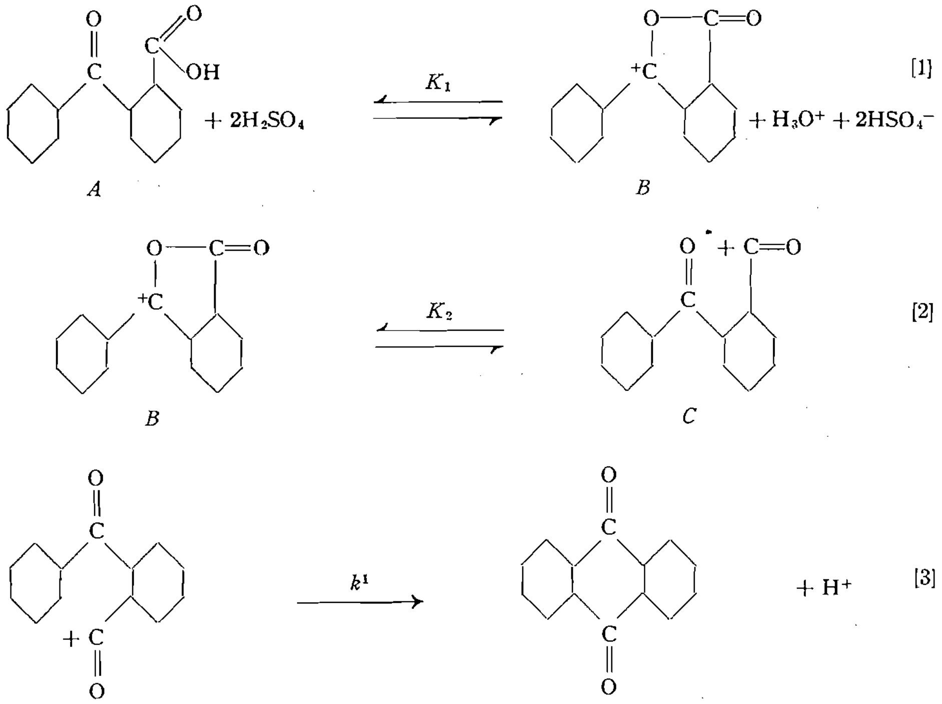
[3] *A thickness such that all β particles originating at the bottom of the sample layer are completely absorbed by the overlaying sample itself. The sample thus exhibits saturation activity. For C^{14}, this thickness is not greater than 25 mgm./cm.^{2}*

The limit given for the average value of $k(14)/k(12)$ is the probable error calculated directly from the four separate values obtained.

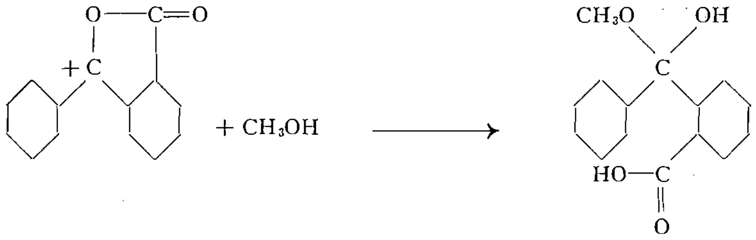
Sources of Error.—The values for $k(14)/k(12)$ are rather insensitive to errors in f, when f is approximately 0.1. A 3% error in f, for any sample, would only change the $k(14)/k(12)$ value for that sample by approximately 0.001. As can be seen from Table I, the probable counting errors are below 1%. The greatest source of error would seem to occur in determining the concentration of the sulphuric acid solutions prepared for counting purposes. The weighing errors were negligible at approximately 0.1%, but the limits given by the manufacturer for the volumes of the 2 ml. graduated tubes are ±0.03 ml., or 1½%.

DISCUSSION

In 1942, Newman (10) commented: "Although ring closure condensations with acids of the *o*-benzylbenzoic and γ-arylbutyric type take place fairly readily in sulphuric acid, anthraquinone formation remains a reaction unique in organic chemistry. The ease and high yield with which this condensation takes place ortho to a ketonic function are indeed remarkable". He proposed the following mechanism for the reaction:



His evidence for the equilibrium in reaction [1] was the fact that after a solution of *o*-benzoylbenzoic acid in cold concentrated sulphuric acid was poured into methanol, a high yield of the pseudo methyl ester was obtained. This reaction was formulated as:



[4]

Conversely, after a sulphuric acid solution of the pseudo ester was poured into water, a good yield of *o*-benzoylbenzoic acid was obtained. (The true ester was only hydrolyzed to a small extent by this latter treatment.) More recently, Newman (11) measured the freezing point depression of solutions of *o*-benzoylbenzoic acid in concentrated sulphuric acid and found that the van 't Hoff "i factor" is 3.8, thus confirming that a carbonium ion is formed in sulphuric acid and also indicating that the equilibrium position in reaction [1] lies far to the right.

Newman's argument for reaction [2] was that ring closure would be a very unlikely reaction for the lactone to undergo because of steric factors, and that since anthraquinone is only formed very slowly unless the solution is heated, the lactone ring is very probably broken on heating. There is some evidence for this reaction since Newman found that on heating a pseudo ester with mineral acid, or thionyl chloride, a large fraction isomerizes to the normal ester.

Reaction [3] may be considered as a benzene substitution reaction involving cationoid attack. The carbonyl group would be expected to be meta directing. However, the mesomeric effect of the carbonyl group in this instance may be shared by the two benzene rings, thus lessening its effect on the monosubstituted ring. The steric advantages to ortho substitution may well be then the determining factor in the substitution orientation.

In terms of this mechanism, the reaction rate, v, may be expressed as follows, using square brackets to indicate concentrations.

[1] $$v = k^1\,[C]$$

[2] $$= k^1K_2\,[B]$$

[3] $$= k^1K_1K_2\,[A]$$

The rate constant ratio determined experimentally is in terms of a different rate constant, k, which is defined by the equation

[4] $$v = k\{[A] + [B] + [C]\}$$

[5] $$= k\left\{\frac{[C]}{K_1K_2} + \frac{[C]}{K_2} + [C]\right\}$$

[6] $$= k[C]\left\{\frac{1}{K_1K_2} + \frac{1}{K_2} + 1\right\}.$$

From [1] and [6],

$$k^1 = k\left\{\frac{1}{K_1K_2} + \frac{1}{K_2} + 1\right\}.$$

A much simpler relation between these two rate constants may be obtained by making an approximation. Newman's work indicates that K_1 is large and K_2 small, so that $[A]$ and $[C]$ are both small quantities compared with $[B]$. Equation [4] above may thus be written,

$$v = k\,[B]. \tag{7}$$

From [2] and [7], $k = k^1K_2$, and hence, as a good approximation,

$$\frac{k(14)}{k(12)} = \frac{k^1(14)}{k^1(12)}\cdot\frac{K_2(14)}{K_2(12)}\,.$$

On the basis of the theory of absolute reaction rates developed by Eyring (9), the ratio of the reaction rate constants for two isotopic molecules undergoing a given reaction in the same reaction vessel may be expressed as:

$$\frac{k_1}{k_2} = \frac{\kappa_1}{\kappa_2}\cdot\left(\frac{m_2{}^*}{m_1{}^*}\right)^{\frac{1}{2}}\cdot\frac{Q_{A2}}{Q_{A1}}\cdot\frac{Q_1{}^\ddagger}{Q_2{}^\ddagger}\cdot\frac{\delta_2}{\delta_1}\,.$$

In this equation the κ's are transmission coefficients, the m^*'s are the effective masses of the activated complexes along the coordinate of decomposition, the δ's are the lengths of the tops of the potential energy barriers, and the Q's are complete partition functions. $Q^\ddagger$ refers to the activated complex molecules and Q_A to the reactant molecules. The subscripts 1 and 2 refer to the reactions of the two isotopic molecules respectively. The factor m^* is usually calculated as the reduced mass, $mm^1/m + m^1$, of the two atoms involved in the bond being broken or formed in the rate controlling step of the reaction.

Bigeleisen and Mayer (4) have shown that the ratio of the partition functions of two isotopic molecules can be expressed as a simple function of the vibrational energy levels of the molecules. Using various approximations, Bigeleisen (3) obtains the equation

$$\frac{k_1}{k_2} = \left(\frac{m_2{}^*}{m_1{}^*}\right)^{\frac{1}{2}}\left(1 + \sum_i^{3N-6} G(u_i)\Delta u_i - \sum_i^{3N^1-6} G(u_i{}^\ddagger)\Delta u_i{}^\ddagger\right)$$

for the reaction rate constant ratio for isotopic molecules where the Δu's are small. $u = hc\omega/kT$, $\Delta u = hc/kT(\omega_1 - \omega_2)$, and $G(u) = 1/2 - 1/u + 1/(e^u - 1)$. In the derivation of this equation, it is assumed that the effect of isotopic mass on the potential energy surface of the reacting molecules is negligible and that the transmission coefficients, as defined in reaction rate theory, are practically identical for the two isotopic molecules, so that $\kappa_1 = \kappa_2$ and $\delta_1 = \delta_2$. For calculation, all the fundamental vibrational frequencies of the isotopic reactant and activated complex molecules, the ω_i's, would have to be known.

Bigeleisen's equation separates isotope effect into two factors: (1) a "reduced-mass effect" which expresses the effect of mass on the frequency of rupturing or forming the critical bonds in the activated complexes, and (2) a "zero-point energy effect" which expresses the effect of mass change on the equilibrium between the reactant molecules and the activated complexes.

Usually the lighter isotopic molecule will have the greater reaction rate constant. This is because the reduced mass effect factor $(m_2^*/m_1^*)^{\frac{1}{2}}$ is greater than unity (if the subscript 1 refers to the lighter molecule) and because, especially in bond cleavage, the reacting molecules are generally more "tightly bound" than the activated complex molecules, which results in

$$\sum_i^{3N-6} G(u_i)\Delta u_i \text{ being greater than } \sum_i^{3N^\ddagger-6} G(u_i^\ddagger)\Delta u_i^\ddagger.$$

The condition for the heavier molecule to have the greater reaction rate constant, i.e. for a "reverse" isotope effect to occur, according to the Bigeleisen equation, is:

$$\sum^{3N^\ddagger-6} G_i(u_i^\ddagger)\Delta u_i^\ddagger > \sum^{3N-6} G(u_i)\Delta u_i + \tfrac{1}{2}\ln(m_2^*/m_1^*).$$

The "reverse" C^{14} isotope effect observed in the condensation of *o*-benzoylbenzoic acid appears explicable in terms of the Bigeleisen theoretical treatment on the basis of the reaction mechanism proposed by Newman, if bond formation, equation [3], is the rate controlling step. The two isotopic reactant carbonium ions, species *C*, must be compared with the two corresponding isotopic activated

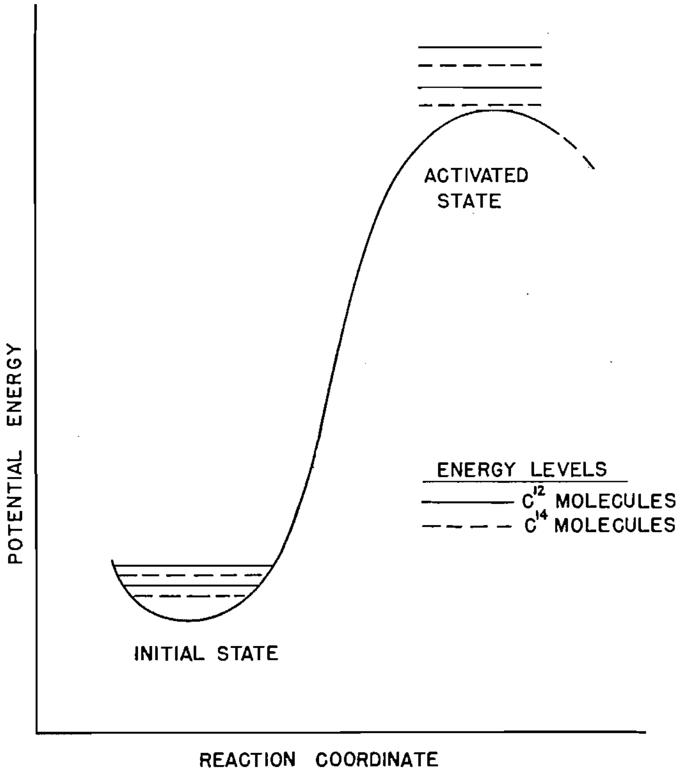


FIG. 2. Potential energy diagram.

complex molecules. Owing to the partial formation of a carbon–carbon bond, an activated complex molecule is then more "tightly bound" than a corresponding reactant molecule. Certain internal rotational degrees of freedom present in the reactant molecule go over into bending vibrational modes in the activated state. The $G(u^{\ddagger})\ \Delta u^{\ddagger}$ terms for these modes can be expected to be larger than the corresponding terms for the reactant molecule. It may be expected therefore that $\sum_i^{3N^{\ddagger}-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}$ will be greater than $\sum_i^{3N-6} G(u_i)\Delta u_i$ for this reaction.

The situation may perhaps be more easily understood in terms of a potential energy curve, Fig. 2. In the initial state, the energy levels of the two isotopic molecules are different, with the levels for the heavier molecule lying below those for the lighter molecules. The same situation holds in the activated state, but because the molecule is now more tightly bound as a result of incipient carbon–carbon bond formation, the energy levels in the activated state are more widely separated than in the initial state.[4] The energy requirement to attain the activated state is therefore greater for the lighter molecules than for the heavier molecules, even though the lighter molecules have the higher energy content in the initial state. The net result is that the concentration of activated complex molecules, relative to reactant molecules, is greater for the heavier isotopic species than for the lighter isotopic species, and the heavier species reacts more rapidly than the lighter species on this account.

The magnitude of the experimental value for the isotope effect, as expressed by the ratio $k(14)/k(12)$, is somewhat surprising, however, for two reasons. Firstly, one might have expected that the "reduced-mass effect" factor, which is a measure of the relative rates of passage of activated complexes over the energy barrier, would counteract the "zero-point energy effect" factor to a large extent. Secondly, it is almost certain that the ratio $K(14)/K(12)$ is less than unity, perhaps having a value as low as 0.95. (This follows from the same argument already given above to hypothesize a higher relative concentration of activated complex molecules for the heavier isotopic molecules than for the lighter isotopic molecules.)

The significant fact is that a value even larger than the experimentally determined 1.07 is indicated for $k^1(14)/k^1(12)$, the reaction rate constant ratio for the unidirectional bond-formation process in this reaction.

One additional point may be worth noting. As previously stated, in the development of the expression for the ratio of reaction rate constants for isotopic molecules, it has been assumed that the transmission coefficients are identical. Calculations (1) using simple hypothetical molecules have shown, however, that transmission coefficients for isotopic molecules can differ appreciably. The possibility that some of the isotope effect observed in this condensation reaction is due to differences in transmission coefficients cannot be ignored even though calculations for this example are completely impractical.

[4] *It might be noted that the departure of the hydrogen atom from a reacting molecule contributes almost exactly the same energy changes to both isotopic molecular species since the hydrogen is attached at an unlabeled position.*

The only logical conclusion which can be drawn from the reverse isotope effect observed, as far as reaction mechanism is concerned, is that bond formation is the rate controlling step in the condensation of *o*-benzoylbenzoic acid to anthraquinone. The mechanism proposed by Newman is thus supported. The measurements are of interest also because only one other "reverse" isotope effect has been reported[5] for C^{14} (12).

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[5] *A "reverse" C^{14} isotope effect reported by Daniels and Myerson (7) was later reported as "normal" (13). The authors understand that reverse isotope effects in a Schmidt reaction and in a pinacol rearrangement were reported by Roe and co-workers at the 124th Meeting of the American Chemical Society in Chicago, September, 1953.*

AN EXAMINATION OF MAYER'S THEORY OF IONIC SOLUTIONS

THE CALCULATION OF THE RELATIVE APPARENT MOLAL HEAT CONTENT AND APPARENT MOLAL VOLUME OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°C.[1]

By G. C. Benson

ABSTRACT

Mayer's theory gives a good representation of the apparent molal volume ϕ_V of sodium chloride in aqueous solution at 25°C. up to a concentration 0.4 molar. Representation of the relative apparent molal heat content ϕ_L is also satisfactory but over a smaller range of concentration. The shape of the ϕ_L curve is strongly influenced by the temperature dependence of the distance of closest approach of oppositely charged ions in the solution. Methods of evaluating this term are considered. The utility of Mayer's theory for the extrapolation of experimental data to infinite dilution is illustrated in the case of ϕ_V and of intermediate heats of dilution.

I. INTRODUCTION

A theory of ionic solutions based on a virial expansion of the osmotic pressure of a solution has been published recently by Mayer (10). The statistical development is similar to that used in treating imperfect gases. A model of hard spherical ions with coulombic interactions in a dielectric continuum is assumed. According to Mayer, the resulting expression for the concentration dependence of the logarithm of the activity coefficient retains terms correct up to and including $c^{3/2}$. Scatchard (16) has discussed the theory in some detail and compared it with the Debye-Hückel theory and its various extensions.

Formulae for the thermodynamic properties of a solution in terms of the Mayer theory have been derived by Poirier (13). In a second paper, Poirier (14) has tabulated the functions necessary for numerical evaluation of these formulae and has applied them to the calculation of the stoichiometric mean ionic molar activity coefficients of several different valence type electrolytes in aqueous solution at 25°C. For sodium chloride, agreement between theory and experiment is good up to about 0.4 molar, where the deviation amounts to 1.5%. The representation for higher valence electrolytes in dilute solution is also quite reasonable, but the discrepancy between theory and experiment becomes noticeable at lower concentrations with increasing complexity of the valence type.

The success of the Mayer theory, as indicated by Poirier's calculations, is sufficient to justify its further examination. In particular, since all the numerical computations have been restricted to activity coefficients at 25°C., an investigation of other thermodynamic properties should be of interest. In this paper, the relative apparent molal heat content ϕ_L and the apparent molal volume ϕ_V of sodium chloride in water at 25°C. are calculated from Mayer's theory. Comparison of the results with experimental data provides a check,

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for a 1–1 electrolyte, on the temperature and pressure dependence predicted by the theory.

The notation and values of the numerical constants employed by Poirier in his two papers (13, 14) have been adopted in the present work and are summarized for convenient reference in the next section. The calculation of ϕ_L is described in Section III and that of ϕ_V in Section IV. This is followed by a discussion of the results in Section V.

II. SUMMARY OF NOTATION AND FORMULAE

In this paper, the set of "natural" variables used to described the thermodynamic state of a two-component system are the temperature, T, external pressure, P, moles of solvent, n_1', and moles of solute, n_2'.[2] Parenthesis with a natural variable written as subscript indicates differentiation of the enclosed quantity with respect to that variable, keeping the other members of the natural set constant.

Mayer's theory leads to the following expressions[3]:

$$\phi_L = \phi_{H_2} - \phi_{H_2}{}^{\circ} = \tau_1 + (\ln a)_T\,\tau_2, \tag{1}$$

$$\phi_V = \bar{V}_2{}^{\circ} + \omega_1 + (\ln a)_P\,\omega_2 \tag{2}$$

for the relative apparent molal heat content and the apparent molal volume of the solute in an ionic solution at temperature T, pressure P, and concentration c moles per liter.

In equation [1] ϕ_{H_2} and $\phi_{H_2}{}^{\circ}$ are the apparent molal heat contents of the solute in the solution at concentration c and at infinite dilution respectively. The quantities τ_1, τ_2, ω_1, and ω_2 are defined by

$$\begin{aligned}\tau_1 = \nu RT^2\Big\{&[(\tfrac{1}{3})\,\alpha_1 + (\ln K)_T + T^{-1}]\ln f'_D \\ &- [(\ln K)_T + T^{-1}]\frac{A}{2n_2}\sum_{\mu\geqslant 0}\frac{(-)^{\mu}n_{\mu}{}^{2}}{A^{\mu}}[\mu b_{\mu}(\varphi) + (\mu-2)g_{\mu}(\varphi)] \\ &- \alpha_1\frac{A}{2n_2}\sum_{\mu\geqslant 0}\frac{(-)^{\mu}n_{\mu}{}^{2}}{A^{\mu}}[b_{\mu}(\varphi) - g_{\mu}(\varphi)]\Big\},\end{aligned} \tag{3}$$

$$\tau_2 = \nu RT^2\frac{A}{2n_2}\sum_{\mu\geqslant 0}\frac{(-)^{\mu}n_{\mu}{}^{2}}{A^{\mu}}[(3-\mu)b_{\mu}(\varphi) - (1+\mu)g_{\mu}(\varphi)], \tag{4}$$

$$\begin{aligned}\omega_1 = \nu RT\Big\{&[(\tfrac{1}{3})\,\beta_1 - (\ln K)_P]\ln f'_D \\ &+ \frac{(\ln K)_P\,A}{2n_2}\sum_{\mu\geqslant 0}\frac{(-)^{\mu}n_{\mu}{}^{2}}{A^{\mu}}[\mu b_{\mu}(\varphi) + (\mu-2)\,g_{\mu}(\varphi)] \\ &- \frac{\beta_1 A}{2n_2}\sum_{\mu\geqslant 0}\frac{(-)^{\mu}n_{\mu}{}^{2}}{A^{\mu}}[b_{\mu}(\varphi) - g_{\mu}(\varphi)]\Big\},\end{aligned} \tag{5}$$

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[2] *Poirier (13, 14) denotes moles of solvent and solute by n_1 and n_2 respectively. A dash has been added to avoid any confusion with the quantities n_{μ} to be defined later.*

[3] *Equation [2] is a more general form of equation 94 in reference 13 where the $(\ln a)_P$ term has been neglected. Also, an omission appears to have been made in printing equation 94. The first term on the right-hand side should be $[(1/3)\beta_1 - (\ln K)_P]\ln f'_D$ in order that ϕ_V have the Debye-Hückel limiting slope $(2/3)\mathscr{S}_{(V)}$ at high dilutions (see reference 7, pp. 50, 596). This has been confirmed by repeating Poirier's derivation.*

$$[6] \qquad \omega_2 = \nu RT \frac{A}{2n_2} \sum_{\mu>0} \frac{(-)^{\mu} n_{\mu}^{2}}{A^{\mu}} [(\mu - 3) b_{\mu}(\varphi) + (\mu + 1) g_{\mu}(\varphi)] = - T^{-1} \tau_2.$$

In equations [1] to [6] the Debye-Hückel limiting expression for the logarithm of the activity coefficient

$$[7] \qquad \ln f'_D = - \frac{n_2 \epsilon^2 \kappa}{2KkT}$$

where

$$[8] \qquad \kappa = \left(\frac{4\pi N_0 \epsilon^2 n_2 \nu c}{1000\, KkT} \right)^{\frac{1}{2}}$$

is used as a convenient parameter. The quantities α_1, β_1, and K are respectively the coefficient of thermal expansion, the coefficient of isothermal compressibility, and the dielectric constant, all for the pure solvent at temperature T and pressure P. $\bar{V}_2^{\circ}$ is the partial molal volume of the solute in an infinitely dilute solution at temperature T and pressure P. The symbols R, k, N_0, and ϵ have their usual meanings (i.e. gas constant per mole, Boltzmann constant, Avogadro's number, and electronic charge, respectively).

A solute molecule dissociates into ν_s ions of type s, each having charge Z_s in protonic units. The total number of ions formed by the dissociation of one molecule is

$$[9] \qquad \nu = \sum_{s} \nu_s.$$

The quantity n_2 is a special case of the set n_{μ} defined by

$$[10] \qquad n_{\mu} = \frac{1}{\nu} \sum_{s} \nu_s Z_s^{\mu}$$

for all positive integral values of the index μ.

The distance of closest approach of oppositely charged ions in the solution is represented by "a" and is related to the parameters A and φ by the equations

$$[11] \qquad a = \frac{\varphi}{\kappa} = \frac{A\epsilon^2}{KkT}.$$

The functions $b_{\mu}(\varphi)$, $g_{\mu}(\varphi)$, and $h_{\mu}(\varphi)$ are defined by certain definite integrals which have been tabulated (14) numerically at rounded values of φ for μ in the range 0 to 16.

The formula for the logarithm of the stoichiometric mean ionic molar activity coefficient of the solute in the solution at temperature T and pressure P is

$$[12] \qquad \ln f = \ln f' - P_{\mathrm{osm}} [\bar{V}_2^{\circ}/\nu RT + \{\ln f'\}_K (\ln K)_P - \beta_1]$$

where

$$[13] \qquad \ln f' = \ln f'_D - \frac{A}{n_2} \sum_{\mu>0} \frac{(-)^{\mu} n_{\mu}^{2}}{A^{\mu}} b_{\mu}(\varphi),$$

$$[14] \qquad \{\ln f'\}_K = - (3/2) \ln f'_D + \frac{A}{2n_2} \sum_{\mu>0} \frac{(-)^{\mu} n_{\mu}^{2}}{A^{\mu}} [2\mu b_{\mu}(\varphi) - g_{\mu}(\varphi) + h_{\mu}(\varphi)],$$

and the osmotic pressure is given by

$$[15]\quad P_{\text{osm}} = \frac{\nu c RT}{1000}\left\{1 + (\tfrac{1}{3})\ln f_D' - \frac{A}{2n_2}\sum_{\mu \geqslant 0} \frac{(-)^{\mu} n_{\mu}^{\;2}}{A^{\mu}}\,[b_{\mu}(\varphi) - g_{\mu}(\varphi)]\right\}.$$

The stoichiometric mean ionic molal activity coefficient f_m can be calculated from

$$[16]\qquad \ln f_m = \ln f - \ln d_1 - \ln\,(m/c)$$

where d_1 is the density of the pure solvent and m is the molality corresponding to the molarity c.

The numerical values of the constants taken from Birge (1) and used in the computations of Sections III and IV are

$R = 8.31436 \times 10^7$ erg deg.$^{-1}$ mole^{-1} $= 1.98646_7$ cal.$_{15}$ deg.$^{-1}$ mole^{-1},
$k = 1.38047_4 \times 10^{-16}$ erg deg.$^{-1}$,
$N_0 = 6.0228_3 \times 10^{23}$ mole^{-1},
$\epsilon = 4.8025_1 \times 10^{-10}$ abs. e.s.u.

The required properties of pure water and of the solute in aqueous sodium chloride solutions are summarized in Table I. For a 1–1 electrolyte n_{μ} is equal to unity for all even values of μ and vanishes for all odd values.

The quantity a which occurs implicitly in the above formulae through A and φ must be treated as a disposable parameter. For sodium chloride in water at 25°C., Poirier (14) used the experimental value of f_m at $m = 0.1$ (given in Table I) in equations [12] to [16] to determine the value of A. The result $A = 0.5464_1$ is equivalent to $a = 3.90$ Å. The use of this value in equation [12] gives a reasonable representation of the activity coefficient up to 0.4 molar as mentioned in Section I. Poirier's value for A at 25°C. is adopted in the present calculations.

TABLE I
DATA FOR PURE WATER AND FOR SODIUM CHLORIDE IN AQUEOUS SOLUTIONS

Property	Temperature			Units	Reference
	20°C.	25°C.	30°C.		
Water					
K	80.36_2	78.54	76.76_5		20
$(\ln K)_T$		$-4.57_9 \times 10^{-3}$		deg.$^{-1}$	20
$(\ln K)_P$	5.936×10^{-11}	5.854×10^{-11}	5.788×10^{-11}	(dynes/ cm.^{2})$^{-1}$	12
β_1	$4.629_9 \times 10^{-11}$	$4.564_6 \times 10^{-11}$	$4.514_3 \times 10^{-11}$	"	4, 12
d_1	0.998234	0.997075	0.995678	gm. ml.$^{-1}$	17
α_1		2.570×10^{-4}		deg.$^{-1}$	17
Aqueous NaCl Solutions					
$\bar{V}_2{}^{\circ}$	16.20	16.62	16.97	cm.^{3} mole^{-1}	2, 3, 5, 8, 9, 18
$f_m(m = 0.1)$	0.779	0.778	0.777		7, p. 557
$c(m = 0.1)$	0.09964_0	0.09951_7	0.09938_4	mole l.$^{-1}$	7, p. 556

III. THE RELATIVE APPARENT MOLAL HEAT CONTENT OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°C.

The quantities τ_1 and τ_2 in equation [1] can be calculated as functions of the concentration, using the data listed for 25°C. in Table I, along with Poirier's value of A and tables of the functions $b_\mu(\varphi)$ and $g_\mu(\varphi)$. Complete evaluation of ϕ_L however requires a knowledge of $(\ln a)_T$. A similar term in the Debye-Hückel theory is frequently neglected (6, 12). After a discussion of this quantity, Poirier (13) concludes that there is no reason why $(\ln a)_T$ should be negligibly small, though evaluation of it "is somewhat problematical".

An examination of the results of Harned and Ehlers (6) for aqueous hydrochloric acid solutions indicates that values of $(\ln a)_T$ of the order of 10^{-3} deg.$^{-1}$ are quite possible. The results of assuming $10^4(\ln a)_T = 0, 5, 8, 10, 12, 15,$ and 20 in equation [1] are plotted against $c^{\frac{1}{2}}$ in Fig. 1. For comparison, the Debye-Hückel limiting slope $\frac{2}{3}\mathscr{S}_{(H)}$ (see page 596, reference 7) and the "experimental data"[4] tabulated in reference 7 (see pp. 539–40) are also indicated in this figure. It can be seen that the shape of the ϕ_L curve is quite sensitive to the value of $(\ln a)_T$. Also, it is obviously impossible to reproduce the experimental ϕ_L curve over an extended concentration region such as 0 to 0.4 molar with anything like the success achieved in the case of the activity coefficient. A value of $10^4(\ln a)_T$ in the range 8 to 10 gives a fairly good fit up to 0.1 molar.

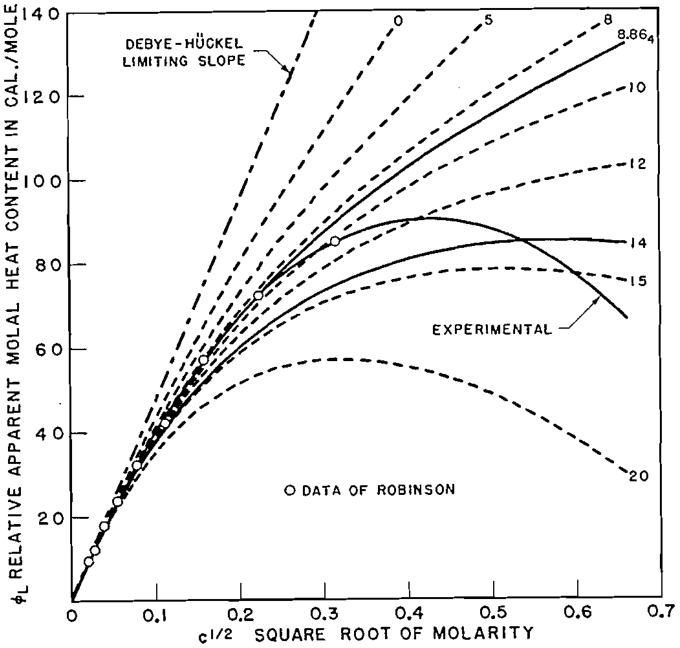

FIG. 1. Relative apparent molal heat content of sodium chloride in aqueous solutions at 25°C. The values of $10^4(\ln a)_T$ are indicated on the calculated curves.

After this preliminary examination it is interesting to investigate possible methods of estimating the best value of $(\ln a)_T$ from experimental data. Two distinct ways appear possible. Briefly these are (*a*) through use of experimental data for activity coefficients at other temperatures around 25°C., and

[4] *These data are actually the results of processing experimental heats of dilution in accordance with the Debye-Hückel theory. Later, in Section III of this paper, it is shown that a similar treatment using Mayer's theory leads to essentially the same data.*

(*b*) through the use of experimental heats of dilutions (or equivalent data) at 25°C. These possibilities will be considered in turn.

(*a*) *Determination of* $(\ln a)_T$ *from Activity Coefficient Data at 20° and 30°C.*

At each temperature the value of $\ln f_m$ (for $m = 0.1$) can be calculated using Poirier's tables of $b_\mu(\varphi)$, $g_\mu(\varphi)$, and $h_\mu(\varphi)$ at four round values of φ so chosen that two of the results are greater and two less than the experimental value given in Table I. Lagrangian interpolation at 20°C. leads to $A = 0.5459_3$. A similar calculation at 30°C. gives $A = 0.5469_4$.[5] From these values and $A = 0.5464_1$ at 25°C., $(\ln A)_T$ is found to be 1.8×10^{-4} deg.$^{-1}$ at 25°C. The corresponding value of $(\ln a)_T$ calculated from

[17] $(\ln a)_T = (\ln A)_T - T^{-1} - (\ln K)_T$

is

[18] $(\ln a)_T = [1.8 - 33.5_4 + 45.7_9] \times 10^{-4} = 14.0 \times 10^{-4}$ deg.$^{-1}$.

The plot of ϕ_L against $c^{\frac{1}{2}}$ for $10^4(\ln a)_T = 14$ deg.$^{-1}$ is also shown in Fig. 1. At high dilutions the calculated curve agrees well with the experimental one. Around 0.01 molar the theoretical curve is a few calories per mole lower. This difference increases to 10 cal. mole^{-1} at 0.1 molar and then decreases to zero where the curves cross near 0.3 molar. Above this concentration the theoretical values are higher than the experimental curve. Although $10^4(\ln a)_T = 14$ deg.$^{-1}$ gives a fit to about ±12% up to nearly 0.4 molar, the more empirical calculations outlined at the beginning of this section indicate that a

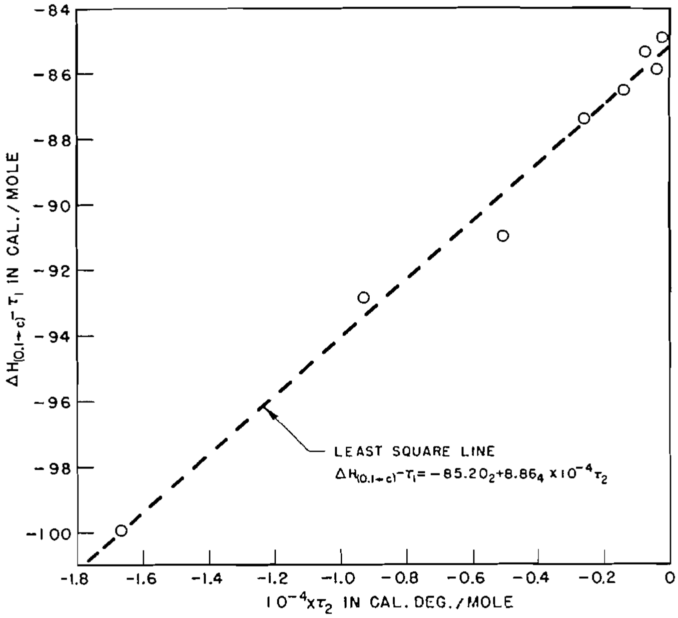

FIG. 2. Extrapolation of intermediate heats of dilution and the determination of $(\ln a)_T$ for aqueous sodium chloride solutions at 25°C.

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[5] *Since it is unlikely that a five degree change in temperature will shift the "concentration limit of validity" below 0.1 from the value 0.4 molar established at 25°C. by Poirier, no attempt was made to test the values of A at 20° and 30°C. by comparing calculated and experimental values for the activity coefficient over a range of concentration at each temperature.*

somewhat lower value would give a much better fit over the low concentration range.

(*b*) *Determination of* $(\ln a)_T$ *from Intermediate Heats of Dilution at 25°C.*

The calculation described in part (*a*) does not appear to be a good method of finding the best value of $(\ln a)_T$ since it is subject to large errors resulting from small relative uncertainties in the data employed. Accordingly, it is preferable to evaluate $(\ln a)_T$ more directly from experimental heats of dilution.

From equation [1], $\Delta H_{(0.1 \rightarrow c)}$ the intermediate heat of dilution from 0.1 molar to concentration c can be written as

[19] $$\Delta H_{(0.1 \rightarrow c)} - \tau_1 = \phi_{H_2}{}^{\circ} - \phi_{H_2}(c = 0.1) + (\ln a)_T \tau_2 .$$

Employing Robinson's data ((15), see also (7), p. 225) for $\Delta H_{(0.1 \rightarrow c)}$ at 25°C., the left-hand side of equation [19] is plotted against τ_2 in Fig. 2. The results show a definite linear trend, although some scatter arising from experimental error is apparent. Using the method of least squares the results can be expressed by the linear form

[20] $$\Delta H_{(0.1 \rightarrow c)} - \tau_1 = -85.20_2 + 8.86_4 \times 10^{-4}\,\tau_2 .$$

From the slope and intercept of this line the values

[21] $$10^4(\ln a)_T = 8.86_4 \text{ deg.}^{-1}$$

and

[22] $$\Delta H_{(0.1 \rightarrow 0)} = -85.20_2 \text{ cal. mole}^{-1}$$

are obtained at 25°C. The relative apparent molal heat content corresponding to $10^4(\ln a)_T$ given by equation [21] has been added to Fig. 1. The resulting curve, as expected, agrees very well with the experimental curve within the experimental error up to about 0.07 molar; beyond this concentration the deviation increases rapidly.

Values of the relative apparent molal heat content determined from Robinson's results extrapolated to zero as just described can be calculated from the equation

[23] $$\phi_L = -\Delta H_{(0.1 \rightarrow 0)} + \Delta H_{(0.1 \rightarrow c)} = 85.20_2 + \Delta H_{(0.1 \rightarrow c)} .$$

These points are also plotted in Fig. 1.

IV. THE APPARENT MOLAL VOLUME OF SODIUM CHLORIDE IN AQUEOUS SOLUTIONS AT 25°C.

In evaluating ϕ_V from equation [2], the quantity $(\ln a)_P$ introduces difficulties similar to those associated with $(\ln a)_T$ in the previous section. Poirier (13) has concluded that $(\ln a)_P$ is quite small and in deriving the formula for ϕ_V assumed that it could be neglected. A similar assumption is usually made in corresponding treatments (11, 12) by the Debye-Hückel theory. However, Wirth and Collier (19) have found that apparent molal volume data for perchloric acid, sodium perchlorate, and hydrochloric acid can be fitted better by using values of $(\ln a)_P = -2.68 \times 10^{-11}$, -0.15×10^{-11}, and -0.7×10^{-11} (dynes/cm.^{2})$^{-1}$, respectively. Accordingly, in the present case $(\ln a)_P$ is retained and the magnitude of it will be chosen to give agreement with experimental results.

Another problem that becomes apparent after a few computations is that the value of $\bar{V}_2°$ at 25°C. used by Poirier (14) and employed so far in these calculations is not consistent with the application of the present theory to available experimental data (9, 18) on the apparent molal volumes of sodium chloride in moderately dilute solutions. The value $\bar{V}_2° = 16.62$ cm.^{3} mole^{-1} has presumably been obtained by extrapolation of a ϕ_V vs. $c^{\frac{1}{2}}$ plot. Owen and Brinkley (12) and Owen (11), investigating the problem from the point of view of the Debye-Hückel theory, concluded that such extrapolations might lead to considerable errors. In the present case the most consistent course is to determine $\bar{V}_2°$ by processing the experimental data in a fashion compatible with Mayer's theory.

In Fig. 3 the difference between the experimental values of ϕ_V and values of ω_1 calculated from equation [5] are plotted against ω_2 calculated from equation

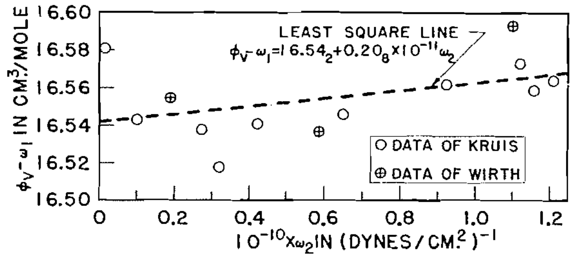

FIG. 3. Extrapolation of the apparent molal volumes of sodium chloride in aqueous solutions at 25°C. to infinite dilution.

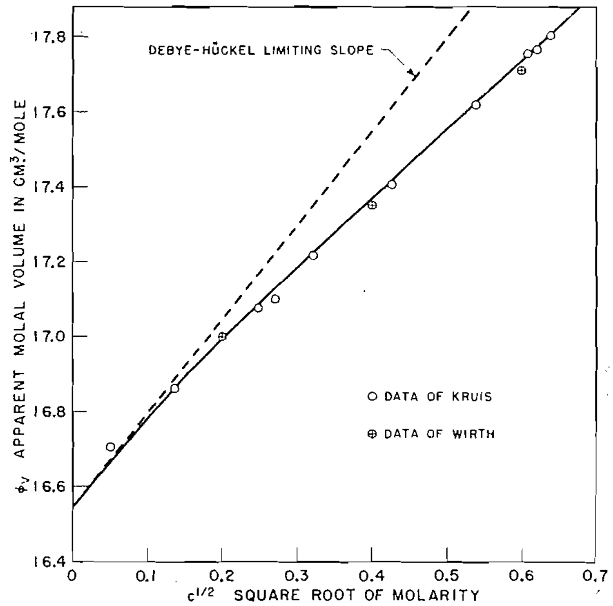

FIG. 4. Apparent molal volume of sodium chloride in aqueous solutions at 25°C. Curve is calculated from Mayer's theory using $\bar{V}_2° = 16.54_2$ cm.^{3} mole^{-1} and $(\ln a)_P = 0.20_8 \times 10^{-11}$ (dynes/cm.^{2})$^{-1}$.

[6]. If the experimental data were perfect and the theory correct, a straight line should result. The equation of the least square line is

[24] $$\phi_V - \omega_1 = 16.54_2 + 0.20_8 \times 10^{-11}\,\omega_2$$

and from this the values

[25] $$(\ln a)_P = 0.20_8 \times 10^{-11}\ (\text{dynes/cm.}^2)^{-1},$$

and

[26] $$\bar{V}_2^\circ = 16.54_2\ \text{cm.}^3\ \text{mole}^{-1}$$

are obtained.[6] The theoretical curve for ϕ_V based on the values given in equations [25] and [26] is plotted against $c^{\frac{1}{2}}$ in Fig. 4. The agreement with experimental data is very good and within experimental error over the whole range up to $c = 0.4$ molar.

V. DISCUSSION

The calculations outlined in the preceding sections indicate that Mayer's theory gives a very satisfactory representation of the apparent molal volume of the solute in aqueous sodium chloride solutions at 25°C. up to the concentration limit of validity (0.4 molar) set by Poirier from a study of activity coefficients. The temperature dependence of the theory is not as good as this, though a good representation of ϕ_L up to about 0.07 molar can be obtained with $10^4(\ln a_T) = 8.86$ deg^{-1}.

There is no independent check on the values of $(\ln a)_T$ and $(\ln a)_P$ given in equations [21] and [25]. The maximum of the ϕ_L curve appears to be connected intimately with the term $(\ln a)_T$, though in the present case the theory starts to fail before the maximum is reached. The assumption that $(\ln a)_T = 0$ is quite poor and if heats of dilution or other data are not available to determine $(\ln a)_T$ it would probably be better to assume $(\ln A)_T = 0$ (see equation [18]). The value of $(\ln a)_P$ is small and, though comparable in magnitude, has the opposite sign to values for other electrolytes obtained by Wirth and Collier (19) from an application of the Debye-Hückel theory. The quantity ω_2 is approximately proportional to c and at $c = 0.4$ molar the term $(\ln a)_P\,\omega_2$ makes a contribution of only 0.02_5 cm.^{3} mole^{-1} to ϕ_V.

It appears that Mayer's theory may be of use in extrapolating experimental data to infinite dilution. This has been illustrated for $\Delta H_{(0.1 \rightarrow c)}$ and for ϕ_V. If only the intercept is required it is sufficient to replace the abscissae in Figs. 2 and 3 by c since τ_2 and ω_2 are approximately proportional to the molarity. The values resulting from these extrapolations are in good agreement with the most recent extrapolations based on the Debye-Hückel theory by Owen and

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[6] *It does not seem possible to reconcile the previous value $\bar{V}_2^\circ = 16.62$ with the data treated in this way. If, instead of determining the least square line, an arithmetic mean is taken of $\phi_V - \omega_1$ the value of $\bar{V}_2^\circ$ is 16.55_2 cm.^{3} mole^{-1}.*

The osmotic correction term in equation [12] is strongly dependent on $\bar{V}_2^\circ$; however the whole contribution of this term to $\ln f$ at 0.1 molar is only about $\frac{1}{2}$% and variations due to a decrease of $\frac{1}{2}$% in $\bar{V}_2^\circ$ will have a negligible effect on the previous calculations and in particular on the value used for A.

Brinkley (12)—(see also reference 7, pp. 595–9). These authors obtained the values $\bar{V}_2^\circ = 16.538$ cm.^{3} mole^{-1} and $\Delta H_{(0.1\rightarrow 0)} = -85.0_1$ cal. mole^{-1}.[7]

Evidently ϕ_H, and ϕ_V for sodium chloride solutions at 25°C. can be represented by either Mayer's theory or the Debye-Hückel theory with very nearly equal success; however, the following difference should be noted. In the present work based on Mayer's theory the terms $(\ln a)_T$ and $(\ln a)_P$ are retained and must be treated as adjustable parameters since independent evaluation is not available. In the calculations of Owen and Brinkley (12, see equations 32 and 31) both $(\ln a)_T\ \theta c$ and $(\ln a)_P\ \theta c$ are put equal to zero but terms $\frac{1}{2}K_H c$ and $\frac{1}{2}K_V c$ are retained. K_H and K_V can be related to the B-coefficient (and its temperature and pressure derivatives) of the empirical linear term in the Debye-Hückel expression for the activity coefficient (see equations 3–8–8 and 3–9–5 of reference 7) but must also be treated as adjustable parameters. Since θ can be expressed as a power series in κa with leading term unity (12, see equation 24a), the procedure used by Owen and Brinkley may partially retain the $(\ln a)_T$ and $(\ln a)_P$ terms hidden in the coefficients K_H and K_V. From this point of view, the terms of the representation by Mayer's theory are more closely related to the theoretical model than in the corresponding Debye-Hückel treatment.

Although it is dangerous to generalize on the basis of the single example studied in this paper, the above conclusions are probably applicable to other 1–1 electrolytes and in a more restricted range to higher valence types.

ACKNOWLEDGMENT

The author wishes to thank Barbara A. Benson for assisting with the calculations.

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[7] *Equation 44 of reference 12 appears to contain a misprint which has been copied in equation (B-4-10) of reference 7. The value attributed above to Owen and Brinkley was calculated at* $c = 0.1$ *from their equation 44 rewritten as*

$$\phi_H - \phi_H^\circ = 471.8\,\Omega_H c^{\frac{1}{2}} - 217c.$$

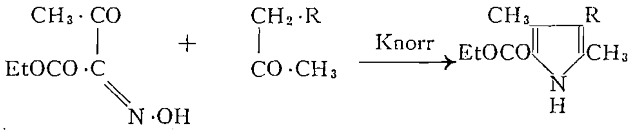
NOTES

A MODIFIED KNORR PYRROLE SYNTHESIS*

By S. F. MacDonald and R. J. Stedman

Intermediates for the synthesis of porphyrins are obtained by combining isonitroso-ketoesters with ethyl, benzyl, or *t*-butyl acetoacetates in the Knorr synthesis, and converting the products into pyrroles with a free β position by partial hydrolysis and pyrolysis (2), catalytic debenzylation and pyrolysis (3), or pyrolysis (5), respectively.

Another modification has been found in which isonitrosoacetoacetic ester and *p*-toluenesulphonylacetone are combined in the Knorr synthesis to give I*a* in 4% yield. Although this was converted into I*b* in 76% yield by Raney nickel desulphurization, the method was not extended beyond this model in view of the low yield in the Knorr synthesis. The method would be useful in cases where the high temperature necessary for decarboxylation was to be avoided.



I*a*, R = $SO_2C_6H_4 \cdot CH_3(p)$
b, R = H

EXPERIMENTAL

p-Toluenesulphonylacetone

A 54% yield of recrystallized product m.p. 51–52° was obtained according to Otto and Otto (4).

2,4-Dimethyl-3-p-toluenesulphonyl-5-carbethoxypyrrole (*Ia*)

Sodium nitrite (7.5 gm.) in a little water was added to ethyl acetoacetate (13 gm.) in acetic acid (30 cc.) at 4–8° and the excess nitrite destroyed with ammonium sulphamate. After the addition of acetic acid (70 cc.), ammonium acetate (15 gm.), and *p*-toluenesulphonylacetone (21.2 gm.), the mixture was warmed to 60° and held at that temperature by cooling and stirring while zinc dust (30 gm.) was added in portions. After a further 15 min. the solution was decanted into ice water (2 liters) and the zinc washed with acetic acid (50%, then glacial). After four hours at 0°, the precipitate was collected, washed with *N* sodium hydroxide to remove unchanged sulphone and zinc salts, dried, and extracted with petrol ether (b.p. 60–75°) (thimble) to remove 2,4-dimethyl-3,5-dicarbethoxypyrrole. When the residue was extracted with ethanol (thimble), the extract concentrated to 20 cc. and kept at 0°, the pyrrole (1.2 gm., 4%) separated as small colorless plates, m.p. 185–186°, unchanged by recrystallization. Ehrlich's reaction was positive hot. Calc. for $C_{16}H_{19}O_4NS$:

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C, 59.79; H, 5.96; N, 4.36; S, 9.98%. Found in material dried at 100° *in vacuo*: C, 59.87; H, 6.15; N, 4.38; S, 9.94%.

2,4-Dimethyl-5-carbethoxypyrrole (*Ib*)

The pyrrole sulphone (1.22 gm.) was refluxed for four hours with freshly prepared W-6 catalyst (1) (20 cc.) in absolute ethanol (60 cc.). The catalyst was separated and washed by centrifuging, and the ethanol evaporated. The residue was extracted with petrol ether (b.p. 60–75°, 50 cc.) (thimble), giving the pyrrole as colorless prisms (0.342 gm.) m.p. 123–124° on cooling of the extract; concentration gave a second crop (0.143 gm.; total 76%) m.p. 122.5–123.5°. Both crops gave a positive Ehrlich's reaction cold, and did not depress the melting point of authentic material of m.p. 123–124°. Calc. for $C_9H_{13}O_2N$: C, 64.65; H, 7.83; N, 8.38%. Found in material recrystallized from hexane and dried *in vacuo*: C, 64.44; H, 7.54; N, 8.37%; Lassaigne test for sulphur, negative.

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ORGANIC DEUTERIUM COMPOUNDS
XII. BENZENE-d_6*

BY L. C. LEITCH

Several methods of preparing benzene-d_6 were reviewed and evaluated by Ingold and Wilson (3). These authors reported that the exchange reaction between benzene and 50 mole % deuterium sulphate – deuterium oxide solution gave benzene-d_6 of higher deuterium content than any other method. They pointed out that the nickel catalyzed vapor phase exchange between benzene and deuterium oxide discovered by Horiuti and Polanyi (2) and developed by Bowman, Benedict, and Taylor (1) gave benzene-d_6 which contained 14 mole % C_6D_5H.† Notwithstanding this criticism by Ingold and Wilson, it seemed desirable to reinvestigate the heterogeneous exchange reaction between benzene and deuterium oxide on account of its simplicity. After exchanging benzene four times with deuterium oxide at 110°C. in the presence of platinum black, a product was obtained which contained less than 4 mole % C_6D_5H and was 99.2% deuterated. Such material is satisfactory for most purposes. The advantages of the present method are that the reaction

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†*Shortly after this paper had been submitted for publication Dixon and Schiessler (J. Am. Chem. Soc. 76: 2197. 1954) reported the method of preparation of benzene-d*$_6$ *of Ingold and Wilson (3) to be superior to that of Bowman, Benedict, and Taylor (1).*

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time is shortened and the rather tedious preparation of deuterium sulphate is avoided.

EXPERIMENTAL

Benzene-d_6

A mixture of benzene (5.0 ml., previously dried and distilled over sodium), deuterium oxide (10.0 ml., 99.5%), and platinum black (0.3 gm., prepared by reducing Adams' catalyst with deuterium) was heated in a sealed tube with a re-entrant joint in a rocking furnace for 12 hr. at 110°C. After the tube had been opened with a magnetic hammer while attached to a vacuum line the deuterated benzene was fractioned and then distilled through a U-tube containing Drierite into a trap. The benzene was recovered nearly quantitatively. A small sample was removed for mass spectrometric analysis and the balance was distilled into another reaction tube containing platinum black and fresh deuterium oxide. This operation was repeated twice more. The deuterium content after each exchange is shown in Table I.

TABLE I
DEUTERIUM CONTENT IN MOLE PER CENT AFTER EACH EXCHANGE

	1st	2nd	3rd	4th
C_6D_6	19.8	65.6	86.7	95.24
C_6D_5H	42.7	31.8	12.0	3.96
$C_6D_4H_2$	37.6	3.18	2.4	—

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HYDROLYSIS OF CELLULOSE ACETATE SULPHATE IN ACETONE[1]

BY KARL KEIRSTEAD AND JOHN MYERS

ABSTRACT

When cellulose acetate sulphate is dissolved in acetone the hydrolysis of the sulphate ester is rapid compared with that of the acetate ester. In 70% acetone the relative rates are reversed. Hydrolysis of the sulphate ester in acetone is greatly affected by the temperature. At 25°C. or greater the hydrolysis is complete after 24 hr. A potentiometric titration method has been developed for the estimation of sulphuric acid in the presence of smaller amounts of acetic acid.

INTRODUCTION

The nitration of cellulose by a mixture of nitric and sulphuric acids results in a nitrocellulose containing about one per cent of sulphate. The sulphate content depends on the composition of the mixed acids and on other factors. In spite of considerable experimentation, there is some doubt about the form of the sulphate which is variously described as mechanically held (2), inorganic (7), fixed sulphuric acid (4), or an acid ester and a neutral ester (5). The majority of workers have assumed the existence of some type of chemical bonding without providing direct evidence. Sheppard (8) estimated the sulphate content of unstabilized nitrocellulose by dissolving the ester in acetone and reprecipitating it with water. The acid liberated was titrated directly in the presence of the precipitate. The results obtained were said to correspond to the acidity extracted with dilute sodium bicarbonate solution. The present work was suggested by an argument advanced by Chédin and Tribot (2) to the effect that the removal of sulphuric acid by solution in acetone and reprecipitation in water supports the idea that the acid is mechanically held. The inference appears to be based on the assumption that sulphate cleavage in acetone is not the likely reaction of a cellulose mixed ester containing sulphate groups. There is however considerable evidence to show that the rate of solvolysis of the sulphate ester of a cellulose mixed ester depends on several factors of which the liquid medium appears to be the most important. The solvolysis of both the sulphate ester and the acetate ester in acetic acid is well known (6). Cleavage of the acetate ester in water is more rapid than decomposition of the sulphate ester (3).

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Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec.

Similar evidence for nitrocellulose is somewhat ambiguous because of the uncertainty regarding the relative amounts of free sulphuric acid and sulphate ester in a given sample. Several examples, however, will serve to illustrate the importance of the liquid medium. In water, prestabilized nitrocellulose produces mainly nitric and sulphuric acids as a result of the decomposition of the respective esters, the relative amounts of the two acids depending on the age of the sample (5). The slow release of the free sulphuric acid or combined ester in water is in contrast to the rapid release of sulphuric acid in ethanol (1).

The acetylation of cellulose using sulphuric acid as a catalyst produces a mixed ester of acetic and sulphuric acids. While commercial methods are designed to produce a cellulose acetate having a minimum sulphate content, it is possible, by selection of the appropriate conditions, to prepare a product containing 2% or more of sulphate. Malm *et al.* (6) have shown that the sulphate in well washed unstabilized cellulose acetate consists entirely of a sulphuric acid ester, RSO_4H. Samples can be dissolved in acetic acid and precipitated with only slight loss in sulphate (6). Titration and ion displacement reactions recently reported in detail (3) show one equivalent of acidity for each atom of sulphur.

A review of the literature yields little information about the properties of cellulose acetate sulphate in various liquid media. According to Malm *et al.* (6), the sulphate content of cellulose acetate sulphate may be reduced to about 0.05% sulphur by dissolving the mixed ester in 99% acetone and precipitating it with water. This is in contrast to the relatively slow decomposition of the sulphate ester in acetic acid. The present investigation was carried out to study the hydrolysis in acetone of the sulphate ester of cellulose acetate sulphate with a possible application to the reaction of nitrocellulose in the same solvent.

EXPERIMENTAL

Fibrous cellulose acetate sulphate was thoroughly washed with distilled water and a portion removed for sulphate determination. The preparation of the cellulose acetate sulphate and the determination of sulphate content have been described previously (3). A known weight of damp cellulose acetate sulphate (approximately 1.5 gm. dry weight) was added to redistilled acetone (100 ml.) and the solution maintained at 25° ± 0.1°C. for varying periods of time. The degree of hydrolysis during that period was estimated by determining the amount of acetic and sulphuric acid formed, using a special potentiometric titration method.

Titrimetric Analysis of a Mixture of Acetic and Sulphuric Acids

The method is based on the fact that the ionization constant of acetic acid can be sufficiently depressed in a nonaqueous solution to permit its estimation in the presence of a strong acid. Known mixtures of dilute sulphuric and acetic acid in 70% acetone were titrated with $N/100$ sodium hydroxide using a model H-2 pH meter and a glass and saturated calomel electrode system. The pH curves shown in Fig. 1 are typical of those obtained in 70% acetone. An inflection in the curve at about pH 5 is noticeable in the presence of as little as 5% acetic acid but it is not sharp enough to permit direct estimation

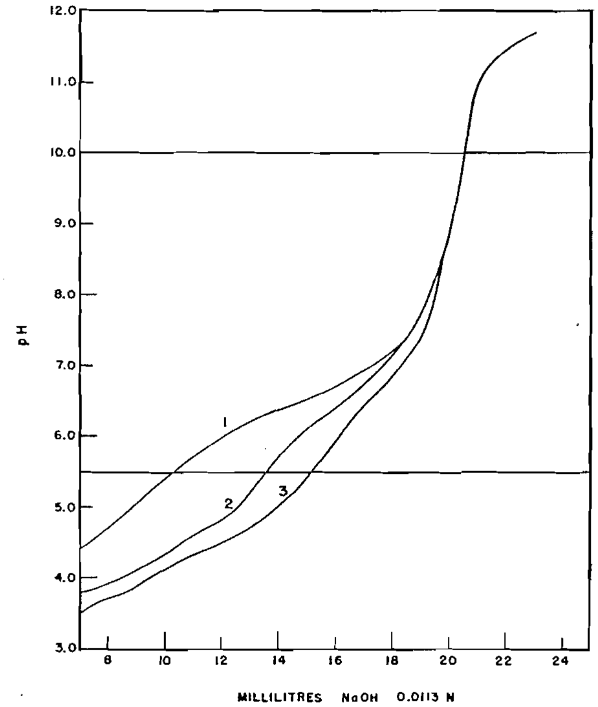

FIG. 1. Titration curves of mixtures of acetic and sulphuric acids in 200 ml., 70% acetone.
Curve 1—50% acetic
Curve 2—30% acetic
Curve 3—20% acetic

of the sulphuric acid equivalence point. Experiments showed, however, that the ratio of the titers at two selected pH readings was proportional to the acetic acid content. In 70% acetone the acetic acid content was proportional to the ratio of the titers at pH 5.5 and 10. The titer at pH 10 was also equivalent to the total acidity providing a small correction was made for a blank on the acetone solution.

Some experiments were also carried out using 50% acetone and 90% acetone solutions. In 50% acetone the ratio of the titers at pH 5 and 8 was found to be proportional to the acetic acid content but the method was not as sensitive for small amounts of acetic acid. In 90% acetone the method was found to be unsuitable since the pH curve exhibited inflections at pH 4, 7.5, and 10.

The acetic acid content of unknown mixtures of the two acids in 70% acetone was determined from a calibration curve (see Fig. 2) showing the relationship between the per cent acetic acid and the ratio of the titers found at pH 5.5 and 10. In all titrations the initial volume was 200 ml.

Procedure for Estimating the Degree of Hydrolysis of Cellulose Acetate Sulphate

(*a*) *In Acetone Solution*

When the cellulose acetate sulphate sample had remained in acetone for the desired time the volume was adjusted to 200 ml. and the acetone concentration

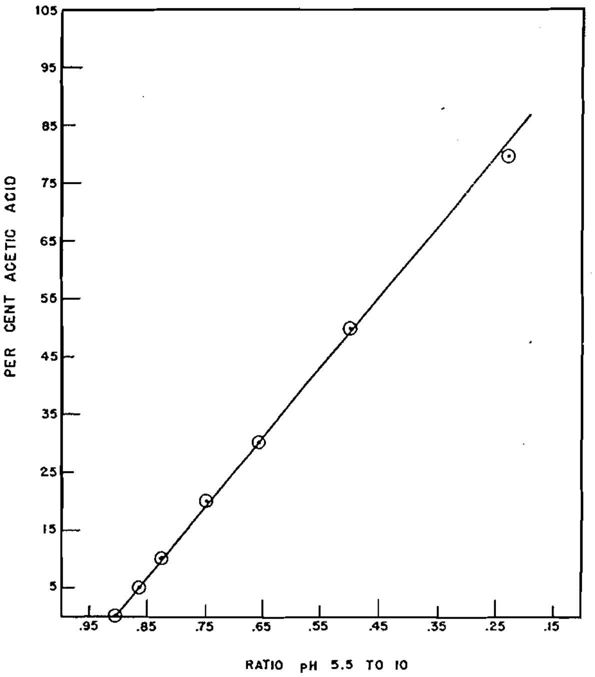

FIG. 2. Calibration curve showing per cent acetic acid in 200 ml. acetone (70%).

to 70%. A precipitate of cellulose acetate usually formed when the sample had been in contact with acetone for three days or more. The precipitate was not usually removed prior to titration unless some additional data were required. The mixture or filtrate was titrated with 0.0113 *N* sodium hydroxide using a Beckman Model H-2 pH meter with a glass and saturated calomel electrode system. The titers at pH 5.5 and 10 were recorded and the per cent acetic acid calculated with the aid of the calibration curve (Fig. 2). The sulphuric acid content was taken as the difference between the total acidity (at pH 10) and the acetic acid content.

The per cent hydrolysis is given by $(a/x) \times 100$ where "a" represents the number of millimoles of sulphate ester (RSO_4H) which has been converted to H_2SO_4, and "x" represents the number of millimoles of sulphate ester in 100 gm. of the original sample. It should be pointed out however that when the precipitate is not filtered off prior to titration the mixture contains "$x - a$" millimoles of RSO_4H plus "a" millimoles of H_2SO_4 which on titration will require $x - a + 2a = x + a$ milliequivalents. The milliequivalents of acid found on titration therefore represent $x + a$, not "a". If, on the other hand, the precipitate is removed prior to titration the milliequivalents of acid found represent $2a$ since the precipitate containing $x - a$ has been removed.

(*b*) *Hydrolysis in Acetone Followed by Precipitation with Petroleum Ether*

After the cellulose acetate sulphate sample had remained in acetone for the desired time, 100 ml. of petroleum ether was slowly added to the well agitated mixture. The resulting precipitate was filtered off and its sulphate content determined gravimetrically (3). The sulphate content thus found was a measure of the unchanged sulphate ester.

RESULTS AND DISCUSSION

Hydrolysis of Cellulose Acetate Sulphate in Acetone

The results shown in Table I indicate that when cellulose acetate sulphate remains dissolved in acetone for 24 hr. or more, the sulphate ester is completely hydrolyzed. The amount of acid found is about double that of the original sulphate ester providing a correction is made for the acetic acid formed by the partial hydrolysis of the acetate ester.

TABLE I
HYDROLYSIS OF CELLULOSE ACETATE SULPHATE IN ACETONE

Expt. No.	Time in acetone (days)	Acetic acid found (% of total acidity)	Sulphuric acid found (m.e.*/100 gm.)	Original sulphate ester content (m.e./100 gm.)	Hydrolysis, %
1	4	10	39.7	20.4	94.6
2	5	20	42.5	20.4	108.3
3	7	32	39.2	20.4	92.1
4	11	30	40.0	20.4	96.0
5	1	9.5	40.8	20.2	102.0
6	1	8.0	41.4	20.2	105.0
7	2½	18.0	39.8	20.2	96.0
8	1	13.0	37.5	20.2	85.6
9	1	13.0	35.5	18.0	97.2
10	7	51.0	20.8	10.4	100.0
				Average:	97.7

**Milliequivalents.*

In experiments 1 to 4 the cellulose ester was precipitated on dilution of the acetone and it was possible to remove it by filtration, so that the titration was carried out on the filtrate. In experiments 5 to 9 no precipitate was formed. In experiment 10 a precipitate was formed but it was not removed prior to titration. The fact that similar results were obtained whether or not the cellulose ester was removed prior to titration is further evidence that hydrolysis of the sulphate ester was complete within the limits of experimental error. Since the acid found after complete hydrolysis is a measure of the original sulphate ester, it is evident that this method could be used for estimating the sulphate ester content of cellulose acetate. It is not as convenient however as the methods described earlier (3).

Accuracy of the Titrimetric Method in Acetone

The accuracy of this method of estimating sulphate content was checked by comparing it with the sulphate found in the filtrate by a gravimetric method the accuracy of which has already been verified (3). Five samples of cellulose acetate sulphate were allowed to stand in acetone for varying times after which water was slowly added and the precipitated cellulose acetate carefully removed by filtration. The sulphuric acid in the filtrate was first determined by the titrimetric method and the same filtrate was then evaporated to dryness and the sulphate content determined gravimetrically. As shown in Table II, the average difference between the two methods was about two per cent. This would indicate that the titrimetric method of estimating sulphuric acid in the presence of acetic acid is fairly reliable.

TABLE II

COMPARISON OF TITRATION AND GRAVIMETRIC METHODS OF DETERMINING SULPHURIC ACID IN THE PRESENCE OF ACETIC ACID AND ACETONE*

Expt. No.	Time in acetone (days)	Acetic acid (% of total acidity)	Sulphate, m.e./100 gm.* Gravimetric	Titration	Difference, %
1	4	10.0	39.8	38.3	−3.8
2	4	9.5	39.2	41.8	+6.6
3	5	13.5	42.4	42.8	+0.9
4	7	23.0	39.2	40.5	+3.3
5	11	30.0	39.2	41.0	+4.6
				Average difference =	+2.3

**In filtrate, after removal of precipitated cellulose acetate.*

Effect of Temperature on Rate of Hydrolysis

Results of hydrolysis experiments at 25°C. (Curve *B*) and at 34°C. (Curve *A*) for various periods up to five hours are shown in Fig. 3, each point representing a separate experiment. It is evident that hydrolysis of the sulphate ester takes place with considerable rapidity during the first two hours and is greatly influenced by the temperature.

Effect of Acetone Concentration

Considerable importance is attached to the amount of water present during the hydrolysis. Two similar samples were simultaneously diluted to 70% acetone. One sample was titrated immediately while the second sample was titrated one hour later. The amount of acetic acid in each sample was 11.5% and 30.5% respectively but the sulphate content was identical. It would appear that hydrolysis of the acetate ester in 70% acetone is similar to hydrolysis in water alone where cleavage of the acetate ester is the more rapid reaction (3). It should be noted that damp samples weighing 2.2 to 2.8 gm. were used throughout and contained 1.2 to 1.6 gm. water. The addition of a sample to 100 ml. of acetone resulted in a solution containing about 1.5% of water.

Effect of Precipitating Agents Other than Water

In some experiments the cellulose acetate sulphate was precipitated from acetone with petroleum ether instead of water. The extent of sulphate cleavage was estimated by a gravimetric determination of the sulphate in the precipitate after filtration and washing. As shown in Table III, the results of these experiments were not very consistent but they did indicate that at least 75% of the sulphate was split off. It is probable that the actual extent of cleavage was greater than this since the precipitate obtained with petroleum ether was very

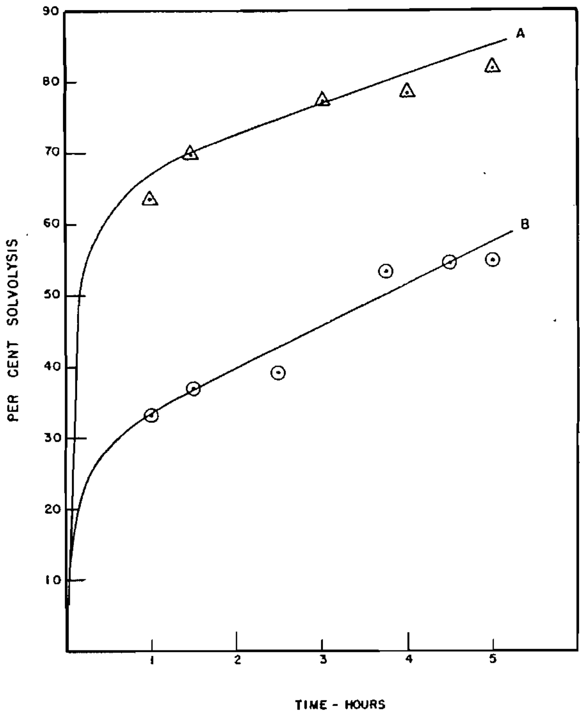

FIG. 3. Rate curve for solvolysis of cellulose acetate sulphate (sulphate cleavage) in acetone.
Curve *A*—Reaction at 34°C.
Curve *B*—Reaction at 25°C.

gelatinous and quite possibly retained some of the free sulphuric acid from the solution. At one time it was felt that the sulphate cleavage occurred during the precipitation with water. These experiments indicated however that the sulphate cleavage is not dependent on the presence of water.

TABLE III
CELLULOSE ACETATE PRECIPITATED FROM ACETONE BY PETROLEUM ETHER

Expt. No.	Time in acetone	Sulphate content of sample (m.e. H_2SO_4/100 gm.)	Precipitate (m.e. H_2SO_4/ 100 gm.)	Sulphate hydrolyzed (m.e. H_2SO_4/ 100 gm.)	Hydrolysis, %
1	21 hr.	42.6	11.0	31.6	74
2	5 days	40.8	10.0	30.8	75
3	1 day	20.0	8.4	11.6	58
4	6 days	20.0	2.9	17.1	86

Comparative Hydrolysis of the Salts of Cellulose Acetate Sulphate

The salt form of the sulphate ester is more stable than the acid both in respect to thermal stability and hydrolysis in water (3). Some data on the hydrolysis in acetone of several salt forms are shown in Table IV. The replace-

TABLE IV
HYDROLYSIS OF SALTS OF CELLULOSE ACETATE SULPHATE IN ACETONE

Expt. No.	Cation	Time in acetone	Hydrolysis, %
1	NH_4	2½ hr.	20
2	"	17½ hr.	74
3	"	9 days	88
4	Na	5 hr.	16
5	"	9 days	88
6	Ca	7 days	96

ment of H^+ by a metallic ion increases the time for complete hydrolysis from about eight hours to more than eight days. More study is required to determine whether the hydrolysis is affected by the type of cation present.

ACKNOWLEDGMENT

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SYNTHESES AND ABSORPTION SPECTRA OF 2-SUBSTITUTED-3-HYDROXY-5-PYRAZOLONES

4-*n*-HEXYL-5-PYRAZOLONES-4-C^{14} [1]

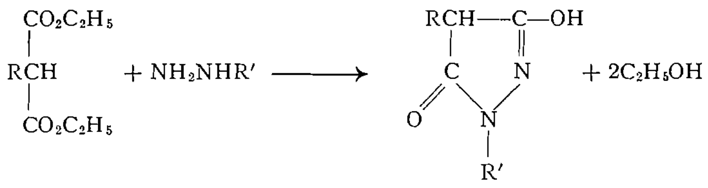
By Paul E. Gagnon, Jean L. Boivin[2], Roderick MacDonald[3],
and Leo Yaffe[4]

ABSTRACT

2-Monosubstituted-3-hydroxy-5-pyrazolones were prepared from diethyl malonate itself and diethyl malonates monosubstituted with methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, and benzyl groups by condensation of the esters with *o*-, *m*-, and *p*-chlorophenylhydrazines, and *n*-hexylhydrazine. By using diethyl *n*-hexyl malonate-2-C^{14} and *o*-, *m*-, and *p*-chlorophenylhydrazines, and *n*-hexylhydrazine as starting materials the corresponding pyrazolones labelled with C^{14} were obtained. Their specific activities were 7.0, 8.8, 9.0, and 8.8 μc./gm. respectively. Ultraviolet absorption spectra were determined in neutral and alkaline solution and the infrared spectra were also obtained. From the data it was possible to ascribe the tautomeric structures best suited for the compounds.

INTRODUCTION

The condensation of diethylmalonates (I) with hydrazine and hydrazine derivatives in the presence of sodium ethylate produces pyrazolones (II) and ethanol according to the following equation:



I II

The first pyrazolone of this type was isolated by Michaelis and Burmeister (10) as a product of the reaction between ethylchloromalonate and phenylhydrazine. It was erroneously concluded that it was a hydrazinedihydroindoxyl because of its acidic character and its facility to form salts.

Other authors (11, 12) assigned the correct formula to the pyrazolone (III), and it was again prepared from diethylmalonate and phenylhydrazine by Conrad and Zart (3).

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Contribution from the Department of Chemistry, Laval University, Quebec, Que., and the Department of Chemistry, McGill University, Montreal, 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.

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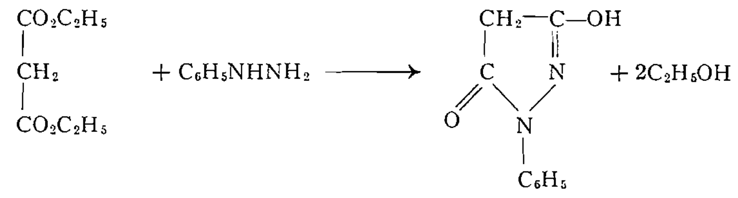


III

In 1950, Gagnon, Boivin, and Boivin (4) prepared several 3-hydroxy- and 3-oxopyrazolones by reacting phenylhydrazine with mono- and disubstituted malonates. It was shown by these authors that the monosubstituted pyrazolones existed as monobasic acids.

In the present investigations other new 4-monosubstituted-3-hydroxy-5-pyrazolones were prepared from diethyl malonate itself and diethyl malonates monosubstituted with methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, and benzyl groups by condensation of these esters with *o*-, *m*-, and *p*-chlorophenylhydrazines and *n*-hexylhydrazine. When diethyl *n*-hexyl malonate-2-C^{14} was used as starting material, the corresponding pyrazolones labelled with C^{14} were obtained and their specific activities determined.

The structure of the pyrazolones were studied with the aid of ultraviolet and infrared absorption spectra; it is well known that such pyrazolones may exist in many tautomeric forms. Pyrazolones bearing N-chlorophenyl and N-hexyl substituents were prepared to study the effect of N-aromatic and N-aliphatic substituents on the pyrazolone ring.

The starting esters were obtained by condensing alkyl halides with diethyl malonate in the presence of sodium ethylate. *o*-, *m*-, and *p*-Chlorophenylhydrazines were prepared by diazotization of their respective anilines followed by reduction with sodium sulphite. *n*-Hexylhydrazine was produced from *n*-hexylbromide and hydrazine hydrate in ethanol.

In the presence of sodium ethylate, diethylmalonates substituted with methyl, ethyl, and propyl radicals did not yield the corresponding pyrazolones when treated with the hydrazines. Fusion of the esters with the hydrazines at 165°C., and heating for a period of three hours was necessary.

The individual properties and analyses of all the pyrazolones prepared are given in Tables I, II, III, and IV.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of all pyrazolones were determined in neutral and alkaline solutions. The results obtained are given in Tables I, II, III, and IV and shown graphically in Figs. 1, 2, 3, and 4.

The spectra of the *o*-, *m*-, and *p*-chlorophenylhydrazines are quite similar in their characteristics. In neutral solution these pyrazolones exhibit two maxima, one of high intensity at short wave length and one of low intensity at longer wave length. The spectra given by the *n*-hexyl pyrazolones do not exhibit definite maxima in many cases. In neutral solution a broad absorption band of low intensity is seen at short wave length. The ethyl, propyl, and butyl

TABLE I

2-*o*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $RC_9H_7O_2N_2Cl$

R	M.p., °C.	Yield, %	Formula	Analysis						Ultraviolet absorption maxima			
				Calculated			Found			Neutral		Alkaline	
				C	H	N	C	H	N	Å	E_m	Å	E_m
H	181–182	38	$C_9H_8O_2N_2Cl$	51.17	3.79	13.20	51.70	3.39	13.82	2860 2340	3.41 4.10	2820 2380	3.92 3.88
CH_3	181–183	25	$C_{10}H_{10}O_2N_2Cl$	53.21	4.43	12.41	52.79	4.55	11.77	2880 2360	3.39 4.13	2840 2400	3.56 3.65
C_2H_5	160–162	28	$C_{11}H_{12}O_2N_2Cl$	55.22	5.01	11.69	55.70	5.42	11.20	2860 2360	3.48 4.20	2820 2380	4.08 3.98
C_3H_7	161–163	29	$C_{12}H_{14}O_2N_2Cl$	56.80	5.52	11.04	56.55	5.79	11.38	2880 2400	4.40 4.08	2780 2380	3.99 3.89
C_4H_9	169–170	52	$C_{13}H_{16}O_2N_2Cl$	58.32	5.97	10.37	58.80	5.97	9.72	2840 2360	3.49 4.19	2820 2360	4.15 4.03
C_5H_{11}	150–151	56	$C_{14}H_{18}O_2N_2Cl$	59.68	6.38	9.97	58.96	6.51	9.91	2860 2440	3.35 3.77		
C_6H_{13}	154–155	62	$C_{15}H_{20}O_2N_2Cl$	60.91	6.81	9.49	61.30	6.67	9.16	2860 2360	3.27 3.99	2540 2860	3.78 3.42
C_7H_{15}	131–133	51	$C_{16}H_{22}O_2N_2Cl$	62.02	7.15	9.06	61.15	6.82	8.64	2460	3.73	2500 2600	3.51 3.69
$C_6H_5CH_2$	197–199	45	$C_{16}H_{14}O_2N_2Cl$	63.68	4.64	9.28	63.55	4.46	9.11	2480	3.59	2560	3.69

TABLE II
2-*m*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $RC_9H_7O_2N_2Cl$

R	M.p., °C.	Yield, %	Formula	Analysis						Ultraviolet absorption spectra			
				Calculated			Found			Neutral		Alkaline	
				C	H	N	C	H	N	Å	E_m	Å	E_m
H	174–175	74	$C_9H_8O_2N_2Cl$	51.17	3.79	13.20	51.81	3.63	13.55	2740 2520	3.86 4.03	2840 2600	4.00 4.12
CH_3	210–211	32	$C_{10}H_{10}O_2N_2Cl$	53.21	4.43	12.41	52.73	4.30	12.10	2900 2440	3.41 4.09	2840 2540	3.86 3.81
C_2H_5	196–198	23	$C_{11}H_{12}O_2N_2Cl$	55.22	5.01	11.69	55.38	5.49	11.66	2980 2540	3.39 3.85	2840 2440	3.93 4.31
C_3H_7	239–240	26	$C_{12}H_{14}O_2N_2Cl$	56.80	5.52	11.04	56.06	5.47	11.28	2880 2420	3.38 4.20	2860 2480	3.82 3.86
C_4H_9	155–156	57	$C_{13}H_{16}O_2N_2Cl$	58.32	5.97	10.37	57.78	5.68	10.08	2820 2420	3.69 4.10	3000 2440	3.68 4.19
C_5H_{11}	132–134	62	$C_{14}H_{18}O_2N_2Cl$	59.68	6.38	9.97	58.92	6.34	9.87	2880 2400	3.41 4.08	2840 2460	3.89 3.88
C_6H_{13}	110–111	62	$C_{15}H_{20}O_2N_2Cl$	60.91	6.81	9.49	60.72	6.49	9.67	2780 2440	3.92 4.08	2840 2540	4.06 4.07
C_7H_{15}	106–108	60	$C_{16}H_{22}O_2N_2Cl$	62.02	7.15	9.06	62.13	7.13	9.16	2760 2460	3.94 4.05	2880 2560	3.96 4.04
$C_6H_5CH_2$	187–189	64	$C_{16}H_{14}O_2N_2Cl$	63.68	4.64	9.28	63.27	4.50	9.33	2780 2460	3.86 4.12	2860 2380	2.84 3.29

TABLE III

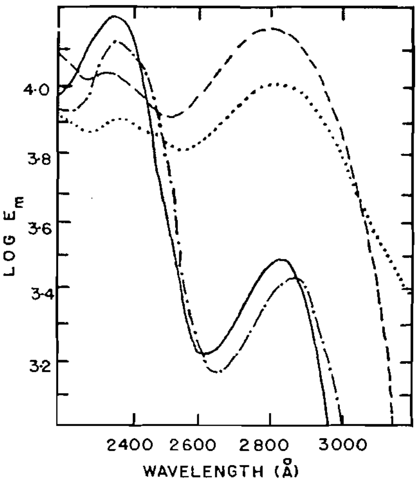
2-*p*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $RC_9H_7O_2N_2Cl$

R	M.p., °C.	Yield, %	Formula	Analysis						Ultraviolet absorption maxima			
				Calculated			Found			Neutral		Alkaline	
				C	H	N	C	H	N	Å	E_m	Å	E_m
H	207–209	32	$C_9H_8O_2N_2Cl$	51.17	3.79	13.20	51.51	3.61	13.41	2760 2460	3.94 4.13	 2640	 4.14
CH_3	220–222	30	$C_{10}H_{10}O_2N_2Cl$	53.21	4.43	12.41	53.22	4.50	11.94	2840 2440	3.79 4.19	3000 2560	3.71 4.10
C_2H_5	202–203	28	$C_{11}H_{12}O_2N_2Cl$	55.22	5.01	11.69	54.24	5.40	11.34	2880 2460	3.75 4.14	3000 2580i	3.75 4.20
C_3H_7	193–195	28	$C_{12}H_{14}O_2N_2Cl$	56.80	5.52	11.04	56.66	5.42	11.18	2840 2460	3.24 4.12	2920 2520	3.82 4.19
C_4H_9	193–195	63	$C_{13}H_{16}O_2N_2Cl$	58.32	5.97	10.37	58.31	5.49	10.08	2860 2460	3.81 4.25	3000 2560	3.68 4.13
C_5H_{11}	174–175	60	$C_{14}H_{18}O_2N_2Cl$	59.68	6.38	9.97	59.68	6.38	9.60	2840 2460	3.79 4.14	3000 2540	3.74 4.17
C_6H_{13}	147–148	69	$C_{15}H_{20}O_2N_2Cl$	60.91	6.81	9.49	61.05	6.95	9.61	2780 2440	3.86 4.13	2860 2520	3.95 4.12
C_7H_{15}	160–162	38	$C_{16}H_{22}O_2N_2Cl$	62.02	7.15	9.06	61.51	7.28	9.03	2920 2420	3.17 4.23	2920 2440	2.97 3.56
$C_6H_5CH_2$	181–182	31	$C_{16}H_{14}O_2N_2Cl$	63.68	4.64	9.28	63.89	4.13	8.93	2760 2480	3.94 4.15	2840 2480i	4.29 4.06

TABLE IV

2-HEXYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES, $RC_9H_{15}O_2N_2$

R	M.p., °C.	Yield, %	Formula	Analysis						Ultraviolet absorption maxima			
				Calculated			Found			Neutral		Alkaline	
				C	H	N	C	H	N	Å	E_m	Å	E_m
H	250–251	80	$C_9H_{16}O_2N_2$	58.70	8.68	15.22	58.01	8.48	15.20	2660	3.81	2750	4.06
CH_3			$C_{10}H_{18}O_2N_2$	60.60	9.09	14.14	59.73	8.62	14.71	2440	3.24	2800i 2540i	3.10 3.21
C_2H_5			$C_{11}H_{20}O_2N_2$	62.26	9.43	13.20	62.64	9.77	12.84	2800i 2520i	3.34 3.32	2800 2520	3.44 3.29
C_3H_7	83–84	38	$C_{12}H_{22}O_2N_2$	63.71	9.73	12.53	63.38	9.65	12.41	2560	3.53	2800 2560	3.50 3.64
C_4H_9	94–95	69	$C_{13}H_{24}O_2N_2$	65.54	10.00	11.66	65.47	9.95	11.69	2780 2520	3.34 3.29	2780 2560	3.48 3.47
C_5H_{11}	93–95	95	$C_{14}H_{26}O_2N_2$	66.14	10.23	10.98	65.11	10.25	10.68	2540	3.57	2780i 2560	3.49 3.61
C_6H_{13}	91–92	60	$C_{15}H_{28}O_2N_2$	67.16	10.44	10.41	66.80	10.17	10.31	2580	3.46	2880i 2580	3.43 3.47
C_7H_{15}	81–83	38	$C_{16}H_{30}O_2N_2$	68.09	10.64	9.93	68.09	10.64	9.81	2560	3.46	2760i 2540	3.48 3.51
$C_6H_5CH_2$	155–156	79	$C_{16}H_{22}O_2N_2$	70.03	8.08	10.21	70.00	8.03	10.12	2520	3.50	2840i 2500	3.36 3.79



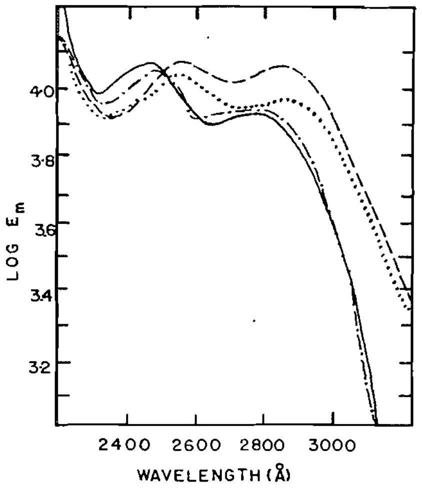
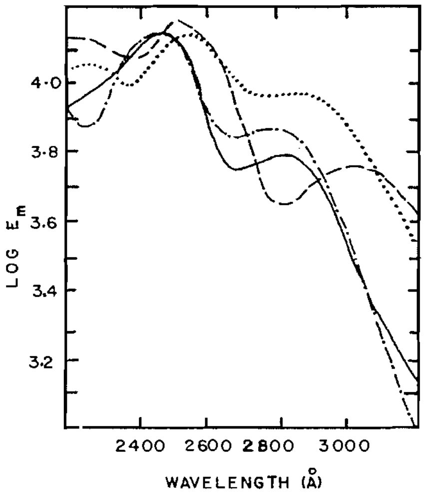


FIG. 1. (Left) Ultraviolet absorption spectrum of: 2-*o*-chlorophenyl-3-hydroxy-4-*n*-propyl-5-pyrazolone; ———— in neutral solution - - - - - - in alkaline solution; 2-*o*-chlorophenyl-3-hydroxy-4-*n*-butyl-5-pyrazolone; —·—·— in neutral solution · · · · · · in alkaline solution.

FIG. 2. (Right) Ultraviolet absorption spectrum of: 2-*m*-chlorophenyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone; ———— in neutral solution - - - - - - in alkaline solution; 2-*m*-chlorophenyl-3-hydroxy-4-*n*-heptyl-5-pyrazolone; —·—·— in neutral solution. · · · · · in alkaline solution.



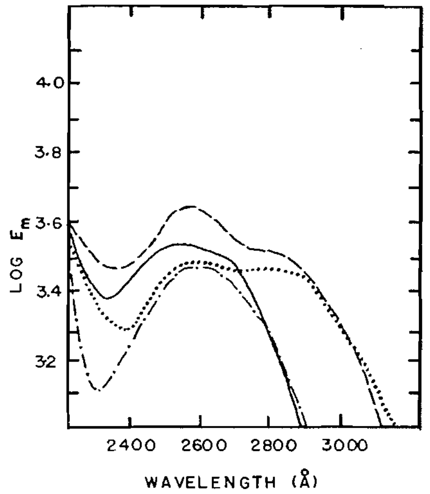
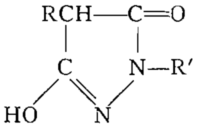


FIG. 3. (Left) Ultraviolet absorption spectrum of: 2-*p*-chlorophenyl-3-hydroxy-4-*n*-amyl-5-pyrazolone; ———— in neutral solution - - - - - - in alkaline solution; 2-*p*-chlorophenyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone; —·—·— in neutral solution · · · · · · in alkaline solution.

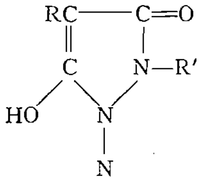
FIG. 4. (Right) Ultraviolet absorption spectrum of: 2-*n*-hexyl-3-hydroxy-4-*n*-propyl-5-pyrazolone; ———— in neutral solution - - - - - - in alkaline solution; 2-*n*-hexyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone; —·—·— in neutral solution · · · · · · in alkaline solution.

monosubstituted hexyl pyrazolones show a second maximum of equal intensity at long wave length. In alkaline solution a number of the *n*-hexyl pyrazolones exhibit two maxima, one at short and one at long wave lengths but of equal intensity.

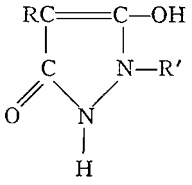
Several structures may be postulated for 4-monosubstituted-3-hydroxy-5-pyrazolones. The following are theoretically possible (IV–VIII) owing to tautomeric displacement.



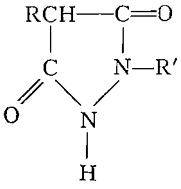
IV



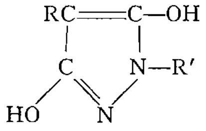
V



VI



VII



VIII

It is possible to disqualify a few of the above structures by examining the chemical and physical properties of the compounds actually obtained. An examination of the ultraviolet absorption spectra has been very useful as a means of postulating the structures of many pyrazolones.

Biquard and Grammaticakis (2) showed that 1-phenyl-2,3,4-trimethyl-5-pyrazolone and 1-phenyl-3,4,4-trimethyl-5-pyrazolone which differ in the position in which the double bond is fixed in the ring gave different ultraviolet spectra.

The spectra exhibited by many pyrazolones have been studied intensively by Gagnon and co-workers (4, 5, 6, 8). These authors related the position of the double bond in the pyrazolone ring to the wave length and the intensity of the absorption. It was found that a high intensity maximum at short wave length corresponded to a double bond between the two carbon atoms 3 and 4, while a low intensity maximum at long wave length was indicative of a single bond between these two carbon atoms. A compound giving two maxima was shown to exist in two tautomeric forms (9).

In 1950, Gagnon, Boivin, and Boivin (4) studied the properties of several 4-monosubstituted-3-hydroxy-5-pyrazolones. They found that the pyrazolones exhibited two maxima in neutral and alkaline solutions and that they were best represented by structures V and VI. A pK_a value of 4 to 5 revealed that the compounds were monobasic acids thereby eliminating the diketo and dienol forms VII and VIII theoretically possible.

The results of the present work compares favorably with that of Gagnon, Boivin, and Boivin (4). Two maxima, indicative of two structures are found in neutral and alkaline solutions in the case of the chlorophenyl pyrazolones. An absorption band of high intensity at short wave length, indicative of an ethylenic double bond may be represented by structures V and VI, while another maximum at low intensity at long wave length satisfy the requirements of structure IV.

The *n*-hexyl-3-hydroxy-5-pyrazolones do not exhibit absorption spectra identical to those 2-chlorophenyl-3-hydroxy-5-pyrazolones. An attempt to explain their structure will be dealt with in the section on infrared absorption spectra.

Infrared Absorption Spectra

The infrared absorption spectra of the pyrazolones were determined with a Perkin-Elmer spectrophotometer. The results obtained are given in Tables V, VI, VII, and VIII and some of the data are plotted in Figs. 5, 6, 7, and 8.

TABLE V

INFRARED MAXIMA OF *o*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$											
H	3300	1700	1698	1645	1600	1565	1490	1322	1300	1235	1203	1155
CH_3	3300	1710	1670	1650	1600	1526	1490	1310	1287	1270	1148	1135
C_2H_5	3300	1710	1680	1650	1600	1535	1490	1320	1305	1235	1205	1155
C_3H_7	3300	1705	1680	1638	1600	1538	1490	1365	1305	1270	1163	1135
C_4H_9	3300	1750	1680	1680	1590	1530	1490	1421	1310	1270	1178	1148
C_5H_{11}	3320	1750	1700	1680	1590	1530	1490	1422	1312	1270	1210	1135
C_6H_{13}	3310	1710	1690	1610	1590	1535	1485	1420	1365	1230	1210	1136
C_7H_{15}	3240	1745	1655	1600	1585	1484		1335	1325	1270	1205	1142
$C_6H_5CH_2$	3328	1738	1700		1590		1490	1358	1320	1290	1205	1148

TABLE VI

INFRARED MAXIMA OF *m*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$										
H	3120	1730	1683	1596	1490	1405	1345	1295	1723	1165	1136
CH_3	3300	1710	1670	1602	1490		1340	1310	1220	1165	1139
C_2H_5	3310	1750	1700	1600	1490	1425	1355	1295	1242	1192	1137
C_3H_7	3260	1675		1605	1492	1407	1349	1285	1232	1157	1142
C_4H_9	3320	1745	1695	1590	1492	1418	1304	1290	1224	1182	1138
C_5H_{11}	3260	1735	1670	1605	1490	1423	1330	1273	1205	1165	1145
C_6H_{13}	3120	1735	1675	1600	1495	1420	1330	1305	1216	1162	1100
C_7H_{15}	3310	1731	1680	1600	1490	1415	1326	1303	1220	1161	
$C_6H_5CH_2$	3120	1745	1690	1600	1490	1418	1355	1295	1270	1170	

TABLE VII

INFRARED MAXIMA OF *p*-CHLOROPHENYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$										
H	3310	1770	1695	1600	1500	1420	1360	1300	1230	1190	1152
CH_3	3320	1750	1690	1600	1545	1418	1335	1300	1240	1185	1145
C_2H_5	3320	1750	1700	1600	1505	1425	1345	1300	1236	1186	1133
C_3H_7	3331	1745	1690	1600	1464	1425	1345	1292	1235	1185	1136
C_4H_9	3320	1745	1690	1600	1500	1425	1340	1295	1228	1175	
C_5H_{11}	3320	1750	1700	1605	1500	1430	1345	1292	1236	1186	
C_6H_{13}	3320	1740	1680	1605	1505	1418	1335	1290	1225	1190	1138
C_7H_{15}	3310	1720	1620	1590	1500	1405		1285	1225	1195	1124
$C_6H_5CH_2$	3315	1750	1675	1590	1490	1415	1330	1305	1225	1182	1137

TABLE VIII

INFRARED MAXIMA OF *n*-HEXYL-3-HYDROXY-4-MONOSUBSTITUTED-5-PYRAZOLONES

R	Absorption bands, cm.$^{-1}$							
H	3210	1705	1610	1550	1361	1300	1190	1115
CH_3	3110	1745	1660	1490	1340	1298	1185	1140
C_2H_5	3100	1740	1650	1490	1351	1271	1172	1122
C_3H_7	3110	1730	1665	1490	1342	1305	1186	1122
C_4H_9	3310	1745	1670	1490	1310	1260	1160	1125
C_5H_{11}	3150	1750	1670	1505	1340	1300	1187	1140
C_6H_{12}	3300	1760	1665	1495	1342	1265	1168	1132
C_7H_{15}	3270	1750	1680		1325			1142
$C_6H_5CH_2$	3230	1752	1685	1500	1305		1180	1132

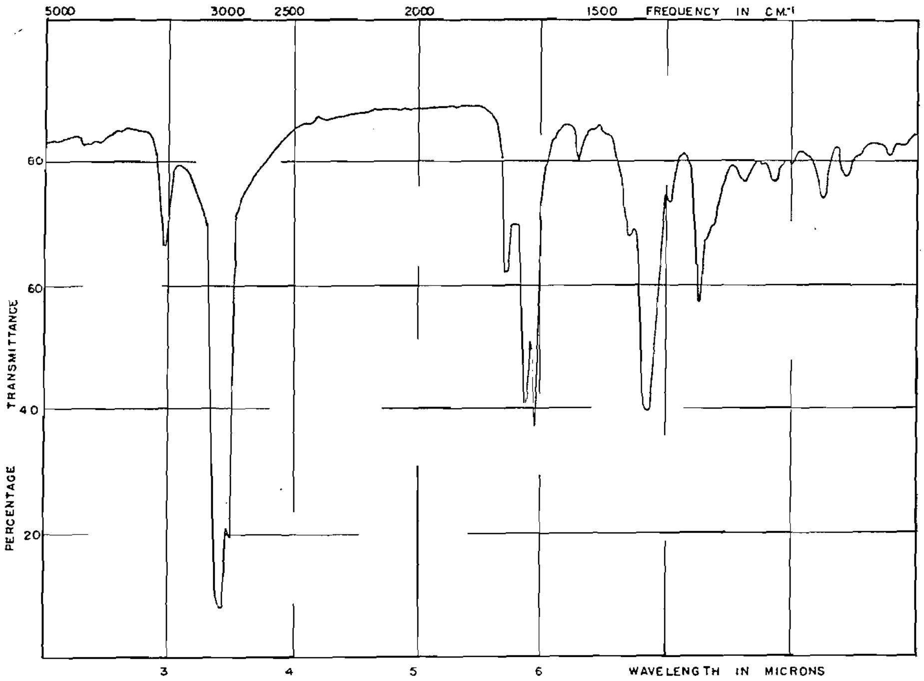


FIG. 5. Infrared absorption spectrum of 2-*o*-chlorophenyl-3-hydroxy-4-*n*-butyl-5-pyrazolone.

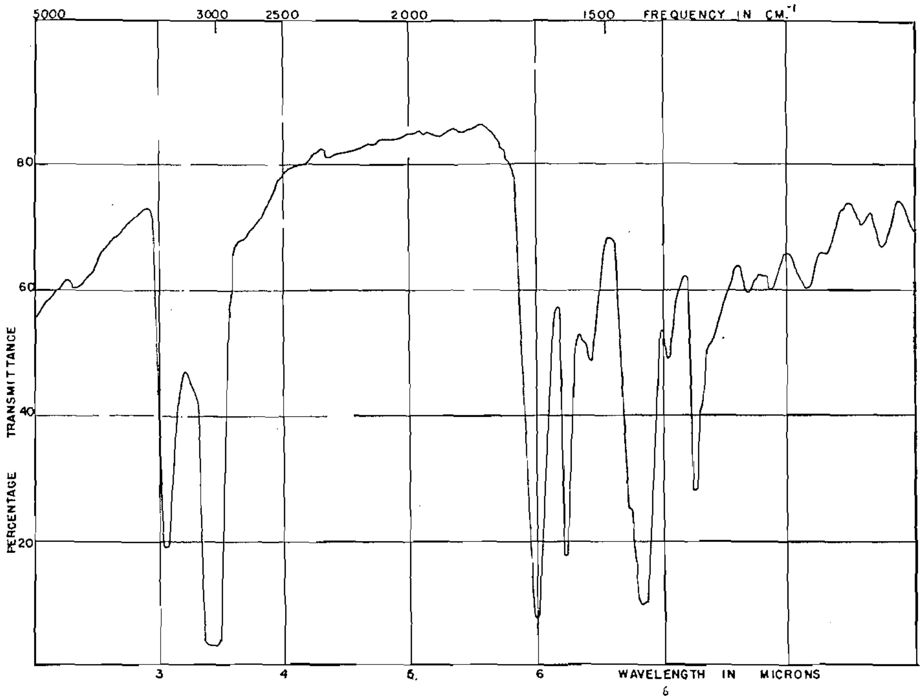


FIG. 6. Infrared absorption spectrum of 2-*m*-chlorophenyl-3-hydroxy-4-*n*-amyl-5-pyrazolone.

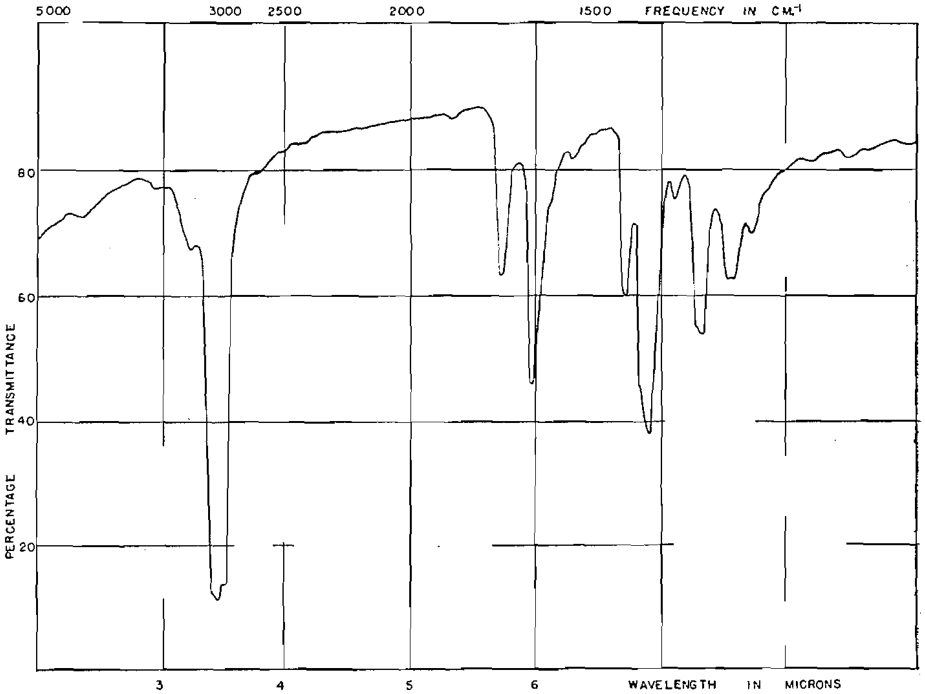


FIG. 7. Infrared absorption spectrum of 2-*p*-chlorophenyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone.

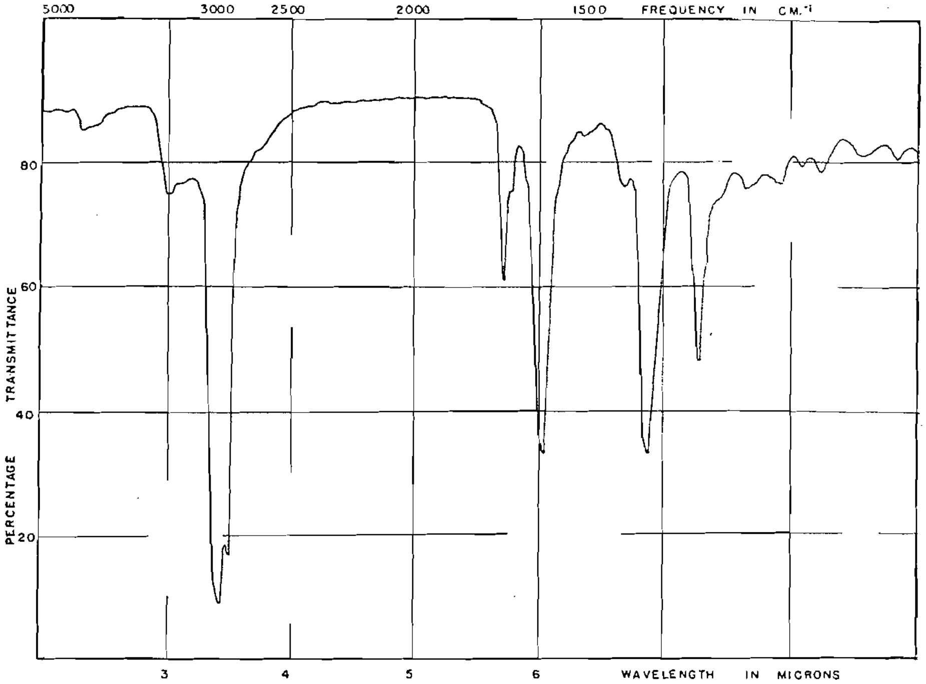


FIG. 8. Infrared absorption spectrum of 2-*n*-hexyl-3-hydroxy-4-*n*-hexyl-5-pyrazolone.

Because of the tautomeric structures theoretically possible for 3-hydroxypyrazolones, the pyrazolones may be expected to give rise to very complicated infrared spectra. The problem of interpretation is also difficult since very few reference spectra for pyrazolones are available. Randal and his co-workers (13) reported the absorption spectrum of 3-methyl-5-pyrazolone but only gave an assignment for a cyclic C=N band. The infrared spectra of several 4-monosubstituted-3-phenyl-5-pyrazolones and 4-monosubstituted-1,3-diphenyl-5-pyrazolones were given by Gagnon, Boivin, and Paquin (7). They assigned an absorption peak which appeared at 3300 cm.$^{-1}$ in the spectra of the 3-phenyl-5-pyrazolones to an OH group. This seemed plausible since no band for a carbonyl group was present, and pyrazolones may exist in the enolic form. Two or more peaks in the double bond region were interpreted as a sign of conjugation. The spectra of 1,3-diphenyl-5-pyrazolones were less complicated. Bond assignments were made tentatively for the C=O group at 1700 cm.$^{-1}$, and the C=N group at 1600 cm^{-1}.

In the present investigation, bond assignments have been made for several functional groups. The *o*-, *m*-, and *p*-2-chlorophenyl pyrazolones exhibit very complicated spectra, but the positions of the peaks are quite similar for the three homologous series. A band of medium to high intensity occurs in the spectra of the compounds at 3300 cm^{-1}. It is easy to assign this band to the absorption of a definite NH or OH group. It has already been mentioned that the pyrazolones prepared in this work are monobasic acids. With this chemical evidence in mind it is reasonable to attribute this band to an OH group.

An absorption band of high intensity occurs in the range 1675–1770 cm^{-1}. This is the region in which the C=O group absorbs. Randal and his co-workers have attributed the absorption in this range to the carbonyl group of lactams, therefore it is reasonable to do the same for pyrazolones.

A second band of very high intensity always occurs in the double bond region and absorbs in the range 1670–1700 cm^{-1}. This band is much too strong to be attributed to C=C absorption or vibrational ring influences, both of which could occur at this place. Randal studied the absorption spectra of many nitrogen compounds such as thiazolidines, imidazolines, pyridines, oxazolones, and 3-methyl-5-pyrazolone and found that the C=N group in these cyclic structures occurred in the region 1590–1680 cm^{-1}. Therefore we may ascribe this peak to that of a cyclic C=N.

A very constant absorption peak of low to medium intensity occurs at 1490 cm^{-1}. This band appears in both the 2-chlorophenyl and the 2-*n*-hexyl pyrazolones and therefore cannot be ascribed to the absorption of the phenyl ring. The absorption of the C=C group is in almost every case found in this region but usually at lower wave length. In the absorption spectrum of α-phenylazoacetoacetic acid ethyl ester, Randal assigns a peak at 1510 cm.$^{-1}$ to the influence of an enolic carbon double bond. Since this structure is possible in the compounds prepared we may assign the peak to a $-C=C-OH$ enolic structure. Other peaks present at 1600 cm.$^{-1}$, 1640 cm.$^{-1}$, and 1530 cm.$^{-1}$ may be caused by the phenyl ring vibrations.

From a consideration of the infrared spectra and assignments made we must consider the following formulae to represent the 2-chlorophenyl pyrazolones. An enolic $-C=C-OH$ bond and an OH absorption peak indicate the partial structure of a phenol $-C=C-OH$. Structures V and VI satisfy this postulation since they both have an enolic structure.

The infrared spectra also shows the presence of a C=N group. The only possibility for a bond of this nature is formula IV.

The spectra of the *n*-hexyl pyrazolones are not as complicated as those of the 2-chlorophenyl pyrazolones. A peak in the region of 3100–3300 cm.$^{-1}$ may be ascribed to the vibration of the OH group. An absorption band at 1735–1750 indicates the presence of a C=O group while an intense band at 1660–1685 cm.$^{-1}$ is ascribed to a cyclic C=N. A very constant absorption band which appears in all the pyrazolones at 1490 cm.$^{-1}$ indicates the presence of an enolic $-C=C-OH$ grouping.

The *n*-hexyl pyrazolones can then be given the same structures as the 2-chlorophenyl pyrazolones.

EXPERIMENTAL PART*

2-o-Chlorophenyl-3-hydroxy-4-monosubstituted-5-pyrazolones

Diethyl malonates (0.05 mole) and *o*-chlorophenylhydrazine (0.05 mole) were condensed in two different ways. The malonates containing the substituents, butyl, amyl, hexyl, heptyl, and benzyl were condensed with *o*-chlorophenylhydrazine in the presence of sodium ethylate in absolute ethyl alcohol.

**All melting points are uncorrected.*

The reaction time varied from 18 to 20 hr. The excess alcohol was then removed and the remaining residues dissolved in water. The aqueous solutions were well extracted with ethyl ether and acidified with dilute acetic acid (33%), whereupon the pyrazolones were obtained usually as crystalline solids. The compounds were purified by crystallization from either xylene or petroleum ether.

The malonates bearing the substituents methyl, ethyl, and propyl and unsubstituted ethyl malonate did not yield pyrazolones when condensed with *o*-chlorophenylhydrazines in the above manner. Heating of the esters with *o*-chlorophenylhydrazine at 165°C. yielded the pyrazolones in small amounts. Heating was continued until no more ethanol was evolved from the reaction mixture. This usually required three hours. The mixture was then cooled and dissolved in sodium hydroxide solution (5%). Insoluble material was filtered off and the alkaline solution was extracted several times with ethyl ether. Upon acidification with acetic acid (33%), the pyrazolones were obtained. The pyrazolones are listed together with their melting points, analyses, and ultraviolet absorption maxima in Table I and the infrared data are given in Table V. Typical ultraviolet absorption curves are plotted in Fig. 1 while some infrared data are plotted in Fig. 5.

2-m-Chlorophenyl, 2-p-Chlorophenyl, and 2-n-Hexyl-3-hydroxy-4-monosubstituted-5-pyrazolones

Diethyl malonates and *m*-chloro, *p*-chloro, and *n*-hexylhydrazines were condensed in a manner similar to that used to obtain the 2-*o*-chlorophenyl pyrazolones. The melting points, analyses, and ultraviolet absorption maxima are given in Tables II, III, and IV. The infrared absorption bands are given in Tables VI, VII, and VIII.

Preparation of Diethyl-n-hexyl Malonate-2-C^{14}

To a solution of sodium metal (5.6 gm., 0.242 mole) in ethanol (400 ml.) was added diethyl malonate (20 gm., 0.125 mole) and 9.3 mgm. of diethyl malonate-2-C^{14} containing 0.1 mc. of activity. Hexyl bromide (21 gm., 0.125 mole) was added and the mixture was refluxed until acidic to wet litmus paper. The excess ethanol was then removed under reduced pressure and the inorganic salts dissolved in water. The oil which separated was extracted with ether and the extract was washed with water and dried over sodium sulphate. The ether was removed by distillation and the substituted ester distilled under reduced pressure: b.p. 154–156°C. at 10 mm. There was obtained 23 gm. of product, yield, 63.3%. A small sample of the product (18.4 mgm.) was taken and converted to carbon dioxide, absorbed in barium hydroxide, and counted as barium carbonate. The specific activity was calculated to be 12.4 μc. per gram of material.

Preparation of 2-Substituted-3-hydroxy-4-n-hexyl-5-pyrazolones-4-C^{14}

Diethyl *n*-hexyl malonate-2-C^{14} (4.0 gm., 0.017 mole) was reacted with *o*-, *m*-, and *p*-chlorophenylhydrazine (2.4 gm., 0.017 mole) and *n*-hexylhydrazine (2.0 gm., 0.017 mole) in the presence of sodium metal (2.4 gm., 0.11 mole) in absolute ethanol (200 ml.). After a reaction time of 18 hr. the excess alcohol was evaporated and the remaining residue dissolved in water. The aqueous solution was purified by extracting several times with ethyl ether. Acidification with dilute acetic acid (33%) gave the labelled pyrazolones. The chemical yields varied from 60 to 70%, after purification from petroleum ether. Their specific activities were determined by conversion of the compounds to carbon dioxide and counting as barium carbonate.

Combustion of C^{14} Products, Plating, and Counting

All the compounds were completely transformed to carbon dioxide by dry combustion. Samples weighing from 20 to 30 mgm. were burned in the presence of oxygen in a closed system. The carbon dioxide evolved was absorbed in two traps containing carbonate free barium hydroxide solution. When combustion was complete the absorbers were removed from the apparatus and the barium carbonate separated by centrifuging. A sample of the active barium carbonate and water was transferred to an aluminum counting plate and dried under an infrared lamp. Continuous agitation was necessary to ensure even distribution throughout the mount. Sufficient barium carbonate was added to each plate to ensure "infinite thickness". When dry the samples were counted using an end window Geiger-Mueller counter. The counting rates were corrected as suggested by Andrews and Mannet (1). The results obtained are given in Table IX.

TABLE IX
COUNTING DATA OF 2-SUBSTITUTED-3-HYDROXY-4-*n*-HEXYL-5-PYRAZOLONES-4-C^{14}

2-Substituent	Weight, mgm.	Total count	Time, min.	Count rate per min.	Specific activity, μc./gm.
o-Chlorophenyl	21.3	7,565	5	1491	7.0
m-Chlorophenyl	19.4	8,110	5	1600	8.8
p-Chlorophenyl	22.0	10,010	5	1980	9.0
n-Hexyl	24.7	10,450	5	2070	8.8

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the pyrazolones were taken on a Beckman Spectrophotometer Model DU. The method has been previously described (6). The solvents used were ethanol (95%) and a solution of sodium hydroxide (0.01 *N*) in ethanol. The results are listed in Tables I, II, III, and IV and some of the data are plotted in Figs. 1, 2, 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 method has been described in the literature (7).

The spectra covering the range from 5000 to 1100 $cm.^{-1}$ only are given in Figs. 5, 6, 7, and 8. The curves all show the four specific bands of Nujol. The other absorption bands are listed in Tables V, VI, VII, and VIII, and have been discussed in the theoretical part.

ACKNOWLEDGMENTS

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MOLTEN SALTS

VISCOSITY OF SILVER NITRATE[1]

By F. A. Pugsley and F. E. W. Wetmore

ABSTRACT

Precise values for the viscosity of silver nitrate show that Frenkel's relation for comparison of the temperature dependence of viscosity and conductivity is valid for this system and that the energy of activation for viscous flow is proportional to that for electrical transport over a range of temperature.

Values of the viscosity of silver nitrate melts reported earlier by Goodwin and Mailey (4) are not of sufficient precision to be useful in making minute examination of the temperature dependence. Previous work (6) showed that the energy of activation for electrical transport decreases with rise in temperature. In order to compare the two processes of transport, the viscosity of silver nitrate has been determined with an apparatus capable of giving relative values precise to within 0.15%.

EXPERIMENTAL

The viscosimeter used was of a modified Ostwald type with bulb and capillary tube of silica. The working volume of the cell was 3.4 cc., the capillary tube 100 mm. long and of 0.2 mm. bore. In order to reduce the lack of precision associated with use of the liquid head as the sole driving force, suction from a controlled source provided 98% or more of the total driving force. The pressure difference created by the suction was read on a precise manometer. A plunger and probe electrode served for setting the head of liquid outside the bulb to the same level before each determination; the change of liquid head during a measurement was kept small by having a large volume of liquid surrounding the bulb. The working volume of the bulb was defined by two probe electrodes; contact of the rising melt with the lower probe started a timing device which was shut off by contact of the melt with the upper probe.

The cell was calibrated at 25° with normal aqueous sodium chloride, for which Jones and Christian (5) have obtained the viscosity, η, and the density, d. Several determinations of the time of filling were made at each of three pressures. These data were substituted in the expression $pt = \eta/a - bd/at$ in order to determine the values of a and b, the constants characteristic of the cell behavior. Small temperature corrections were applied to adjust a and b for use at 275°; corrections over a range of ±50° from this temperature were calculated to be negligibly small.

All materials used were of reagent quality. The liquids were filtered through porous Pyrex discs; for the melts a cylindrical furnace surrounded the filter. The temperature of the viscosimeter was maintained constant in a furnace built about a 65-lb. copper cylinder and measured within 0.1° with a calibrated thermocouple.

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Contribution from the Electrochemical Laboratory, University of Toronto, Toronto 5, Ontario.

TABLE I
VISCOSITY AND CONDUCTIVITY OF SILVER NITRATE

°C.	η	log η	log κ	C
256.8	3.606	0.5571	−0.0610	0.4732
258.5	3.571	0.5528	−0.0570	0.4744
258.9	3.556	0.5509	−0.0565	0.4732
259.5	3.541	0.5491	−0.0550	0.4734
261.8	3.494	0.5434	−0.0501	0.4744
262.1	3.487	0.5425	−0.0496	0.4742
279.0	3.128	0.4953	−0.0168	0.4722
280.3	3.123	0.4946	−0.0137	0.4758
299.8	2.784	0.4446	0.0212	0.4738
300.0	2.782	0.4443	0.0216	0.4740
300.2	2.775	0.4433	0.0220	0.4736
320.2	2.503	0.3985	0.0546	0.4736

$C = \log \eta + 1.376 \log \kappa$

In Table I is given the viscosity of silver nitrate relative to that of water at 25°. The values are lower than those of Goodwin and Mailey by a few per cent, but are estimated to be reliable to about 0.7 per cent. The probable relative error, of consequence for the comparison to be made, is estimated to be not greater than 0.15 per cent. Conductivity data were taken from Reference 6.

DISCUSSION

Andrade (1), Frenkel (2), and Glasstone, Laidler, and Eyring (3) have derived expressions for the expected dependence of viscosity on temperature. Unfortunately the expressions are not identical. Moreover, the last mentioned authors defined energy of activation through an expression involving finite quantities, but calculated it as a differential coefficient. The inconsistency of this treatment will be dealt with elsewhere. Frenkel (Reference 2, p. 441) has suggested a method of comparing viscosity and specific conductivity data. He assumed the equations $\kappa = A.\exp(-E_1/RT)$ and $\eta = B.\exp(E_2/RT)$ to hold, with A, B, E_1, and E_2 constant. This would require that log κ and log η be strictly linear in T^{-1}, which they are not. However, if E_1 and E_2 are admitted to be temperature dependent the nonlinearity can be recognized and the development continued: $E_1 = RT\ln A - RT\ln\kappa$, $E_2 = RT\ln\eta - RT\ln B$. If E_2 is proportional to E_1 over the range of temperature ($E_2 = mE_1$), it follows that $\log\eta + m\log\kappa =$ constant (Frenkel's relation). Even if the activation energy is defined as the differential coefficient $-R\,d(\ln f)/dT^{-1}$, in which f stands for either the conductivity or fluidity, proportionality of the activation energies leads to the equation $d\ln\eta + m\,d\ln\kappa = 0$, which leads to Frenkel's relation also. From the data of Table I, m was determined by the method of L.M.S. to be 1.376. The last column of the table shows the value of $\log\eta + 1.376\log\kappa$, which has the mean value 0.4738 with standard deviation only 0.0008, i.e. within the precision of the data. The energy of activation for viscous flow is therefore taken to be proportional to that for electrical transport over the range of temperature.

ACKNOWLEDGMENT

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SOME THERMODYNAMIC PROPERTIES OF HYDROCARBONS ADSORBED ON RUTILE[1]

By H. P. Schreiber[2] and R. McIntosh[3]

ABSTRACT

Differential thermodynamic properties of methane, ethane, propane, and *n*-butane adsorbed on rutile have been determined from isotherms over appreciable temperature ranges. Ordinary experimental techniques failed to yield reliable data in low temperature and surface coverage regions, but essentially simple modifications of these resulted in accurate thermodynamic values. For methane, the results compared well with similar ones computed by Pace, Heric, and Dennis from data obtained by means of calorimetry. Maximum error in isosteric heats of adsorption was 60 cal. mole^{-1}; in differential molar entropies 0.8 cal. mole^{-1} degree^{-1}. The thermodynamic properties of methane and ethane are similar but there is a departure in the set pattern for propane. A large change was observed in the heat of adsorption of propane, near 185° K. and surface coverages lower than 0.6 of the monolayer. A phase transition is suggested to account for this occurrence.

INTRODUCTION

Thermodynamic and statistical analyses of adsorption data have been found useful for the description of the states of physically adsorbed films. The methods have been developed principally by Hill (10, 11) and Everett (6) and full details are given in their papers. So far, however, few detailed applications of the methods have been made. Everett (7) and Everett and Young (8) have applied a scheme of analysis to a limited number of systems adsorbed on charcoals. Hill, Emmett, and Joyner (12) have evaluated the thermodynamic functions for nitrogen adsorbed on Graphon from isotherms in a limited temperature range. Morrison, Los, and Drain (14) and Drain and Morrison (3, 4, 5) have determined thermodynamic properties of argon, nitrogen, and oxygen on rutile from isotherm, heat capacity, and heat of adsorption measurements obtained by calorimetry. More recently Pace, Heric, and Dennis (15) and Pace, Sasmor, and Heric (16) have carried out a calorimetric study of the properties of methane on rutile, so augmenting the trend toward this form of experimental approach.

Data sufficiently accurate to warrant the labor of thermodynamic analysis are best obtained by calorimetry. This is an expensive experimental tool, however, and it was thought to be of interest to refine the techniques of obtaining adsorption isotherms sufficiently to obtain accurate thermodynamic data. In this paper the steps taken to obtain useful data are recounted and some thermodynamic properties of methane, ethane, propane, and *n*-butane adsorbed on rutile are presented and discussed. The hydrocarbons were chosen for study because it seemed probable that a useful comparison of the properties in the homologous series could be made. In doing so, one was aware

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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 fulfilment of the requirements for the Ph.D. degree.

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of difficulties which would be encountered in eventual application of statistical concepts to such complex molecules.

EXPERIMENTAL

Materials and Apparatus

The rutile was obtained from Dr. J. A. Morrison of the National Research Council, Ottawa, and has been described earlier (14). Throughout these experiments, one sample of 2.581 gm. was used. All the hydrocarbon vapors were obtained from the Ohio Chemical Company (Cleveland). The vapors were purified by repeated distillations from dry ice to liquid air, and only middle cuts were used in the determinations. In order to eliminate unsaturated impurities, methane and ethane were bubbled through illuminated scrubbing towers containing bromine water. Infrared spectra demonstrated that no unsaturated impurities were present in the ethane, propane, and *n*-butane. Helium, used in determinations of dead space, was purified by passage over activated charcoal at liquid air temperatures.

The apparatus used in this work differed from those generally employed, in that neither stopcock lubricants nor mercury vapors were present in the adsorption system. Stopcock lubricants had to be eliminated because the solubility of hydrocarbon vapors in these would result in error. All stopcocks in the adsorption system were therefore replaced by greaseless metal vacuum valves. The presence of mercury vapor in the adsorption system was undesirable in principle. Pressure measurements and methods of introducing adsorbate which complied with this principle were therefore devised. Equilibrium vapor pressures were read by two methods. Pressures greater than 2–3 cm. Hg were read to ±0.01 cm. Hg by means of a spoon gauge used as a null instrument. Pressures lower than 2 cm. Hg were read on a multirange McLeod gauge. The errors in such readings varied from ±15 per cent at 10^{-5} cm. Hg to about 0.2 per cent at 2 cm. Hg.

The rutile sample was contained in a cell which was designed to provide easy access of adsorbate vapors and eliminate temperature gradients within the adsorbent bed. Details of the cell construction may be found in the Appendix (see also Fig. 6). The assembly was operated with ease in the thermal region 83.2°–300° K. This was done by immersing the assembly in a Dewar flask containing a suitable refrigerant and balancing the cooling action by the heat input. Manual control was effective in maintaining temperatures constant to ±0.05° over long periods of time. Four single junction copper–constantan thermocouples placed at various positions in the cell were used to determine the temperature. Temperature gradients over the length of the cell were generally less than 0.1°, but exceeded this value slightly near the liquid air temperature.

Procedure

Methods of determining isotherms and compiling equilibrium pressure–volume data in low surface coverage regions were different from conventional means. They were developed because in regions in which the vapor pressure over the adsorbed film was less than 0.1–0.2 cm. Hg, conventional methods of investigation consistently led to absurd thermodynamic values. This was most pronounced at low temperatures. A description of these techniques is given in the Appendix.

RESULTS AND DISCUSSION

Adsorption Isotherms

The adsorption of the hydrocarbons was studied to the following extent:

methane—five isotherms covering the range	83.2°–133.2° K.
ethane—six isotherms covering the range	133.2°–203.2° K.
propane—nine isotherms covering the range	166.3°–273.2° K.
n-butane—seven isotherms covering the range	193.2°–298.2° K.

The isotherms for butane adsorbed below 273° K. led to absurd thermodynamic values, however, and so cannot be considered valid. This matter is further discussed in the Appendix.

Thermodynamic functions of adsorption are most readily interpreted in the region near and below V_m, the monolayer capacity. Particular attention was therefore given to this region. Coverages beyond 1.5 V_m were only sketchily studied for propane and *n*-butane, and not at all for the other two vapors. In all pressure readings, the mercury was assumed to be at 298° K.; values of the volume of vapor adsorbed were always corrected to N.T.P. conditions. Ideal gas laws were used for methane and ethane because even at the highest pressures nonideality corrections were negligible. The propane and *n*-butane data were corrected for nonideality using the van der Waals equation of state. Thermomolecular pressure effects, often important in such experiments, were not significant here.

All the isotherms appeared to be of the type II (1). They obeyed the B.E.T. (Brunauer, Emmett, and Teller (2)) and Huttig (13) equations in the range $0.05 < P/P^0 < 0.250$, and slightly beyond these limits in a few cases. The B.E.T. and Huttig monolayer capacities were computed, as well as the surface areas, using liquid state densities for the adsorbates. Some of these values are compiled in Table I. The values computed from the methane data were based on isotherms near 100° K.; for the other hydrocarbons from isotherms near 200° K. Values reported by Morrison, Los, and Drain (14) from the adsorption of argon and nitrogen at 77.3° K. on rutile from the same stock as that used here are included for comparison.

TABLE I
MONOLAYER VOLUMES AND SURFACE AREAS FROM ADSORPTION OF HYDROCARBONS ON RUTILE

	V_m (cc. N.T.P./gm.)		Area (m.^{2}/gm.)	
Adsorbate	B.E.T.	Huttig	B.E.T.	Huttig
Methane	12.9	13.3	60.6	62.5
Ethane	7.7	8.2	46.0	49.0
Propane	6.8	7.4	49.5	54.0
n-Butane	5.7	6.1	48.0	51.4
Nitrogen (M.L.D.)	—	—	85.0	—
Argon (M.L.D.)	24.9	—	—	—

The difference between the nitrogen and hydrocarbon areas may be due to nonuniformity in the particle size of various portions of the rutile stock. A greater similarity in the argon and methane values of V_m might have been expected, however. The difference in these values is very difficult to interpret. It appears to be a function not only of the configuration of the adsorbed molecule, but also of the substrate configuration and, within broad limits, the temperature.

Thermodynamic Analyses

Hill (10) has pointed out that two sets of thermodynamic functions for the adsorbed phase may be computed, depending on the choice of independent variables used to describe the state of this phase. If the surface concentration Γ (or the surface area A) is chosen as one such variable, the differential or isosteric functions are involved. If the film spreading force ϕ is chosen, integral thermodynamic functions are derived. The integral functions are more meaningful (6), but the differential functions are more easily obtained and provide good indication of the precision of the data from which they stem. In this paper, only the differential functions are presented.

Isosteric heats, differential molar entropies and, in some cases, the differential free energies of adsorption were computed. The isosteric heat of adsorption may be evaluated from

$$[1] \qquad (q_{st})_\theta = R \ln \frac{(p_2 - p_1)_\theta}{1/T_1 - 1/T_2}$$

where q_{st} is the isosteric heat at surface concentration $\theta = V/V_m$, where V is the volume of vapor adsorbed, and p_1, p_2 and T_1, T_2 are the equilibrium pressures and temperatures of the isotherms involved.
Writing

$$[2] \qquad -q_{st} = (H_g - \bar{H}_s)$$

the differential molar entropy is obtained from

$$[3] \qquad (H_g - \bar{H}_s) + RT \ln p/p^0 = T(S_g - \bar{S}_s)$$

and the free energy of adsorption from

$$[4] \qquad (F_g - \bar{F}_s) = -RT \ln p/p^0$$

where $\bar{H}_s$, $\bar{S}_s$, $\bar{F}_s$ refer to the differential molar quantities of the adsorbed species.

The calculations were performed by the method of Hill, Emmett, and Joyner (12). This yields, in effect, quantities for a mean isotherm $\bar{T}$ characterized by pressures $\bar{p}$, where by arbitrary definition

$$[5] \qquad 1/\bar{T} = 1/2\ (1/T_1 + 1/T_2)$$

and

$$[6] \qquad \log \bar{p} = 1/2\ (\log p_1 + \log p_2).$$

T_1, T_2, p_1, and p_2 refer to equilibrium temperatures and pressures of the two isotherms under consideration.

Pairs of isotherms, usually not differing by more than 20 degrees were employed in the calculations. On occasion, the isosteric heat obtained for an isotherm pair could be considered constant in the given temperature range, thus leading to values of $(S_g - \bar{S}_s)$ for actual isotherms. Except where otherwise indicated, the thermodynamic functions were obtained using pure vapor at 1 cm. Hg pressure as standard state. The quantities are expressed as a function of θ. The B.E.T. value of V_m is thereby inherently involved.

The isosteric heat, the free energies, and the differential molar entropies of adsorbed methane are plotted as functions of θ in Figs. 1A, 1B, and 1C re-

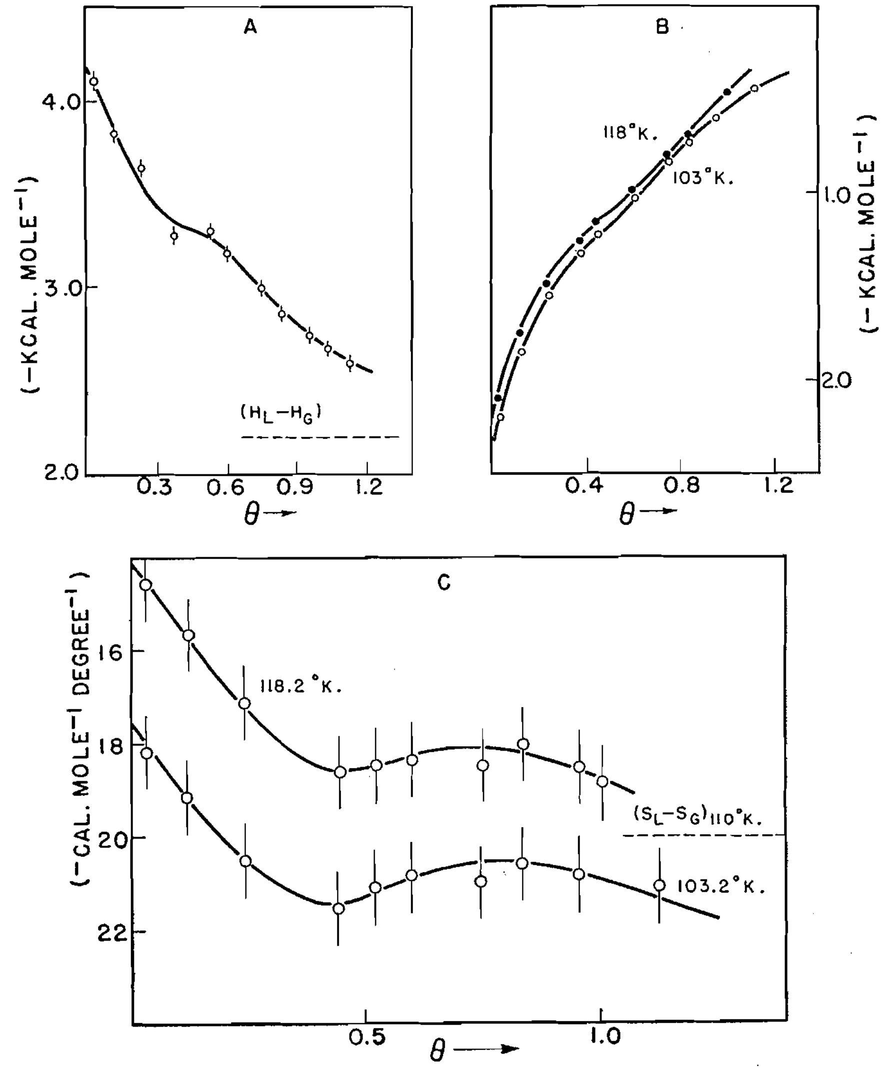

FIG. 1A. Isosteric heat of adsorption of methane on rutile at 110.2° K.
B. Differential molar free energy of adsorption of methane on rutile at 103.2° and 118.2° K.
C. Differential molar entropy of adsorption of methane on rutile at 103.2° and 118.2° K.

spectively. Heat and entropy relationships for adsorbed ethane are shown in Figs. 2A and 2B and the isosteric heat for butane is shown in Fig. 3. In all systems, the experimental errors were ±60 cal. mole^{-1}, ±30 cal. mole^{-1}, and ±0.8 cal. mole^{-1} degree^{-1} for the heats, free energies, and entropies respectively.

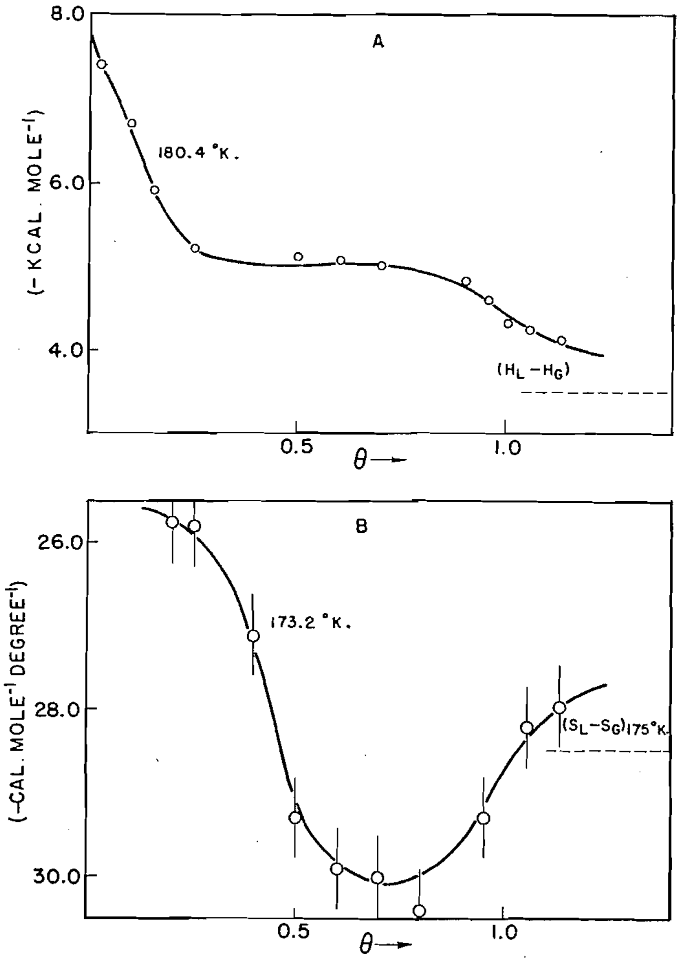

FIG. 2A. Isosteric heat of adsorption of ethane on rutile at 180.4° K.
B. Differential molar entropy of adsorption of ethane on rutile at 173.2° K.

The isosteric heats of adsorption for methane, ethane, propane below 185° K. (see Fig. 4B), and butane in the range 273°–298° K. are all of similar shape. The case of propane is discussed in greater detail below. Data for butane below 273° K. showed large, random variations and therefore were not considered acceptable. Isosteric heat relationships of a similar form have previously been reported (3, 15). The rapid initial decrease was observed in all systems, and was more pronounced the larger the adsorbate molecule. This decrease in the heat of adsorption is generally considered to be a characteristic of a heterogeneous substrate. The topic has been discussed recently

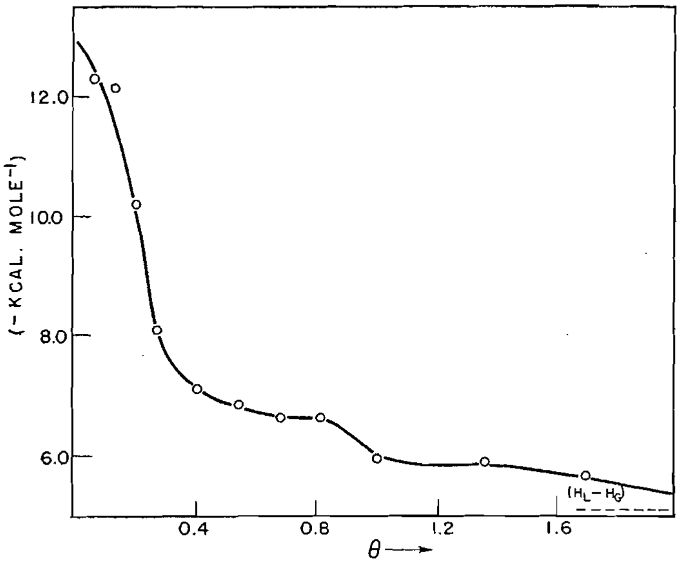

FIG. 3. Isosteric heat of adsorption of *n*-butane on rutile at 273.2° K.

in some detail by Drain and Morrison (3), and in accord with their conclusions it is postulated that the rutile presents a heterogeneous surface to the adsorbing matter. The more gradual decrease beyond 0.5 θ is likely due, in part, to repulsive interactions caused by the close packing of the adsorbed films. In all cases, the heats of liquefaction of the adsorbates are approached at high surface concentrations. The isosteric heat of methane is unique in the region 103.2°–133.2° K. Differences between the values at the two extreme temperatures did not exceed 50 cal. mole^{-1} and so could have been due to experimental errors. A significant difference in the heats of adsorption of ethane at the average temperatures 134.7° and 180.4° K. was detected however; the values at the lower temperature are about 300 cal. mole^{-1} greater. A difference of about 100 cal. mole^{-1} existed between the heats at $\bar{T}$ = 134.7° and $\bar{T}$ = 156.9° K. Thus, for the larger adsorbate molecule, the sensitivity of the isosteric heat to temperature variation was somewhat increased.

The free energies and differential molar entropies of adsorption of methane are shown in Fig. 1B and 1C at two temperatures in order to indicate the magnitude of temperature variation inherent in these quantities. The free energy plots are characteristic for the adsorption process and the entropy curves are of much the same shape as those for ethane, exemplified in Fig. 2B. The entropy data for propane adsorption are dealt with later. The entropies of the adsorbed methane and ethane are negative with respect to the corresponding vapors over the entire surface coverage region investigated. They are positive with respect to those of the liquids, except in the region $0.30 < \theta < 0.55$ for methane and $0.50 < \theta < 0.80$ for ethane, where they are also negative and pass through minima. The minimum in the differential entropy curve of adsorbed methane occurs near 0.50 θ; that for ethane occurs near

0.65 θ, is somewhat deeper and is formed more abruptly. At higher surface coverages, as the free energy change diminishes toward zero, the entropies of liquefaction are approached. In the absence of the integral entropies, the interpretation of the differential quantities becomes difficult. Some similarity may be noted, however, between our differential entropy curves and those derived by Hill, Emmett, and Joyner (12) from concepts of the B.E.T. theory. On that basis, the minima were indicative of progressive close packing of the adsorbed films and consequent restrictions in the configurations of the monolayer films. The subsequent rise in the entropy was then due to the onset of multilayer formation.

Methane on Rutile

It is of interest to compare the thermodynamic properties of this system as calculated here and by Pace and co-workers (15, 16) using calorimetrically obtained data. In order to effect comparison, our data have been computed using the vapor pressure of bulk liquid as standard state. A complication arises because of differences between the two samples of rutile involved. The adsorbent used by Pace was of somewhat greater subdivision than ours, giving a B.E.T. methane area of about 84m^2. gm^{-1}. Thus, exact agreement in the thermodynamic functions should not necessarily be expected. The comparative differential thermodynamic functions in the range $0.20 < \theta < 1.10$ at 110° K. are shown in Table II. We are indebted to Dr. E. L. Pace, Western Reserve University, Cleveland, for kindly supplying the necessary data.

TABLE II

COMPARISON OF DIFFERENTIAL THERMODYNAMIC PROPERTIES OF METHANE ADSORBED ON RUTILE AT 110° K.

	q_{st}(−cal. mole^{-1})		ΔF(−cal. mole^{-1})		ΔS(−cal. mole^{-1} degree^{-1})	
θ	Pace *et al.*	This work	Pace *et al.*	This work	Pace *et al.*	This work
0.268	3920	3680	1320	1350	23.6	19.2
0.567	3470	3300	1087	1050	21.7	19.9
0.694	3410	3150	992	900	22.0	19.3
0.839	3110	2850	748	720	21.5	19.0
0.876	2970	2820	675	660	20.8	19.1
1.031	2520	2600	451	480	18.8	19.5
Errors:	±30	±60	±10	±30	±0.3	±0.8

The variation of the isosteric heat with surface concentration in the two cases is nearly identical. Our values, however, are displaced by about 300 cal. mole^{-1} towards lower heats of adsorption in the region below 0.8 θ. Thereafter the two sets of values merge and approach the heat of liquefaction. It may thus be concluded that the nature of heterogeneity in the two adsorbents is nearly identical, although it is somewhat less pronounced in our sample. The free energies of adsorption are in very satisfactory agreement. In all cases, except at 0.694 θ, the values are within the experimental error of each other. The agreement would likely be further improved if the comparison were made at truly "equal" surface coverages. There exists some uncertainty in calculating values of V_m so that the comparison may, in fact, be based on slightly discrepant values of θ. The differential molar entropies are in some disagreement. This is a result of the numerical differences in the isosteric heats. The discrepant entropies attest with greater sensitivity to differences existing in the two adsorbed films. These differences presumably are a result of the distinct nature of the two adsorbents.

The calorimetric data are somewhat more accurate than the present set (see Table II). The better definition of the heats of adsorption, for example, detects variations with temperature over 10° ranges. This could not be done with our data. The more sharply defined entropy values are another significant outcome of applying calorimetric techniques. On the other hand, the two sets of results are certainly comparable in usefulness. The present data may then be judged to constitute a marked improvement over similar ones obtained from experiments employing standard adsorption techniques.

Propane on Rutile

The results obtained for this system are rather surprising. In the region of surface coverage below about 0.6 θ, the isosteric heats of adsorption fell into two well defined categories. At any surface coverage in this region, isotherms below about 185° K. ($1/T = 5.4 \times 10^{-3}$) yielded one heat value; above this temperature another heat of adsorption, as much as 3–4 kcal. mole^{-1} lower, was computed. In order to illustrate this situation, the isosteric heats were evaluated from the slopes of log p vs. $1/T$ plots, on which data from all isotherms were included. Three typical plots of this type are shown in Fig. 4A. The discontinuity in the slope of this plot remains invariant with respect to the $1/T$ axis, but diminishes in magnitude at higher surface coverages. Beyond 0.6 θ, a characteristic single straight line plot is obtained. The resulting isosteric heat relationships are exemplified by the data at 174.8° and 210.3° K.

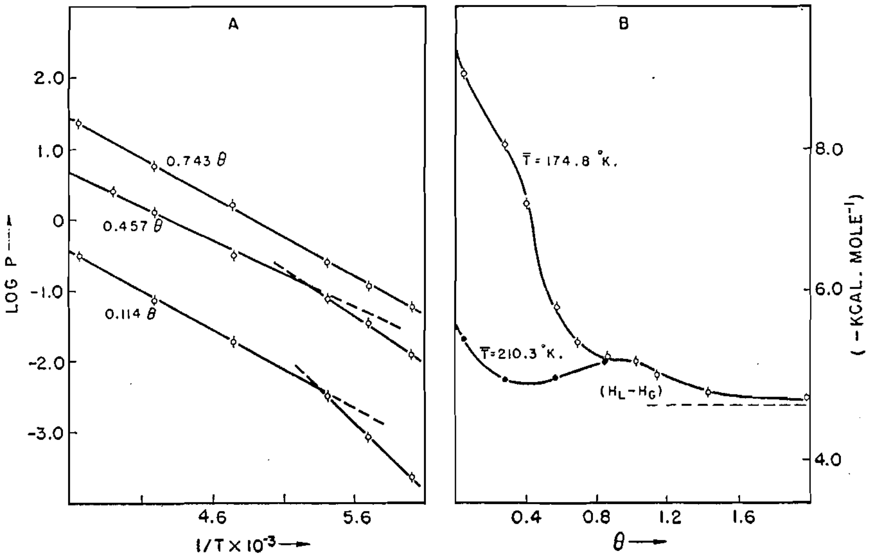

FIG. 4A. Log p vs. $1/T$ for propane adsorbed on rutile, as a function of surface coverage.
B. Isosteric heat of adsorption of propane on rutile at 174.8° and 210.3° K.

These are shown in Fig. 4B. The heat of adsorption at the lower temperature is of the general form already described; on the other hand, the curve at the higher temperature is of notably altered form.

A thorough attempt was made to establish the validity of the phenomenon. Other experimental methods of investigation were not feasible but a painstaking re-examination of the experimental techniques revealed no determinate errors capable of accounting for this occurrence. The possibility always exists that indeterminate errors were responsible. For example, in carrying out the experiments, the refrigerating liquid was changed near 185° K. from liquid air to dry ice – acetone. Thus, possibly, some spurious temperature effects may have arisen. The construction of the cell (see Fig. 6) and the absence of appreciable temperature gradients in the cell at this temperature, however, tend to reduce the likelihood of such effects being undetected. It seems unlikely, moreover, that indeterminate effects could occur with a regularity leading to the observed results. Two legitimate causes for an appreciable change in the isosteric heat of adsorption are recognized. One is the transition of the adsorbed film from a localized to a mobile one, the other a phase change in the adsorbed film. Hill (9) has shown that the transition from localized to mobile films occurs over wide temperature regions, so that the present case

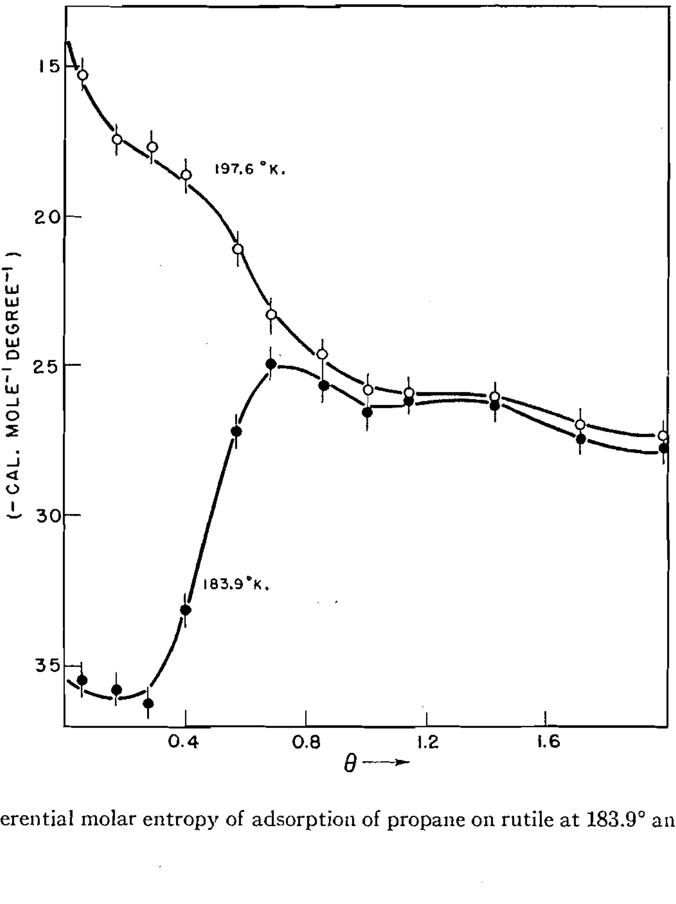

FIG. 5. Differential molar entropy of adsorption of propane on rutile at 183.9° and 197.6° K.

cannot reasonably be an example of it. The phase change in the adsorbed film is, therefore, the more plausible cause for the dual heats of adsorption. At the lowest surface coverages, where complicating factors such as molecular interactions should contribute little to the over-all heat effect, the difference between the high and low temperature isosteric heats equals nearly 3.5 kcal. mole^{-1}. This is of the general order of magnitude of the heat of liquefaction of propane at 185° K. Thus, one might postulate the transition, near 185° K., of the adsorbed film from a two dimensional vapor to a two dimensional liquid. At higher surface coverages, the continuously increasing degree of close packing of the vapor film reduces the transitional heat effect. Finally, near 0.6 θ, the existence of the vapor film is ended and a unique heat of adsorption is observed. Without heat capacity or entropy data which are independent of the heat function, it is unfortunately impossible either to confirm or reject the above hypothesis.

The differential molar entropy of adsorbed propane reflects the dual heat relationship. In Fig. 5, the results at 183.9° and 197.6° K. are plotted as a function of θ. It will be noted that below about 0.6 θ, the entropy of the suggested two dimensional liquid film is appreciably lower than that of the vapor. The two quantities approach each other and merge at the postulated disappearance of the vapor film. Neither of the two entropy functions bears much resemblance to the methane and ethane counterparts. This suggests that in the adsorption of propane, the physical pattern set in the adsorption of the lower hydrocarbons is altered. A closer examination of this point is deferred for a future publication.

APPENDIX

Cell Assembly

The cell and the heater arrangement are shown in Fig. 6. The small perforations in the inner cell wall allowed multifold access of vapor to adsorbent. Equilibrium pressure over the adsorbed film was thereby established more speedily. The thin glass rod sealed to the bottom of the inner cell wall was wound with gold foil to eliminate vertical temperature gradients near the center of the sample. Strips of gold foil, extending from the glass rod to the inner cell wall at short intervals, tended to overcome lateral gradients. Copper strips placed between inner and outer cell chambers made heat transfer from the outside more efficient. The total metallic surface in the cell was less than 0.01 per cent that of the rutile, so that the effect of adsorption on the metals could be neglected. Temperature gradients on the outer surface of the cell were reduced by 1/32 inch lead sheeting wound to a height about two inches above the rutile. A lead umbrella (not shown) fastened to the capillary some six inches above the rutile level and extending to the heater wall was used to cut down conduction of heat by the capillary lead.

Detail of Experimental Techniques

The rutile was first degassed near 300° C. for about 30 hr. The residual pressure after such treatment was 10^{-6} mm. Hg. Then, for surface coverages

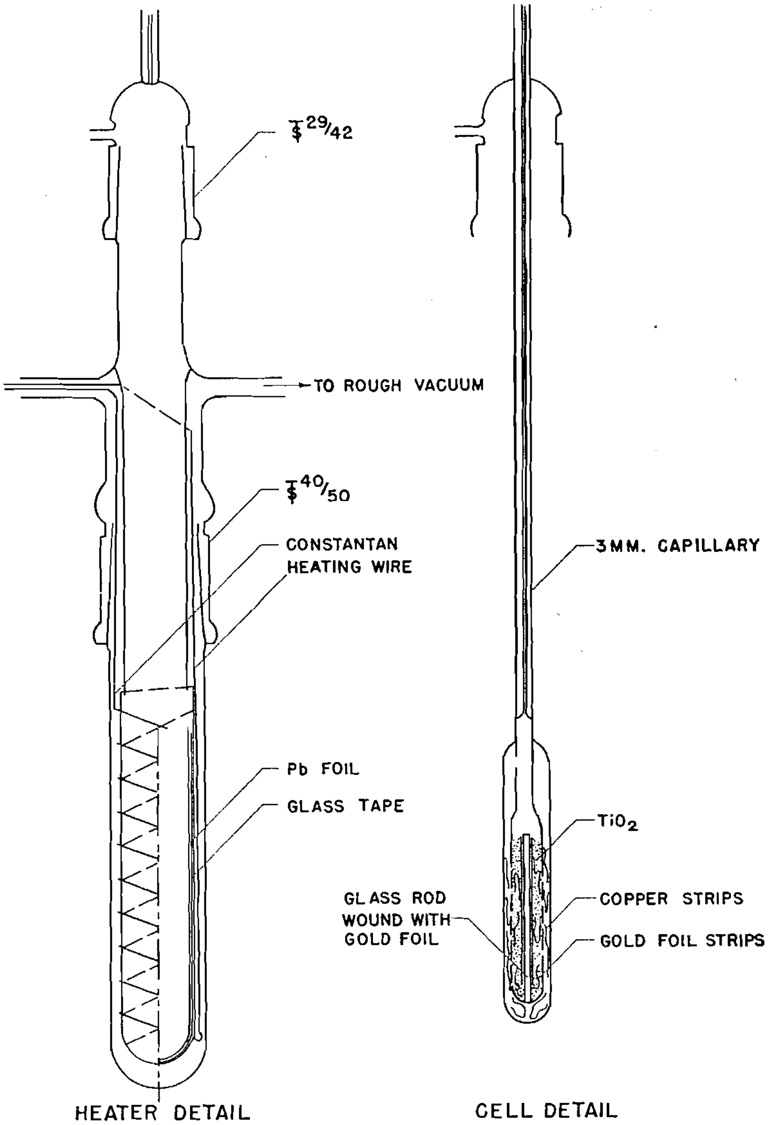

FIG. 6. Cell assembly, showing details of heater and cell construction.

for which the vapor pressures were lower than 0.5 cm. Hg, the following procedure had to be followed rigorously if equilibrium pressures were to be obtained. A known volume of vapor was allowed to come into contact with the adsorbent at room temperature. The temperature was then adjusted to that of the lowest isotherm for the particular adsorbate. It was found that the recorded pressure was a function of the rate of cooling of the adsorbent. Therefore, the rate of cooling had to be diligently controlled, so that the required temperature was reached in a period of time greater than the "critical" mentioned below. The rutile was maintained at the desired temperature for 15–25 min. before the equilibrium pressure was read. The sample was next warmed to room temperature so that the system was restored to the condition obtaining prior to the first cooling. The procedure was then repeated, attaining this time the next higher selected temperature. After points on all required isotherms were determined, the rutile was outgassed and a series of points at the next higher surface coverage determined by the same procedure.

TABLE III

DEPENDENCE OF APPARENT EQUILIBRIUM PRESSURES ON COOLING PERIOD

Adsorbate	Temp. of isotherm, ° K.	Volume vapor adsorbed (cc. N.T.P.)	Cooling time (min.)	Apparent equi'm pressure (mm. Hg)	Critical cooling period (min.)
CH_4	103.2	3.9	20	7.22×10^{-3}	$\geqslant$ 40
			40	5.08	
			60	5.05	
			90	5.13	
			120	5.00	
C_2H_6	153.2	3.8	30	1.82×10^{-2}	$\geqslant$ 70
			55	1.40	
			70	1.15	
			90	1.20	
			120	1.13	
C_3H_8	173.2	4.1	60	9.08×10^{-2}	$\geqslant$100
			100	8.68	
			120	8.70	
			180	8.74	
n-C_4H_{10}	208.2	2.4	45	3.58×10^{-3}	180*
			80	1.70	
			100	1.10	
			180	1.00	

**Isosteric heats computed from isotherms below 273° K. showed large random variations. It was concluded, therefore, that a cooling period of 180 min. was not sufficient to establish equilibrium conditions in this system, even though the data above tend to suggest this. It was not considered practicable to extend the duration of the cooling period beyond 180 min.*

The dependence of apparent equilibrium pressures on critical cooling times is shown in Table III. The cooling times varied from adsorbate to adsorbate. They decreased somewhat at higher temperatures and, as a rule, at surface coverages characterized by pressures greater than 0.3 cm. Hg, equilibrium was attained rapidly regardless of the temperature.

A further peculiarity of adsorption at low surface coverages and low temperatures is the slow rate at which equilibrium pressures may be obtained by desorption. Periods comparable with the critical cooling periods were entirely inadequate to establish equilibrium conditions, when a selected temperature was approached by gradual heating. This is illustrated in Fig. 7, where the approach to equilibrium by adsorption and desorption methods is shown for 4.1 cc. propane adsorbed at 173.2° K. A desorption period of about 20 hr. was needed to attain the equilibrium pressure. Thus, while the process is

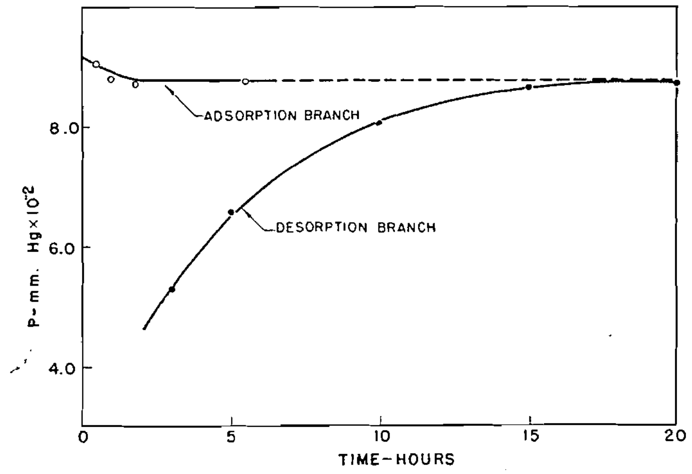

FIG. 7. Approach to equilibrium pressure by adsorption and desorption for 4.1 cc. propane adsorbed on rutile at 173.0° K.

clearly reversible, serious errors would be committed if the low pressure regions had been investigated by desorption methods analogous to the adsorption techniques.

The method of compounding isotherms used in this research may be termed "isosteric and discreet". This is in contrast with the usual "isothermal and continuous" methods, in which an entire isotherm is determined by successive increments of adsorbate onto a partially covered substrate. The present method constitutes some improvement, when the thermodynamic functions are sought. For example, the behavior of the isosteric heat of adsorption at low surface coverages is of particular interest (3, 17). The isosteric method tends to define q_{st} more precisely in this region. The argument is illustrated with the aid of Fig. 8. The solid lines represent two hypothetical error free isotherms at temperatures T_1 and T_2 ($T_1 < T_2$). The broken lines represent "experimental" isotherms determined at the same temperatures by the two methods. The sections of the isotherms under consideration are generally determined by the initial two or three experimental points. In the isothermal method it is possible that the values of volume adsorbed in the one isotherm are all affected by error in one direction, and those in the neighboring isotherm by error in the opposite direction. An isosteric section through the isotherms then yields an experimental value of $\Delta P'$ which is appreciably different from ΔP—the error free value. It is evident from equation [1] that the value of q_{st} will be in some error.

Such a situation cannot arise when the isosteric procedure is employed. The greatest proportion of error in the value of the volume of vapor adsorbed arises from the determination of the initial volume of vapor admitted to the evacuated sample. In this procedure, that error is unique on all isotherms for every series of points at given surface concentration. Thus if one isotherm is again in error in one direction, the ensuing procedure guarantees that at the given surface coverage, neighboring isotherms are in error in the same direction, if not to the same extent. Therefore, the isosteric section through the isotherms now yields a value of $\Delta P'$ which nearly equals the error free ΔP. The error in q_{st} is consequently reduced.

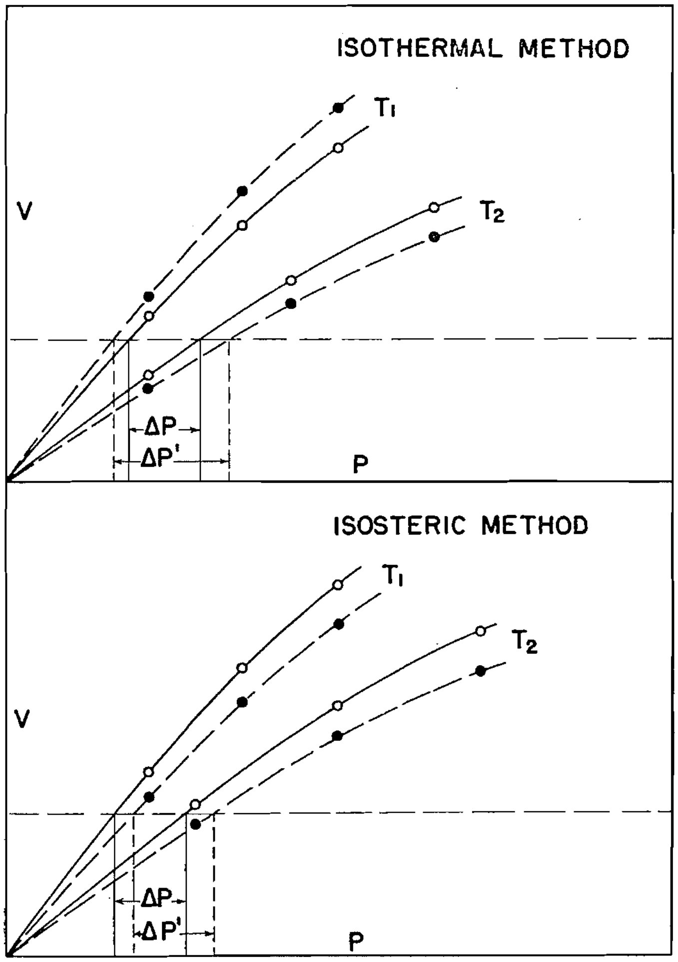

FIG. 8. Types of error inherent in isothermal and isosteric methods of isotherm determinations.

A theoretical calculation illustrates the point quantitatively. The adsorption of a hydrocarbon vapor on rutile was considered at $T_1 = 273°$ K. and $T_2 = 293°$ K. for three low values of surface coverage. Volumes adsorbed and equilibrium pressures were computed on the basis of operations consistent with the isosteric and isothermal methods. The errors were assigned on the basis of uncertainties inherent in pressure readings and volume calibrations. The isotherms were constructed as in Fig. 8 and the isosteric section made at $\theta = 0.1$. The values of q_{st} listed below indicate the magnitude of improvement achieved:

$$q_{st}\text{ ideal} = -3400 \text{ cal. mole}^{-1}$$
$$q_{st}\text{ isosteric} = -3390 \pm 30 \text{ cal. mole}^{-1}$$
$$q_{st}\text{ isothermal} = -3380 \pm 80 \text{ cal. mole}^{-1}$$

Regions of an isotherm determined only after a considerable number of experimental points has been obtained (generally more than five), will deviate little from the ideal form, regardless of the procedure used, because of random cancellations of errors.

The discreet technique has a distinct advantage over the continuous. If a point on an isotherm is in serious error, then this error will affect all subsequent points determined by the continuous method. That section of the isotherm will then tend to be distorted. In the discreet method, each point is independently determined; thus a point in great error would fail to fall upon the smooth curve fitting a series of neighboring points.

ACKNOWLEDGMENTS

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INFRARED STUDY OF THE N—OH GROUP IN ALPHA AND BETA OXIMES[1,2]

By Ann Palm and Harold Werbin[3]

ABSTRACT

The O–H bending and N–O stretching vibrations were studied in four pairs of isomeric oximes. A band at 1265 cm.$^{-1}$, characteristic of the solution spectra of the α oximes, is identified with the O–H bending mode. Tentative assignments for the N–O stretching vibration both in solid and solution spectra are advanced. The β isomers show a distinct shift of the band associated with the N–O mode from about 950 cm.$^{-1}$ in the solid to about 930 cm.$^{-1}$ in solution.

The results of a recent investigation (13) of the infrared spectra of five pairs of isomeric oximes demonstrated that the most pronounced difference between the geometric isomers was the position of the band associated with the O–H stretching vibration which occurred near 3250 cm.$^{-1}$ in the α and near 3115 cm.$^{-1}$ in the β oximes. Although the isomers could not be distinguished from one another on the basis of their frequencies in the 1300 cm.$^{-1}$ and 900 cm.$^{-1}$ regions, tentatively attributed to the O–H deformation and N–O stretching modes, more detailed examination of these absorption bands seemed desirable in order to verify these assignments. This was attempted in the present study by examining the spectra of eight isomeric oximes as Nujol mulls and in benzene and chloroform solutions. The spectra of several N- and O-methyl ethers as well as the sodium salts of some of the oximes were also obtained in order to complement this work.

EXPERIMENTAL

The preparation of the oximes has been described previously (13). The method of Goldschmidt and Kjellin (8) was used in making the β-O-methyl ether of *p*-nitrobenzaldoxime. For the syntheses of the α-O- and -N-methyl ethers of *p*-nitro- and *p*-chlorobenzaldoximes the procedures of Brady *et al.* (3) were adopted. The melting points of the ethers agreed with those reported in the literature, the one exception was the N-methyl ether of α-*p*-nitrobenzaldoxime, m.p. 215–216°C. (lit.: 208°C. (3)). Calc. for $C_8H_8O_3N_2$: N, 15.4%. Found: N, 15.0%. The sodium salts of α-benzaldoxime, α-*p*-nitro-, and α-*p*-chlorobenzaldoximes were prepared in the following manner. Slightly less than one millimole of sodium methoxide in methanol was added to one millimole of the oxime. After standing for one to two minutes, the oxime salt was precipitated with copious amounts of anhydrous ether and filtered. The salt was washed several times with ether to remove unreacted oxime and was dried over phosphorous pentoxide. The infrared spectra demonstrated that the unreacted oximes had been completely removed from the salts. No attempt was made to obtain analytically pure salts since they were used

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solely to aid in establishing the O–H bands. Analytical reagent grade benzene was distilled over sodium before use.

The spectra were recorded with a Perkin-Elmer Model 21 double-beam spectrometer equipped with a rock-salt prism. Sodium chloride cells of 0.10 and 0.20 mm. thickness were employed for the solution studies, while the crystalline compounds were mulled with Nujol. Saturated solutions were prepared of those oximes which had a limited solubility in benzene and chloroform.

RESULTS AND DISCUSSION

The frequencies of the principal absorption bands of the oximes and the ethers between 800–1400 cm.$^{-1}$ are listed in Tables I–III. The salient feature of the solution spectra of the three α benzaldoximes is a band at 1265 cm.$^{-1}$ which is present neither in the solid spectra of these compounds nor in any of the β oximes. This band does not occur in N-benzylidineaniline, in the sodium salts of the α oximes, nor in any of the ethers, but it is found in the benzene spectra of α-*o*-chloro- and α-*m*-nitrobenzaldoximes. These observations suggest its assignment to the in-plane O–H bending mode, hitherto unreported for oximes. A variety of solvents such as benzene, chloroform, carbon tetrachloride, chlorobenzene, and nitrobenzene did not appreciably affect the frequency of the 1265 cm.$^{-1}$ band which is in accord with previous studies of the solvent effect on the O–H stretching vibration in oximes (13).

TABLE I

PRINCIPAL ABSORPTION BANDS OF BENZALDOXIMES AND BENZILMONOXIMES FROM 800–1400 CM.$^{-1}$

Benzaldoxime				Benzilmonoxime			
α		β		α		β	
Liquid	Benzene	Nujol	Benzene	Nujol	Benzene	Nujol	Benzene
	1363(w)	1350(m)	1363(w)		1358(m)		1358(m)
1318(m)	1313(s)		1321(m)	1326(m)	1312(m)		1313(s)
1305(vs)	1303(vs)		1311(s)	1303(s)	1303(m)	1307(w)	1298(s)
1290(s)	1288(s)	1293(w)		1288(w)	1278(w,bd)	1292(w)	1281(m)
	1263(s)						
				1222(w)		1226(s)	1222(s)
1212(s)	1210(s)			1212(s)	1204(s)		1207(w)
1178(m)		1188(m)				1176(m)	
1159(m)	1149(m)		1149(m)				
1104(w)	1102(w)			1105(w)			
1074(s)	1073(m)			1072(w)		1067(w)	
1028(m)	1010(m)	1027(w)		1026(m)		1026(w)	
				1010(s)	1011(s)	1011(w)	1011(s)
		993(w)		1000(m)	992(m)	1001(w)	
958(vs)	965(vs)	963(m)	972(m)	977(m)	975(m)		972(w)
948(vs)	945(vs)	950(s,bd)				951(s)	
			930(s)	932(w)		940(w)	934(m)
915(w)	910(w)	912(w)		927(m)	919(w)	924(w)	916(w)
		895(w)	907(m)			908(m)	900(s)
870(s)				873(vs)		873(w)	
	866(vs)			856(w)	861(s)		861(s)
843(m)	848(m)	847(s)	848(s)	842(w)			

Intensities: weak (w), medium (m), strong (s), very strong (vs), and broad (bd). These symbols have the same significance in all the tables.

TABLE II

PRINCIPAL ABSORPTION BANDS OF *p*-NITROBENZALDOXIMES FROM 800–1350 CM.$^{-1}$

α					β			
Oxime		O-Methyl ether		N-Methyl ether	Oxime		O-Methyl ether	
Nujol	Benzene	Nujol	Benzene	Nujol	Nujol	Benzene*	Nujol	Benzene
1349(s)	1347(s)	1349(m)	1348(vs)	1343(m)	1343(m)	1347(m)	1348(s)	1348(vs)
			1334(m)					
1317(m)	1310(w)	1312(w)	1314(m)	1308(w)	1315(m)	1309(w)	1317(m)	1317(m)
1293(m)			1299(w)		1293(m)		1295(m)	1295(s)
	1265(m)							
1217(m)	1214(w)	1217 (w,bd)	1214(m)					
		1181(w)		1185(w)	1192(m)		1186(w)	
1172(m)	1176(s)	1173(m)	1176(s)		1169(w)	1177(w)	1171(w)	1176(s)
1157(w)		1157(w)		1162 (m,bd)	1157(w)			
1114(w)					1112(w)			
1106(s)	1108(m)	1107(w)	1108(m)	1109(w)	1104(m)		1110(m)	1109(m)
		1057(m)	1051(vs)				1055(s)	1051(vs)
1009(m)	1010(m)	1010(w)	1013(w)		1014(m)			
973(s)		976(m)	972(m)	973 (m,bd)	968(m)	970(m)	968(w)	969(w)
967(vs)	968(m)				955(s)			
942(s)	938(w)	934(s)	932(vs)	947(m)			931(w)	930(w)
909(w)	901(w)				910(s)		916(s)	914(s)
883(m)		890(w)					894(m)	898(m)
		870(w)						
852(s)	850(m)			866(m)	866(m)		856(s)	855(vs)
846(s)		851(m)	850(vs)		854(m)	859 (s,bd)	847(m)	
833(m)	838(m)	831(m)	830(vs)	837(m)	840(s)		831(w)	830(w)
							801(m)	800(s)

**Limited solubility.*

The O–H bending mode has been examined in different types of compounds (1, 10, 14), but not as extensively as the O–H stretching vibration, and has been found between 1020–1420 cm.$^{-1}$ (10, 14). A comparison of the Nujol spectra of α-*p*-chloro- and α-*p*-nitrobenzaldoximes and their corresponding O- and N-methyl ethers and sodium salts indicated that a band near 1300 cm.$^{-1}$ could possibly be ascribed to an O–H bending mode. Evidence favoring such an assignment stems from the work of Voter *et al.* (18). The Nujol spectra of 1,2-cyclohexanedionedioxime and 1,2-cycloheptanedionedioxime presented by these investigators show that deuteration of these compounds caused the disappearance of, among others, an intense band around 1300 cm^{-1}. If the O–H deformation gives rise to a band near 1300 cm.$^{-1}$, then its shift to 1265 cm.$^{-1}$ in the solution spectra is not unexpected since it has been noted in several instances that hydrogen bonding causes a frequency shift opposite to that occurring in the bands due to the O–H stretching mode (4, 15). A constraint imposed upon the bending motion in the solid state could account for such an increase in frequency.

A band at 1350 cm.$^{-1}$ in the Nujol spectrum of β-benzaldoxime seems to be displaced to 1321 cm.$^{-1}$ in the solution spectrum. In β-*p*-chlorobenzaldoxime

TABLE III

Principal absorption bands of *p*-chlorobenzaldoximes from 800–1400 cm.$^{-1}$

α				β	
Oxime		O-Methyl ether	N-Methyl ether	Oxime	
Nujol	Benzene	Liquid	Benzene	Nujol	Benzene
1398(w)	1393(s)	1398(m)			
					1355(w)
		1342(m)		1341(m)	
1317(m)	1311(m)				1323(w)
1300(m)	1298(w)	1295(w)	1304(m)	1303(w)	1309(w)
1281(w)	1278(w)	1273(w)	1281(m)		
	1263(m)				
	1251(w)				1248(m)
1216(m)	1213(m)		1214(w)		
1200(w)		1204(m)			
1172(m)	1177(s)	1179(m)	1172(s)		1177(s)
	1148(m)	1160(w)			1149(m)
1119(w)					
1106(w)	1102(w)		1101(m)	1105(w)	
1089(s)	1090(s)	1084(vs)	1087(s)	1087(s)	1090(m)
	1035(vs)	1047(vs)			
1012(m)	1015(s)	1010(m)	1011(s)	1015(vs)	1011(w)
	992(m)				992(m)
974(vs)				969(m)	972(m)
955(s)	956(s)	960(w)		957(s,bd)	
935(s)	932(w)	947(m)	948(m)		935(m)
896(w)	895(w)	914(s)		898(m)	912(m)
875(s)	867(s)	862(w)		859(m)	
	848(s)	842(s)			849(s,bd)
822(s)	825(s)		831(vs)	827(w)	
		817(s)		817(m)	818(w)

a similar shift from 1341 cm.$^{-1}$ to 1323 cm.$^{-1}$ is observed, while in β-*p*-nitrobenzaldoxime the N=O stretching band at 1343 cm.$^{-1}$ precluded the confirmation of this observation. These bands are tentatively assigned to the in-plane O–H bending mode. The fairly strong bands at 1342 cm.$^{-1}$ and 1334 cm.$^{-1}$ in the spectra of the O-methyl ethers of α-*p*-chloro- and α-*p*-nitrobenzaldoximes respectively, are ascribed to a C–H bending vibration of the methyl group.

There is evidence in the literature for the assignment of the N–O stretching mode to the 900 cm.$^{-1}$ (7, 9, 12) and the 800–850 cm.$^{-1}$ regions (5, 11, 16). The oximes and the N- and O-methyl ethers studied exhibit a strong band near 940 cm.$^{-1}$ and 850 cm^{-1}. The former, which is missing from the spectra of the corresponding aldehydes, is tentatively assigned to the N–O stretching vibration (see Table IV), and the latter is believed to be due to a C–H bending mode. The data in Table IV indicate that the N–O band is not considerably shifted from the solid to the solution spectra of the α oximes while the β isomers show a displacement from about 950 cm.$^{-1}$ in the solid to 930 cm.$^{-1}$ in the solution spectra.

Among the several remaining intense bands observed that are not due to the phenyl or the N–OH groups are those characteristic of the C–O in the methyl ethers, the NO_2 in the nitrobenzaldoximes, and the C–Cl in the

TABLE IV

TENTATIVE ASSIGNMENT OF THE N–O STRETCHING VIBRATION (CM.$^{-1}$)

Benzaldoximes	Nujol		Benzene	
	α	β	α	β
Unsubstituted	948 (vs)	950 (s,bd)	945 (vs)	930 (s)
p-Chloro	935 (s)	957 (s,bd)	932 (w)	935 (m)
p-Nitro	942 (s)	955 (s)	938 (w)	*n.d.*
o-Chloro	935 (m)	*n.i.*	935 (m)	*n.i.*
m-Nitro	942 (m)	*n.i.*	945 (m)	*n.i.*
Benzilmonoxime	927 (m)	951 (s)	——	934 (m)

n.d.—Not detected because of limited solubility.
n.i.—Not investigated.

chlorobenzaldoximes. The C–O band occurring at approximately 1050 cm.$^{-1}$ shows a slight shift in going from solid to solution analogous to the displacement of the N–O absorption in oximes. The NO_2 stretching vibrations absorb at 1525 cm.$^{-1}$ and 1345 cm.$^{-1}$, and a strong band arising possibly from the NO_2 bending vibration is present at about 830 cm.$^{-1}$ (6). The bands associated with the C–Cl modes are found near 1090 cm.$^{-1}$ and 820 cm^{-1}. All the above group frequencies remained rather constant throughout the various spectra investigated.

The spectra of the benzilmonoximes differ from those of the benzaldoximes in the following respects. The α isomer does not have a band in the solution spectrum at 1265 cm.$^{-1}$ characteristic of the α benzaldoximes, but the β isomer shows the displacement of the N–O band from 951 cm.$^{-1}$ in the solid to 934 cm.$^{-1}$ in the solution spectrum, a shift distinctive for the β benzaldoximes. There are data in the literature indicating intramolecular O–H---O bonding in β-benzilmonoxime (17). Since the spectra of β-benzilmonoxime and the β benzaldoximes show a close resemblance in the O–H and N–O regions, i.e. near 3100 cm.$^{-1}$ and 950 cm.$^{-1}$, it is conceivable that the type of association in the β benzaldoximes is via intermolecular O–H---O bridges, whereas the α oximes may possibly form O–H---N hydrogen bonds (2, 7). In β-benzilmonoxime the C=O mode occurs at the same frequency, 1675 cm.$^{-1}$, in both the solid and the solution spectra, offering further evidence for intramolecular hydrogen bonding. This vibration shifts from 1645 cm.$^{-1}$ in the solid to 1670 cm.$^{-1}$ in the solution spectra of the α isomer.

The data presented in this paper evince that the 1265 cm.$^{-1}$ band in the solution spectra of α benzaldoximes and the frequency shift of the N–O stretching mode of the β benzaldoximes may be of value in differentiating unknown geometric oximes. The applicability of these observations will depend upon their confirmation in a greater number of isomers.

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MOLTEN SALTS

COMPLEX ION FORMATION IN THE SYSTEM SILVER CHLORIDE – SILVER NITRATE[1]

BY S. HILL AND F. E. W. WETMORE

ABSTRACT

Conductivity data have been combined with transport fractions to show that silver chloride in dilute solutions in silver nitrate can be regarded as being almost completely in the form of complex cation. The mobility of the complex ion is shown to be about one-half that of silver ion.

It has frequently been suggested that deviations from simplicity in the behavior of binary salt melts should be ascribed to complex ion formation, but the descriptions have been only qualitative. The conductivity of the system silver chloride – silver nitrate (4) shows considerable deviation from simplicity, as shown in Fig. 1 by the separation between the dashed line and the curve for Λ. Schwartz (2) determined the e.m.f.'s of cells of the type $Ag/AgNO_3//AgCl,AgNO_3/Ag$ and found the electrode in the binary melt to be the negative electrode of the cell. Spooner (3) obtained similar results in a more detailed study. The results suggest that chloride is involved in a cationic complex. Spooner pointed out the difficulties encountered in attempting to assess the e.m.f. data quantitatively. Measurements of relative transport fractions have now been made by Hittorf's method. These data have been combined with the conductivity data to yield some quantitative ideas about the complex formation.

The constituents of the binary melt are first assumed to be Cl', NO_3', and Ag^+, with transport fractions θ_1, θ_2, and θ_3, respectively. Passage of z Faradays of charge through silver electrodes immersed in a melt having the initial composition N_1 (equivalent fraction) AgCl and N_2 $AgNO_3$ should lead to anolyte having weight and composition related to the transport fraction by the expression

$$[1] \qquad (n_1 + n_2)(N_1 - N_1')/z = \phi = N_1\theta_2 - N_2\theta_1,$$

in which n_1 and n_2 are the equivalents of AgCl and $AgNO_3$ in the anolyte and N_1' its composition after electrolysis. Reference (1) gives details for a melt with common anion.

The experimental procedure for determining ϕ was essentially the same as used earlier (1), save for the form of the furnace. Tests showed that a considerable concentration gradient could be caused in this system by a thermal gradient (Ludwig-Soret effect). The cell was therefore encased in close-fitting copper blocks. Determinations were made at 270°C. with $N_1 = 0.118$, 0.232, and 0.437. The reproducibility was very poor for the most concentrated melt. For the other melts, $\phi = 0.05 \pm 0.01$ at $N_1 = 0.12$, $\phi = 0.088 \pm 0.02$ at $N_1 = 0.23$. Despite the lack of precision of these results, they are informative.

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Contribution from the Electrochemical Laboratory, Department of Chemistry, University of Toronto, Toronto 5, Ontario.

From equation [1], $\theta_1 = (N_1\theta_2 - \phi)/N_2$. It has been shown that θ_2 is very small in $AgNO_3$ (1) and therefore $N_1\theta_2$ must be negligibly small for the dilute solutions used here. Hence $\theta_1 = -0.057 \pm 0.01$ at $N_1 = 0.12$, $\theta_1 = -0.115 \pm 0.03$ at $N_1 = 0.23$. It is evident that chloride migrates toward the cathode. Assumption of a cation containing chloride is necessary to avoid a negative transport fraction; let the choice be the simplest possible, Ag_2Cl^+.

The constituents will then be assumed to be Ag^+, Ag_2Cl^+, NO_3', and either AgCl or Cl′. The choice of the last constituent depends on the model chosen for the association:

$$\text{(A)}\quad AgCl + Ag^+ = Ag_2Cl^+ \qquad \text{or (B)}\quad Cl' + 2Ag^+ = Ag_2Cl^+.$$

The two choices lead to different quantitative expressions, but both lead to the same result ultimately, as it happens. The first will be used to exemplify the treatment. Let β be the fraction of the silver chloride associated to form complex ion and let θ_4 denote the transport fraction of the complex ion. It can be shown that $\phi = N_1\theta_2 + N_2\theta_4$, i.e. that $\theta_4 = -\theta_1$. Let U_3 and U_4 denote the mobilities (cm.^{2}sec.$^{-1}$v.$^{-1}$) of the constituents Ag^+ and Ag_2Cl^+, respectively, multiplied by the Faraday constant 96500. Additivity of the conductivities leads to

$$[2]\qquad \Lambda = (N_2 - \beta N_1)U_3 + \beta N_1 U_4.$$

Also, $\beta N_1 U_4 = \theta_4\Lambda$. Combination of this with equation [2] yields

$$[3]\qquad (N_2U_3 - \Lambda)/N_1 = \beta U_3 - \theta_4\Lambda/N_1.$$

Without knowledge of the variation of U_3 with N_1, equation [3] cannot be used to determine β at various concentrations. However, a limiting value at $N_1 = 0$ can be obtained by finding the limiting values of the first and third members. For this purpose U_3 is assumed to vary with N_1 in the same way that the melt would in the absence of interaction of the components (the dashed line of Fig. 1). This assumption may be incorrect for high values of N_1, but should be appropriate for dilute solutions. The first member has the limiting value 19 (see Fig. 1). The third member has the value 19 ± 3 at $N_1 = 0.12$, 19 ± 5 at $N_1 = 0.23$; the limiting value is taken as 19 ± 6. The limiting value of β is then $(19 + 19 \pm 6)/40 = 0.95 \pm 0.15$. From equation [3], the limiting value of U_4 is $40 - 19/(0.95 \pm 0.15) = 20 \pm 3$.

Acceptance of model B and the assumption that unassociated Cl′ contributes negligibly to the conductivity will lead to

$$\Lambda = (1 - 2\beta N_1)U_3 + \beta N_1 U_4$$

and $(U_3 - \Lambda)/N_1 = 2\beta U_3 - \theta_4\Lambda/N_1$. The limiting value of the first member is 60 (see Fig. 1). The limiting value of β is $(60 + 19 \pm 6)/80 = 0.99 \pm 0.08$; the limiting value of U_4 is $80 - 60/(0.99 \pm 0.08) = 20 \pm 5$.

Both models A and B meet the requirements that β lie between 0 and 1 and that U_4 be substantially less than U_3. Model A is more appealing as a mechanism; it is also consistent with the concept of conduction of the silver ion by repeated rotation of the complex and transfer of a silver ion to an adjacent silver chloride ion-pair on the cathode side.

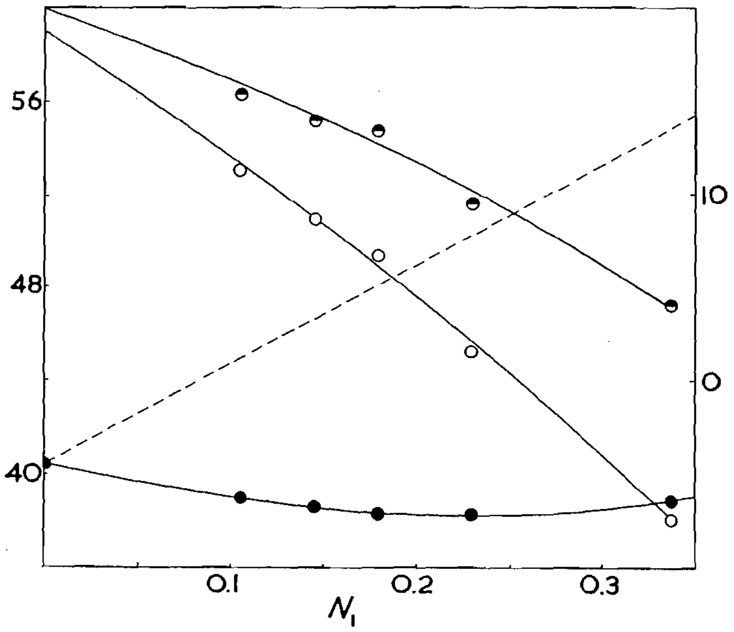

FIG. 1. Conducting properties of the system AgCl–$AgNO_3$ at 270°.
○ $(N_2U_3 - \Lambda)/N_1$ (right scale) (Model A)
◓ $(U_3 - \Lambda)/N_1$ (left scale) (Model B)
● Λ (left scale)
– – – U_3 (Λ for undercooled AgCl at $N_1 = 1$) (left scale).

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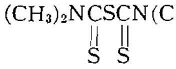
THE STRUCTURE OF THE THIURAM OXIDES[1]

BY ROBERT W. WHITE[2]

ABSTRACT

The compounds identified by previous investigators as thiocarbamyl oxides (commonly known as "thiuram oxides") are shown to be, instead, the isomeric thiocarbamyl carbamyl sulphides.

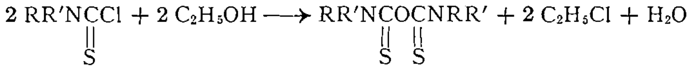
In connection with an investigation of the infrared spectra of certain of the dithiocarbamate fungicides, it became necessary to prepare analogues of the well-known tetramethylthiuram monosulphide (I) in which oxygen replaced sulphur at any or all positions. Of the five possible analogues, the only one referred to in the literature is bis(dimethylthiocarbamyl)oxide, the so-called "tetramethylthiuram oxide", in which the central atom of I has been replaced by an oxygen atom.



$$(CH_3)_2N\underset{\underset{S}{\|}}{C}S\underset{\underset{S}{\|}}{C}N(CH_3)_2$$

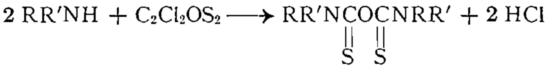
I

In 1887, Billeter (1) prepared two members of a new series of compounds which he designated as "thiuram oxides". His synthesis was a simple one, making use of the action of absolute ethanol on an N,N-disubstituted thiocarbamyl chloride. He explained the formation and structure of these new compounds by equation [*A*].



$$2\,RR'N\underset{\underset{S}{\|}}{C}Cl + 2\,C_2H_5OH \longrightarrow RR'N\underset{\underset{S}{\|}}{C}O\underset{\underset{S}{\|}}{C}NRR' + 2\,C_2H_5Cl + H_2O \qquad [A]$$

More recently, Delépine and co-workers (2) produced a series of compounds by the reaction of a group of secondary amines with carbon sulphoxy chloride[3], a derivative of dimeric thiophosgene. Two members of this series proved to be identical with Billeter's compounds, and Delépine explained their formation by equation [*B*].



$$2\,RR'NH + C_2Cl_2OS_2 \longrightarrow RR'N\underset{\underset{S}{\|}}{C}O\underset{\underset{S}{\|}}{C}NRR' + 2\,HCl \qquad [B]$$

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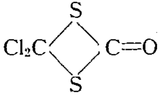
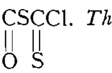
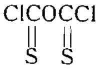
[1] *Manuscript received June 2, 1954.*
Contribution No. 34, Science Service Laboratory, Canada Department of Agriculture, University Post Office, London, Ontario. Presented before the 37th Annual Meeting of the Chemical Institute of Canada, Toronto, June 21–23, 1954.

[2] *Assistant Chemist.*

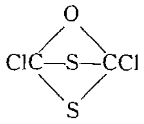
[3] *The name "carbon sulphoxy chloride" has been used throughout this paper to avoid any structural implications, since this investigation casts some doubt on such previously advanced formulas as II, IIA, or*  *(5). The results of this work give some credence to the formula suggested by the work of Rathke (4), i.e.,*  $Cl\underset{\underset{O}{\|}}{C}S\underset{\underset{S}{\|}}{C}Cl$. *The results of a more complete investigation will be reported in due time.*

From this, Delépine was able to deduce to his satisfaction the structure of carbon sulphoxy chloride to be either II or IIA.



$$\mathrm{Cl\underset{\underset{S}{\|}}{C}O\underset{\underset{S}{\|}}{C}Cl}$$

or

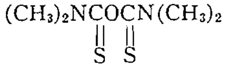


II

IIA

Apart from a brief reference by Klöpping and van der Kerk (3) who did not question the validity of Billeter's and Delépine's identification, no further work on this series appears to have been reported.

In the present work, both methods of synthesis were followed, the expected product in both cases being bis(dimethylthiocarbamyl)oxide, (III).



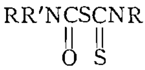
$$\mathrm{(CH_3)_2N\underset{\underset{S}{\|}}{C}O\underset{\underset{S}{\|}}{C}N(CH_3)_2}$$

III

A. *Billeter's Method*

The product of the action of absolute ethanol on dimethylthiocarbamyl chloride, obtained in yields of up to 50%, contained no oxygen and proved to be identical in every respect with an authentic sample of (I). No alteration of reaction conditions was effective in producing the desired compound. No simple mechanism has been found to explain this wholly unexpected reaction. However, it was felt that the behavior of dimethylthiocarbamyl chloride, the lowest disubstituted member, could not be assumed to be characteristic of the whole series or to be an indication of the inaccuracy of Billeter's report, since his starting materials were both of the mixed aliphatic–aromatic type and possibly quite different from the dimethyl derivative in behavior. The next step, then, was to check Billeter's work by the preparation of one of the two compounds actually synthesized by him.

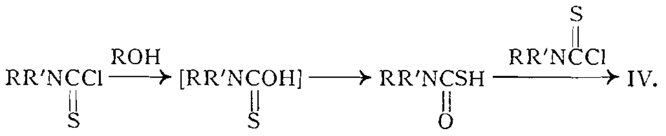
To this end, methylphenylthiocarbamyl chloride was prepared from N-methylaniline and thiophosgene and then treated with absolute ethanol. The product of this reaction was identical with Billeter's methylphenylthiuram oxide in so far as the melting point checked and the elemental analysis was similar and indicated the presence of an atom of oxygen. The infrared spectrum of this compound, however, showed strong absorption at 1670 cm^{-1}. The strength and position of this absorption indicated the presence of a carbonyl group. This, in turn, pointed not to the "thiuram oxide" structure, but to the thiocarbamyl carbamyl sulphide structure, IV.



$$\mathrm{RR'N\underset{\underset{O}{\|}}{C}S\underset{\underset{S}{\|}}{C}NRR'}$$

IV

This being the case, it is evident that the reaction must involve the electronic shift $\underset{\underset{S}{\|}}{\mathrm{C}}\text{—O}$ to $\underset{\underset{O}{\|}}{\mathrm{C}}\text{—S}$, possibly as in equation [*C*].

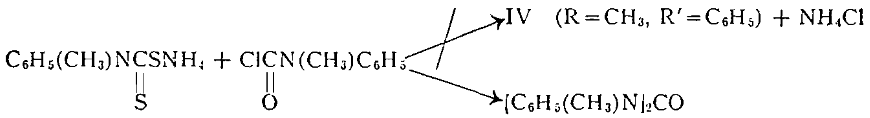


$$RR'N\underset{\underset{S}{\|}}{C}Cl \xrightarrow{ROH} [RR'N\underset{\underset{S}{\|}}{C}OH] \longrightarrow RR'N\underset{\underset{O}{\|}}{C}SH \xrightarrow{RR'N\overset{\overset{S}{\|}}{C}Cl} IV. \qquad [C]$$

B. *Delépine's Reaction*

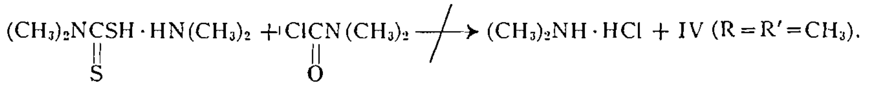
The reaction of dimethylamine with carbon sulphoxy chloride resulted in the formation of a compound identical with that produced by Delépine in his original work. Elemental analysis indicated the presence of one atom of oxygen and supported the empirical formula advanced by Delépine. However, as in the case of the previous compound, the infrared spectrum of this derivative showed a strong band at 1670 cm.$^{-1}$, again pointing to structure IV.

An unequivocal proof of structure by direct synthesis was next sought. Delépine, in his original work, in an attempt to prove that his compounds did *not* have structure IV, tried unsuccessfully to form IV ($R=CH_3$, $R'=C_6H_5$) through the reaction of ammonium methylphenyldithiocarbamate with methylphenylcarbamyl chloride as in equation [*D*]. The only product that he was able to isolate was identified as 1,3-dimethyl-1,3-diphenylurea.



$$C_6H_5(CH_3)N\underset{\underset{S}{\|}}{C}SNH_4 + Cl\underset{\underset{O}{\|}}{C}N(CH_3)C_6H_5 \begin{array}{l} \not\nearrow IV \quad (R=CH_3,\ R'=C_6H_5) + NH_4Cl \\ \searrow [C_6H_5(CH_3)N]_2CO \end{array} \qquad [D]$$

A similar attempt by Delépine to obtain IV ($R=R'=CH_3$), as in equation [*E*], yielded no identifiable product.



$$(CH_3)_2N\underset{\underset{S}{\|}}{C}SH\cdot HN(CH_3)_2 + Cl\underset{\underset{O}{\|}}{C}N(CH_3)_2 \not\longrightarrow (CH_3)_2NH\cdot HCl + IV\ (R=R'=CH_3). \qquad [E]$$

Subsequent to Delépine's work, however, the use of the sodium salt in place of the ammonium or dimethylammonium salts of equations [*D*] and [*E*] was described in the patent literature (6). This modification, when adapted to the present requirements, afforded the desired compound in good yield.

Comparison of this substance with the "thiuram oxide" produced by Delépine's reaction from carbon sulphoxy chloride and dimethylamine showed them to be identical with respect to infrared spectrum, melting point, and elemental analysis. A mixture of the two showed no depression of melting point.

The identity of these two compounds confirms the spectroscopic evidence that the "thiuram oxides" do indeed contain a carbonyl group. The conclusion, therefore, is that the compounds of Billeter and of Delépine here re-examined are, in fact, thiocarbamyl carbamyl sulphides and not, as previously believed, bis(N,N-disubstituted thiocarbamyl) oxides. There is also every reason to assume that the same conclusion is valid for those members not individually examined in this work.

EXPERIMENTAL[4]

Carbon Sulphoxy Chloride

This intermediate was prepared by the method of Schönberg and Stephenson (5).

Attempted Preparation of bis(Dimethylthiocarbamyl) oxide (III)

Dimethylthiocarbamyl chloride was warmed on a steam-bath for 30 min. with double its weight of absolute ethanol. The solution was then diluted with five times the volume of water and the resultant mixture extracted with ether. The ether solution was dried with anhydrous sodium sulphate and the solvent removed by evaporation. There was left a bright yellow powder which, when recrystallized several times from absolute ethanol, melted at 108.5–109°C. A mixture of this with authentic tetramethylthiuram monosulphide (I) showed no depression of melting point. The infrared spectra of the two were identical. Calc. for $C_6H_{12}N_2S_3$: S, 46.15%. Found: S, 46.1%.

Variation of reaction time and temperature, substitution of water for absolute ethanol, the use of a solvent other than the excess ethanol, and the introduction of sodium carbonate to take up hydrogen chloride, if and when formed, did not change the product. Yields varied between 30–50% in all experiments.

Methylphenylthiocarbamyl Methylphenylcarbamyl Sulphide (IV, $R = CH_3$, $R' = C_6H_5$)

To thiophosgene (1.15 gm., 0.01 mole) in chloroform (20 ml.) was added, slowly with frequent shaking, N-methylaniline (1.07 gm., 0.01 mole) in chloroform (20 ml.). The mixture was shaken frequently over a period of two hours at room temperature and then absolute ethanol (10 ml.) was added. The mixture was warmed on a steam-bath for 30 min. The cooled solution was then extracted with water to remove any amine hydrochloride and dried with anhydrous sodium sulphate. The dried, filtered solution was then evaporated to a small volume. Upon the introduction of 100 ml. of petroleum ether, crystallization took place. The yellow precipitate was filtered off, washed with petroleum ether, and recrystallized several times from absolute ethanol. Yield: 0.8 gm. (52%, assuming no amine hydrochloride formed). M.p.: 117.0°C. (lit.: 116.5° C. (1)). Calc. for $C_{16}H_{16}N_2OS_2$: S, 20.25%. Found: S, 20.2%.

The infrared spectrum of this compound showed a strong band at 1670 cm^{-1}.

Dimethylthiocarbamyl Dimethylcarbamyl Sulphide (IV, $R = R' = CH_3$)

(*a*) A solution of carbon sulphoxy chloride (1.75 gm., 0.01 mole) in benzene (40 ml.) was added to a solution of dimethylamine (about 1.8 gm., 0.04 mole) in benzene (40 ml.). The mixture was shaken at room temperature for 30 min. and then warmed on the steam-bath for a like period. The benzene solution was then washed with dilute hydrochloric acid and with water and then dried over anhydrous sodium sulphate. Most of the benzene was then evaporated off and 100 ml. of petroleum ether was added to induce crystallization. The pre-

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[4] *All melting points are uncorrected and were obtained on the Fisher-Johns block. Infrared spectra were determined with a Perkin-Elmer Model 21 equipped with sodium chloride prism.*

cipitate was recrystallized several times from absolute ethanol. Yield: 1.1 gm. (58%). M.p.: 76.5–77°C. (lit.: 79° C.(2)). Calc. for $C_6H_{12}N_2OS_2$: N, 14.6%; S, 33.3%. Found: N, 14.65%; S, 33.6%.

(*b*) Sodium dimethyldithiocarbamate (1.4 gm., 0.01 mole) was dissolved in the minimum amount of water (about 5 ml.) and to this was added dimethylcarbamyl chloride (1.08 gm., 0.01 mole). The mixture was heated on the steam-bath for 45 min. The yellow-brown oil that formed in the cooled mixture was taken up in ether. The ether solution, after being dried with sodium sulphate, was evaporated to a small volume. Addition of 100 ml. petroleum ether yielded a bright yellow precipitate. Recrystallization from absolute ethanol gave a yellow powder. M.p.: 76.5–77°C. Yield: 1.3 gm. (68%).

A mixture of the compounds from (*a*) and (*b*) gave m.p. 76.5–77°C. Their infrared spectra were identical and showed a strong peak at 1670 cm^{-1}.

ACKNOWLEDGMENTS

The author is indebted to Dr. G. D. Thorn for his advice and criticism, and to Mrs. K. Bongart for the microanalyses. Samples of dimethylcarbamyl chloride and of dimethylthiocarbamyl chloride were generously supplied by Monsanto Chemicals Company and Sharples Chemical Inc., respectively.

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THE AERATION PRODUCTS OF DISODIUM ETHYLENEBISDITHIOCARBAMATE[1]

By G. D. Thorn[2] and R. A. Ludwig[3]

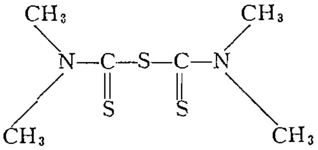
ABSTRACT

The aeration of dilute solutions of disodium ethylenebisdithiocarbamate yields hexahydro-1,3,6-thiadiazepine-2,7-dithione (I), polymeric I, 2-imidazolidinethione, and elemental sulphur. I with ammonia gives mainly hexahydro-1,3,5-triazepine-2,4-dithione. I and polymeric I have high antifungal activity.

The anomalous protective fungicidal action of the highly water-soluble disodium ethylenebisdithiocarbamate (nabam) has been investigated in this laboratory. It has been shown (9, 10) that the aeration of dilute solutions of nabam results in the formation of a yellow insoluble fungicidal material consisting mainly of a polymer, $(C_4H_6N_2S_3)_n$, together with up to 20% of the corresponding monomer and varying amounts of elemental sulphur. The filtrate of the reaction mixture yields further amounts of the monomer and nonfungicidal 2-imidazolidinethione (ethylenethiourea). The latter had been identified previously by Barratt and Horsfall (1) as a breakdown product of nabam.

The compound $C_4H_6N_2S_3$(I) gives a positive sodium azide – iodine test (4) for thioketones and mercaptans. Reaction of I with Grote's reagent (5) gives a red-brown color. According to Grote, a red coloration indicates the presence of thiol, while a green or blue color is obtained with thioketones.

The ultraviolet absorption spectra of I and tetramethylthiuram monosulphide (II) are distinctly similar. For compound I, the peaks are at 280 mμ, E_m = 19600, and at 227.5 mμ, E_m = 8800; for tetramethylthiuram monosulphide maximum absorption is at 280 mμ, E_m = 16300, and at 210 mμ, E_m = 17000.



II

Reaction of I either with concentrated aqueous ammonia at room temperature or with liquid ammonia yields a compound $C_4H_7N_3S_2$, for which the structures III*A* and III*B* can be written. The reaction in aqueous ammonia

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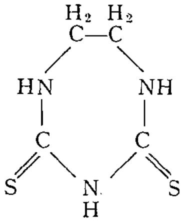
[2] *Senior Chemist.*

[3] *Principal Plant Pathologist.*



III*A*

$$SCN{-}CH_2CH_2{-}NHCSNH_2$$

III*B*

$$H_2NCSNH{-}CH_2CH_2{-}NHCSNH_2$$

IV

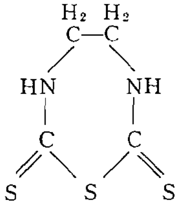
yields also a compound $C_4H_{12}ON_4S_2$, probably the monohydrate of the open-chain diamide, ethylenebisthiourea (IV). The attempted preparation of IV through reaction of excess concentrated aqueous ammonia with ethylenebisisothiocyanate gave, surprisingly, the compound III in good yield. Petersen (13) has shown that the reaction of excess hexamethylenebisisocyanate with ammonia yields 6-ureido-hexylisocyanate (V), which with excess ammonia is converted to the expected diurea. Structure III*B* for the compound

$$OCN{-}(CH_2)_6{-}NHCONH_2$$

V

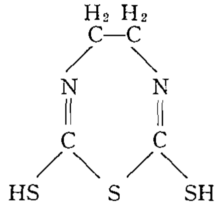
$C_4H_7N_3S_2$ is however ruled out, as the infrared spectrum of the compound shows no absorption in the 2100 cm.$^{-1}$ region attributable to the isothiocyanate grouping. Further, the spectrum in the "finger-print" region shows a very close similarity to that of ethyl dithiobiuret.[4] The compound $C_4H_7N_3S_2$ must be therefore ethylenedithiobiuret (hexahydro-1,3,5-triazepine-2,4-dithione[5]) (III*A*).

From the foregoing, especially the reaction of I with ammonia and the independent synthesis of ethylenedithiobiuret, it can be concluded that the compound $C_4H_6N_2S_3$(I) is ethylenethiuram monosulphide (hexahydro-1,3,6-thiadiazepine-2,7-dithione[5]):



I*A*

or



I*B*

The structure may be that of the thioamide, I*A*, or of the enethiol, I*B*. Our interpretation of the infrared spectrum favors the latter structure. The strong band at 1610 cm.$^{-1}$ is taken as indicative of C=N (3); the bands attributable to the thioamide group (3, 14) are absent, and there is no evidence of N—H stretching in the 3200 cm.$^{-1}$ region.

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[4] *Sample kindly supplied by Dr. G. Woolfe, Boots Pure Drug Co. Ltd., West Bridgford, Notts., England.*

[5] *Named in accordance with Patterson and Capell (12).*

Ethylenethiuram monosulphide forms a hydrochloride, m.p. 210–211°C., a picrate, m.p. 171–172°C., a perchlorate, m.p. 182–183°C., and an acetyl derivative, m.p. 151–152°C.

The insoluble yellow polymeric ethylenethiuram monosulphide is obtained simply by removal of the more soluble components of the precipitate from the aeration of nabam by washing with water, drying the residue, and washing with cold chloroform. The material appears to be quite insoluble in all organic solvents tested. Its infrared spectrum shows the same bands of the monomer, some with slight shift in wave length. Digestion of the polymer with hot chloroform or acetone gives rise to a change in the elemental analysis (increased carbon and hydrogen values) of the residue together with the disappearance of the 1610 cm.$^{-1}$ band of the spectrum and the appearance of bands at 1475 cm.$^{-1}$ and at 3210 cm.$^{-1}$ (N—H), and also at 1705 cm.$^{-1}$ (C=O), when acetone is used as the digestion solvent. The nature of the materials formed was not investigated further.

The polymer can be obtained also in a crystalline form by allowing a 1000 p.p.m. solution of nabam to evaporate slowly (room temperature) in a shallow tray to about one half its volume, filtering, and washing as above. The material has a decomposition point of 145–147°C.

It was hoped that a convenient method of analysis of micro amounts of ethylenethiuram monosulphide and its polymer might be based on carbon disulphide evolution through acid hydrolysis (2). However, only roughly 10% of the theoretical amount of carbon disulphide was obtained on digestion with 1 *N* sulphuric acid for one hour. Lower recoveries resulted with stronger acid. The use of sodium bisulphite (6) was of no avail.

The synthesis of ethylenethiuram monosulphide was attempted using several methods. The reaction of ethylenethiourea with carbon disulphide at elevated temperatures and pressures (up to 20 atm.) yielded at best a small amount of odiferous brown material. More promising are the reaction of ethylenebisisothiocyanate with hydrogen sulphide, of sodium β-aminoethyldithiocarbamate with thiophosgene, and of thiophosgene, sodium sulphide, and ethylenediamine. This work is as yet incomplete, but low yields have been obtained of yellow material possessing the required sulphur and nitrogen content, and showing a good measure of toxicity towards *Sclerotinia fructicola*.

The oxidation of nabam with the usual mild oxidizing agents—hydrogen peroxide, persulphate, iodine—resulted in the formation of the polyethylenethiuram disulphide (8).

EXPERIMENTAL[6]

Aeration of Nabam Solutions

The course of breakdown of nabam is affected markedly by solution concentration. It was found that 1000 p.p.m. nabam is optimal for the preparation of the fungicidal yellow precipitate without external control of pH. Accordingly, 150 liters of 0.1% nabam was aerated vigorously in a wooden cask.

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[6] *All melting points are uncorrected and were obtained on the Fisher-Johns block. E.D. 50 values were obtained by the spore drop technique using* Sclerotinia fructicola *as the test organism.*

The pH, initially about 8.5, dropped rapidly to about 7.0, and slowly rose to between 8 and 9. The solution first turned orange in color, then became milky, and finally the yellow material separated out. The "reaction time" varied, but was usually three to four days. The solid was separated by basket centrifugation. The air-dried yield was 30 to 65 gm. The material obtained in this way analyzed 62% S (av.) and has been given the code G.D. 26 (10). It gave an E.D. 50 of 12–15 p.p.m.[7]

Polyethylenethiuram Monosulphide

The yellow material above was washed with water, dried, then allowed to stand with successive amounts of chloroform to remove the more soluble sulphur and ethylenethiuram monosulphide, to leave 70 to 80% by weight as insoluble material, m.p. 145–147°C. (decomp.). Found: C, 27.6; H, 3.27; N, 16.0; S, 54.6%. Calc. for $(C_4H_6N_2S_3)_n$: C, 27.0; H, 3.37; N, 15.7; S, 53.9%. The E.D. 50 value was 8–10 p.p.m.

Fractional crystallization of the chloroform soluble portion yielded elemental sulphur (up to 15% of total) and ethylenethiuram monosulphide.

Ethylenethiuram Monosulphide (*I*)

The filtrate from G.D. 26 was extracted by vigorous stirring with about 3 liters of chloroform. The lower layer was siphoned off, dried with anhydrous sodium sulphate, and the solvent removed *in vacuo* to leave a yellow residue, 6 to 15 gm., anal. 48 to 51% S. Repeated crystallization from chloroform–ethanol, and chloroform alone, yielded ethylenethiuram monosulphide, m.p. 125–6°C. Found: C, 27.3; H, 2.97; N, 15.9; S, 54.2%; mol. wt., 176 (isopiestic (11)). Calc. for $C_4H_6N_2S_3$: C, 27.0; H, 3.37; N, 15.7; S, 53.9%; mol. wt., 178. The E.D. 50 value was 1.5 p.p.m.

Concentration of the extracted aqueous portion to small volume and extraction with ether gave ethylenethiourea, 7 gm. (after removal of a small amount of ethylenethiuram monosulphide with chloroform and crystallization from ethanol), m.p. 197–198°C., not depressed on admixture with authentic ethylenethiourea. Calc. for $C_3H_6N_2S$: S, 31.4%. Found: S, 31.5%.

Ethylenedithiobiuret (*Hexahydro-1,3,5-triazepine-2,4-dithione*) (III*A*)

A. Ethylenethiuram monosulphide, 0.94 gm., was covered with about 5 ml. liquid ammonia and the mixture allowed to stand for 24 hr. Evaporation of the ammonia from the resulting solution left a pale yellow residue, which after crystallization from ethanol gave white material, m.p. 190–192°C. The compound can be sublimed at 140°C. under 0.001 mm. without apparent decomposition, but without sharpening of the melting point. Found: C, 29.9; H, 4.60; N, 26.1; S, 39.7%. Calc. for $C_4H_7N_3S_2$: C, 29.8; H, 4.35; N, 26.1; S, 39.8%. The material gave an E.D. 50 value of 75–80 p.p.m.

B. The reaction of ethylenethiuram monosulphide with aqueous concentrated ammonia at room temperature gave mainly the cyclic imide, ethylenedithiobiuret, with some open-chain amide, ethylenebisthiourea. The total yield was about 90%.

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[7] *E.D. 50—effective dosage required for 50% inhibition of spore germination.*

On one occasion, the amide was the main reaction product. A constant melting point of 195–196°C. (decomp.) was obtained after two crystallizations from 95% ethanol. Found: C, 24.7; H, 6.25; N, 28.4; S, 32.6%. Calc. for $C_4H_{10}N_4S_2 \cdot H_2O$: C, 24.5; H, 6.13; N, 28.6; S. 32.7%. E.D. 50 value was above 100 p.p.m., the highest concentration tested.

C. The reaction of the polyethylenethiuram monosulphide with concentrated aqueous ammonia at room temperature also gave ethylenedithiobiuret in the same order of yield as in *B*; high analytical figures for N and low for S in the crude reaction product indicated, here also, the formation of some amide.

D. Ethylenebisisothiocyanate (8), 0.2 gm., was covered with 4 ml. conc. ammonium hydroxide and rubbed against the side of the flask with a glass rod. The white crystalline material formed was removed by filtration, washed with water, and crystallized from ethanol, giving 0.15 gm., m.p. 190–192°C., not depressed on admixture with material from *A*. Found: C, 30.2; H, 4.69; N, 26.1; S, 39.7%. Calc. for $C_4H_7N_3S_2$: C, 29.8; H, 4.35; N, 26.1; S, 39.8%.

Interaction of I with Hydrogen Chloride

A mixture of 0.95 ml. conc. hydrochloric acid and 0.10 gm. ethylenethiuram monosulphide in 25 ml. chloroform was shaken for five minutes. The solid was removed by filtration, washed with chloroform, and dried over sodium hydroxide *in vacuo*. The yield was 0.12 gm. of pale yellow material melting at 210–211°C. after crystallization from ethanol. The E.D. value was found to be 1–1.5 p.p.m. Found: C, 22.2; H, 3.01; N, 13.3; S, 44.6; Cl, 16.7%. Calc. for $C_4H_6N_2S_3 \cdot HCl$: C, 22.4; H, 3.26; N, 13.1; S, 44.7; Cl, 16.6%.

Addition of an equivalent of sodium hydroxide to a chloroform suspension of the compound gave back the ethylenethiuram monosulphide. The use of a greater excess of hydrochloric acid did not give a dihydrochloride.

Interaction of I with Acetic Anhydride

Ethylenethiuram monosulphide, 0.20 gm., was suspended in 8 ml. acetic anhydride and the mixture allowed to stand at room temperature for two hours. The resulting solution was poured over a small quantity of crushed ice. The orange precipitate was removed, washed well with water, and dried; yield, 0.16 gm. It melted at 151–152°C. (decomp.) after crystallization from chloroform. Found: C, 33.1; H, 3.23; N, 12.7; S, 43.2%. Calc. for the monoacetyl derivative, $C_6H_8ON_2S_3$: C, 32.7; H, 3.63; N, 12.7; S, 43.6%. The E.D. 50 value was above 100 p.p.m., the highest concentration tested.

The use of elevated temperatures for the reaction resulted in much decomposition with the formation of a tarry material.

I and Perchloric Acid

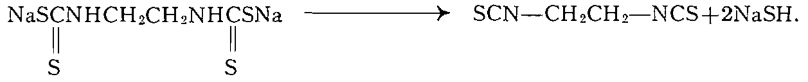
The addition of excess concentrated perchloric acid to a chloroform solution of ethylenethiuram monosulphide gave yellow material, which, when washed well with chloroform and ether, melted at 182–183°C. (decomp.). The yield was quantitative. Found: N, 10.1; S, 33.7; Cl, 12.8%. Calc. for $C_4H_6N_2S_3 \cdot HClO_4$: N, 10.1; S, 34.5; Cl, 12.8%.

I with Picric Acid

The addition of excess picric acid in ethanol to ethylenethiuram monosulphide in minimum chloroform solution gave on standing yellow crystals, m.p. 171–172°C. out of ethanol. Found: S, 24.2%. Calc. for $C_4H_6N_2S_3 \cdot C_6H_3O_7N_3$: S, 23.8%.

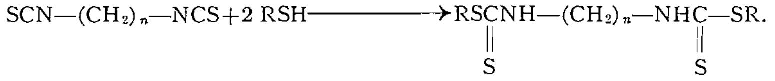
DISCUSSION

The formation of the yellow material, G.D. 26, would appear to explain the prolonged fungicidal activity when nabam is sprayed in the field. It does not however give any insight into the actual mode of fungicidal action. On the basis of fungistatic tests involving different mold species, Klöpping and van der Kerk (7, 8) concluded that "the antifungal activity of the bisdithiocarbamates is due to their transformation into the corresponding diisothiocyanates":



$$NaS\underset{\underset{S}{\|}}{C}NHCH_2CH_2NH\underset{\underset{S}{\|}}{C}SNa \longrightarrow SCN{-}CH_2CH_2{-}NCS + 2NaSH.$$

Sijpesteyn and van der Kerk (15) have shown that nabam and tetramethylenebisisothiocyanate are rendered inactive by the addition of thiols to the culture medium. They believe this to be brought about by the formation of (stable) dithiocarbamate esters:

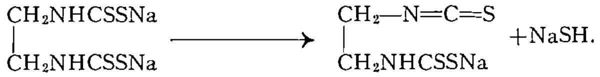


$$SCN{-}(CH_2)_n{-}NCS + 2\,RSH \longrightarrow RS\underset{\underset{S}{\|}}{C}NH{-}(CH_2)_n{-}NH\underset{\underset{S}{\|}}{C}{-}SR.$$

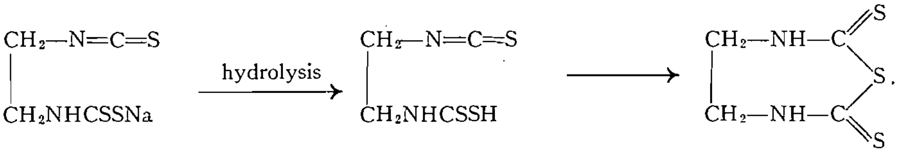
These authors have shown also that there is a marked decrease in toxicity for the reaction products of thioglycollic acid with the ethylene- and tetramethylenebisisothiocyanates. They suggest therefore that the antifungal action of the bisdithiocarbamates and the bisisothiocyanates is through reaction of these compounds with essential —SH compounds in the cells.

The present authors have found dimethyl ethylenebisdithiocarbamate to possess an E.D. 50 value of 200 p.p.m. In contrast to this, nabam shows an apparent E.D. 50 value of 2–5 p.p.m., and ethylenebisisothiocyanate an E.D. 50 value well below 1 p.p.m. This can be taken as evidence in support of the Dutch workers' theory.

Sijpesteyn and van der Kerk (15) consider that the formation of ethylenethiuram monosulphide serves as a direct indication for the transitory appearance of isothiocyanate groups. They offer the following equations:



$$\begin{array}{l} CH_2NHCSSNa \\ | \\ CH_2NHCSSNa \end{array} \longrightarrow \begin{array}{l} CH_2{-}N{=}C{=}S \\ | \\ CH_2NHCSSNa \end{array} + NaSH. \qquad [1]$$

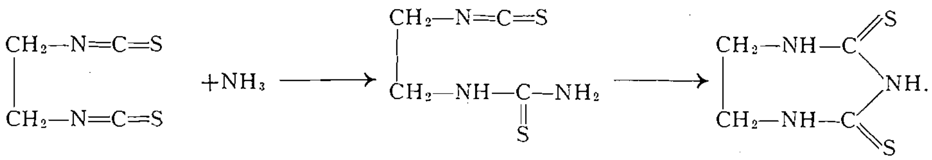


. [2]

VI

IA

The formation of ethylenedithiobiuret (III*A*) from ethylenebisisothiocyanate and ammonia very likely proceeds by analogy with the equations above, and so lends support to the proposal of Sijpesteyn and van der Kerk:[8]



Moreover, the fungicidal action of ethylenethiuram monosulphide is antagonized by thiol compounds (15) in the same way as was demonstrated for nabam and tetramethylenebisisothiocyanate. Sijpesteyn and van der Kerk state that this fact points to a common biochemical mode of action. They consider a reversal of the ring closure presented in equation [2] above (presumably induced by RSH) to form the isothiocyanate group (VI) requisite to their theory. Similarly, ethylenedithiobiuret should undergo the same ring fission and display the same order of fungitoxicity as ethylenethiuram monosulphide. The observed E.D. 50 value of ethylenedithiobiuret is rather high in comparison with that of the thiuram monosulphide. This would suggest that the modes of fungicidal activity are quite different, or perhaps that the dithiobiuret is more stable towards ring opening than is ethylenethiuram monosulphide. No chemical or physical evidence has yet been gathered to establish the formation of isothiocyanate through the proton-wandering postulated by Sijpesteyn and van der Kerk.

The actual demonstration of the presence of the isothiocyanate grouping is rendered difficult because of its high reactivity. This does not detract, however, from the possibility that the biochemical action of nabam and of the thiuram monosulphide is through transitory isothiocyanate which acts on —SH groups in the fungus cell.

ACKNOWLEDGMENTS

The authors are indebted to Dr. H. Martin for his encouragement of this work, to R. W. White for the determination of infrared spectra, to (Mrs.) Dorle Bongart for microanalyses, and to C. H. Unwin for the bioassays.

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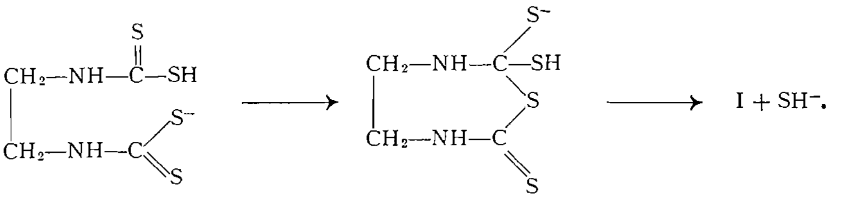
[8] *The referee has expressed skepticism of the formatiion of isothiocyanate in dilute aqueous solution, and suggested that the thiuram monosulphide could form as follows:*



We tend to concur, however, with the proposal of van der Kerk and Sijpesteyn in the light of the considerable evidence, albeit mainly circumstantial, for the momentary existence of isothiocyanate.

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THE VAPOR PHASE PARTIAL OXIDATION OF *n*-BUTANE—EFFECT OF PRESSURE, REACTION TIME, AND INLET GAS COMPOSITION[1]

By D. Quon[2], I. Dalla Lana,[3] and G. W. Govier[4]

ABSTRACT

Data are presented on the product yields and the general course of the partial oxidation of *n*-butane at an ambient temperature of 725°F., at pressures ranging from 50 to 175 p.s.i.a., reaction times of 1.0 to 4.5 sec., and inlet reactant compositions of 1.5 to 6.0 mole % *n*-butane and 1.5 to 6.0 mole % oxygen (the remainder being diluent nitrogen). Conditions were neither isothermal nor adiabatic and peak temperatures as much as 70 Fahrenheit degrees higher than the inlet temperatures were encountered. The reactor consisted of a 24-ft. length of ¼-in. stainless steel pipe, immersed in a bath of boiling Aroclor 1254. Under optimum conditions, a 20% conversion of the butane to methanol, ethanol, acetaldehyde, acetone, and formaldehyde was obtained. In all the tests, an induction period of approximately 0.75 sec. was observed.

INTRODUCTION

The vapor phase partial oxidation of the ordinarily gaseous paraffin hydrocarbons, including *n*-butane, has been the subject of numerous investigations and forms the basis of several commercial processes. Despite this, the literature offers little definite information and no systematic correlation of the many variables affecting the course and rate of the reaction. This paper, the first of a series on the partial oxidation of *n*-butane, gives the results of experimental studies on the reaction in a flow system at a constant ambient temperature but over a range of pressures, reaction times, and reactant concentrations.

THEORETICAL CONSIDERATIONS

Little published work appears specifically on the partial oxidation of *n*-butane. Wiezewich and Frolich (10) identified one-, two-, three-, and four-carbon-atom alcohols, acetaldehyde, propionaldehyde, acetone, acetic acid, and propyl acetate in their liquid products from the reaction of a 95% *n*-butane—5% oxygen mixture at pressures of 33–160 atmospheres and temperatures of 410–490°F. Commercial installations using the partial oxidation process employ lower pressures (10–20 atmospheres) and higher temperatures (750°F. and higher). Reaction time is of the order of a few seconds. For example, a Celanese Corporation patent (1) suggests operation at 20 atmospheres pressure, a reaction time of 1.15 sec., and an initiation temperature of 750°F., using a feed made up of 1 part (by volume) of *n*-butane, 10 parts air, and 110 parts steam. Nitrogen may also be used as a diluent. Other

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reports (9) indicate substantial yields of formaldehyde, acetaldehyde, methanol, acetone, organic acids, and smaller quantities of other compounds.

In addition to these desirable products, water is formed and there is considerable further oxidation to carbon monoxide and carbon dioxide. Free energy data (8) indicate that at the range of temperatures and pressures used, all of the oxygenated organic compounds are inherently unstable and that the equilibrium end products are carbon dioxide and water. In order to obtain high yields of useful products, the reaction must consequently be stopped before it goes to completion. Factors which tend toward increased yields of oxygenated organic compounds include: close control of reaction time, operation under pressure, low oxygen concentrations (to limit the amount available for secondary oxidations), and large amounts of diluent in order to absorb the heat of reaction and to permit survival of the intermediate products by limiting the temperature rise.

Attempts to predict the course of the reaction or the product distribution from assumed reaction mechanisms have not been too successful. In the broad field of hydrocarbon oxidation there are, in general, three postulations as to mechanism (3).

(1) *Hydroxylation*—in which an oxygen atom attacks the carbon–hydrogen bond at the end of the hydrocarbon chain to produce an alcohol. This step is followed by further oxygen attack and subsequently by thermal decompositions. One of the weaknesses of this theory, however, is that the formation of atomic oxygen is difficult to explain.

(2) *Peroxide*—in which an oxygen molecule attacks a carbon–hydrogen bond to give a peroxide which, being inherently unstable, decomposes to yield alcohols, aldehydes, acids, water, and carbon oxides.

Both of the above mechanisms have chain-initiating and chain-terminating steps to account for inhibition by surfaces.

(3) *Atomic chain theory of Norrish* (7)—in which the reaction is propagated by atoms and radicals rather than by an energy chain mechanism.

All of these mechanisms involve a number of steps and give a variety of products, the distribution of which depends upon the relative reaction rates of the individual steps. However, the problem of validating a proposed mechanism for such a complex reaction represents an extremely difficult task. Even in the case of methane, the simplest hydrocarbon and the one most thoroughly studied, there is no general agreement on mechanism. The partial oxidation of *n*-butane is much more complex since there are carbon–carbon bonds to be attacked as well as carbon–hydrogen bonds.

EXPERIMENTAL PROGRAM

The initial studies reported below were planned to determine the reaction conditions under which the partial oxidation of *n*-butane would produce substantial yields of oxygenated organic products and to enable observation of the general characteristics of the reaction. The obvious variables to be investigated were temperature, pressure, reaction time, and inlet gas composition. The present experimental program was concerned only with the effect of the last three variables, the initiation temperature being held constant in all cases. It was found that the reaction took place not isothermally, but over a range of temperatures, the temperature gradient within the reactor being a function of the heat transfer characteristics of the reactor and of the

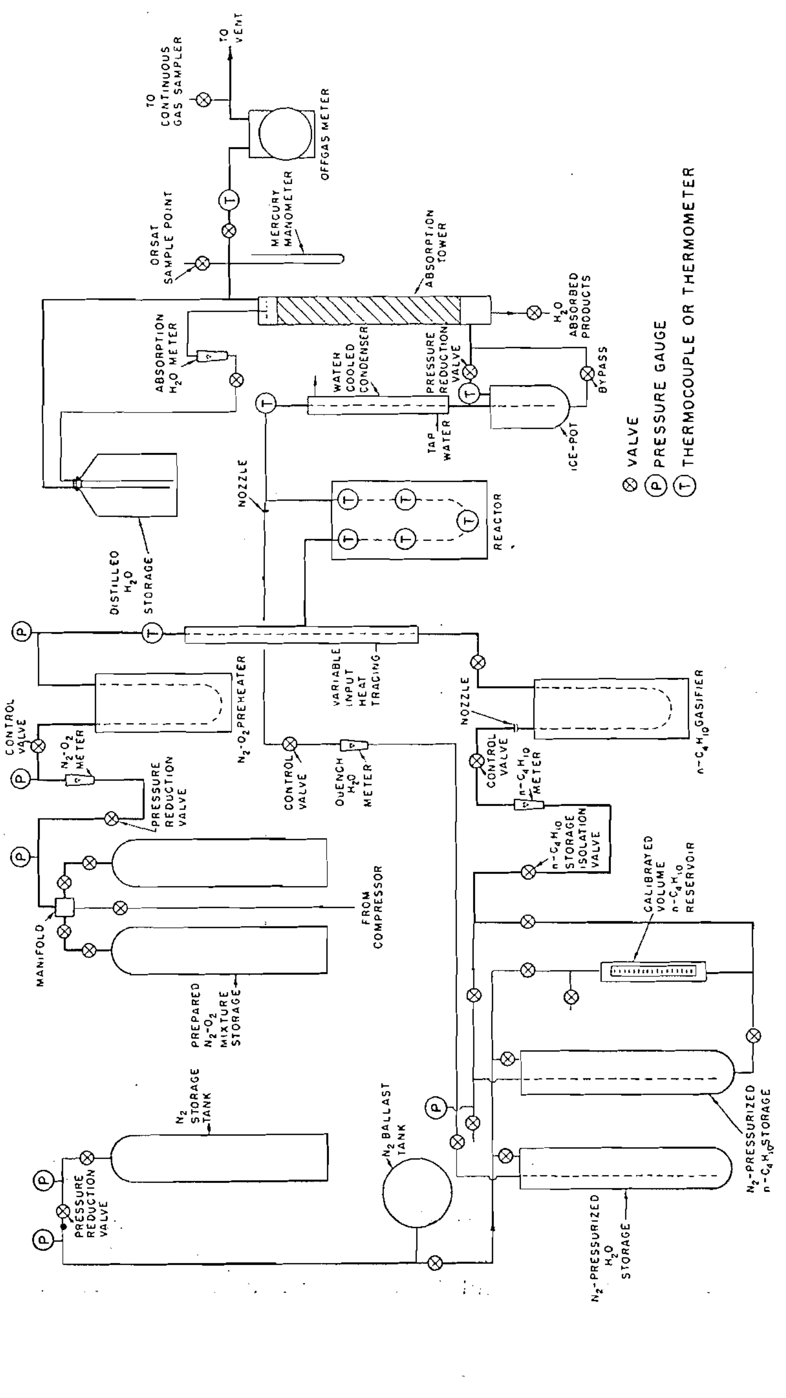


FIGURE I

SCHEMATIC DIAGRAM OF N-BUTANE PARTIAL OXIDATION EQUIPMENT.

extent of reaction. Work is currently under way to investigate the effect of temperature in a reactor of modified design.

Equipment and Procedure

The reaction system had the following design features:

(1) A flow system was used because of the low reaction times.

(2) A boiling liquid bath (Aroclor 1254*) was used to maintain a constant ambient temperature around the reactor.

(3) Gas flow was in the turbulent region (Reynolds numbers ranging from 2500 to 8000) to minimize concentration and temperature gradients in a direction perpendicular to flow and to give reasonably high heat transfer coefficients from the reactant gas to the reactor wall.

(4) A direct water quench effectively stopped the reaction.

A schematic diagram of the equipment is shown in Fig. 1. Nitrogen and oxygen from commercial cylinders, mixed to give the required oxygen concentration, were passed into a gasholder. The mixture was drawn from the holder, compressed in a three-stage gas compressor, and stored in high pressure cylinders. From here, the mixed nitrogen and oxygen was passed through a pressure reduction valve, metered at 300 p.s.i.a., and brought up to reaction temperature in an electrically heated preheater which consisted of a 7-ft. length of ¼-in. stainless steel pipe. The heated nitrogen–oxygen mixture was then contacted and mixed with the gaseous *n*-butane stream and fed into the main reactor. The *n*-butane, as supplied by the Phillips Petroleum Co., was specified to be 99% pure. The butane was stored as a liquid in a pressurized vessel, metered as a liquid, and vaporized and preheated in a bath of boiling Aroclor 1254. The reactor itself consisted of a 24-ft. length of ¼-in. (nominal) type 304 stainless steel pipe (outside diameter 0.540 in. and inside diameter 0.364 in.), arranged in the form of a helical coil having an inside diameter of 4 in. The reactor thus had a surface-to-volume ratio of 132 ft^{-1}. Five thermocouple wells were spaced at 6-ft. intervals along the coil. The coil was immersed in a boiling Aroclor bath contained in a 4-ft. section of 6-in. steel pipe. The bath was heated electrically by a chromel wire winding wrapped around the pipe. The condenser for the Aroclor bath consisted of a 3-ft. length of 2-in. steel pipe, the outer surface bared to the atmosphere. An internal water cooler serving as a "cold finger" and made of ¼-in. O.D. copper tubing, extended downwards inside the pipe. The pressure inside the bath could be varied from 5 to 50 p.s.i.a.

The off-gases from the reactor were cooled, first quickly by a direct water quench, and further by a water-jacketed cooler. The pressure was then reduced to nearly atmospheric by an adjustable back pressure valve, and the gases were scrubbed in a water absorption tower. The latter consisted of a 4-ft. length of 3-in. I.D. Pyrex glass, packed with ¼-in. ceramic Raschig rings. The scrubbed gases were measured in a dry test meter and discharged to atmosphere.

**A mixture of chlorinated diphenyl and diphenyl oxide manufactured by the Monsanto Chemical Co.*

TABLE

PARTIAL OXIDATION

Series		I					II			
Test	A12*	A1	A4	A9	A10	A11	A2	A6	A24	A28
Variable studied		Pressure					Reaction time			
Duration of test, min.	57.6	35.3	68.0	50.4	39.9	43.3	36.2	44.8	69.1	54.6
Bath temperature, °F.	724	727	727	723	723	724	723	723	726	724
Reaction temperature, °F.										
Inlet	726	727	727	724	726	724	723	723	729	726
¼ Point	786	727	747	811	775	774	723	724	726	756
½ Point	737	727	738	734	735	737	723	724	763	733
¾ Point	730	727	729	725	724	726	723	726	744	722
Outlet	725	725	728	723	722	722	723	733	724	722
Reaction pressure, p.s.i.a.	100	50	75	125	150	175	100	100	100	100
Reaction time, † sec.	3.0	3.0	2.9	3.0	2.9	3.1	1.0	1.2	1.4	4.5
Space velocity, sec.$^{-1}$	0.948	0.475	0.705	1.20	1.39	1.62	2.84	2.39	1.90	0.609
Feed rate, lb.moles/hr.	0.1645	0.0824	0.122	0.208	0.243	0.287	0.491	0.416	0.331	0.105
Feed gas composition,										
mole % n-butane	2.84	3.04	3.00	3.08	3.00	2.97	3.04	2.92	3.20	3.36
Oxygen	3.02	3.00	2.98	3.00	3.00	3.00	3.02	3.10	2.91	3.02
Nitrogen (by diff.)	94.14	93.96	94.02	93.92	94.00	94.03	93.94	93.98	93.89	93.62
Off-gas rate, c.f.m. (N.T.P.)	0.98	0.491	0.725	1.23	1.42	1.68	2.93	2.49	1.98	0.622
lb.moles/hr.	0.163	0.082	0.121	0.205	0.238	0.281	0.490	0.416	0.331	0.104
Off-gas composition,										
mole % n-butane	2.11	3.0	2.66	1.92	1.86	1.74	3.0	2.48	2.28	2.32
Unsaturated hydrocarbons	0.44	—	0.35	0.48	0.52	0.61	—	0.14	0.27	0.38
Oxygen	1.54	3.00	1.97	0.78	0.24	0.05	3.01	2.69	2.49	1.18
Carbon monoxide	0.70	—	0.45	0.89	1.07	1.35	—	0.20	0.57	0.83
Carbon dioxide	0.64	—	0.52	0.62	0.63	0.58	—	0.12	0.32	0.66
Nitrogen (by diff.)	94.57	—	94.05	95.31	95.68	95.70	—	94.37	94.07	94.63
Fraction oxygen reacted	0.494	—	0.346	0.744	0.920	0.983	—	0.131	0.144	0.612
Carbon balance (ratio carbon out to carbon in)	1.05	‡	1.06	0.96	0.96	0.97	‡	0.97	0.92	1.00
Hydrogen balance§ (ratio hydrogen out to hydrogen in)	0.94	‡	0.92	0.95	0.99	1.00	‡	0.97	0.94	0.91

**This test is common to all series.*

†Based upon ideal gas volume of feed gas.

‡Amount of reaction small; material balances not made.

§Water produced is calculated from oxygen balance.

Reaction times were determined from the measured flow rates of the nitrogen–oxygen and the n-butane streams. The butane flow was determined by observing the change in butane liquid level over a timed interval in a calibrated Jerguson sight gauge used as a storage vessel. An independent check of the total flow was obtained by a dry test meter.

The boiling point of Aroclor, and hence the bath or ambient reaction temperature, was adjusted by varying the pressure exerted on the bath. In the present series of runs, the bath temperature was maintained at approximately 725°F. The heat input (supplied electrically) to the nitrogen–oxygen preheater was adjusted so that the initiation temperature (measured at a point just inside the reactor and several inches from the junction of the nitrogen–oxygen and butane gas streams) was the same as the bath temperature. The temperature gradient immediately following reaction initiation was dependent on the extent of reaction and on the heat transfer characteristics of the reactor, and could not be controlled independently. Temperatures were measured at five points along the reactor using chromel–alumel thermocouples and a recording multipoint potentiometer.

A continuous sample was taken of the gases leaving the scrubber and analyzed afterwards with a precision Orsat apparatus to an accuracy of about 0.02 mole %. As a further check, three or four spot samples were taken during the course of a run and analyzed immediately for oxygen, carbon monoxide, carbon dioxide, and unsaturated hydrocarbons. The total hydrocarbon content

I

OF n-BUTANE

III			IV			V		
A22	A15	A21	A17	A16	A26	A3	A7	A27
Oxygen concentration			n-Butane concentration			Total reactant concentration		
74.6	52.4	70.9	50.1	41.0	72.7	30.4	41.8	73.7
713	733	712	730	727	725	727	727	725
715	730	714	726	722	729	727	727	725
714	783	790	764	805	750	767	805	758
715	745	725	736	739	735	732	746	746
713	735	715	729	729	728	725	728	733
712	732	714	719	722	692	724	728	711
100	100	100	100	100	100	100	100	100.
2.9	2.8	3.1	3.1	3.0	3.4	3.0	2.9	3.3
1.04	0.978	0.950	0.909	0.960	0.892	0.936	0.989	0.897
0.180	0.170	0.164	0.157	0.167	0.155	0.162	0.172	0.156
2.83	2.56	2.85	1.37	4.59	7.37	1.50	4.63	6.35
1.58	4.65	5.85	3.06	3.09	3.58	1.52	4.67	6.15
95.59	92.79	91.30	95.57	92.32	89.05	96.98	90.70	87.50
1.08	1.00	0.967	0.940	0.985	0.913	0.970	1.00	0.904
0.180	0.168	0.161	0.157	0.164	0.152	0.162	0.167	0.151
2.8	1.44	1.95	1.17	3.33	5.41	1.5	3.17	3.87
—	0.41	0.42	0.19	0.64	0.97	—	0.70	0.76
1.34	2.38	2.69	1.83	0.66	0.43	1.50	1.15	0.39
0.04	0.71	1.20	0.29	0.63	1.04	—	1.22	2.63
0.15	0.72	0.83	0.43	0.61	0.68	—	0.90	1.13
—	94.34	92.91	96.09	94.13	91.47		92.98	91.22
0.158	0.749	0.549	0.405	0.755	0.883	—	0.760	0.937
‡	0.91	1.05	1.17	0.96	0.91	‡	1.09	0.91
‡	1.16	1.08	1.00	1.01	0.90	‡	1.02	1.03

of the "off-gases" was determined by the complete oxidation of a measured volume over a promoted copper oxide catalyst (6). The carbon dioxide formed was absorbed in a 2 N potassium hydroxide solution and the latter back-titrated with $N/10$ hydrochloric acid; methyl orange was used for the first end point, and a mixed indicator of cresol red and thymol blue for the final end point.

The aqueous solutions containing the oxygenated organic compounds were sent to the Consolidated Engineering Corporation, Pasadena, California, and analyzed with a mass spectrometer. Detection of all the major components is claimed to be positive but the accuracy of the analysis is limited owing to the high degree of dilution. The total organic concentration in most of the tests was of the order of 1 mole %. Mass transfer calculations indicated that the absorption of all the organic vapors was nearly quantitative with the possible exception of acetaldehyde. As a further check, an aliquot portion of the scrubbed gases was passed through a solution of 2,4-dinitrophenylhydrazine. The precipitate formed was a measure of the aldehyde content of the gas (2).

RESULTS

The experimental results of a total of 19 tests, which permitted material balances to be established, are presented in Table I and Figs. 2 to 6. The data are grouped in five series, reflecting the different variables studied (pressure,

FIGURE 2a

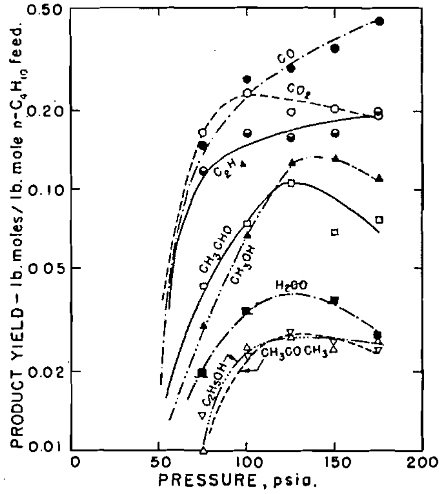


FIGURE 2b

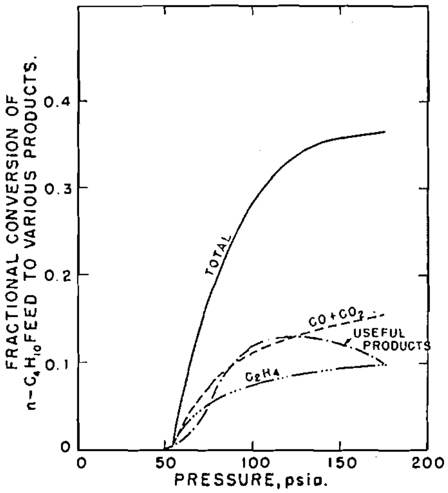


FIGURE 2c

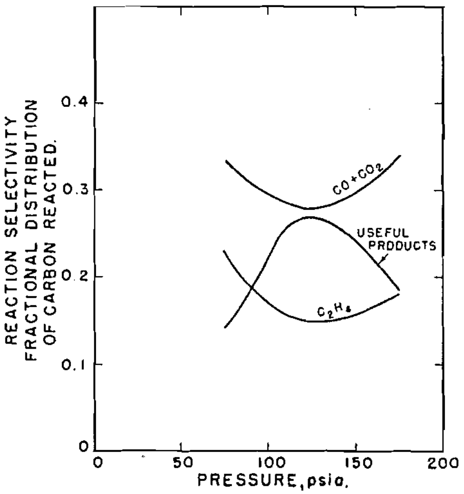


FIGURE 3a

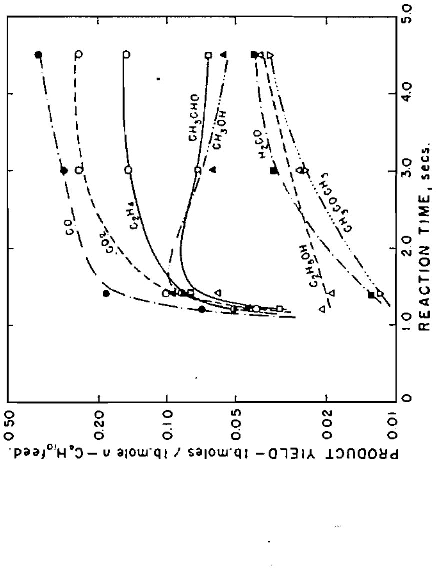


FIGURE 3b

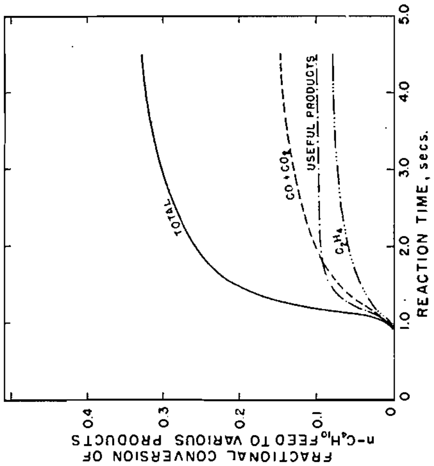


FIGURE 3c

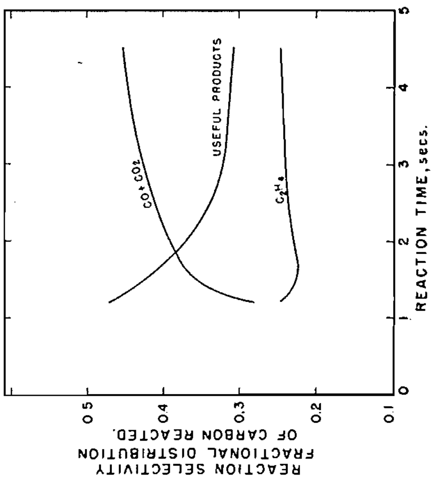


FIGURE 4a

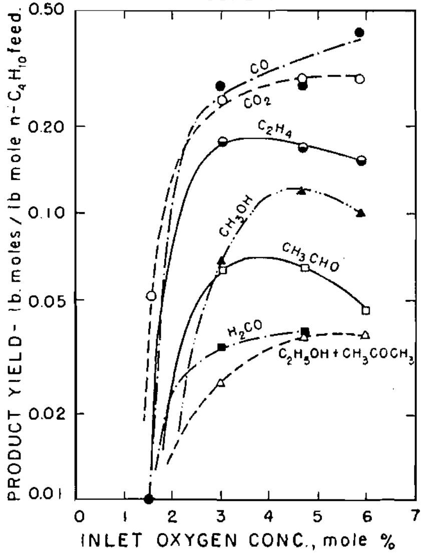


FIGURE 4b

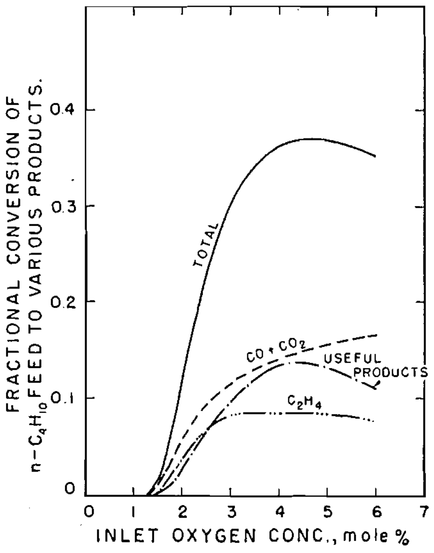


FIGURE 4c

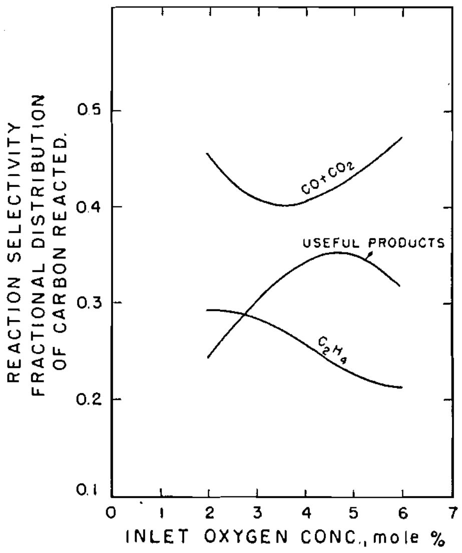


FIGURE 5a

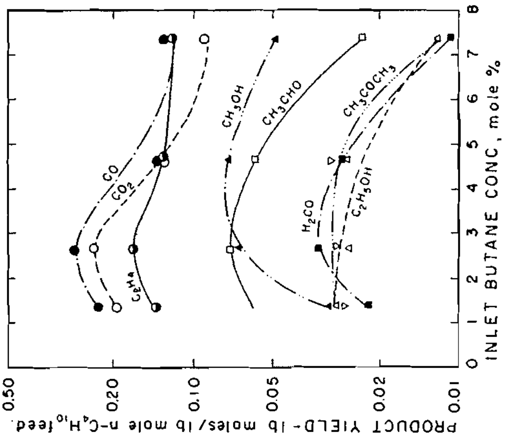


FIGURE 5b

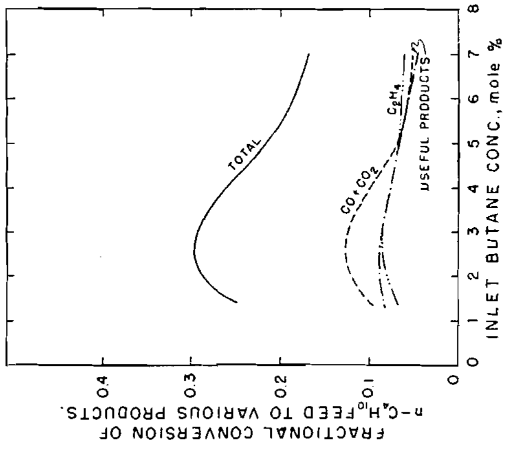


FIGURE 5c

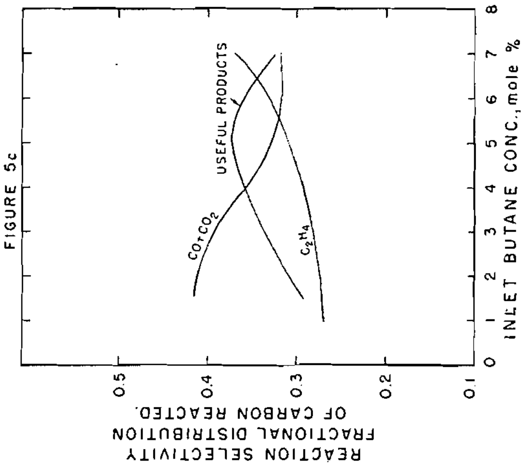


FIGURE 6a

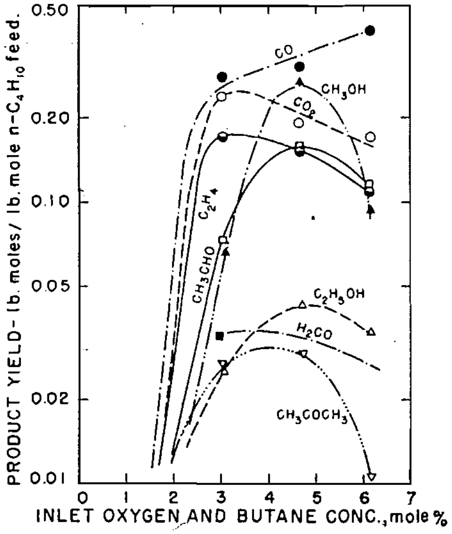


FIGURE 6b

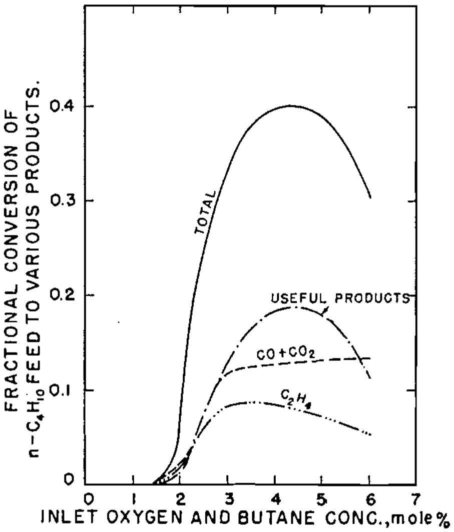
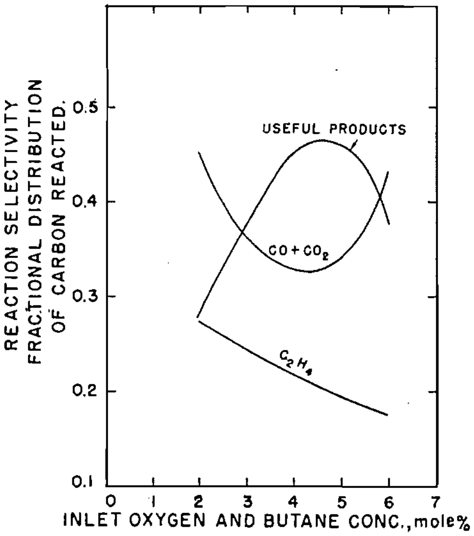


FIGURE 6c



reaction time, and inlet gas composition). A "control" test was carried out at a pressure of 100 p.s.i.a., a reaction time of 3.0 sec., and a gas inlet composition of 3 mole % butane, 3 mole % oxygen, and 94 mole % nitrogen.

Figs. 2 to 6 show the effect of each variable on the yields of the various products. Yield data are presented in several ways. The actual experimental data showing individual products yields per unit mole of butane feed are given in Figs. 2*a* to 6*a*. The smoothed curves then formed the basis of calculation for the over-all product yields in terms of both the butane feed and the butane converted. The latter are shown in Figs. 2*b* to 6*b* and Figs. 2*c* to 6*c*, respectively.

Effect of Pressure

Six tests (Series I in Table I) were carried out at pressures ranging from 50 to 175 p.s.i.a. (in 25 p.s.i. intervals). At 50 p.s.i.a., there was no evidence of reaction. As the pressure was increased, the over-all fractional conversion (shown in Fig. 2*b*) increased rapidly up to a pressure of about 125 p.s.i.a., and then more slowly up to a pressure of 175 p.s.i.a. The fractional conversion to useful products exhibited a maximum (somewhat diffuse) at a pressure of 125 p.s.i.a. In fact, as shown by Fig. 2*a*, all of the individual oxygenated organic products showed a maximum yield at about this pressure. No definite effect of pressure on the distribution of these organic products was indicated, but pressures above 125 p.s.i.a. tended to favor the formation of carbon oxides. This is clearly shown on the reaction selectivity curves in Fig. 2*c*. As a result, the useful products curve goes through a marked maximum at a pressure of 125 p.s.i.a.

The increasing severity of the reaction as the pressure is raised is also shown clearly by the increase in the fractional consumption of oxygen. Table I shows that at 100 p.s.i.a. only 49.4% of the original oxygen had reacted. At 150 p.s.i.a. this had risen to 92.0%, and at 175 p.s.i.a. to 98.3%. It is evident that higher pressures would lead to complete exhaustion of the oxygen.

Increasing the total pressure means proportionate increases in the individual reactant partial pressures, and the data could have been analyzed on a reactant partial pressure basis. However, comparison of individual tests in this series with other tests having similar reactant partial pressures but different total pressures (for example tests A10 and A7) showed a wide difference in the product yields. Consequently, total pressure was used as the correlating variable.

Effect of Reaction Time

The effect of reaction time is shown in the tests of Series II. The times were varied from 0.8 to 4.5 sec. while all other variables were held constant. Below a residence time of 1.0 sec., little or no reaction was observed. However, increasing the reaction time to 1.5 sec. brought a rapid increase in the amount of reaction (Fig. 3*b*). After about 2.0 sec., further increases in reaction time caused little further increase in reaction. This was surprising since the exit gas stream in all cases contained over 1 mole % oxygen. The explanation may be that after the oxygen content has been reduced below a certain critical value in the first part of the reactor, no further oxidation can occur (for a given temperature and pressure). Under the conditions of pressure, temperature, and butane concentration employed in this series of runs, this value appeared to be between 1.0 and 1.5 mole %.

It is difficult to draw any definite conclusions from the individual product curves in Fig. 3*a*. Methanol and acetaldehyde appear to be formed in the early part of the reaction but the evidence is not conclusive.

Fig. 3*c* shows that the optimum reaction selectivity occurs with the shorter contact times (1.0 to 1.5 sec.) and there is a sharp drop in the fraction of useful products as the reaction time is increased. This is logical since longer reaction times provide more time for secondary oxidations to occur.

The reactor temperature profiles (Table I) show clearly that the reaction temperature peak moved further from the reactor inlet as the residence time was decreased. On a time basis, however, the interval between the instant when the reactant streams contacted each other and the temperature peak remained substantially constant. The presence of an induction period of from 0.5 to 1.0 sec. is indicated.

With the present reaction system, the reaction time was varied by changing the gas velocity through the reactor. Higher mass velocities meant higher heat transfer coefficients from gas to reactor wall resulting in a greater ability to dissipate the heat of reaction, and tended toward a more nearly isothermal reaction and lower reactor temperature peaks. This may well have been one of the main reasons for the high yields of useful products at short contact times, which corresponded to high mass velocities.

EFFECT OF INLET GAS COMPOSITION

(1) *Oxygen Concentration*

In the tests of Series III, the inlet oxygen concentration was varied from 1.5 to 6.0 mole % while the inlet butane concentration and other variables were held constant. Although the data were more scattered for this series of runs than for any other, some trends were evident.

At an inlet oxygen concentration of 1.5 mole %, very little reaction occurred (Fig. 4*b*). This appears to be the lower limit of oxygen concentration necessary to initiate the reaction. The over-all conversion increased sharply as the inlet oxygen concentration was raised to 3.0 mole %, then started to level off (and even decrease) at oxygen concentrations above 4.5 mole %. While Fig. 4*b* shows that the yield of oxygenated organic compounds passed through a maximum at an inlet oxygen concentration of 4.5 mole %, no great significance should be attached to this owing to uncertainties in the analysis of the liquid products.

The optimum reaction selectivity also occurred at this oxygen concentration (Fig. 4*c*).

These results are consistent with Egloff's findings (4) that excess oxygen tends to inhibit the reaction and to lead to lower yields of intermediate oxygenated compounds.

(2) *Butane Concentration*

In the tests of Series IV, the effect of inlet *n*-butane concentration over the range of 1.5 to 6.0 mole % was studied. Definite signs of reaction were noted with butane concentrations as low as 1.5 mole %. Fig. 5*b* shows that the fractional conversion of the butane feed passed through a maximum at an inlet butane concentration of about 2.5 mole %. However, the total amount of reaction (based upon a unit mass of feed) continued to increase up to an inlet butane concentration of about 4.5 mole %. The optimum reaction selectivity (Fig. 5*c*) occurred at an inlet butane concentration of 4.5 mole %. It is interesting to note that as the inlet butane concentration is increased the fraction of the total butane reacted which was converted to unsaturated hydrocarbons increased sharply.

(3) *Total Reactant Concentration*

In the tests of Series V, a one-to-one butane-to-oxygen molal ratio was maintained, but the concentration of each component was varied from 1.5 to 6.0 mole %. The results are consistent with those obtained for Series III and Series IV. In Series III, with a constant butane inlet concentration of 3.0 mole %, the optimum useful products yield was at an oxygen inlet concentration of 4.5 mole %; similarly in Series IV, with a constant inlet oxygen concentration of 3.0 mole % the optimum yield was at a butane concentration of 4.5 mole %. It might be expected that with inlet oxygen and butane concentrations both at 4.5 mole % the yields would be even higher. This is indeed the case. The "useful products" curve showed a sharp maximum at a concentration of 4.5 mole % for both *n*-butane and oxygen in the fractional conversion curves (Fig. 6*b*) as well as in the reaction selectivity curves (Fig. 6*c*). The detrimental effect of high oxygen concentrations—leading to high yields of carbon dioxide and carbon monoxide at the expense of intermediate oxygenated compounds—is again evident when the inlet concentration of oxygen exceeds 4.5 mole %. As might be expected, no reaction occurred when the *n*-butane and oxygen inlet concentrations were both at 1.5 mole %.

GENERAL DISCUSSION

The primary purpose of this phase of the investigation was to define approximately the reaction conditions under which the partial oxidation of butane would give substantial yields of oxygenated organic products. No attempt has been made at this time to treat the data kinetically or to postulate a reaction mechanism. However, several distinctive features of the reaction have been noted:

(1) At a temperature of 725°F., using a reactor with a surface-to-volume ratio of 132 ft.$^{-1}$ and the reactant gases flowing with a Reynolds number of the order of 5000, the optimum conditions are roughly as follows:

Pressure, 120–140 p.s.i.a.
Reaction time, 1.2–1.8 sec.

Inlet gas composition, 4–5 mole % *n*-butane, 4–5 mole % oxygen, remainder nitrogen.

Under these conditions, a fractional conversion of over 20% of the original carbon to useful oxygenated organic products in one pass might be expected. About 50% of the total carbon reacted should go to useful products.

(2) In all the runs, the reaction followed a characteristic course. After the *n*-butane and oxygen streams had been mixed, they remained at the bath temperature for a definite interval of time (assumed to be the "induction" period and estimated to be of the order of 0.5 to 1.0 sec.). From this point, the reaction rates increased very sharply and assumed the characteristics of a "run-away" reaction. Peak temperatures of 75 or more Fahrenheit degrees higher than the bath temperature were observed. The bulk of the reaction took place over a comparatively short period of time (less than a second). After the reaction peak had passed, the gases once more cooled down to the bath temperature.

(3) Reactor design may have two effects upon the reaction. First, the amount of surface may be a factor in determining the course of the reaction—for example, in the case of a free radical chain mechanism, the surface may act as a chain initiator or chain breaker. Second, the heat transfer characteristics of the reactor would unquestionably affect the reaction temperature profile, and this would in turn have an important bearing on the over-all reaction. With the reactor used, conditions were neither isothermal nor adiabatic. It would appear to be very difficult to achieve isothermal operation unless the reaction were almost completely suppressed.

The heat transfer coefficient from the outer reactor wall to the liquid bath was measured to be of the order of 30 B.t.u./(hr.) (sq. ft.) (°F.). As calculated from the Dittus–Boelter equation (5), the corresponding coefficient from the reacting gases to the inner reactant wall in these tests should range from 12 to 25 B.t.u./(hr.) (sq. ft.) (°F.). These individual coefficients would give over-all heat transfer coefficients of 8 to 14 B.t.u./(hr.)(sq. ft.)(°F.).

Actually, the great bulk of the heat is transferred to the reactor rather than absorbed by the reactant gases. In some of the runs, the adiabatic temperature rise (calculated from the over-all heats of reaction) would have been as much as 400 Fahrenheit degrees.

(4) Careful control of the oxygen concentration appears to be one of the most important factors in directing the reaction towards high yields of oxygenated organic products. There is a critical oxygen concentration (around 1.5 mole % at 100 p.s.i.a., 725°F., and 3 mole % *n*-butane) below which no reaction will take place. On the other hand, high oxygen concentrations (relatively speaking) favor formation of the more completely oxidized products, namely, carbon dioxide and carbon monoxide.

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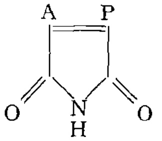
THE SYNTHESIS OF UROPORPHYRIN I[1]

By S. F. MacDonald and (in part) R. J. Stedman[2]

ABSTRACT

The analytical proof of H. Fischer's structure for uroporphyrin I has been completed, and the structure confirmed by synthesis.

Uroporphyrin I, an octacarboxylic acid, may be partially decarboxylated to coproporphyrin I (II, A = CH_3), and oxidized to a carboxylated hematinic acid. Synthesis eliminated two of the three possible structures for the latter, thus shown to be I. Uroporphyrin I has accordingly been formulated as II (8) on the assumption that each of the four pyrrole nuclei bore an acetic acid and a propionic acid residue. Because the oxidation of uroporphyrin I gave no more than two molecules of I, the assumption that all four pyrrole nuclei bore the same substituents was unproven (cf. (5,6,9)); alternative structures such as one in which one pyrrole nucleus bore a methyl and a succinic acid residue could not be excluded. This uncertainty remained after the synthesis of I by oxidization of a synthetic porphin-tetraacetic acid – tetrapropionic acid mixture (13). Although in the porphyrin mixture obtained from porphobilinogen with acid (1) all four pyrrole nuclei must have the same substituents, the status of this as a mixture of uroporphyrins has not been confirmed by the isolation of recognizable uroporphyrin isomers from it.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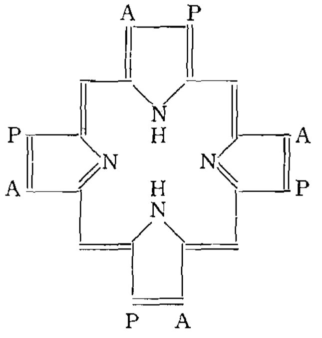
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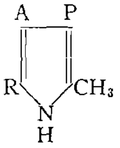
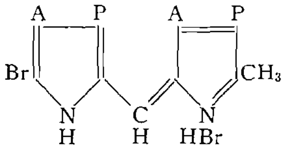

IIIa, R = COOH
b, R = H


IV

A = CH_2COOH
P = $CH_2CH_2 \cdot COOH$

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3348.
This work was reported at the Summer Seminar in the Chemistry of Natural Products, University of New Brunswick, August, 1953, and in a preliminary communication (14).

[2] *National Research Laboratories Postdoctorate Fellow 1952–1954.*

This uncertainty in Fischer's structure II for uroporphyrin I has been eliminated by Kuhn–Roth determinations. The number of C-methyl groups found in the methyl esters were: natural uroporphyrin I, 0.0; synthetic porphin-tetraacetic acid – tetrapropionic acid (mixed isomers (13)), 0.0; synthetic coproporphyrin I, 3.46; 2.93. In addition, analytical *meso*-porphyrin IX showed 5.05. The first two results show that the porphyrin nucleus, propionic acid residues, and acetic acid residues do not contribute to the C-methyl values. The four equivalent methyl groups in coproporphyrin I must then each contribute 0.8 to the C-methyl groups found in it, and none of these can be present in uroporphyrin I, which must be II.

After seed had been prepared, the pyrromethene IV was easily obtained crystalline by brominating (cf. (7)) either of the pyrroles III*a* or III*b* (cf. (13)). With methylsuccinic acid at 118°, the pyrromethene gave porphin-1,3,5,7-tetraacetic acid – 2,4,6,8-tetrapropionic acid, II, isolated as its methyl ester. This method had been used in the synthesis of the isomeric 1,3,5,7-tetramethyl-porphin-2,4,6,8-tetrasuccinic acid where a moderate temperature was necessary to avoid partial decarboxylation (11). Working up such melts has sometimes been difficult because highly carboxylated porphyrins may form colloidal solutions in water, and are too insoluble in ether for fractionation with hydrochloric acid. It was found that colloidal solutions are avoided if enough water is used in dissolving the melt, and the nearly pure porphyrin ester results when its chloroform solution is washed with 50% aqueous resorcinol; lower concentrations are less effective and higher concentrations extract the porphyrin as well as the impurities.

Neither analysis of the methyl ester nor paper chromatography of the free acid with lutidine (15) gave any indication of heptacarboxylic or lower acids in the product. In analogous cases, this method of synthesis has given type I porphyrins exclusively. Here, the type and purity were confirmed by paper chromatography of the ester with kerosene-dioxan (see below) and by partial decarboxylation to coproporphyrin I (10). The latter was obtained as its methyl ester, identical with an authentic synthetic specimen by the following criteria: crystal form, insolubility in ether, visible spectra, melting point and mixed melting point, infrared spectra in Nujol mull, and X-ray powder photographs.

The synthetic porphin-1,3,5,7-tetraacetic acid – 2,4,6,8-tetrapropionic acid methyl ester was identical with the purest natural uroporphyrin I methyl ester by the following criteria: visible spectra, paper chromatography with kerosene-dioxan (2), melting point and mixed melting point, the formation of a crystalline hydrochloride (4), infrared spectra in Nujol mull, and X-ray powder photographs. This confirms the structure II for uroporphyrin I.

Now, with the proof of the structure of uroporphyrin I, the mixture of porphin-tetraacetic acid – tetrapropionic acid isomers previously synthesized (13) is known to be a mixture of uroporphyrins. There was, at the time, direct evidence for this: X-ray powder photographs and infrared spectra in Nujol mull had indicated that the synthetic mixture was identical with an atypical uroporphyrin mixture from human urine (12). However, as both samples were mixtures, and particularly because the natural mixture might not be found again, their identity was an unsatisfactory proof that the natural uroporphyrins were porphin-tetraacetic acid – tetrapropionic acids.

EXPERIMENTAL

Melting points are uncorrected unless otherwise specified. Those of the porphyrins were determined on a micro hot-stage, heating rapidly at first, then at 2°/min. from about 10° below the melting point. The range indicates the temperature at which sintering began and that at which the crystals lay in pools of melt.

5-Bromo-5'-methylpyrromethene-4,3'-diacetic Acid – 3,4'-Dipropionic Acid Hydrobromide, IV

A suspension of the pyrrole III*a* (1 gm.) in acetic acid (6 ml.) was warmed in a bath at 40–50°, and bromine in acetic acid (2 ml. containing 1 gm. bromine) added in two portions. After 20 min. the solution was cooled to 25° and seeded. Next day the pyrromethene (579 mgm., 51%) was filtered off and well washed with acetic acid, then with ether. It formed golden-yellow microscopic plates, capillary m.p. *ca.* 210–215° (decomp.), unchanged by recrystallization from acetic acid (60 parts; recovery 60%), stable when kept dry. Found: C, 41.75; 41.64; H, 4.23; 3.94; N, 4.84; 4.91; Br, 27.07%. Calc. for $C_{20}H_{22}N_2O_8Br_2$: C, 41.54; H, 3.84; N, 4.85; Br, 27.64%.

The original seed crystals were obtained by the same method of bromination.

Porphin-1,3,5,7-tetraacetic Acid – 2,4,6,8-Tetrapropionic Acid, II (Uroporphyrin I) Methyl Ester

The pyrromethene IV (2.5 gm.) and methylsuccinic acid (10 gm.) were ground together, dried *in vacuo*, and kept for six hours while protected from moisture in a tube heated with boiling acetic acid. The melt was dissolved in water (800 ml.), the solid separated and washed with water (2 × 250 ml.) (centrifuge), dried, and left overnight in saturated methanolic hydrogen chloride (125 ml.). This was poured into ice water, extracted with chloroform, and the chloroform washed with water. The chloroform was filtered through a column of alumina (grade IV; 3 × 15 cm.) which was washed with more chloroform as long as porphyrin came through. The chloroform was washed with 50% (w/w) aqueous resorcinol (6 × 50 ml.), which was in turn washed with a little chloroform. The combined chloroform solutions were washed with water, with dilute sodium hydroxide, with water, dried over sodium sulphate, filtered, and the chloroform boiled off while hot methanol was added. The porphyrin ester (120 mgm., 5.9%) m.p. 284–285°, which separated was recrystallized thrice from chloroform–methanol giving micro needles (115 mgm.), m.p. 285–286.5°. A second preparation on a different hot-stage showed m.p. 285–286° (291–292° corr.). Found in material dried at 100° for eight hours at 5×10^{-4} mm.: C, 61.00; H, 5.85; N, 5.76; OMe, 26.38; C-Me, 0.0%. Calc. for $C_{48}H_{54}O_{16}N_4$: C, 61.14; H, 5.77; N, 5.94; OMe, 26.33; C-Me, 0.0%. The halogen content, 1.6% as Cl compared to 0.7% found in natural uroporphyrin I, is presumably derived from the solvent.

This product was compared with the uroporphyrin I methyl ester obtained from the urine of a case ("Lev.") of human congenital porphyria by Rimington and Miles (16), which has been characterized by its infrared spectrum (3) and X-ray powder photograph (12).

For this natural ester, (m.p. 293° corr. (16)) we found m.p. 284–286°, mixed melting point with the synthetic ester, 284–286°. When heated more slowly, there was partial or complete darkening of all samples, and the darkened parts did not melt below 340°. As darkening was noted by Fischer and Hofmann (6), the higher melting point they record (302°, 311° corr.) may be spurious.

When the synthetic ester was dissolved in methanolic hydrogen chloride (16 parts, saturated at 25°), the ester-hydrochloride crystallized after six weeks at 0°.

Coproporphyrin I Methyl Ester from the Synthetic Uroporphyrin

The synthetic uroporphyrin ester (18 mgm.) in 1% hydrochloric acid was heated for four hours at 185–190° in a sealed tube. The porphyrin was precipitated with sodium acetate, filtered off, and washed with water acidified with acetic acid. It was dissolved in pyridine, ethereal diazomethane added, the porphyrin ester extracted with hydrochloric acid, and brought into chloroform with ammonia. The chloroform was washed with dilute sodium hydroxide, then with water, dried with sodium sulphate, filtered, and the chloroform boiled off while hot methanol was added. The coproporphyrin I methyl ester (6 mgm.) formed needles, some of which were slightly bent, m.p. 251–252°. This was combined with a second lot (7.2 mgm. from 19 mgm. of the synthetic uroporphyrin), dissolved in chloroform, filtered through alumina (grade IV), crystallized and recrystallized from chloroform–methanol, giving 10.2 mgm., m.p. 251–252° (252–253° corr.) alone or mixed with authentic coproporphyrin I methyl ester. Found: C, 67.52; H, 6.49%. Calc. for $C_{40}H_{46}O_8N_4$: C, 67.59; H, 6.52%.

Both the free porphyrin and its ester were too insoluble in ether to be fractionated between ether and hydrochloric acid.

The authentic coproporphyrin I methyl ester was a synthetic specimen (bent needles) obtained from the late Professor Hans Fischer, further purified by filtration of its chloroform solution through alumina, crystallization, and recrystallization from chloroform–methanol. It then formed needles, some of which were slightly bent, m.p. 251–252°.

ACKNOWLEDGMENT

The paper chromatography was carried out through the courtesy of Prof. C. Rimington, to whom we are also indebted for a sample of natural uroporphyrin I. We thank Mr. R. Lauzon for the infrared spectra and Dr. W. H. Barnes for the X-ray powder photographs.

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DIPHENYLCYANAMIDE DERIVATIVES

II. 4,4′-DIMETHOXYDIPHENYLCYANAMIDE[1]

By J. R. Robinson[2]

ABSTRACT

The synthesis of 4,4′-dimethoxydiphenylcyanamide has been accomplished by treatment of 4,4′-dimethoxydiphenylamine with cyanogen chloride or alternatively by removal of the elements of water from N,N-bis(4-methoxyphenyl)urea. These reactions may be reversed by hydrolysis of the cyanamide with alcoholic or aqueous alkali, respectively. This nitrogen analogue of methoxychlor exhibits a very slight toxic effect on mosquito larvae (*Aedes aegypti* (L.)).

DISCUSSION

Paralleling an earlier report of a nitrogen analogue of DDT (2), the present communication describes the synthesis of 4,4′-dimethoxydiphenylcyanamide (I, Fig. 1) which is similarly analogous to the insecticide methoxychlor (1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane). The material was prepared from 4,4′-dimethoxydiphenylamine (II) by treatment with cyanogen chloride at approximately five atmospheres pressure. The limitations inherent in the type of pressure-vessel used led to a low yield (43%) since the reaction was necessarily run at a temperature below that of the melting-point of the amine. This resulted in a system of three phases which could not be adequately mixed.

A second method of synthesis involved the intermediate compound N,N-bis(4-methoxyphenyl)urea (III) which was obtained by the addition of cyanic acid to 4,4′-dimethoxydiphenylamine (II). A pyridine solution of this substituted urea was treated with benzenesulphonyl chloride, after the method of Kurzer (1), resulting in a 73% yield of 4,4′-dimethoxydiphenylcyanamide.

The extent of the alkaline hydrolysis of the substituted cyanamide may be controlled by choice of hydrolyzing medium. In 10% aqueous sodium hydroxide the reaction proceeds only as far as the carbamide stage (III), whereas the use of saturated methanolic potassium hydroxide results in a complete degradation to 4,4′-dimethoxydiphenylamine (II), presumably through the unstable carbamic acid.

4,4′-Dimethoxydiphenylcyanamide is a very weak base; it forms an unstable hydrochloride salt which decomposes immediately on moistening or warming, and within a few hours on standing at room temperature in a desiccator. In this respect it closely resembles diphenylcyanamide but is a much weaker base than diphenylamine or 4,4′-dimethoxydiphenylamine, both of which form stable (dry) hydrochlorides.

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[1] *Manuscript received June 2, 1954.*
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[2] *Holder of a C.I.L. Fellowship 1950–52. Present address: Science Service Laboratory, Canada Department of Agriculture, University Sub Post Office, London, Ontario.*

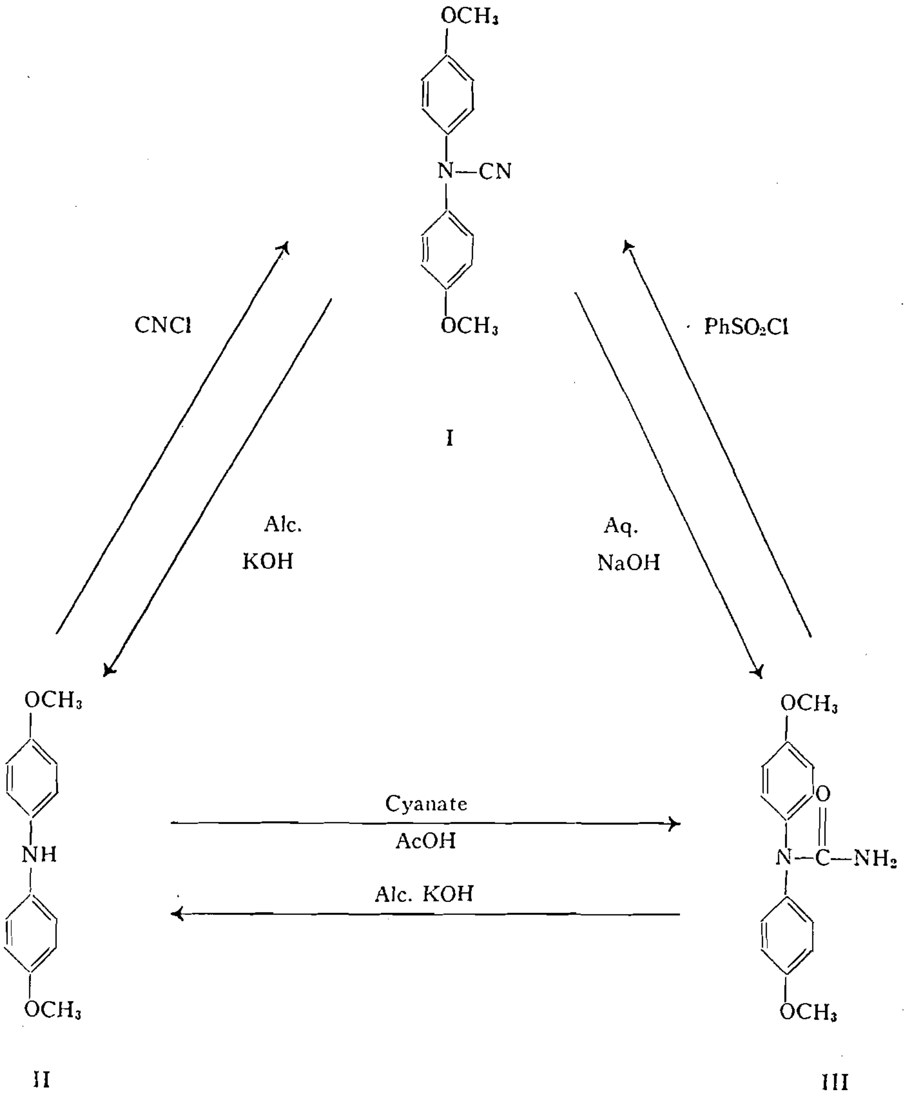

FIG. 1. The synthesis and hydrolysis of 4,4′-dimethoxydiphenylcyanamide and N,N-bis(4-methoxyphenyl)urea.

TOXICOLOGY*

The larvae of mosquitos, *Aedes aegypti* (L.), were used to compare the toxic effect of the cyanamide (I) with that of methoxychlor, DDT, and DDC (chemical names are given in Table I). Solutions ranging in concentration from 0.0012 to 2.5 p.p.m. were made up by first dissolving the materials in acetone and then diluting them with water to give the desired concentrations. Twenty

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The toxicological data were determined by Dr. R. W. Fisher, Division of Entomology, Science Service Laboratory, London, Ontario.

larvae (second instar) were placed in each solution. Acetone–water controls were used, and each test solution was duplicated. The dead larvae were counted after a 24-hr. exposure. The results, shown in Table I, indicate the lethal concentrations of both cyanamide derivatives to be of the same order of magnitude, namely about one hundred times that of methoxychlor, and more than one hundred times that of DDT.

TABLE I

A COMPARISON OF THE TOXIC EFFECTS OF METHOXYCHLOR, DDT, DDC, AND 4,4′-DIMETHOXYDIPHENYLCYANAMIDE ON MOSQUITO LARVAE

Materials tested	% kill at various concentrations (p.p.m.)									
	2.5	1.25	0.625	0.312	0.156	0.025	0.012	0.006	0.003	0.0012
Methoxychlor (1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane)	—	—	—	—	100	95	45	20	0	0
DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane)	—	—	—	—	100	100	100	95	85	60
DDC (4,4′-dichlorodiphenylcyanamide)	100	70	0	0	0	—	—	—	—	—
4,4′-dimethoxydiphenylcyanamide	70	40	5	0	0	—	—	—	—	—

EXPERIMENTAL*

N,N-bis(4-Methoxyphenyl)urea

A solution of 4,4′-dimethoxydiphenylamine (22.9 gm., 0.1 mole) in 175 ml. of glacial acetic acid was treated with 10 gm. of potassium cyanate each day for five days. A total of 50 gm. (0.62 mole) of cyanate was thus added. The brown slurry was left standing for an additional two days, and then was poured into a solution of 100 gm. of sodium hydroxide in 500 ml. of water, and the resulting suspension was refluxed gently for two hours. After the suspension was cooled the solid material was filtered off and washed with cold water until free of alkali. It was then leached 12 times with 500 ml. portions of boiling water. Adsorbent charcoal was used, and after rapid filtration of each boiling suspension, pink, hair-like crystals appeared in the filtrate. When cold, the solid material from the 12 filtrates was combined, washed, and dried at 105°C. Recrystallization from ethyl acetate (using charcoal) produced 9.5 gm. (36%) of fine, colorless needles, melting at 188°–189°. Anal. calc. for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92; N, 10.29%. Found: C, 66.02; H, 5.99; N, 9.79%.

Hydrolysis of N,N-bis(4-Methoxyphenyl)urea

A solution of N,N-bis(4-methoxyphenyl)urea (4.8 gm., 0.018 mole) in 100 ml. of saturated methanolic potassium hydroxide was refluxed vigorously for 36 hr.

**All melting points have been corrected against reliable standards. Combustion analyses were by Dr. Robert Dietrich, Gartenstrasse 14, Zürich, Switzerland.*

A white precipitate was filtered off and identified as potassium carbonate. As the filtrate cooled, large, lustrous plates of 4,4′-dimethoxydiphenylamine precipitated from solution. After crystallization from petroleum ether (65°–110°) the product weighed 1.6 gm. (40%) and melted at 103°. No depression of the melting point was observed when mixed with an authentic sample.

4,4′-Dimethoxydiphenylcyanamide

(*a*) *From N,N-bis(4-Methoxyphenyl)urea*

A solution of 7.5 gm. (0.027 mole) of N,N-bis(4-methoxyphenyl)urea in 125 ml. of pyridine was treated with 10 ml. (0.08 mole) of benzenesulphonyl chloride and heated for three hours on a boiling water bath. After cooling, the solution was poured into ice water with vigorous stirring. The solid material was filtered off, washed with cold water till acid-free, then dried in a desiccator. Crystallization from petroleum ether (65°–110°) yielded 5 gm. (73%) of pearly plates, melting at 96°–97°. Anal. calc. for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02%. Found: C, 70.66; H, 5.50; N, 11.09%.

(*b*) *From 4,4′-Dimethoxydiphenylamine*

4,4′-Dimethoxydiphenylamine (22.9 gm., 0.1 mole) was placed in a 30 oz. ginger ale bottle and cooled by immersion of the bottle in an ice water bath. Cyanogen chloride (5.7 ml., 0.1 mole) was added and the bottle was sealed with a standard metal cap. The reaction vessel was placed inside a steel-jacketed water bath and the bath was heated slowly to 60°C., maintained at that temperature for six hours, and then left standing overnight to cool. The black, tarry residue was leached three times with boiling petroleum ether (65°–110°) yielding a total of 5.5 gm. (43%) of pearly plates melting at 96°–97°. Admixture with an analytical sample of the material produced by method (*a*) did not depress the melting point.

4,4′-Dimethoxydiphenylcyanamide Hydrochloride

An ethereal solution of 1.0 gm. (0.0039 mole) of the cyanamide was dried over anhydrous sodium sulphate for three days. After the drying agent was filtered off, the solution was saturated with dry hydrogen chloride and left standing at room temperature for three days, during which time the hydrochloride crystallized from the solution. The theoretical yield of 1.1 gm. of the salt was collected by filtration and dried in a desiccator over potassium hydroxide pellets. The colorless crystals were observed to decompose with evolution of gas at 115°–117°, and when moistened with water, a sample of the material was immediately converted to the free cyanamide. The remainder of the material was left standing over calcium chloride for six days, and was found to have completely reverted to 4,4′-dimethoxydiphenylcyanamide(0.9 gm., melting at 96°–97°).

Diphenylcyanamide Hydrochloride

Treated in the manner described for the methoxy analogue, 1.0 gm. (0.005 mole) of diphenylcyanamide produced 0.9 gm. (78%) of hydrochloride salt, which decomposed sharply at 110°. On treatment with water, a sample of the material immediately hydrolyzed to diphenylcyanamide, melting at 73°. After standing over calcium chloride for seven days at room temperature, the remainder of the material had reverted to diphenylcyanamide.

4,4'-Dimethoxydiphenylamine Hydrochloride

A dry ether solution of 4,4'-dimethoxydiphenylamine (1.0 gm. in 50 ml. of ether) was treated with dry hydrogen chloride until precipitation occurred. The product, 1.0 gm. (94%) of long, colorless needles, was quite stable when kept in a dry atmosphere, but it immediately reverted to the free amine on being moistened with water. The material decomposed at 140°–150° with evolution of gas.

Hydrolysis of 4,4'-Dimethoxydiphenylcyanamide

(*a*) *In Aqueous Sodium Hydroxide*

A suspension of 5.5 gm. (0.02 mole) of 4,4'-dimethoxydiphenylcyanamide in 200 ml. of 10% aqueous sodium hydroxide was refluxed vigorously for eight hours, during which time the suspended material changed from an oil to a solid. The product was filtered off, washed free of alkali, dried, and crystallized from ethyl acetate, yielding 4.1 gm. (68%) of fine, colorless needles, melting at 188°–189°. Admixture with an authentic sample of N,N-bis(4-methoxyphenyl) urea did not depress the melting point.

(*b*) *In Alcoholic Potassium Hydroxide*

A solution of 4,4'-dimethoxydiphenylcyanamide (1.27 gm., 0.005 mole) in 34 ml. of saturated methanolic potassium hydroxide was refluxed vigorously for 72 hr. Large crystals precipitated when the solution was cooled to room temperature. After the product was filtered off and dried, it weighed 1.1 gm., and its crystallization from methanol yielded 1.0 gm. (87%) of 4,4'-dimethoxydiphenylamine, melting 102°–103°. The melting point was not depressed on admixture with an authentic sample. Potassium carbonate was identified in the reaction residue.

ACKNOWLEDGMENT

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FREE RADICAL MECHANISMS IN THE MERCURY PHOTOSENSITIZED REACTION OF HYDROGEN WITH ACETYLENE[1]

BY J. K. CASHION[2] AND D. J. LE ROY

ABSTRACT

The Hg($^3P_1$) photosensitized reaction of hydrogen with acetylene has been investigated with particular emphasis being placed on the identification of products and their dependence on hydrogen pressure. The results have been interpreted in terms of a number of elementary reactions in which vinyl and ethyl radicals play an important part.

INTRODUCTION

Although the reaction of H atoms with acetylene has been the subject of a number of investigations, no completely adequate mechanism has been proposed to explain the results obtained under different conditions. With the high H atom concentrations used in the discharge tube method acetylene appeared to act simply as a catalyst for atom recombination (3, 27, 8). However, Geib and Steacie (9) found that when D atoms were used the acetylene was rapidly exchanged. They suggested that the catalytic effect could be explained in terms of one of the following mechanisms:

$$\text{A}\ \begin{cases} H+C_2H_2=C_2H_3, & [1] \\ H+C_2H_3=C_2H_2+H_2, & [2] \end{cases}$$

$$\text{B}\ \begin{cases} H+C_2H_2=C_2H+H_2, & [3] \\ H+C_2H=C_2H_2. & [4] \end{cases}$$

The catalytic effect was confirmed by Tollefson and Le Roy (24) and by Dingle and Le Roy (6). These workers used the hot filament method for producing H atoms and total pressures of the order of 5 mm. The latter, using an improved technique, found the steric factor and activation energy of the rate controlling step, [1] or [3], to be 4×10^{-4} and 1.5 kcal. per mole, respectively.

Le Roy and Steacie (18) used the method of mercury photosensitization to produce H atoms in the presence of acetylene and found that appreciable quantities of ethane, ethylene, and butane were formed, as well as the polymer which had been observed by others.

The wide difference in the nature of the results obtained by the discharge tube and hot filament methods on the one hand and photosensitization on the other undoubtedly arises because of the very great differences in the relative concentrations of H atoms, H_2 molecules, and perhaps certain radicals. Any reasonable mechanism for the formation of the gaseous products of the photosensitization experiments would seem to require the existence of vinyl radicals, regardless of whether the primary reaction is [1] or [3].

In comparison with the saturated alkyl radicals, very little is known about the reactions of free vinyl radicals; the present reinvestigation of the mercury

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photosensitized hydrogenation of acetylene was undertaken with the view of obtaining more information about their behavior. A considerable amount of emphasis has been placed on the identification of products and their dependence on conditions, particularly on hydrogen pressure. In the light of the present and earlier results a number of free radical reactions have been proposed which will serve as bases for future investigations.

Most of the experiments were carried out at room temperature. A few results will be given for 300°C., and a few for experiments in which quenching was entirely by acetylene rather than by hydrogen.

EXPERIMENTAL

A. Apparatus

The reaction was studied in a circulating system which included the usual quartz cell illuminated by a low pressure mercury arc with rare gas carrier. For most of the experiments the system included a buffer volume and had a total volume of 2695 cm^3. The use of the buffer volume made it possible to obtain relatively large amounts of products without carrying the reaction too far in terms of the fraction of acetylene consumed. Pressure measurements were made with a differential mercury manometer having a multiplication ratio of approximately ten.

B. Reagents

Commercial electrolytic hydrogen was purified by passage over platinized asbestos at 500°C. and then through silica gel at the temperature of liquid air.

Tank acetylene was purified by a combination of the methods suggested by Klemenc (14) and Farkas and Melville (7), dried over Anhydrone, and subjected to a number of trap-to-trap distillations. Two impurities remained after this treatment. The first, ethane, was present to the extent of approximately 0.12%. This was reduced by low temperature fractionation (16) until it could no longer be detected by vapor pressure measurements or by its infrared spectrum; it is estimated that not more than about one part in 10^4 remained.

The second impurity in the acetylene was not identified, although its infrared spectrum was obtained by comparing 200 mm. of purified acetylene from a head-cut with an equal pressure from a tail-cut. The concentration of the impurity was somewhat greater in the tail-cut, suggesting that it contained three or four carbon atoms in the molecule. The spectrum showed that it was not propyne, propylene, any of the butenes, butadienes or butynes, vinyl acetylene, diacetylene, 2-methyl-1-butene-3-yne, isoprene or any of the impurities likely to be present in acetylene prepared from calcium carbide (7) such as acetone, formaldehyde, ammonia, or carbon dioxide. The C—H stretching frequency at 3.3 μ was relatively weak and displaced from that for paraffins and olefins, which suggested that it was an unsaturated cyclic hydrocarbon, possibly 1,3-cyclobutadiene. Unfortunately neither this material nor its spectrum were available for comparison, but the spectrum of the impurity showed some similarity to that of 1,3-cyclopentadiene, and the material was shown to react with the olefin reagent (22). More than 40 maxima in the spectrum were observed, but will not be reported here. It was shown during the experiments that the material was neither produced nor consumed during the reaction.

C. Products

The products included a nonvolatile polymer as well as ethylene, ethane, *n*-butane, 1,3-butadiene, butene-1, benzene, and a mixture of hydrocarbons principally of carbon number six; the latter included at least two conjugated dienes, of which one was 1,3-hexadiene. The gas which was not condensable in liquid air was tested for methane by diffusion through palladium (16); methane was only found in the high temperature experiments, and under the same conditions propane and propylene were also found.

At the end of an experiment the hydrogen was pumped off at the temperature of liquid air. The condensable gas was then fractionated by low temperature distillation (16). It was possible to separate the C_2 products into an ethylene-rich and an acetylene-rich fraction. The latter was shown by infrared analysis to contain no ethane or ethylene; the former was analyzed for acetylene (2) and ethylene (22) by chemical means, and the residue was taken to be ethane. The *n*-butane was readily identified by its vapor pressure, infrared spectrum, and its nonreactivity to the olefin reagent (22).

Although the 1,3-butadiene and the butene-1 were present in relatively small amounts they were easily identified by their spectra. The characteristic bands of the former were removed on treatment of the fraction with molten maleic anhydride.

Benzene constituted the major portion of all volatile products having vapor pressures less than that of butane. More than a dozen of its characteristic infrared absorption frequencies were observed. Low temperature distillation showed that the bulk of the remaining volatile products had vapor pressures of the order of that of benzene and therefore probably had carbon numbers of approximately six. The infrared bands characteristic of unsaturation, particularly in the 11 μ region, were very broad, which suggested a multiplicity of products. It was concluded that most of this fraction was made up of benzene and conjugated dienes, since after treatment with molten maleic anhydride absorption in the regions characteristic of unsaturation was reduced to a small fraction of its original value. This decrease was not the result of loss of product, for the optical densities of the benzene bands remained unchanged.

Comparison of the spectrum of the C_6 fraction with that of a mixture of *cis*- and *trans*-1,3-hexadiene showed that at least one of the isomers was present. The fraction also showed strong absorption in the region of the two strongest bands of 2,4-hexadiene (the reference sample contained unknown proportions of the three isomers), but the minima were too ill-defined to make the identification conclusive. The spectrum was also not inconsistent with the presence of 1,3,5-hexatriene, although positive identification was not possible.

No evidence was found for any cyclic unsaturated compound, other than benzene.

The major product, which accounted for approximately 70% of the acetylene consumed at room temperature, was the polymer. Only the polymer formed at room temperature in the presence of hydrogen was studied. Its empirical formula was calculated from the observed pressure drop, the pressure of acetylene consumed, and the composition and pressure of the gaseous products; the average value was $(C_2H_{3.46})_n$.

Some idea of the structure of the polymer was obtained from its infrared spectrum. Translucent particles of the material were removed from the cell by shaking with ether and were placed between two rock salt plates; although the loss of light was quite high, sufficient was transmitted to obtain 15 minima in the spectrum. By using the correlations of McMurray and Thornton (19) a rough estimate of the structure was obtained. From the relative intensities of the bands corresponding to terminal unsaturation (10.94 to 11.02 μ) and to trans unsaturation (10.26 to 10.37 μ) it was concluded that the polymer must contain considerably more of the latter. Also the intensity of the bands at 6.89 and 7.24 μ, which are characteristic of paraffinic structure, suggested a predominance of methylene linkages over unsaturated groups; this was substantiated by the considerable intensity of the C—H stretching band at 3.38 μ relative to the intensity of the unsaturation bands. The fact that terminal unsaturation was discernible at all was taken to mean that the ratio of internal to terminal carbon atoms cannot be excessive. It was concluded that if the average polymer unit contains one terminal double bond then it also contains about three internal double bonds and perhaps nine or more single bonds. The empirical formula given above is in agreement with this estimate. The molecular weight would then be of the order of 200. However, if units of this magnitude were cross linked to other similar units the molecular weight might be many times this. The highly insoluble nature of the polymer suggests that this may be the case.

QUANTITATIVE RESULTS AND DISCUSSION

A. The Primary Reaction

Geib and Steacie (9) suggested two possible primary steps for the reaction of atomic hydrogen with acetylene, reactions [1] and [3]. Since exchange is the predominant process at high values of $(H)/(H_2)$ it was not possible to decide which of these two reactions actually occurs. However, the following evidence obtained in the present investigation suggests that [1] is the primary reaction: (*a*) no gaseous products containing triple bonds could be detected; these would result from the combination of ethynyl radicals with themselves or with other radicals, (*b*) the spectrum of the polymer showed no bands in the region 2200 to 2260 cm.$^{-1}$ characteristic of asymmetric triple bonds, (*c*) by far the larger proportion of ethylene is formed by a process which is independent of hydrogen pressure (Fig. 2), which would not be the case if vinyl radicals, which are undoubtedly the precursors of ethylene, were formed by the reaction

$$C_2H + H_2 = C_2H_3. \quad [5]$$

It will therefore be assumed that [1] is the primary reaction.

B. The Reaction at Room Temperature

The results of a series of experiments for which constant initial pressures of acetylene and hydrogen were used but which were allowed to proceed for various periods of time are shown in Fig. 1. Because of the accumulation of polymer on the cell window the pressure drop, rather than the time, is taken to be a measure of the extent of reaction. It is seen that ethane increases linearly and butane at a continuously increasing rate, while ethylene reaches a maximum concentration at which, presumably, its rate of formation is equal to its rate of consumption. The last observation confirms the results of Le Roy and Steacie (18). The maximum is reached when there is still considerably more acetylene than ethylene in the system, which is in agreement with the fact that the rate of attack of H atoms on acetylene (6) is considerably slower than on ethylene (4, 20).

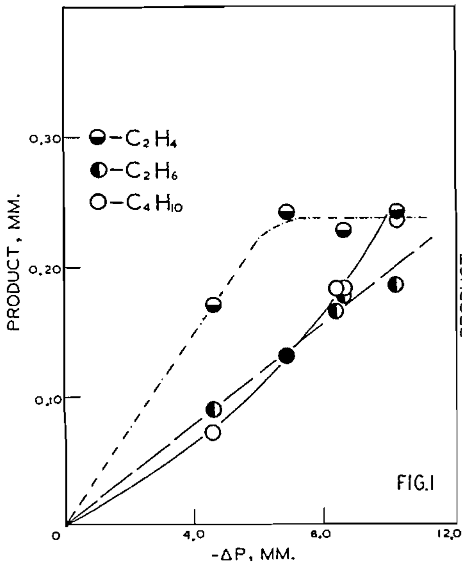


FIG.1

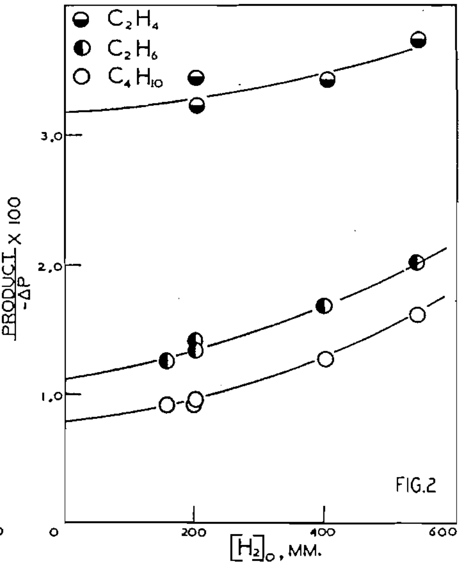


FIG.2

FIG. 1. Variation in products with extent of reaction. Room temperature. Initial conditions: $C_2H_2 = 10.0 \pm 0.05$ mm., $H_2 = 544 \pm 4$ mm. ●, overlapping points for C_2H_6 and C_4H_{10}.

FIG. 2. Effect of hydrogen pressure on the formation of products for a pressure decrease of 4.7 ± 0.2 mm. Room temperature. Initial acetylene pressure, 10.1 ± 0.04 mm.

A second series of experiments was made in which the initial pressure of acetylene (10 mm.) and the pressure drop (4.7 mm.) were kept constant while the hydrogen pressure was varied from 155 to 540 mm. It was found that the number of millimeters of acetylene consumed was a constant fraction 0.69 ± 0.02, of the pressure drop, regardless of the hydrogen pressure. However, the observed rate of pressure drop increased from 0.035 mm. per minute for an initial hydrogen pressure of 155 mm. to 0.050 mm. per minute for an initial hydrogen pressure of 540 mm.

Kahn and Le Roy (11) made a similar study of the effect of hydrogen pressure on the mercury photosensitized hydrogenation of ethylene. They found that the rate of formation of ethane, as well as the rate of pressure drop, was a linear function of the hydrogen pressure above 200°C. and showed that this was the result of two reactions, one of which was independent of hydrogen pressure (disproportionation of ethyl radicals), and one of which was directly proportional to the hydrogen pressure (the reaction $C_2H_5+H_2=C_2H_6+H$). Hoey and Le Roy (10) have observed a similar effect of hydrogen pressure in the mercury photosensitized hydrogenation of propylene.

Unfortunately, in the present experiments the deposition of polymer on the cell window made it impossible to study the effect of hydrogen pressure on rates of reaction at constant light intensity. We have therefore chosen to correlate the hydrogen pressure with the amounts of various products formed per millimeter of pressure drop, as shown in Fig. 2. Curves of a similar shape were obtained when the observed rates of formation of ethylene, ethane, and butane were plotted against the hydrogen pressure, although the slopes were, of course, somewhat steeper. It is believed, therefore, that each of these products arises by at least two processes, one of which is dependent on, and one of which is independent of hydrogen pressure.

It is difficult to see how products like ethane and butane could be formed without the intermediate formation of ethyl radicals. It will therefore be necessary to consider how ethyl radicals might be formed and how they, together with vinyl radicals, atomic and molecular hydrogen and acetylene, might give rise to the observed products and account for their dependence on hydrogen pressure.

Le Roy and Steacie (18) attributed ethylene formation to the reaction

$$C_2H_3+H_2=C_2H_4+H. \qquad [6]$$

This was consistent with their observation that hydrogenated products of acetylene could only be obtained when $(H_2)/(H)$ was large, i.e. under conditions in which [6] might compete favorably with [2]. However, it is evident from Fig. 2 that the predominant ethylene-forming reaction must be independent of hydrogen pressure and therefore cannot be [6].

Reaction [7] is probably of little importance in ethylene formation.

$$H+C_2H_3=C_2H_4. \qquad [7]$$

If it requires a third body its rate would increase with hydrogen pressure, but the observed increase can be accounted for more adequately in another way. If [7] occurred without a third body restriction it would compete with [2] just as effectively when $(H)/(H_2)$ is large as when it is small; this is contrary to experience, since exchange is the predominant process when $(H)/(H_2)$ is large.

It is suggested that the most likely reaction to account for the major portion of the ethylene formed is [8].

$$C_2H_3+C_2H_3=C_2H_4+C_2H_2. \qquad [8]$$

This reaction was postulated by Tickner and Le Roy (23) to account for the fact that equal amounts of ethylene and acetylene were formed when vinyl radicals, produced from vinyl iodide and sodium in the diffusion flame, were allowed to react in the absence of hydrogen. The rate of formation of ethylene by [8] would be independent of hydrogen pressure, and yet it would be negligibly small under the conditions used by Geib and Steacie (9) and Dingle and Le Roy (6). In both investigations the initial H atom concentration was comparable to or even greater than the acetylene concentration and hence very much greater than the vinyl radical concentration; under such conditions [2] would be much more important than [8].

Ethyl radicals are probably formed in at least two different ways:

$$C_2H_3+H_2=C_2H_5, \qquad [9]$$

$$H+C_2H_4=C_2H_5. \qquad [10]$$

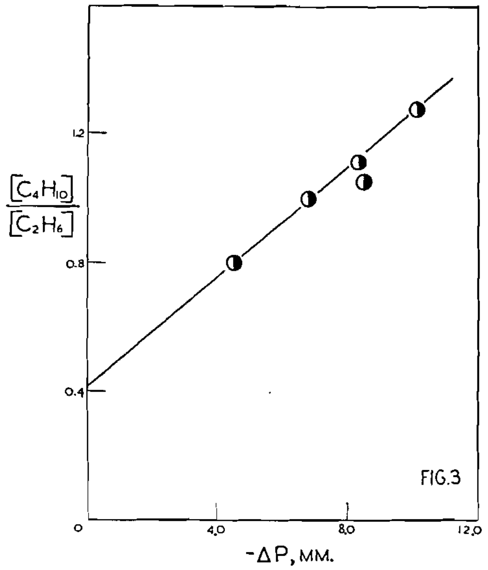
Because of the effect of hydrogen pressure on the rate of [9] the rate of formation of ethylene by [11],

$$C_2H_5+C_2H_5=C_2H_6+C_2H_4, \qquad [11]$$

should increase with hydrogen pressure. This, we believe accounts for the finite slope of the curve for ethylene in Fig. 2. Furthermore, as a result of the two methods of forming ethyl radicals, the production of ethane by [11] and of butane by [12],

$$C_2H_5+C_2H_5=C_4H_{10}, \qquad [12]$$

should then show a dependence on hydrogen pressure similar to that seen in Fig. 2. However, [11] and [12] cannot be the only reactions forming ethane and butane. If this were the case the ratio of butane to ethane would be a constant at fixed temperature.



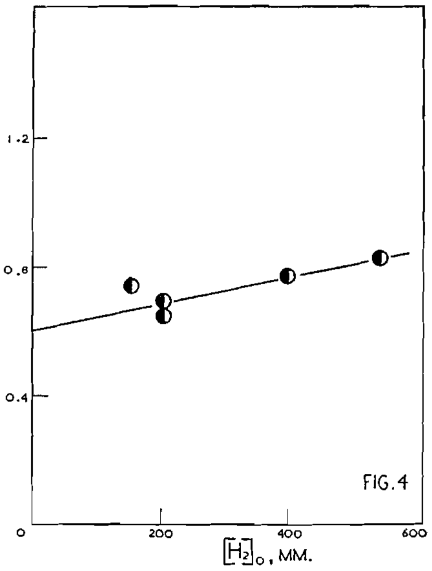


FIG. 3. Variation in butane/ethane ratio with extent of reaction. Room temperature. Initial conditions: $C_2H_2=10.0\pm0.05$ mm., $H_2=544\pm4$ mm.

FIG. 4. Effect of hydrogen pressure on butane/ethane ratio. The observed ratios, for a pressure drop of 4.7 ± 0.2 mm., have been corrected to a constant pressure drop of 4.8 mm. by using the data of Fig. 3. Room temperature. Initial acetylene pressure, 10.1 ± 0.04 mm.

Fig. 3 shows that the ratio of butane to ethane is strongly dependent on the extent of reaction, although Fig. 4 shows that for the same pressure drop it is not greatly influenced by the hydrogen pressure. Even the largest value of the ratio (*ca.* 1.3, Fig. 3) is considerably smaller than values taken from other work. Moore and Taylor (21) found it to be 6.0 in the mercury photosensitized hydrogenation of ethylene at room temperature. Although the primary emphasis of the work of Kahn and Le Roy (11) was in the occurrence of reaction [13] at higher temperatures,

$$C_2H_5+H_2=C_2H_6+H, \qquad [13]$$

their results show that the ratio of butane to ethane in the mercury photosensitized hydrogenation of ethylene at room temperature varied from 2.3 to 4.0, depending on the rate of light absorption.

Dr. K. O. Kutschke (15) has recently summarized the values of k_{12}/k_{11} obtained from the photolysis of diethyl mercury, diethyl ketone, azoethane, and propionaldehyde; here the results were based on the ratio of butane to ethylene. He states that, "the weight of evidence seems in favor of a value $k_d/k_c \sim 0.13$ to 0.14 (i.e. $k_{12}/k_{11} \sim 7.2$ to 7.8) provided the assumptions regarding mechanism are correct". On the other hand Kaplan (12) found a value of approximately 3.2 for butane/ethane in the mercury photosensitized hydrogenation of ethylene and values of 0.54 to 1.0 in the mercury photosensitized hydrogenation of acetylene. Kaplan's hydrogen contained HT, and he found the ratio of the molar activity of the butane to that of ethane to be 0.8 for the acetylene reaction, 1.6 for the ethylene reaction. These results must be accepted with reservation since secondary reactions of the products were probably involved because of prolonged irradiation. Nevertheless we are forced to conclude that reactions in addition to [11] and [12] are involved in the formation of ethane and/or butane. In particular, it seems necessary to postulate that ethane can be formed by some other process in addition to [11].

Trenner, Morikawa, and Taylor (25) and Berlie and Le Roy (1) found that the reaction

$$H+C_2H_5=C_2H_6 \qquad [14]$$

was relatively unimportant under the conditions used in the discharge tube and hot filament methods, respectively. This is undoubtedly because of the much greater rate of the reaction

$$H+C_2H_5=2\ CH_3. \qquad [15]$$

However Darwent and Steacie (5) have pointed out that the actual reactions are more likely to be

$$H+C_2H_5=C_2H_6^*, \qquad [16]$$

$$C_2H_6^*=2\ CH_3, \qquad [17]$$

$$C_2H_6^*+M=C_2H_6+M. \qquad [18]$$

Reaction [18] could be quite important at the high pressures obtaining in photosensitization experiments. Some support for this is given by the data of Fig. 3. Because of the influence of H atom concentration on [10] and [16] the rate of formation of ethane by the sequence [10], [16], [18] would be greatly reduced by a reduction in the steady state H atom concentration. Such a reduction will occur as the ethylene concentration increases and as the H atoms react with the polymer on the walls, as suggested below.

The fact that the butane/ethane ratio is so low compared to the values found in the mercury photosensitized hydrogenation of ethylene suggests the possibility of ethane formation by the reaction

$$C_2H_5+C_2H_3=C_2H_6+C_2H_2. \qquad [19]$$

This is analogous to reaction [8], which has been established with a considerable amount of certainty. The rate of formation of ethane by the sequence [1], [8], [10], [19] would be independent of the hydrogen pressure but strongly dependent on the H atom concentration, in agreement with the data of Fig. 3.

The butene-1 is undoubtedly formed by the combination reaction

$$C_2H_5+C_2H_3=C_4H_8, \qquad [20]$$

and the 1,3-butadiene by

$$C_2H_3+C_2H_3=C_4H_6. \qquad [21]$$

Tickner and Le Roy (23) showed that the latter reaction occurred in diffusion flame experiments with sodium vapor and vinyl iodide.

If one considers the reactants acetylene, ethylene, and vinyl and ethyl radicals, then four different C_4 radicals could be formed by radical addition to the unsaturated compounds:

$$CH_3—CH_2—CH_2—CH_2—,$$
$$CH_3—CH_2—CH{=}CH—,$$
$$CH_2{=}CH—CH_2—CH_2—,$$
$$CH_2{=}CH—CH{=}CH—.$$

Six different straight chain C_6 compounds could then be formed by the combination of vinyl or ethyl radicals with these C_4 radicals: *n*-hexane, 1-hexene, 3-hexene, 1,3-hexadiene, 1,5-hexadiene, and 1,3,5-hexatriene. Of these, 1,3-hexadiene is certainly present in the products and there is good reason to believe that 1,3,5-hexatriene is formed. It was mentioned under Products that the C_6 fraction contained unsaturated compounds which were not removed by treatment with maleic anhydride; these were undoubtedly the hexenes. Because of its much weaker absorption, *n*-hexane could not be detected even if it were present. It seems reasonable to assume, then, that the straight chain C_6 compounds are formed by ethyl or vinyl radical addition to acetylene or ethylene followed by combination of ethyl or vinyl radicals with these C_4 radicals.

Disproportionation of the C_4 radicals with ethyl or vinyl radicals could, conceivably, yield *n*-butane, 1-butene, and 1,3-butadiene, as well as ethyl acetylene, cyclobutane, cyclobutene, cyclobutadiene, and vinyl acetylene. No evidence for the last five compounds was obtained, although, with the exception of cyclobutadiene, their characteristic absorption bands are well known and quite strong. From a probability point of view it is likely that most of the *n*-butane, 1-butene, and 1,3-butadiene are formed by [12], [20], and [21] rather than by disproportionation.

Benzene was the only cyclic hydrocarbon which could be detected, and it accounted for a large proportion of the total gaseous products, as seen

TABLE I[a]

Run	T.°C.	H_2[b]	C_2H_2[b]	$-\Delta p$	$-\Delta H_2$	$-\Delta C_2H_2$	CH_4	C_2H_4	C_2H_6
1	35	484	20.3	20.6	10.0	12.4	nil	0.7	0.2
2	300	396	22.5	21.0	11.6	14.8	1.0	2.3	0.8
7	35	540	10.07	6.75	3.1	4.40	nil	0.24	0.131
17	35	nil	11.87	3.98	−0.06	4.50	nil	0.12	0.008

Run	C_3H_6	C_3H_8	C_4H_6	C_4H_8	C_4H_{10}	C_6H_6	Other[c]	Pol.[d]
1	nil	nil	0.02	0.02	0.3	0.45	0.10	9.3
2	0.1	0.1	0.08	0.04	0.5	0.45	0.10	8.3
7	nil	nil	0.005	0.008	0.13	0.16	0.04	3.2
17	nil	nil	0.001	nil	0.003	0.21	0.01	3.7

[a] *The concentrations are in mm. pressure corrected to 25°C.*
[b] *Initial.*
[c] *C_6 (and higher) compounds other than benzene.*
[d] *Mm. of C_2H_2 which went to form polymer.*

in Table I. It is probably formed by the successive addition of acetylene to a vinyl radical to form the 1,3,5-hexadienyl radical, followed by the elimination of a hydrogen atom and cyclization.

The structure of the polymer has been discussed under Products. Cross linking is probably initiated by the addition of H atoms or free radicals to the highly unsaturated linear polymer; such reactions would occur most readily at the window where, in photosensitization experiments, the concentration of atoms and radicals is greatest.

C. The Reaction at 300°C.

Le Roy and Steacie (18) found that at 300°C. the reaction proceeded several times as rapidly as at 25°C., although an accurate temperature coefficient could not be obtained because of uncertainties in the light absorption. The same difficulty arose in the present work and the experiment at 300°C. was done solely to observe any change in the nature of the products.

As seen from Table I, there is a marked increase in the proportion of ethylene formed. In view of the results of Tickner and Le Roy (23) this can be accounted for by reaction [6]. The increase in ethane production is probably the result of [13]. Kahn and Le Roy (11) found this reaction to be unimportant in the mercury photosensitized hydrogenation of ethylene below approximately 200°C., but of increasing importance above that temperature. Wijnen and Steacie (29) have estimated E_{13} to be 11.5 ± 1 kcal. per mole.

A significant feature of the results for 300°C. is the formation of methane, propane, and propylene. The first step in their formation is probably the atomic cracking of ethyl radicals by [16] and [17] (*vide* Berlie and Le Roy (1)). At this temperature methane would most likely be formed by the reaction of methyl radicals with hydrogen (28),

$$CH_3 + H_2 = CH_4 + H, \tag{22}$$

while propylene and propane would be formed by their combination with vinyl and ethyl radicals. Vanhaeren and Jungers (26) concluded that large amounts of methane were formed at room temperature, although they did not actually separate methane from the other products. If the experiments were prolonged sufficiently to remove all unsaturated gases it is likely that it would be formed at room temperature, but this was not the case in the present experiments.

D. The Reaction in the Absence of Hydrogen

The data for experiment 17 in Table I confirm the earlier work of Le Roy and Steacie (17) who found the reaction to be inhibited by nitric oxide and concluded that it took place by a free radical mechanism. The formation of ethane, ethylene, and benzene is in agreement with the findings of Kemula and Mrazek (13).

Le Roy and Steacie postulated the primary reactions,

$$\begin{aligned} Hg(^3P_1)+C_2H_2 &= C_2H+H+Hg(^1S_0), && [23a]\\ &= C_2H+HgH, && [23b]\\ &= HgC_2H+H. && [23c] \end{aligned}$$

It is now generally conceded that HgH is not formed in the quenching of $Hg(^3P_1)$. Their observation that mercury is consumed in the reaction is evidence in favor of (23*c*). In any event the system will contain H atoms and hence vinyl radicals will be formed by [1]. The hydrogen that is produced is undoubtedly formed by [2]. Le Roy and Steacie (17) found the quantum yield of acetylene consumption to be approximately 4.5 at 40 mm. pressure and their data indicate that it would be approximately 4 at 12 mm. Thus the consumption of 4.5 mm. of acetylene in experiment 17 must have involved the production of about 1.1 mm. of atomic hydrogen. Only 0.12 mm. of this appeared as molecular hydrogen. The rest could not have undergone reaction [4] or there would have been no polymerization; it must therefore have been consumed in forming vinyl radicals and in the other H atom consuming reactions mentioned in section *B*. It is not surprising, then, that the nature of the products is similar to that for the reaction in the presence of hydrogen.

A comparison of the results of experiments 7 and 17 shows that in the latter ethane and butane production is reduced very much more than that of ethylene. The formation of ethyl radicals by [9] will be eliminated and hence the rate of production of butane and ethane by [11] and [12] will be reduced. The rate of formation of ethane by [19] will not be reduced to the same extent because its rate depends only on the first power of the ethyl radical concentration. One would expect the ratio of butane to ethane to be somewhat smaller than the intercept of Fig. 4, and this is the case. The fact that the ratio of butane to ethylene is very much less in experiment 17 than in experiment 7 suggests that ethyl radicals may be consumed in reaction [24]

$$C_2H_5+C_2H = C_2H_4+C_2H_2. \qquad [24]$$

This is analogous to [8], which accounts for the major proportion of the ethylene produced in the experiments with hydrogen at room temperature. It might also account for the absence of gaseous products containing triple bonds in experiment 17.

ACKNOWLEDGMENT

The authors would like to express their appreciation to the National Research Council of Canada for supporting this research, and to Prof. M. R. Fenske for giving us samples of 1,3- and 2,4-hexadiene.

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NOTE

THE ROLE OF BETAINE IN PLANT METHYLATIONS

By M. Sribney[1] and S. Kirkwood

Recent work on the biogenesis of plant substances has shown that methylation processes in the plant are very similar to the well studied methylations which occur in animal tissues. It has been shown that the N-methyl groups of the alkaloids hordenine (10), nicotine (1), ricinine (6), and protopine (15) have the same origin as the labile methyl groups in animal metabolism. The O-methyl groups of the alkaloid ricine (6), of barley lignin (2), and the methylenedioxy groups of the alkaloid protopine (15) have been shown to have a similar origin.

One important difference between animal and plant methylations has been noted. Although choline serves as an excellent methyl donor in the animal (7), it does not function as a methyl donor in barley, the castor bean, or in mature *Dicentra* hybrids (13, 6, 15). It does serve as a fair source of methyl in certain mycological methylations (4) and is an efficient donor in *Nicotiana rustica* (3). Thus there is a great variation in the efficiency of choline as a labile methyl source in the plant kingdom. In the case of barley there can be no doubt that the failure of choline to serve as a methyl donor has metabolic significance, since it has been shown that the plants absorb and translocate administered choline (13).

It has been shown in animals that choline must first be oxidized to betaine before it can transfer its methyls (14). A possible explanation for the failure of choline to serve as a source of labile methyl in barley could be that this plant lacks the enzymic apparatus necessary to convert choline to betaine. The choline oxidase system is responsible for this transformation and is found in many animal tissues. Little is known about the occurrence of choline oxidase in plant tissues, although it has been reported to occur in the roots of the sugar beet (5). An investigation of the ability of betaine methyl to serve as a source of labile methyl in the barley plant should shed considerable light on this question. If betaine contributes labile methyl, then it is very probable indeed that the failure of choline to do likewise is due to lack of an effective choline oxidase system.

Betaine served as a source of labile methyl in the barley plant, as judged by the transfer of its methyls to the alkaloids N-methyltyramine and hordenine (Table I). It failed to serve as a source of labile methyl in the young castor bean. A sample of choline, isolated from barley plants to which methyl-labelled betaine had been fed, proved to bear label only in its methyl groups. This demonstrates conclusively that these plants can synthesize choline methyl from betaine methyl. Whether this is done by transmethylation or by direct reduc-

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TABLE I

SPECIFIC ACTIVITIES

Betaine administered		Alkaloid isolated	Specific activity, counts per minute per millimole		
Wt., mgm.	Total activity, c.p.m.		Original substance	Trimethyl-amine	Homo-anisaldehyde oxime
42	1.2×10^7	Ricinine	0		
60	1.7×10^7	N-methyl-tyramine	4.5×10^3	4.8×10^3	0
		Hordenine	9.4×10^3	8.5×10^3	0
		Choline	1.9×10^4	1.8×10^4	

tion of betaine to choline cannot be determined from these experiments. The comparatively low activity in the isolated choline is perhaps more consistent with a transmethylation than with a direct reduction. In the animal, betaine methyl goes to choline methyl by transmethylation, rather than by direct reduction (8). It should be noted that the barley plants used in these experiments were 11-day-old seedlings. Barley plants may well develop a choline oxidase system as they mature.

EXPERIMENTAL

C^{14}-*Methyl Labelled Betaine*

This compound was prepared by the method of Ferger and du Vigneaud (9). The labelled substance was isolated and purified through the reineckate.

Growth of Plant Material

The barley used in these experiments was the Charlottetown No. 80 strain and the castor beans were a commercial sample of *Ricinus communis*. These materials were grown and harvested as described previously (10, 6).

Isolation and Degradation of Labelled Materials

The alkaloids M-methyltyramine and hordenine were isolated and purified by the method of Leete *et al.* (11). Ricinine was isolated and purified as described by Dubeck and Kirkwood (6). Choline was isolated from the barley plants as described previously (10). To ensure that the choline sample was not contaminated with betaine, it was repeatedly precipitated from alcohol as the chloroplatinate and from aqueous alkali as the reineckate. Betaine chloroplatinate is soluble in 95% ethyl alcohol and betaine reineckate is soluble in aqueous alkali.

The hordenine and N-methyltyramine were degraded according to the method of Leete *et al.* (11) and the choline was degraded by the method of Lintzel and Monasterio (12).

All radioactivity measurements were made with a "Q"-gas counter and appropriate corrections were applied. Adequate care was taken to purify all compounds to constant specific activity.

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ISOTOPE EFFECTS IN THE COMBUSTION OF CARBON MONOXIDE[1]

BY R. W. ATTREE, F. BROWN, G. E. DUNN,[2] AND M. LOUNSBURY

ABSTRACT

The relative rates of reaction of $C^{12}O$, $C^{13}O$, and $C^{14}O$ with oxygen have been measured. When the oxidation proceeds mainly on the walls of the containing vessel the relative rates for $C^{13}O$ and for $C^{14}O$ compared to $C^{12}O$ are respectively 0.985 and 0.959. When reaction proceeds mainly in the gas phase there is no isotope effect within experimental error.

INTRODUCTION

In this investigation the relative rates of combustion of $C^{12}O$, $C^{13}O$, and $C^{14}O$ in oxygen have been studied. The object was to see whether a study of isotope effects could contribute to the understanding of the mechanism of the reaction and more generally to explore the possibility of using isotope effects to investigate gas phase reactions.

The reaction between carbon monoxide and oxygen has been thoroughly investigated (e.g. (6) and references to be found in (6)) and its main features are well known. It is a chain reaction which shows upper and lower pressure limits of explosion and is generally believed to proceed either on the wall of the containing vessel ('slow' reaction) or homogeneously (fast or explosive reaction) according to conditions.

The initiation of explosion by heating the mixed gases in a vessel requires a fairly high temperature, between 500 and 700° C., while the 'slow' reaction taking place on the walls proceeds quite rapidly at temperatures just below the explosion temperature. Mixtures of suitable proportion can be readily exploded by an electric spark. Many other variations in conditions are possible; e.g. admitting a cold mixture to a hot vessel; or mixing the two preheated gases. In general, the chief effect of varying the conditions is to change the relative importance of the heterogeneous and homogeneous reactions.

As an initial step in this investigation the principal features of previous work were repeated in order to test the apparatus and to establish the conditions for thermally induced explosion, slow reaction, spark induced explosion, etc.

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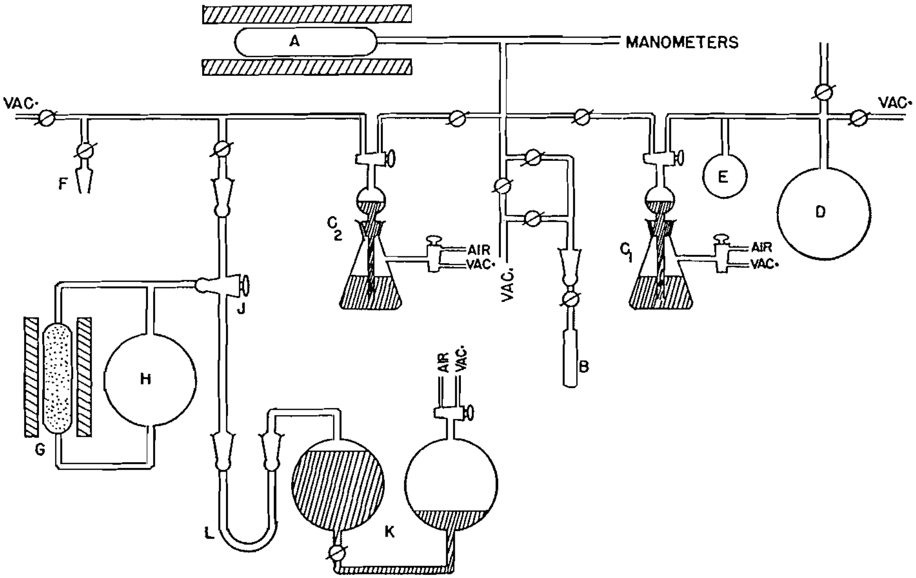
Good agreement was found on points where direct comparison was possible and it is not proposed to describe this part of the work in detail.

The method employed for measuring the isotope effects can be summarized as follows. A supply of carbon monoxide was prepared by complete reduction of carbon dioxide with hot zinc (1). Various types of combustions were carried out using a deficiency of oxygen so that the monoxide was only partially oxidized (usually about 30%). The carbon isotopic compositions of the dioxide samples so produced were then compared mass spectrometrically with that of the initial dioxide from which the monoxide was prepared. Thus the isotopic composition of the monoxide at the start of each reaction and the isotopic composition of the dioxide produced by its partial oxidation were known. By simple pressure measurements the amount of monoxide which had reacted was determined. The relative rates of combustion of $C^{12}O$, $C^{13}O$ (and $C^{14}O$ if present) can be obtained from these data. In the first experiments natural carbon dioxide was the starting material so that only the isotope effect for C^{13} compared with C^{12} was studied. Later the experiments were repeated starting with dioxide containing about one per cent C^{14} so that the effects for both C^{13} and C^{14} could be studied. Details of the experimental methods are given below.

EXPERIMENTAL

The main features of the apparatus are shown in Fig. 1. The silica reaction vessel *A* with volume about 100 ml. was heated by an electric furnace. Its temperature was measured by a thermocouple placed inside the furnace tube against the outer wall of the reaction vessel. Samples of gas from the reaction vessel could be collected in a sampling tube *B*. The pressure in the furnace was measured by two manometers, the first being a simple mercury barometer type and the other a U-tube filled with Kel-F polymer grade 10. In the latter



—FIGURE 1—

case both arms of the U-tube could be opened to the system and then with one arm closed the manometer would indicate any pressure changes which occurred subsequently. The fluorocarbon polymer Kel-F has the advantages of high density and low vapor pressure but its high viscosity means that readings take rather a long time. The manometer, connections, stopcocks, etc. associated with the reaction vessel (*A*) and outside the furnace were made to have the smallest practicable volume which was small compared to the volume of the vessel. A conventional vacuum system was used consisting of liquid nitrogen cold trap, low pressure gauges, mercury diffusion pump, and rotary fore-pump. This system gave a pressure of less than 10^{-4} mm. mercury.

The oxygen was obtained from a cylinder. It was stored in a large bulb *D*, dried by phosphorus pentoxide in *E*, and transferred to the reaction vessel by a simple pump C_1.

The carbon monoxide was prepared by reduction of carbon dioxide with hot zinc (1, 3). The dioxide was generated by heating a dry mixture of sodium carbonate and lead chloride (7) in a tube placed at *F*. A sample of this gas was isolated and retained for mass spectrometry. The remainder was allowed to circulate by convection through the tube *G* which contained glass beads covered with zinc dust and heated to 400°C. by an electric furnace. To test for completion of reduction the contents of *G* and *H* could be drawn repeatedly through a liquid nitrogen cold trap *L* by raising and lowering the mercury in *K*. Reduction was usually allowed to continue overnight by which time no visible amount of dioxide could be condensed in *L*. Nevertheless the condensable contents of *L*, if any, were rejected; this ensured that the monoxide was free from dioxide and from moisture. The monoxide was stored in *G* and *H* and transferred to the reaction vessel by the pump C_2.

The procedure for making a run was briefly as follows. Measured pressures of the two gases were introduced into *A* at room temperature. The furnace was then heated at the desired rate and the temperature and pressure were noted at frequent intervals. A graph of pressure against temperature then showed initially the ordinary gas expansion but as reaction commenced the pressure dropped more or less rapidly according to conditions. Explosions in the reaction vessel were detected by a sharp 'kick' of the manometer followed by an instantaneous drop in pressure. After the reaction was completed the system was allowed to cool to room temperature and the pressure measured. The over-all decrease in pressure gave the measure of the extent of the reaction. In most runs the initial pressures (cold) of monoxide and oxygen would be approximately 10 cm. mercury and 2 cm. mercury respectively. A large proportion of the oxygen would be burned (see Table I for details). When pressure measurements were complete the carbon dioxide produced by the reaction was collected in the sampling bulb at *B*.

The condition which apparently produced the slow or heterogeneous reaction was to heat the reactants at about 550°C. At this temperature the reaction as followed by the pressure–temperature graph proceeded fairly rapidly and was complete, in so far as the proportions of gases allowed, in about an hour.

The condition required to produce an explosion (by heat) was to heat the mixture as rapidly as possible. At about 600°C. which was reached in about eight minutes in this apparatus, the explosion occurred and the furnace was immediately shut off. It is obvious that a certain amount of slow reaction must occur before the explosion takes place and it was observed that if the mixture was heated slowly then the initial slow reaction would proceed so far that no explosion was possible even at temperatures above that normally required to cause explosion.

In a few experiments the carbon monoxide, about 10 cm. mercury pressure, was heated at 700°C. and then a small quantity of oxygen admitted and the furnace shut off. The amount of oxygen admitted was determined by previous calibration experiments.

Experiments on sparking of mixtures were made by using a glass reaction vessel with tungsten wire electrodes across which a spark could be made by applying a high voltage coil. This vessel was filled with gas mixture by attachment to the main apparatus but the pressure of the gas before and after sparking was measured in an auxiliary system equipped with mercury manometer and a simple arrangement for transferring the carbon dioxide produced by the explosion to a sampling bulb.

The carbon dioxide samples so obtained were transferred to another vacuum line where the following operations could be performed by conventional techniques. In the first place the samples were equilibrated with water by being shaken overnight with a few milliliters of water in a sealed bulb. This is to ensure that all carbon dioxide samples have the same O^{16}, O^{17}, O^{18} content; a special stock of water was retained for this purpose. Secondly the samples were dried over magnesium perchlorate. Finally they were transferred to sample tubes designed to fit onto the mass-spectrometer sampling system.

MASS SPECTROMETRY

The carbon dioxide samples were analyzed with a 6-in. radius, 90° deflection mass spectrometer similar to one described by Graham, Harkness, and Thode (5). Mass spectra were obtained by magnetic scanning and were recorded with a Leeds and Northrup type G Speedomax. For each sample, 20 to 30 spectrograms were recorded by scanning alternately from mass 44 to 46 and then in the reverse direction from mass 46 to 44. The resolution of the mass spectrometer was such that the ion peaks were completely resolved. Possible systematic errors arising from mass discrimination and nonlinearity of the amplifying and recording systems were negligible.

Because isotopic abundance ratios, as determined by the mass spectrometer, show small variations from day to day, each sample of carbon dioxide prepared by the combustion of the monoxide was compared mass spectrometrically with a standard sample of carbon dioxide. For the inactive samples the standard was prepared from normal sodium carbonate, and for the active samples from sodium carbonate containing about one per cent C^{14}, as described above. The peak height ratios (45)/(44) and (46)/(44) obtained for each sample were normalized by comparison of the corresponding ratios of the accompanying standard with the average values of these ratios determined from all measurements on the standard.

From the normalized values of the peak height ratios, the C^{13}/C^{12} and C^{14}/C^{12} abundance ratios may be calculated as follows:

$$\frac{(45)}{(44)} = \frac{C^{13}O^{16}O^{16} + C^{12}O^{16}O^{17}}{C^{12}O^{16}O^{16}} = \frac{C^{13}}{C^{12}} + \frac{O^{16}O^{17}}{O^{16}O^{16}}.$$

Therefore,

$$\frac{C^{13}}{C^{12}} = \frac{(45)}{(44)} - \frac{O^{16}O^{17}}{O^{16}O^{16}}. \qquad [1]$$

Similarly

$$\frac{(46)}{(44)} = \frac{C^{14}O^{16}O^{16} + C^{13}O^{16}O^{17} + C^{12}O^{16}O^{18} + C^{12}O^{17}O^{17}}{C^{12}O^{16}O^{16}}$$

$$= \frac{C^{14}}{C^{12}} + \frac{C^{13}}{C^{12}}\cdot\frac{O^{16}O^{17}}{O^{16}O^{16}} + \frac{O^{16}O^{18}}{O^{16}O^{16}} + \frac{O^{17}O^{17}}{O^{16}O^{16}}.$$

Therefore

$$\frac{C^{14}}{C^{12}} = \frac{(46)}{(44)} - \frac{C^{13}}{C^{12}}\cdot\frac{O^{16}O^{17}}{O^{16}O^{16}} - \frac{O^{16}O^{18}}{O^{16}O^{16}} - \frac{O^{17}O^{17}}{O^{16}O^{16}}. \qquad [2]$$

Because all of the carbon dioxide samples and standards were equilibrated with water taken from the same source (a stock of distilled Ottawa River water), their oxygen isotopic ratios were constant. For carbon dioxide gas in equilibrium with Ottawa River water, the ratios ($O^{16}O^{17}/O^{16}O^{16}$), ($O^{16}O^{18}/O^{16}O^{16}$), and ($O^{17}O^{17}/O^{16}O^{16}$) were determined to be 0.000802, 0.004250, and 0.00000016 respectively. The latter ratio is so small that it was neglected in calculating the C^{14}/C^{12} ratio. Equations [1] and [2] may then be expressed as follows:

$$\frac{C^{13}}{C^{12}} = \frac{(45)}{(44)} - 0.000802, \qquad [3]$$

and

$$\frac{C^{14}}{C^{12}} = \frac{(46)}{(44)} - 0.000802\frac{C^{13}}{C^{12}} - 0.004250. \qquad [4]$$

In order to be able to measure the isotope effect by the present method it is necessary that no significant exchange take place between the carbon dioxide produced and the unreacted monoxide under the conditions of the reactions. This was studied in the following manner. The furnace was filled with radioactive carbon monoxide (5.70 cm. mercury) and ordinary inactive carbon dioxide (4.20 cm. mercury). The mixture was heated at 610–630°C. for an hour and then cooled. The dioxide was removed and transferred to a bulb containing 1.5 ml. $N/5$ sodium hydroxide solution. The sodium carbonate solution thus obtained was diluted to 10 ml. and aliquots were counted in a methane filled proportional counter of known efficiency (52%). Knowing the C^{14} content of the initial monoxide and the specific activity of the final dioxide it was calculated that not more than one per cent exchange had occurred. This is not sufficient to cause any trouble in measuring the isotope effect.

RESULTS

Reaction Data

The data for the various runs are summarized in Table I. The table shows the initial pressure of carbon monoxide and oxygen, the temperature conditions, the percentage of the monoxide burned, and whether or not an explosion occurred. It is assumed that for run No. 14 where oxygen was admitted to carbon monoxide preheated at 700° C. an explosion would have occurred; the characteristic 'kick' of the manometer was not observable owing to the abrupt change in pressure caused by admitting the oxygen.

TABLE I
SUMMARY OF REACTION DATA

	Cm. mercury			
Run No.	p, CO	p, O_2	Conditions	CO reacted (%)
Heterogeneous reaction				
12	11.37	2.30	Heat to 700° at ~20°/min.; maintain five minutes; cool	31.3 ± 1.0
13	10.25	2.10	Heat to 600° at ~20°/min.; maintain one hour; cool	36.5 ± 1.0
18	10.40	2.00	Heat to 550° at ~20°/min.; maintain one hour; cool	34.5 ± 1.0
19	10.50	1.85	Heat to 560° at ~50°/min.; maintain one hour; cool	24.7 ± 1.0
Homogeneous (explosive) reaction				
14	19.95	3.95	Admit oxygen to monoxide preheated at 700°; cool	39.7 ± 4.0
15	20.50	4.00	Sparked	61.5
16	21.95	2.15	Sparked	31.0 ± 1.0
17	20.30	3.05	Sparked	28.1 ± 1.0
20	10.30	2.05	Heat to 700° at ~70°/min.; cool (explosion occurred at 580°)	27.0 ± 1.0
22	10.50	1.90	Heat to 630° at ~100°/min.; cool (explosion occurred at 575°)	32.9 ± 1.0

Notes: (*1*) *In run 15 the percentage reaction was uncertain; this is of no consequence since there was no isotope effect for this run.*
(*2*) *If an explosion was observed the reaction is classified as "homogeneous". Where no explosion occurred the reaction is classified as "heterogeneous".*

Mass Spectrometer Analyses

Table II gives a summary of the mass spectrometer data. *Because the standard was a sample of the carbon dioxide from which the monoxide was prepared, it had the same C^{12}:C^{13}:C^{14} content as the monoxide used in all reactions.* The standard was mass-analyzed each time a sample was analyzed. The average values of the (45)/(44) and (46)/(44) ratios obtained from all the measurements on the standard were 0.01200 and 0.01560 respectively, corresponding to C^{13}/C^{12} and C^{14}/C^{12} ratios of 0.01120 and 0.01134 respectively. Over a period of three months, the day-to-day variations in the standard ratios were small, the maximum deviation from the mean being 0.5%. The average values of the standard ratios were used in the normalization of the sample peak height ratios. Table II shows the *normalized* values of peak height ratios, (45)/(44) and (46)/(44), for each of the samples, and also the corresponding values of the isotopic abundance ratios, C^{13}/C^{12} and C^{14}/C^{12}, calculated as explained in the experimental section above.

TABLE II
SUMMARY OF MASS SPECTROMETER DATA (NORMALIZED)

Average values for the standard used in normalizing sample values:*

$$\frac{(45)}{(44)} = 0.01200; \quad \frac{C^{13}}{C^{12}} = 0.01120$$

$$\frac{(46)}{(44)} = 0.01560; \quad \frac{C^{14}}{C^{12}} = 0.01134$$

Run	$\frac{(45)}{(44)}$	$\frac{(46)}{(44)}$	$\frac{C^{13}}{C^{12}}$	$\frac{C^{14}}{C^{12}}$
Heterogeneous reaction				
12	.01186		.01106	
13	.01186		.01106	
18	.01185	.01524	.01105	.01098
19	.01185	.01517	.01105	.01091
Homogeneous (explosive) reaction				
14	.01199		.01119	
15	.01199		.01119	
16	.01202	.01559	.01122	.01133
17	.01198	.01555	.01118	.01129
20	.01203	.01555	.01123	.01129
22	.01204	.01558	.01124	.01132

**The C^{13} ratios for the natural monoxide (runs 12–15) and the monoxide containing C^{14} (runs 16–22) were almost identical, and thus both sets of results have been normalized to the same value.*

Ratio of Rate Constants

Because of the low concentration of $C^{13}O$ (or $C^{14}O$) in the monoxide the reaction will be first order in respect to these species (even though it may not be first order in respect to carbon monoxide). The ratios of the rates of reactions k^{13}/k^{12} and k^{14}/k^{12} were calculated on this assumption and are shown in Table III. The errors quoted are based on the standard deviation of the mass spectrograms. Errors in measuring the extents of the reactions are not important.

TABLE III
RATIOS OF RATE CONSTANTS

Run	k^{13}/k^{12}	k^{14}/k^{12}
Heterogeneous reaction		
12	$0.985_0 \pm 0.002$	
13	$0.984_2 \pm 0.002$	
18	$0.983_6 \pm 0.004$	$0.961_0 \pm 0.006$
19	$0.984_6 \pm 0.002$	$0.956_2 \pm 0.004$
Homogeneous (explosive) reaction		
14	$0.998_4 \pm 0.003$	
15	$0.998_4 \pm 0.002$	
16	$1.002_2 \pm 0.003$	$0.998_4 \pm 0.003$
17	$0.998_0 \pm 0.003$	$0.995_0 \pm 0.005$
20	$1.002_5 \pm 0.004$	$0.994_3 \pm 0.005$
22	$1.004_5 \pm 0.004$	$0.994_4 \pm 0.006$

DISCUSSION OF RESULTS

The outstanding feature of the results is that the homogeneous "explosive" reactions (Runs 14, 15, 16, 17, 20, 22) show no isotope effect whereas the heterogeneous "slow" reactions produce a small but distinct effect, the heavier molecules reacting more slowly. The distinction between the two mechanisms is thus nicely emphasized.

Heterogeneous Reactions

The four observed values for k^{13}/k^{12} are 0.985, 0.984, 0.984, and 0.985. The two observed values of k^{14}/k^{12} are 0.961 and 0.956. Since these apply to heterogeneous reactions it is an obvious step to interpret these ratios in terms of the number of collisions made by $C^{12}O$, $C^{13}O$, and $C^{14}O$ molecules with the walls of the vessel. It is most interesting to carry out this interpretation in terms of Eyring's theory of rate processes because this approach is the one which has been used with some success in the interpretation of isotope effects in general.

According to Eyring (4) the activated complex for an adsorption process in which the adsorbed layer is mobile may be considered as the gas molecule just before it strikes the surface. In this case the vibrational and rotational partition functions of the reactant and of the activated complex are the same. On the other hand the reactant has three degrees of translational motion whilst the activated complex has only two so that the ratio of the partition functions of the complex to those of the reactant reduces to

$$\frac{2\pi m\,k\,T/h^2}{(2\pi m\,k\,T)^{3/2}/h^3} = \frac{h}{(2\pi m\,k\,T)^{1/2}}\,.$$

The rate of adsorption, v, thus becomes

$$v = C_g\frac{kT}{h}\cdot\frac{h}{(2\pi\,m\,k\,T)^{\frac{1}{2}}}\,e^{-\epsilon/kT}$$

where C_g is the concentration of reactant in the gas, ϵ is the zero point energy of the molecule, and the other symbols have their usual meaning.

The ratio of the rates of adsorption for two isotopically distinguished molecules m_1 and m_2 will be

$$\frac{v_1}{v_2} = \left(\frac{m_2}{m_1}\right)^{\frac{1}{2}} e^{-(\epsilon_1-\epsilon_2)/kT}.$$

This will give the ratio of the rates of reaction provided adsorption is the rate controlling step and the adsorbed layer is mobile. Since $(\epsilon_1 - \epsilon_2)$ is a small quantity and T is large, 900° Kelvin in the present experiments, this expression leads to the conclusion that the rates of reaction should be inversely proportional to the square roots of the mass of the molecules. In this case k^{13}/k^{12} should be $\sqrt{28/29} = 0.983$ and k^{14}/k^{12} should be $\sqrt{28/30} = 0.966$. The agreement with experiment in the case of k^{13}/k^{12} is very good and in the case of k^{14}/k^{12} is reasonable considering the experimental errors. The same conclusion could of course have been reached by considering the classical collision frequencies of the various molecules with the walls of the vessel and neglecting any differences in the energy of activation of adsorption.

Homogeneous Reactions

An accepted mechanism for the reaction (6) involves the following chain propagating and branching steps:

$$CO + O_3 = CO_2 + O + O,$$
$$O + O_2 = O_3.$$

The activated complex for the reaction can in this case be represented as

$$O\text{—}C\ldots O\text{—}M$$

where M is O_2 treated as a point mass. If it is assumed that this complex is linear, which is reasonable, the vibration frequencies may be readily calculated for any given set of masses and potential constants. The isotope effect can then be obtained using Bigeleisen's formula (see Ref. 2 where the derivation and significance of this equation is described)

$$\frac{k_1}{k_2} = \frac{K_1}{K_2}\left(\frac{\nu_{1L}}{\nu_{2L}}\right)\left[1 + \sum_i G(u_i)\Delta u_i - \sum_i G(u_i^{\ddagger})\Delta u_i^{\ddagger}\right].$$

In using this formula it is necessary to neglect the effect of mass on transmission coefficients K_1/K_2. At the temperatures of the present reactions the "free energy" term $(1 + \sum_i G(u_i)\,\Delta u_i - \sum_i G(u_i^{\ddagger})\,\Delta u_i^{\ddagger})$ is effectively unity. Using the proposed model it can also be shown that the ratio of the frequencies along the reaction co-ordinate ν_{1L}/ν_{2L} is also very close to unity for a wide range of potential constants and $M = O_2$ (i.e. O_3 as reactant). It is also very close to unity if M is taken as a "third body" with no O—M bond but having a weak repulsion between M and the carbon atom.

It follows that, assuming the ratio of transmission coefficients to be unity, there will be no isotope effect, in agreement with the experimental results.

It is interesting to look briefly at the situation from the point of view of simple collision theory, i.e. using the expression:

$$\frac{k_1}{k_2} = \frac{P_1 Z_1}{P_2 Z_2}\,e^{-\Delta E/RT}$$

where ΔE is the difference in experimental activation energies for the isotopic molecules. Since ΔE is presumably small and T is large the term $e^{-\Delta E/RT}$ should be close to unity. On the other hand the term Z_1/Z_2 (ratio of collision frequencies) is not unity. Table IV shows the value of Z_1/Z_2 for $C^{13}O$ compared to $C^{12}O$ and for $C^{14}O$ compared to $C^{12}O$ assuming in one case (column 1) that the collisions occur between carbon monoxide and oxygen atoms and in the other case (column 2) between monoxide and ozone molecules.

TABLE IV
RATIOS OF COLLISION FREQUENCIES

	O	O_3
$C^{13}O/C^{12}O$	0.9937	0.9891
$C^{14}O/C^{12}O$	0.9878	0.9787

Comparison of Tables IV and III shows differences which are probably significant, i.e. the ratios of rate constants expected on the basis of collision numbers only is not in agreement with the measured values. Part or even all of this discrepancy could be accounted for by allowing that the term $e^{-\Delta E/RT}$ is not unity, ΔE being negative in just the amount required to compensate for the Z_1/Z_2 term. Unfortunately there is no simple way of estimating ΔE. Furthermore there is no knowledge of the effect of isotope substitution on the factor P. For these reasons the simple collision theory is of little use in considering isotope effects.

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GLUTAMIC ACID AS AN ADDITION AGENT IN THE ELECTRODEPOSITION OF COPPER[1]

BY S. ADAMEK AND C. A. WINKLER

ABSTRACT

The polarization–time curves obtained in the presence of glutamic acid generally showed two distinct polarization levels, one corresponding to an induction period following an initial rapid increase of polarization from the standard surface value, and the other corresponding to a steady state period following a second rapid increase of polarization. The polarization at both levels increased with increase of glutamic acid concentration and decreased with increase of sulphuric acid concentration in the electrolyte. In general, the induction period increased, and eventually became irreproducible, with increased sulphuric acid and copper sulphate concentrations, decreased glutamic acid concentration, decreased current density, increased temperature, and addition of chloride. Addition of sufficient chloride prolonged the induction period indefinitely at a polarization level corresponding to the presence of chloride alone. Following the induction period, the concentration polarization increased with glutamic acid concentration and was considerably higher than the value obtained during the induction period. Addition of chloride decreased the concentration polarization.

INTRODUCTION

Several previous papers from this laboratory have discussed the changes in cathode polarization during the deposition of copper when gelatin alone, or gelatin plus chloride ion, are present as addition agents in the electrolyte (5, 6, 12, 14). The increase in polarization observed in the presence of gelatin alone has been interpreted as a consequence of an increase in true current density when the active area of the cathode is reduced by adsorption of gelatin. A marked decrease in polarization below the value observed with gelatin alone, when small quantities of chloride ion (of the order 2 mgm. per liter) are added with the gelatin, was attributed to an increase of active area by attack of the halide ion on less active parts of the cathode surface.

A recent study of the initial changes in cathode polarization (13) has shown that, in the presence of gelatin but not in its absence, these changes were dependent upon the time the cathode was in contact with the electrolyte before electrolysis was begun. There was just a suggestion from this behavior that corrosion processes, with accompanying formation and adsorption of copper–gelatin complexes, might play a significant part in the addition agent effect of gelatin. Other workers have concluded that substances which function as addition agents form complexes with metal ions in the solution (3, 4, 7–9, 11).

To obtain further information about the way in which complex formation might be concerned in the mechanism of addition agent action, it seemed reasonable to study the behavior of a simple amino acid, rather than gelatin, as the addition agent. The ability of many such acids to form heavy metal complexes is well recognized, and copper complexes with several of them have been isolated. It was also hoped that further study of the effect of chloride ion,

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with the simpler addition agent, might enable a better understanding of the way in which chloride ion exerted its profound effect on the cathode polarization.

Although experiments were made with several amino acids, the increases of polarization appeared to be more pronounced with glutamic than with the other acids used. Hence, it is with glutamic acid that the present paper is primarily concerned.

EXPERIMENTAL AND RESULTS

All polarization measurements were made in a modified Haring cell of the type described previously (12). The auxiliary equipment and procedure for making the measurements have been indicated in several of the earlier papers. The volume of electrolyte used was always 150 ml.

The chemicals used in preparation of the electrolytes were Merck reagent grade copper sulphate pentahydrate, Baker's analyzed C. P. sulphuric acid, reagent grade sodium halides and amino acids, and laboratory distilled water that was redistilled from alkali. Before they were used all electrolytes were brought to the temperature of the thermostat (25 ± 0.1°C.).

Prior to an experiment, the cathode was polished with emery cloth, etched in 1:1 concentrated nitric acid – water solution, and thoroughly washed with distilled water. The surface was then brought to a standard condition by electrodeposition at 25°C. from an electrolyte containing 125 gm. copper sulphate pentahydrate and 90 gm. concentrated sulphuric acid per liter of solution. The deposition was continued for 30 min. at 3 amp./dm.^{2}, then for one hour at 2 amp./dm^2. The polarization at the end of the surfacing procedure was 105 ± 5 mv.

In the presence of glutamic acid, in an electrolyte containing 125 gm./liter copper sulphate pentahydrate and 180 gm./liter sulphuric acid, the polarization generally increased rapidly (within two minutes) to a relatively constant value, (cf. Fig. 1*A*, 1*B*) where it remained for a time which, for brevity, may be referred to as the induction period. Following this induction period, there was observed a second rapid increase to a steady state value which, for given conditions of electrolysis, was reproducible within ±7 mv. The length of the induction period, on the other hand, was generally quite irreproducible with this electrolyte. Occasionally, families of curves were obtained that showed definite trends of polarization with change of addition agent concentration, especially if the same stock electrolyte were used throughout a given series of experiments. However, use of the same stock electrolyte was no guarantee that reproducibility would be realized. The reproducibility remained poor with different batches of copper sulphate, sulphuric acid, or glutamic acid, and with differently prepared batches of distilled water. A decrease in the sulphuric acid content of the electrolyte (Fig. 1*A*) increased the polarization at both the steady state and induction period levels, and improved the reproducibility considerably. With several different batches of electrolyte containing 200 mgm./liter glutamic acid and 90 gm./liter sulphuric acid, an extreme variation in the induction period from 4 to 10 min. was observed, whereas with electro-

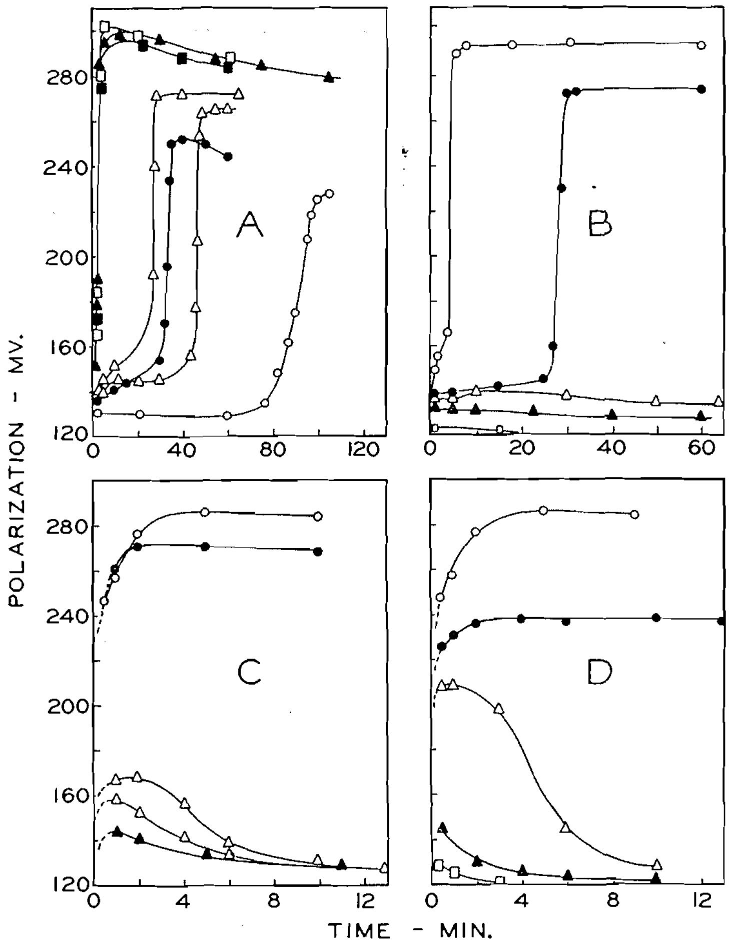

FIG. 1. Effect of various factors on cathode polarization in the presence of glutamic acid.
A. Effect of sulphuric acid concentration. H_2SO_4 conc. (gm./liter): ○ 180; ● 150; △120; ▲ 90; □ 50; ■ 35.
B. Effect of chloride concentration. H_2SO_4 conc., 90 gm./liter. Chloride conc. (mgm./liter): ○ nil; ● 0.145; △0.165; ▲ 0.33; □ 4.
C. Effect of immersion time (cathode surface first subjected to maximum polarization). H_2SO_4 conc., 90 gm./liter. Immersion time (min.): ○ nil; ● 0.5; △ 1.0; ▲ 5.0.
D. Effect of chloride concentration (cathode surface first subjected to maximum polarization). H_2SO_4 conc., 90 gm./liter. Chloride conc. (mgm./liter): ○ 0.5; ● 1.0; △ 1.5; ▲ 2.0; □ 8.0.

lyte containing 180 gm./liter sulphuric acid the variation in induction period was often 10-fold or more, for given conditions of electrolysis. When the sulphuric acid concentration was varied at a low glutamic acid concentration (4 mgm./liter), the induction period again increased with increase of sulphuric acid concentration, but irreproducibility was quite evident at acid concentrations as low as 90 gm./liter.

At a reduced current density of 1 amp./dm.^{2}, a very pronounced increase in induction period (from about 5 min. to 100 min.) resulted when the sulphuric acid concentration was increased from 35 gm./liter to 90 gm./liter.

The effect of glutamic acid concentration on the cathode polarization was determined with an electrolyte containing 90 gm./liter sulphuric acid. (Unless otherwise stated, the electrolyte used in all subsequent experiments contained 125 gm./liter copper sulphate pentahydrate and 90 gm./liter concentrated sulphuric acid). For glutamic acid concentrations above 50 mgm./liter, the induction period varied only slightly, but for smaller concentrations of glutamic acid, it increased considerably as the glutamic acid concentration was decreased, and eventually, for concentrations of glutamic acid below about 5 mgm./liter, erratic induction periods were again observed. Similar trends were noted in electrolytes containing 180 gm./liter sulphuric acid when, by chance, systematic behavior was observed in this more strongly acid solution. Erratic induction periods were not accompanied by erratic behavior of the steady state polarization, as indicated by the relation between the steady state polarization and glutamic acid concentration shown in Fig. 2*A*. In this figure are plotted also the polarization values after one minute, corresponding roughly to the polarization at the induction period plateau. The increase in its value with increased glutamic acid concentration is evident. The data of Fig. 2*A* can be well represented as linear relations between the logarithm of the cathode polarization and logarithm of the glutamic acid concentration.

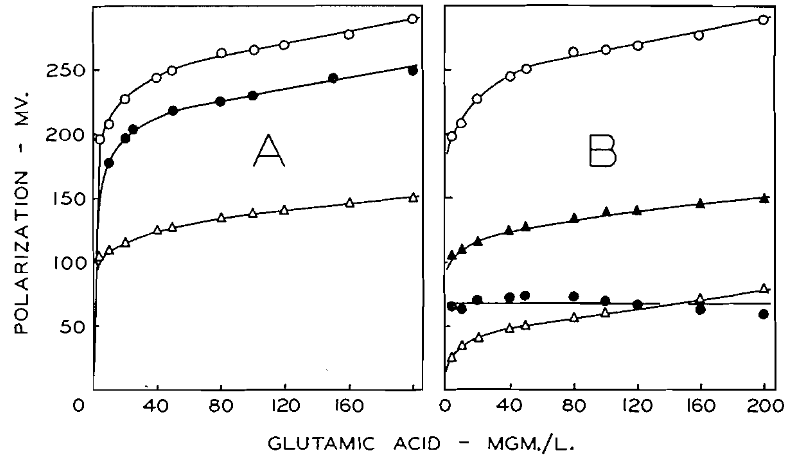

FIG. 2. Effect of glutamic acid on cathode polarization.
A. ○ Steady state polarization. H_2SO_4, 90 gm./liter.
● Steady state polarization. H_2SO_4, 180 gm./liter.
△ Polarization after one minute. H_2SO_4, 90 gm./liter.
B. H_2SO_4, 90 gm./liter.
○ P_T (total steady state polarization in presence of glutamic acid).
△ P_C (concentration polarization following induction period).
▲ P_A (total polarization during induction period).
● $P_T - (P_C + P_A)$.

With 200 mgm./liter glutamic acid in the electrolyte, the induction period appeared to increase with a decrease of current density and to become erratic at low current densities, as shown by the following results:

Current density (amp./dm.^{2})	Induction period (min.)	Steady state polarization (mv.)
3.0	2	330
2.0	4	295
1.5	8	268
1.3	17	240
1.2	26, 60	240, 228
1.1	20	238
1.0	95	234

A decrease in copper sulphate concentration was found to decrease the induction period and increase the polarization in an electrolyte containing 200 mgm./liter glutamic acid. The results were as follows:

Copper sulphate conc. $CuSO_4 \cdot 5H_2O$ (gm./liter)	Induction period (min.)	Steady state polarization (mv.)
Current density = 1 amp./dm.^{2}		
40	<1	330
80	4	244
125	90	234
Current density = 2 amp./dm.^{2}		
125	4	295
190	12	256

The effect of temperature on the polarization behavior at 2 amp./dm.^{2} in the presence of 200 mgm./liter glutamic acid was examined at 19°, 25°, 30°, and 36°C. Without presenting the results in detail, it might be mentioned that increase of temperature decreased the polarization from 320 mv. to 205 mv., and increased the induction period from 5 min. to 60 min., over the range studied. The most marked changes in both quantities appeared to be in the interval 30°–35°C.

Experiments were made to determine whether the second increase in polarization observed in the presence of glutamic acid might be the result of some product formed at the anode and carried to the cathode by convection. One milliliter of glutamic acid solution was added carefully from a pipette, at the base of the anode, while an electrolysis was in progress in the absence of addition agent. Approximately one hour elapsed before any increase of cathode polarization was observed. Repetition of the experiments with gelatin solution instead of glutamic acid solution gave a similar result. Since the induction periods observed in the polarization–time curves discussed previously were frequently much less than one hour for similar conditions of electrolysis, the second increase in polarization apparently is not due to formation of anodic products and their subsequent action at the cathode.

Although it seemed rather unlikely, there was a possibility that the induction period bore some relation to the time required for the acidity of the cathode film to attain a steady concentration. The drainage method described by Brenner (1) was used, and experiments were made at 0.5, 1.0, and 2.0 amp./dm.^{2} in electrolyte containing 90 gm./liter sulphuric acid, and at 2.0 amp./dm.^{2} in electrolyte containing 180 gm./liter sulphuric acid. Since a relatively steady acid concentration in the film was attained in less than two minutes, there appears to be no relation between this time and the induction period observed in the polarization–time curves. In agreement with Brenner, the acid concentration in the film increased with increase of current density; the percentage increase was approximately the same at the two bulk electrolyte acid concentrations used.

The effect of chloride ion on the cathode polarization in the presence of glutamic acid was studied over a range of conditions. Typical behavior is illustrated in Fig. 1*B*. With addition of chloride in concentrations less than about 0.2 mgm./liter, the induction period with 2 amp./dm.^{2} was increased, but the second increase of polarization did occur to somewhat lower steady state values than in the absence of chloride. With chloride concentrations greater than about 0.2 mgm./liter, however, the induction period appeared to be prolonged indefinitely, and with chloride concentrations of 4 and 8 mgm./liter, and 200 mgm./liter glutamic acid, the polarization followed closely the values in the presence of chloride alone.

When sufficient chloride (6 mgm.) was added at the base of the cathode after the polarization had reached the steady state value in electrolyte containing glutamic acid alone, the polarization began to decrease immediately and rapidly. At the end of 10 min., in a typical experiment, it had decreased some 45 mv., and after 40 min. had fallen to the value characteristic of chloride alone in the electrolyte.

The very high sensitivity of the system to the presence of chloride ion suggested the possibility that the induction period was due to the presence of an impurity (particularly chloride ion) and that the end of the induction period represented depletion of this depolarizer. However, prolonged electrolysis (up to $1\frac{1}{2}$ hr.) at 2 amp./dm.^{2} failed to attain the second increase of polarization when 0.16 mgm./liter chloride was present; with increase of the current density to 3 amp./dm.^{2} the increase of polarization occurred after 10 min. When a fresh cathode was inserted and the current density restored to 2 amp./dm.^{2} the normal induction period was again observed. This type of behavior, which was observed several times, does not indicate consumption of a depolarizer during the induction period.

It is interesting to note that the second increase of polarization could be promoted readily at 3 amp./dm.^{2} with 0.16 mgm./liter chloride, but required 4 amp./dm.^{2} when 0.3 mgm./liter chloride was present. Also, if the higher polarization were induced by a higher current density in the presence of 0.3 mgm./liter chloride, it could also be attained when the current density was restored to 2 amp./dm.^{2} provided current flow was not interrupted. With 0.16 mgm./liter chloride, similar procedure allowed the second polarization increase to occur at the lower current density even after short periods of current interruption.

The behavior summarized briefly above apparently had no relation to the surface condition of the cathode. Cathodes were prepared with quite different surface grain sizes, by polishing and etching and by deposition at current densities of 1.0, 2.0, and 3.0 amp./dm^2. There were no significant differences in the polarization–time curves with the different cathodes in an electrolyte containing 200 mgm./liter glutamic acid and with a current density of 2 amp./dm^2.

The effect of chloride on the polarization was investigated further with cathodes that were given the usual standard surface, after which they were subjected to deposition from electrolyte containing glutamic acid (200 mgm./liter) until the polarization had attained its maximum value. The cathode was then transferred to fresh electrolyte containing both glutamic acid and chloride, where it was allowed to remain for various immersion times before current flow was begun. The results for several immersion times at given chloride concentration, and for several chloride concentrations at zero immersion time, are shown in Figs. 1*C* and 1*D*. The behavior, in general, suggests two competitive processes, one of which tends to increase, the other to decrease the polarization.

The effect of halides, other than chloride, on the polarization in the presence of glutamic acid was also studied, but the results will not be presented in detail. It suffices to mention that fluoride ion had no effect whatever, which is reminiscent of its behavior when gelatin was the addition agent (12), whereas both bromide and iodide ions reduced the polarization in a manner similar to chloride, although with less effectiveness. With iodide, the decrease in polarization was followed by an increase as electrolysis was continued.

The change in concentration polarization brought about by the presence of glutamic acid in the electrolyte was estimated by the method outlined in a previous paper (13). Briefly, it consisted of measuring with a calibrated oscilloscope the extent of relatively slow polarization decay when current flow through the Haring cell was interrupted.

When the polarization in the presence of glutamic acid was allowed to attain its maximum value before electrolysis was stopped, the concentration polarization was linearly related to the glutamic acid concentration:

Glutamic acid conc. (mgm./liter)	Concentration polarization (mv.)
0	20
40	28
100	40
200	60

On the other hand, decrease of the copper sulphate concentration from 125 gm./liter to 60 gm./liter, or the sulphuric acid concentration from 90 gm./liter to 45 gm./liter, in the presence of 200 mgm./liter glutamic acid, had no effect on the concentration polarization.

Concentration polarization during the induction period in electrolyte containing 200 mgm./liter glutamic acid was approximately 30 mv.

Addition of a small amount of chloride (e.g. 1 mgm.), with 200 mgm./liter glutamic acid resulted in a decrease of concentration polarization to values comparable with the value obtained in the absence of addition agent.

It is of particular interest to note that the quantity $P_T - (P_C + P_A)$ is essentially constant, where

P_T = Total steady state polarization in the presence of glutamic acid.
P_C = Concentration polarization following the induction period.[2]
P_A = Total polarization during the induction period.

The behavior is illustrated in Fig. 2*B*. Extrapolated values of the concentration polarization were used for glutamic acid concentrations below 40 mgm./liter.

The changes in polarization brought about by several compounds related to glutamic acid were studied in an electrolyte containing 125 gm./liter copper sulphate, 90 gm./liter sulphuric acid, and 200 mgm./liter of the addition agent. The compounds studied were glycine, α-amino-n-butyric acid, α-amino-n-valeric acid, serine, β-phenylalinine, leucine, valeric acid, glutaric acid, and aspartic acid. Briefly summarized, the results indicated that mono-amino dicarboxylic acids (aspartic and glutamic) are much more effective as addition agents than the mono-amino monocarboxylic acids. Also, it would appear that in an homologous series of amino acids of increasing chain length (glycine, α-amino butyric, α-amino valeric, and also aspartic and glutamic), the effectiveness as an addition agent increased with chain length. Glycine and α-amino butyric had relatively little effect on the polarization and failed to produce the second increase in polarization that was characteristic of the other amino acids studied. Valeric and glutaric acids were without effect on the polarization, serine gave an initial increase (40 mv.) which gradually returned to the standard state value, and β-phenylalinine gave a gradual increase that eventually amounted to about 40 mv.

DISCUSSION

The rapidity of the first increase of polarization in the presence of glutamic acid, together with the relation between the polarization during the induction period and the concentration of glutamic acid (Fig. 2*A*), suggest that adsorption of some species on the active centers of the cathode is responsible for the increase in polarization to the induction period plateau. Since the length of the induction period was found to be independent of the surface for surfaces prepared in the absence of glutamic acid, but not for surfaces prepared in its presence, the indications favor a copper–glutamic complex as the adsorbed species. Further, the complex involved would probably be with cuprous ion[3] if deposition is assumed to occur by a sequence of single electron transfers (2) from the cathode

$$Cu^{++} + e \rightarrow Cu^{+}, \qquad [1]$$

$$Cu^{+} + e \rightarrow Cu, \qquad [2]$$

or by the first of these followed by a chemical change (dismutation) on the surface (10),

$$2\,Cu^{+} \rightarrow Cu + Cu^{++}. \qquad [3]$$

The second increase in polarization following the induction period suggests initiation of a new process corresponding to a higher deposition potential.

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[2] *P_C may be regarded as the sum of the concentration polarization (practically independent of glumatic acid concentration) during the induction period and an increment in concentration polarization (dependent upon addition agent concentration) following the induction period.*

[3] *In the absence of oxygen, a light blue color developed in a solution of cuprous chloride to which glutamic acid was added.*

There are several indications that this might be a consequence of cuprous ion depletion adjacent to the cathode face. With passage of current several factors tend to reduce the cuprous ion concentration in the cathode film below the value determined in the absence of current flow by the equilibrium $Cu^{++} + Cu \rightleftarrows 2\,Cu^{+}$. These include increase of current density and decrease of copper sulphate concentration, for obvious reasons, together with decrease of temperature, which operates by reducing the rates of diffusion and convection into the film and by altering the equilibrium constant of reaction (4). These same factors have been found to decrease the induction period during deposition in the presence of glutamic acid. It will also be recalled that the concentration polarization was considerably higher after, than during, the induction period, and that the concentration polarization after the induction period was observed to increase with increase of glutamic acid concentration. This behavior might be expected if cuprous–glutamic complex formation occurred, as suggested previously, with an accompanying decrease in cuprous ion concentration.

While, as indicated by these arguments, the induction period appears to be associated with depletion of cuprous ions, a reasonable explanation has not been found on this basis for the observed large variations in induction period, particularly with change of sulphuric acid concentration. However, attempts to interpret the induction period from other points of view, such as adsorption phenomena, appear to encounter equally formidable difficulties.

Whatever might be its cause, it is suggested that the second increase of polarization initiates the discharge of cuprous–glutamic complexes, at a potential corresponding to the steady state polarization. Accordingly, the steady state polarization (P_T) might be regarded as the sum of:

(*a*) polarization corresponding to the potential level of the induction period (P_A), postulated to involve adsorption of copper–glutamic complexes,
(*b*) concentration polarization (P_C) following the induction period,
(*c*) polarization due to discharge of complexes following the induction period.

The value of (*c*) alone, given by $P_T - (P_C + P_A)$, should then be independent of the glutamic acid concentration. This was indeed found to be essentially true (Fig. 2*B*).

The very small quantities of chloride ion necessary to reduce markedly the polarization in the presence of glutamic acid, together with the high rate with which the polarization is reduced, do not encourage the view expressed in previous papers that chloride exerts its influence through a corrosion type of process. An alternative suggestion is that chloride ion might facilitate electron transfer by acting as an electron "bridge", in the manner suggested by Heyrovsky (10) to account for the accelerated deposition of zinc on a mercury cathode in the presence of chloride ion. In the present system, the electron "bridges" might be assumed to facilitate electron transfer from the cathode to copper–glutamic complexes on the surface or to operate between complexes to promote their decomposition,

$$2\,[\mathrm{Cu-Glutamic}]^{+} \rightarrow \mathrm{Cu}^{++} + \mathrm{Cu} + 2\,[\mathrm{Glutamic}].$$

Failure of the fluoride ion to function in the manner of the other halides to reduce the polarization can be ascribed simply to its relative unpolarizability. Obviously, the decrease in polarization brought about by chloride ion when gelatin is the addition agent, though not the subsequent increase at higher chloride concentrations, might be explained in a similar way, by assuming adsorption of copper–gelatin complexes. It must be emphasized, however, that glutamic acid and gelatin differ considerably in their behavior as addition agents. It is hoped that studies now in progress with other simple compounds which produce addition agent effects more closely simulating those of gelatin will permit stronger convictions about the importance of complex formation in systems containing gelatin.

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PHTHALIDE FORMATION

III. CONDENSATIONS WITH 5-HYDROXY-2-METHYLBENZOIC ACID[1]

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ABSTRACT

The product obtained from the condensation of 5-hydroxy-2-methylbenzoic acid with aqueous formaldehyde and hydrochloric acid is dependent on the temperature. If the condensation is carried out at room temperature 3-hydroxy-6-methylphthalide results. This substance can also be obtained by the demethylation of 3-methoxy-6-methylphthalide. If the condensation is carried out at the boiling point the lactone of 8-hydroxymethyl-1,3-benzodioxane-6-methyl-7-carboxylic acid results. Proof of the presence of the *m*-dioxane and phthalide rings in this latter substance has been established by opening these rings in succession. In both cases this has led by a series of degradative steps to 4-methoxybenzene-1,2,3,5-tetracarboxylic acid. The structure of this acid has been confirmed by its synthesis in six unambiguous steps from mesitylene.

INTRODUCTION

When 5-hydroxy-2-methylbenzoic acid (I) is condensed with aqueous formaldehyde and hydrochloric acid at room temperature 3-hydroxy-6-methylphthalide (II) is obtained. However when the condensation is carried out at the boiling point the lactone of 8-hydroxymethyl-1,3-benzodioxane-6-methyl-7-carboxylic acid (III) is produced. The phthalide (II) has also been formed by demethylation with hydriodic acid or aluminum chloride of 3-methoxy-6-methylphthalide (IV) prepared according to the directions of Charlesworth *et al.* (2).

The structure of the dioxanylphthalide (III) has been established from its preparation by further condensation of the phthalide (II) and also by the opening of the *m*-dioxane and phthalide rings in succession, with a study of the degradation products resulting therefrom. When the dioxanylphthalide (III) was oxidized with chromic oxide and acetic acid, the methylene ether – ester (V) was formed. On alkaline hydrolysis of V a molecule of formaldehyde split out and the hydroxy acid (VI) was produced. This could be readily methylated to VII. The free carboxyl groups of either VI or VII could be removed by heating with quinoline and copper chromite to yield the aforementioned phthalides II and IV respectively. By oxidation with alkaline permanganate at 60°C. the phthalide ring of VII was opened and the tricarboxylic acid (VIII) was formed. On more drastic oxidative treatment, the methyl side chain was attacked and the final tetracarboxylic acid (IX) was obtained.

If the dioxanylphthalide (III) was oxidized originally with alkaline permanganate, the dioxane ring is left intact and the phthalide ring was opened to produce the dioxanylphthalic acid (X). This acid readily formed the anhydride (XI) and the imide (XII). The acid (X) on treatment with chromic oxide and

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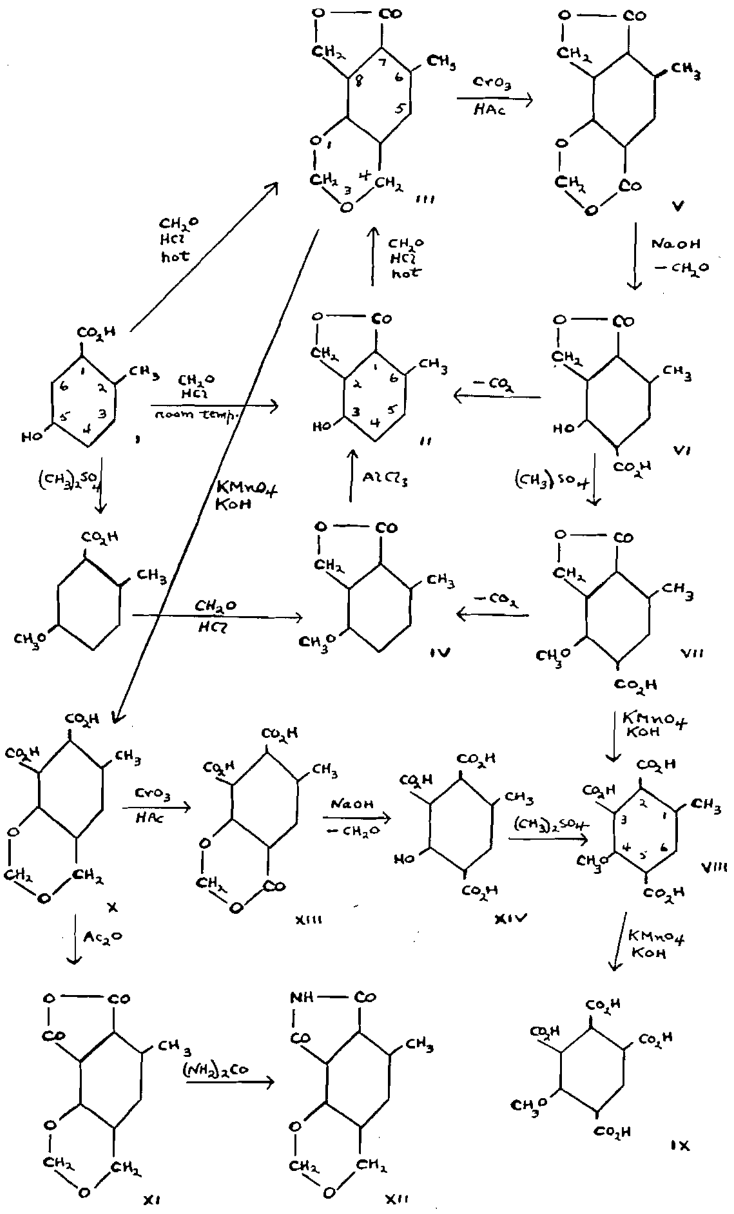
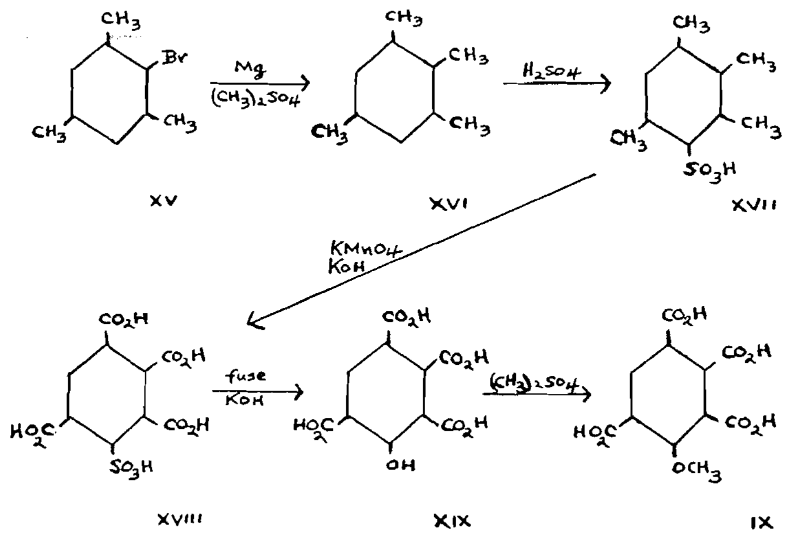


acetic acid gave the methylene ether – ester (XIII) which on alkaline hydrolysis lost formaldehyde and formed the hydroxytricarboxylic acid (XIV). Methylation of XIV gave the previously obtained acid (VIII).

The structure of the acid (IX) has been confirmed by its synthesis in six unambiguous steps from mesitylene. Bromomesitylene (XV) was methylated by treating its Grignard derivative with methyl sulphate to give isodurene (XVI). The sulphonic acid (XVII) of isodurene was oxidized with alkaline permangante to yield the tetracarboxylic sulphonic acid (XVIII). Fusion with



potash gave the phenolic tetracarboxylic acid (XIX) and methylation 4-methoxybenzene-1,2,3,5-tetracarboxylic acid identical with the degradative acid (IX).

Since the publication of Part II (1) the hydrolysis of the lactone of 6-hydroxymethyl-8-methyl-1,3-benzodioxane-4-one-5-carboxylic acid has been accomplished to yield 5-hydroxy-4-methylphthalide-6-carboxylic acid, m.p. 195°C. This has been reported also in the meantime by Duncanson, Grove, and Zealley (3) in connection with their work on gladiolic acid.

EXPERIMENTAL

Most of the 2-methylbenzoic acid used in this research was prepared by the oxidation of *o*-xylene by dilute nitric acid as described by Zaugg and Rapala (9). 5-Hydroxy-2-methylbenzoic acid (I), 5-methoxy-2-methylbenzoic acid (II), and 3-methoxy-6-methylphthalide (IV) were made as described by Charlesworth *et al.* (2) in the first paper of this series.

3-Hydroxy-6-methylphthalide (II)

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

(*a*) A mixture of 3-methoxy-6-methylphthalide (2.0 gm.), hydriodic acid (20 ml., sp. gr. 1.7) and red phosphorus (5.0 gm.) was refluxed gently under an atmosphere of nitrogen for three hours. The solid material was filtered off, washed with water, and dissolved in hot alcohol (charcoal). The hydroxyphthalide was crystallized from the alcohol in fine colorless needles (0.8 gm.) which melted at 223–224°C.

(*b*) A mixture of 3-methoxy-6-methylphthalide (1.1 gm.) and anhydrous aluminum chloride (2.7 gm.) in dry benzene (40 ml.) was refluxed on a water bath for 10 hr. The solid was filtered off, washed with water, and dried. On crystallization from alcohol, needles (0.5 gm.) which melted at 223–224°C.

were obtained. The compound was very soluble in alcohol, acetone, ether, and hot sodium hydroxide solution. It was insoluble in water and 5% sodium bicarbonate solution. On warming this substance with resorcinol and concentrated sulphuric acid followed by sodium hydroxide solution, the greenish fluorescence characteristic of the phthalide ring developed. Found: C, 65.8; H, 4.98%; mol. wt., 168. Calc. for $C_9H_8O_3$: C, 65.8; H, 4.88%; mol. wt., 164.

The above hydroxyphthalide can also be obtained by allowing a well shaken mixture of 5-hydroxy-2-methylbenzoic acid, formaldehyde solution, and concentrated hydrochloric acid to stand overnight at room temperature. The solid then on top of the liquid layer was filtered off, washed, and crystallized from alcohol. It melted at 223–224°C. with no depression on mixing with the above samples.

If a sample of the hydroxyphthalide was refluxed with formaldehyde solution and concentrated hydrochloric acid it was converted to the dioxanylphthalide (III) m.p. 171–172°C.

The Lactone of 8-Hydroxymethyl-1,3,-benzodioxane-6-methyl-7-carboxylic Acid (III)

A mixture of 5-hydroxy-2-methylbenzoic acid (30 gm.) and formaldehyde solution (300 ml., 40%) was heated in a 2 liter flask over a wire gauze until the acid just dissolved. At this point concentrated hydrochloric acid (300 ml.) was added through the top of the reflux condenser and the mixture was boiled. In the first few minutes of heating after the addition of the hydrochloric acid, a flocculent white precipitate separated, a small sample of which was removed and found to be the above hydroxyphthalide (II) m.p. 223–224°C. As the boiling continued, the flocculent precipitate dissolved and then a second product separated in the form of light brown granules. After a total of one hour's boiling the mixture was cooled and the crude dioxanylphthalide (30 gm.) filtered off. It was dissolved in boiling alcohol (*ca.* 2 liters) and filtered from a little insoluble material. On cooling, the dioxanylphthalide separated as coarse, white needles which melted at 171–172°C. A small sample was recrystallized for analysis from acetone from which it separated in characteristic long needles. Found: C, 64.0; H, 4.91%; mol. wt., 204. Calc. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.89%; mol. wt., 206. It gives the phthalide test with resorcinol and concentrated sulphuric acid. When the sample was warmed with phloroglucinol and strong sulphuric acid a reddish precipitate was formed which Mehta and Ayyar (6) have used to confirm the *m*-dioxane ring.

The Lactone of 8-Hydroxymethyl-6-methyl-1,3-benzodioxane-4-one-7-carboxylic Acid (V)

The dioxanylphthalide (III) (10 gm.) was dissolved in warm glacial acetic acid (250 ml.). The reaction flask was cooled externally with cold water, and finely ground chromium trioxide (15 gm.) was added with stirring at such a rate that the temperature was maintained at 65–70°C. When the reaction appeared to be complete the mixture was diluted with water to a volume of 2 liters and allowed to stand overnight. White, fluffy needles (2.5 gm.) separated which were filtered off, dried, and recrystallized from acetone. The white needles thus obtained melted at 184–185°C. Found: C, 60.4; H, 3.64%. Calc. for $C_{11}H_8O_5$: C, 60.0; H, 3.65%.

3-Hydroxy-6-methylphthalide-4-carboxylic Acid (VI)

A mixture of the above methylene ether – ester (V) (5.0 gm.) and sodium hydroxide solution (50 ml., 10%) was refluxed for one hour. A homogeneous solution gradually developed with the evolution of formaldehyde. The reaction mixture was cooled, filtered, and acidified with concentrated hydrochloric acid. The precipitate thus obtained was filtered off and dried. On recrystallization from water the acid was obtained as a white powder (4.0 gm.) which melted at 238°C. and which gave a dark violet color with 1% ferric chloride solution. Found: C, 57.6; H, 3.95%. Calc. for $C_{10}H_8O_5$: C, 57.7, H. 3.87%.

3-Methoxy-6-methylphthalide-4-carboxylic Acid (VII)

The hydroxy compound (VI) (7.5 gm.) was methylated in the usual manner with methyl sulphate and sodium hydroxide solution. After it was boiled with excess sodium hydroxide solution to hydrolyze any methyl ester, the mixture was acidified with hydrochloric acid. The crude acid (7.0 gm.) was twice recrystallized from water, from which it separated in white needles (6.0 gm.); these melted at 150–151°C. and gave no phenolic test with ferric chloride solution. Found: C, 59.6; H, 4.47%; neut. equiv., 218. Calc. for $C_{11}H_{10}O_5$: C, 59.5; H, 4.54%; neut. equiv., 222.

3-Methoxy-6-methylphthalide (IV)

The above 4-carboxylic acid (VII) (1.0 gm.) was decarboxylated by heating at 180°C. for 15 min. with quinoline (15 ml.) and copper chromite (0.01 gm.). The mixture was cooled and poured into 10% hydrochloric acid (150 ml.). The phthalide separated as white needles which were crystallized from alcohol. They melted at 165–166°C. and showed no depression of melting point on being mixed with a sample of the phthalide produced by the method of Charlesworth *et al.* (2) from 5-methoxy-2-methylbenzoic acid.

If a similar decarboxylation with quinoline and copper chromite was carried out on the hydroxy acid (VI), the hydroxyphthalide was obtained, which melted at 223–224°C. and with no depression on being mixed with an authentic sample (II), described earlier in this section.

1-Methyl-4-methoxybenzene-2,3,5-tricarboxylic Acid (VIII)

A solution of the above methoxyphthalide (VII) (3.0 gm.) in 3.5% aqueous potassium hydroxide solution (200 ml.) was heated at 60°C. and stirred while potassium permanganate solution (105 ml., 0.27 *M*) was added over a period of one hour. Excess permanganate was decomposed with sodium bisulphite and the manganese dioxide removed by filtration. The filtrate was acidified with sulphuric acid and the resulting precipitate (2.0 gm.) collected. On crystallization from 50% acetic acid it melted at 238°C. Found: C, 52.0; H, 4.09%; neut. equiv., 83.3. Calc. for $C_{11}H_{10}O_7$: C, 52.0; H, 3.96%; neut. equiv., 84.7.

4-Methoxybenzene-1,2,3,4-tetracarboxylic Acid (IX)

The previous methyl tricarboxylic acid (VIII) (1.0 gm.) was dissolved in 5% aqueous potassium hydroxide solution (80 ml.). The solution was heated on a steam bath and stirred while potassium permanganate solution (242 ml., 0.117 *M*) was added over a four hour period. The excess permanganate was decomposed with bisulphite and the manganese dioxide filtered off. The filtrate was evaporated to a small volume, refiltered, and acidified with concentrated sulphuric acid. The solution was extracted with three successive 50-ml. portions of ethyl acetate. The extract was evaporated to dryness and the residue recrystallized from 50% acetic acid. The tetracarboxylic acid (0.3 gm.) melted at 167–168° with effervescence. Found: C, 45.8; H, 3.00%; neut. equiv., 69. Calc. for $C_{11}H_8O_9$: C, 46.5; H, 2.83%; neut. equiv., 71.

There was no depression of melting point when the above acid was mixed with an authentic sample of 4-methoxybenzene-1,2,3,4-tetracarboxylic acid synthesized from mesitylene as described below.

Isodurene Sulphonic Acid (XVII)

Isodurene (XVI) was prepared by the Grignard methylation of bromomesitylene (XV) according to the directions of Smith (7). The isodurene was then sulphonated as described by Smith and Cass (8).

4-Hydroxybenzene-1,2,3,5-tetracarboxylic Acid (XIX)

The directions given below are a modification of methods outlined in French (4) and German (5) patents for the oxidation and fusion of pseudocumene-5-sulphonic acid.

Isodurene sulphonic acid (15 gm.) and potassium hydroxide solution (5.5 gm. in 250 ml. of water) were placed in a 1 liter three-necked flask equipped with a reflux condenser and stirrer. The flask was heated to 90°C. by a mantle and during vigorous stirring, powdered potassium permanganate (62.8 gm.) was added at such a rate that the temperature did not exceed 95°C. After the addition was complete the oxidation was continued at the stated temperature for a further 24 hr. Excess permanganate was decolorized with alcohol. The manganese dioxide was filtered and washed with two 150-ml. portions of boiling water. The resulting yellow solution was evaporated to dryness and the residue (15 gm.) pulverized. The bulk of the potassium salt was not purified further, but used in the next stage. A small portion of the potassium salt was acidified and extracted with ethyl acetate; the solvent was evaporated and the residue dissolved in a small quantity of hot water. On cooling, the sulphonic acid (XVIII) m.p. 238°C. was obtained, but it was not examined further.

The crude potassium salt of the sulphonic acid (14 gm.) was mixed with potassium hydroxide (40 gm.) and water (5 ml.) and fused at 200–220°C. for five hours in a nickel crucible. The melt was then cooled to a slush, mixed with water (60 ml.), and acidified with concentrated hydrochloric acid. Water (150 ml.) was added and the mixture heated to boiling and filtered. The filtrate was evaporated to dryness and the residue recrystallized from 5% hydrochloric acid (60 ml.). The hydroxy tetracarboxylic acid (6 gm.) melted at 281–282°C. Found: C, 44.4; H, 2.35%. Calc. for $C_{10}H_6O_9$: C, 44.0; H, 2.26%.

4-Methoxybenzene-1,2,3,5-tetracarboxylic Acid

The phenolic carboxylic acid (XIX) (4.0 gm.) was dissolved in sodium hydroxide solution (25 ml., 10%) under an inert atmosphere (propane). Methyl sulphate (5 ml.) was added at such a rate that the temperature did not rise above 40°C. Three additional portions (5 ml.) of methyl sulphate were added under the same conditions, along with solid sodium hydroxide to always maintain an alkaline solution. The solution was allowed to stand overnight and finally boiled to destroy excess methyl sulphate and to saponify any ester. Precipitated sodium sulphate was filtered off and the acidified solution was extracted with three portions (15 ml.) of ethyl acetate. Purification of the crude acid obtained by evaporation of the solvent was difficult. It was dissolved in sodium bicarbonate solution, filtered to remove insoluble material, and decolorized with charcoal. The solution was acidified with hydrochloric acid and extracted with ethyl acetate as before. Repetition of this process gave a product (1.3 gm.) which melted at 164–166°C. and was identical with the product (IX) obtained previously by oxidative degradation. Found: C, 46.1; H, 2.98%. Calc. for $C_{11}H_8O_9$: C, 46.5; H, 2.83%.

The tetraphenacyl ester of this acid was made in the usual manner by treatment of its sodium salt with phenacyl bromide. On crystallization from alcohol it melted at 189–190°C. with previous softening and darkening. Found: C, 68.0; H, 4.27%. Calc. for $C_{43}H_{32}O_{13}$: C, 68.2; H, 4.25%.

6-Methyl-1,3-benzodioxane-7,8-dicarboxylic Acid (X)

The procedure followed was the cold oxidation method of Charlesworth, Anderson, and Thompson (1). If the oxidation is carried out at higher temperature, around 60°C., this phthalic acid could not be isolated.

The dioxanylphthalide (III) (6.0 gm.) was dissolved in warm potassium hydroxide solution (300 ml., 3.5%). The solution was filtered and cooled in an ice-water bath. The temperature was maintained at 5–10°C. while a solution of potassium permanganate (24 gm.) in water (700 ml.) was added over a period of one hour. The resulting solution was allowed to regain room temperature and to stand overnight. The manganese dioxide was filtered off, washed with water, and the combined filtrates made just acid with hydrochloric acid with litmus as indicator. The solution was evaporated at a temperature of 65°C. to a volume of about 100 ml. After the solution was cooled, the separated solid, a mixture of organic and inorganic material, was filtered off. The acidic organic material was dissolved in 5% aqueous sodium carbonate solution and filtered. On acidification a dark brown powder (1.5 gm.) precipitated, which was crystallized from dilute alcohol. The light yellow crystals melted at 223–224°C. with effervescence. Found: C, 55.3; H, 4.16%. Calc. for $C_{11}H_{10}O_6$: C, 55.4; H, 4.20%.

If at any time a solution of the phthalic acid became sufficiently acid to darken Congo red paper, only a dark brown tar was precipitated. Presumably the dioxane ring has opened under the influence of the strong acid and some sort of polymer has resulted. This tar could be converted to the phthalic acid by being boiled with 10 times its weight of 10% sodium hydroxide solution and then carefully acidified.

The Anhydride (XI) *and Imide* (XII) *of 6-Methyl-1,3-benzodioxane-7,8-dicarboxylic Acid*

A mixture of the above phthalic acid (X) (2.0 gm.) and acetic anhydride (20 ml.) was heated on the water bath for one hour. The solution was filtered and allowed to stand in the refrigerator for 24 hr., when the anhydride separated as stout needles (1.3 gm.) of light brown color. These were crystallized from dry toluene and melted at 130°C.

An intimately powdered mixture of the anhydride (2.0 gm.) and urea (2.0 gm.) was heated in an oil bath at 160° until the evolution of ammonia ceased. The molten mixture was poured into boiling water (1 liter) in which it quickly dissolved. Upon cooling the phthalimide separated as orange plates (1.2 gm.) which were crystallized from 50% alcohol. The imide melted at 162°C. Found: C, 60.9; H, 4.13%. Calc. for $C_{11}H_9O_4N$: C, 60.3; H, 4.12%.

Degradation of 6-Methyl-1,3-benzodioxane-7,8-dicarboxylic Acid (X) *to 1-Methyl-4-methoxybenzene-2,3,5-tricarboxylic Acid* (VIII)

The dioxanylphthalic acid (X) (3.0 gm.) was dissolved in glacial acetic acid (80 ml.) and oxidized with chromic oxide at 65–70°C. by the method described above for the oxidation of the dioxanylphthalide (III). At the end of the oxidation water (600 ml.) was added and the solution evaporated *in vacuo* to dryness. Acidic organic material was dissolved by digestion with 5% sodium carbonate solution (50 ml.) and the resulting solution was then filtered off. Careful acidification of the filtrate gave the crude dioxanonephthalic acid (XIII) in the form of a brown tar. It was not possible to purify this further without hydrolysis of the dioxanone ring, so this was accomplished by boiling the tar for one hour with 10% aqueous sodium hydroxide (30 ml.). Acidification gave a small amount of light brown powder which gave a purplish color with ferric chloride solution and was the hydroxy acid (XIV). It was not purified further, but was methylated in alkaline solution in the usual manner. Upon acidification a small amount of light brown powder, m.p. 229°C. was obtained. It was recrystallized from 50% acetic acid and melted at 234°C. A mixed melting point with a sample of the methoxy tricarboxylic acid (VIII) previously described gave no depression.

ACKNOWLEDGMENT

The authors are grateful to the National Research Council of Canada for a grant which has aided in this research, and for a Bursary awarded to E. A. Dudley.

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AROMATIC HYDROXYLAMINES AS ORGANO-ANALYTICAL REAGENTS[1]

BY G. D. LUTWICK AND D. E. RYAN

ABSTRACT

The investigation of the use, as analytical precipitants, of a number of aromatic phenylhydroxylamines is described. In general they react similarly, increasing in selectivity with an increase in acidity of the oxime group. In acid solutions (1% or more) only vanadium, tin, titanium, and zirconium are precipitated. Their variation in reaction with copper and the nature of their reaction with tin are described. All compounds can act as oxidants or reductants with an oxidation potential of approximately −1.2 volts.

INTRODUCTION

The use of cupferron [$C_6H_5NO(NH_4)NO$] as an analytical precipitant was first proposed by Baudisch (1). It is most useful in acid medium for the quantitative precipitation of iron, titanium, zirconium, vanadium, and tin; elements such as aluminum, chromium, manganese, nickel, cobalt, and the alkaline metals with which they are usually associated do not interfere. A marked disadvantage of cupferron, however, is its instability. In addition, complexes precipitated by this reagent cannot be weighed as such but must be ignited to the oxides.*

Schome (4), by substituting a benzoyl for the nitroso group of cupferron, obtained a compound that was stable, and formed complexes with iron, aluminum, and copper that could be dried at 110°C. Ryan and Lutwick (3) extended the use of N-benzoylphenylhydroxylamine to the gravimetric determination of tin. The tin complex was dried at 110°C. and weighed as [$(C_{13}H_{10}NO_2)_2SnCl_2$].

The low solubility of the N-benzoyl derivative of phenylhydroxylamine in water necessitates close control of excess reagent and its basicity prevents the preparation of an ammonium salt. For these reasons a number of N-substituted phenylhydroxylamine compounds, containing a carbonyl alpha to the oxime, were prepared and their reactivities investigated.

COMPOUNDS INVESTIGATED

The following (mono-) N-derivatives of phenylhydroxylamine were prepared: benzoyl ($C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}$—), O-ethoxybenzoyl ($C_8H_9O\overset{\overset{\displaystyle O}{\|}}{C}$—), α-naphthoyl

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Contribution from the Department of Chemistry, Dalhousie University with financial assistance from the National Research Council. Abstracted from the M.Sc. thesis of G. D. Lutwick. Presented at the Annual Conference of the Chemical Institute of Canada, Toronto, June, 1954.

**Duval has shown that the cupferrates of iron (Anal. Chim. Acta, 5: 160. 1951) and copper (Anal. Chim. Acta, 6: 47. 1952) are the most stable of the cupferron complexes and that they may be brought to constant weight. Their usefulness as weighing forms, however, is questionable as the iron complex decomposes very rapidly above 98°C. whilst the copper compound is not stable above 107°C.; it is still advisable to ignite these complexes to the oxide.*

$(C_{10}H_7\overset{\overset{O}{\|}}{C}—)$, 3,5-dinitrobenzoyl $(C_6H_3(NO_2)_2\overset{\overset{O}{\|}}{C}—)$, 2,4-dichlorobenzoyl $(C_6H_3Cl_2\overset{\overset{O}{\|}}{C}—)$, O-iodobenzoyl $(C_6H_4I\overset{\overset{O}{\|}}{C}—)$, α-furoyl $(C_4H_3O\overset{\overset{O}{\|}}{C}—)$, benzenesulphonyl $(C_6H_5\underset{\searrow O}{\overset{O \nearrow}{S}}—)$, and the benzoyl derivative of naphthylhydroxylamine $(C_6H_5—\overset{\overset{O}{\|}}{C}—\overset{\overset{O—H}{|}}{N}—C_{10}H_7)$. These compounds were prepared by the addition of their acid chlorides to phenylhydroxylamine in an ether solution containing pyridine (2); 0.05 moles of the hydroxylamine was present in excess of the theoretical in order to decrease the yield of the di-compound $[(R—\overset{\overset{O}{\|}}{C}—)_2ONC_6H_5]$. The compounds were purified by recrystallization from a water–ethanol solution.

Physical Properties

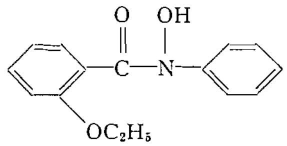
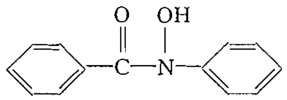
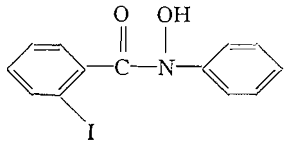
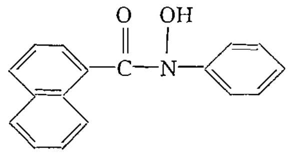
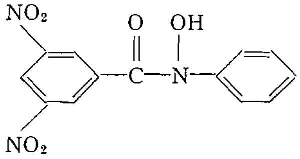
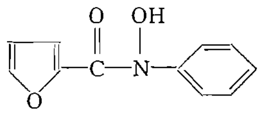
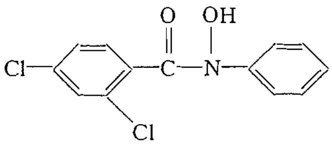
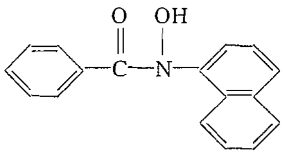
Table I shows the physical properties and structural formula of these compounds. They are soluble in most organic solvents but only slightly in water, the benzoyl derivative showing the highest solubility. The melting points are higher than that of N-benzoylphenylhydroxylamine with the exception of the O-ethoxybenzoyl-derivative; the melting of these compounds is accompanied by decomposition, the material becoming red then black. They can be stored without a preservant for two years or more without any decomposition; this stability is a marked advantage over cupferron.

Chemical Properties

Similar reactions were shown by the compounds of Table I; the benzenesulphonyl derivative did not react. The reactions were carried out by adding 1 ml. of a 1% alcohol solution of the compound under investigation to 100 mgm. of the metal ion in 10 ml. of an acidic and a neutral solution. No color or precipitate was noted with the following: $Cr^{\cdot\cdot\cdot}$, $Co^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Bi^{\cdot\cdot\cdot}$, $Ag^{\cdot}$, $Hg_2^{\cdot\cdot}$, and MoO_4''. In neutral solutions $Mn^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, and $Al^{\cdot\cdot\cdot}$ formed white precipitates, $UO_2^{\cdot\cdot}$ yielded a yellow precipitate, $Cu^{\cdot\cdot}$ a greenish-yellow precipitate, and $Fe^{\cdot\cdot\cdot}$ an orange precipitate. In solutions greater than 1 per cent in concentrated hydrochloric acid only $Sn^{\cdot\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Ti^{\cdot\cdot\cdot\cdot}$, $Zr^{\cdot\cdot\cdot\cdot}$ $(Hf^{\cdot\cdot\cdot\cdot})$, $V^{\cdot\cdot\cdot\cdot\cdot}$ (as VO_4''') reacted to give precipitates. The tin and zirconium complexes are white, the titanium yellow, and the vanadium purple in color.

Oxidation–reduction reactions were observed with Cr_2O_7'', MnO_4', $V^{\cdot\cdot}$, and $Ti^{\cdot\cdot\cdot}$. In acid solutions the orange dichromate was reduced to the green chromic ion and the pink color of permanganate was discharged. The violet hypovanadous ion was oxidized in at least two stages passing through the

TABLE I
PHYSICAL PROPERTIES OF THE COMPOUNDS

Compound	Structural formula	Color	M.p., °C.	Solubility in H_2O, gm./100 ml.
N-O-Ethoxybenzoylphenylhydroxylamine		White	103	0.011
N-Benzoylphenylhydroxylamine		White	121	0.040
N-O-Iodobenzoylphenylhydroxylamine		White	128	0.010
N-Naphthoylphenylhydroxylamine		White	129	0.003
N-3,5-Dinitrobenzoylphenylhydroxylamine		Yellow	133	0.007
N-Furoylphenylhydroxylamine		White	134	0.013
N-2,4-Dichlorobenzoylphenylhydroxylamine		White	137	0.006
N-Benzoylnaphthylhydroxylamine		White	164	0.013

green vanadous to the blue vanadyl; from a purple titanous solution the yellow titanic precipitate was formed.

The N-benzoylphenylhydroxylamine compound is too basic to permit the preparation of an ammonium salt. The enhanced acidity of the furoyl-compound enables such a salt to be prepared and aqueous reagent solutions are thus possible.

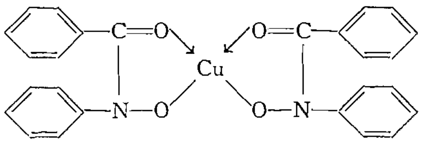
Change of precipitant necessitated a change in acidity for complete precipitation of the common elements. Variations in the acid concentration did not markedly affect the precipitation of the zirconium and vanadium complexes by the different reagents. Vanadium (V) was completely precipitated in 10% concentrated hydrochloric acid solution and zirconium (IV) in 5% by all compounds.

The vanadium complex precipitated by benzoylphenylhydroxylamine decomposed when heated at 110°. Zirconium formed a complex with the empirical formula $[Zr(C_{13}H_{10}NO_2)_4]$ that can be dried at 110°. Titanium was completely precipitated by N-benzoylphenylhydroxylamine in a solution 5% in concentrated hydrochloric acid (4); with the other compounds complete precipitation occurred in solutions only as high as 2% in hydrochloric acid. The complex of titanium was of a variable composition and it is thus not possible to dry to constant weight.

In order to investigate more closely the effects of these substituents, a detailed investigation of the reaction with copper and tin was carried out. These two reactions were investigated as two different types of complexes are involved.

THE COPPER REACTION

Copper reacts with all these compounds by the displacement of the hydrogen of the oxime (shown by a decrease in the pH of the copper solution on adding reagent) to form a planar complex in which the copper is co-ordinatively bonded to the oxygen of the carbonyl.



By measuring the lower pH limit for the complete precipitation of the copper the effect of substituents on the ability to form inner complexes was determined. The results are shown in Table II.

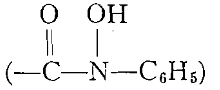
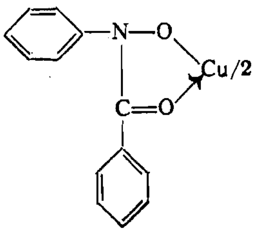
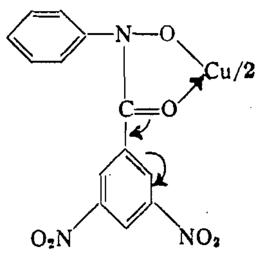
The results show that there is an increase in the pH required for complete precipitation of the copper with an increase in reagent acidity; the furoyl derivative, in which the nature of the ring is changed, is an exception. Therefore attempting to prepare more acidic reagents with this reactive grouping  $(\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—}\overset{\overset{\text{OH}}{|}}{\text{N}}\text{—}C_6H_5)$ is not advantageous because the electrons in the carbonyl become so much less available for bonding that precipitates would either not

TABLE II

Compounds	pH of 1% solution of reagent in ethanol	Lowest pH for complete precipitation of copper
N-Benzoylphenylhydroxylamine	7.5	3.0
O-Ethoxybenzoylphenylhydroxylamine	7.3	3.3
O-Iodobenzoylphenylhydroxylamine	7.3	3.0
Naphthoylphenylhydroxylamine	7.2	3.4
2,4-Dichlorobenzoylphenylhydroxylamine	6.8	3.7
Furoylphenylhydroxylamine	6.1	3.0
3,5-Dinitrobenzoylphenylhydroxylamine	5.8	4.2
Benzoylnaphthylhydroxylamine	4.5	5.5

form at all or would only be stable in a basic medium. For example consider the two compounds N-benzoylphenylhydroxylamine and N-3,5-dinitrobenzoylphenylhydroxylamine.



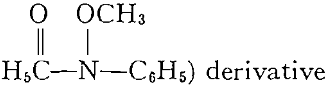


In the nitro-compound there is a shift in the electron density towards these groups so that although the compound becomes more acidic, the electrons on the oxygen of the carbonyl are less available for co-ordination.

THE TIN REACTION

Cupferron reacts with tin by displacement of the hydrogen of the oxime to form SnC_2 and SnC_4 (C is $C_6H_5\overset{\overset{O}{|}}{N}-N=O$) type compounds. It was found on analysis that the N-benzoylphenylhydroxylamine reacted with stannous and stannic tin to form compounds containing chloride and were of the same percentage composition (3); for every gram atom of tin there are two gram atoms of chlorine and two gram molecules of the reagent. The melting points of the dried stannous and stannic complexes were identical, 171°C., and mixed melting points gave no deviation. It is apparent that both stannous and stannic tin form the same complex; for this to be true an oxidation–reduction reaction must take place with one of the two ions.

The question of whether an oxidation or reduction has taken place with these reagents has caused some difficulty. Analysis is not sufficient to distinguish between the stannous and stannic complexes which differ only by two hydrogen atoms. Neither pH measurements for determining displacement of hydrogen as the reaction proceeds, nor tests for the oxime grouping in the precipitated compound are suitable to prove or disprove the presence of the oxime hydro-

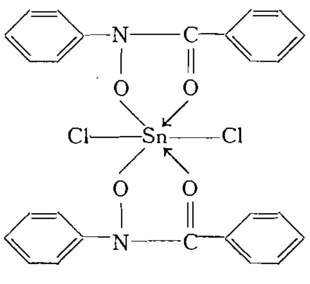


gen; the tin reaction must be carried out in a fairly acid solution to prevent the formation of metastannic acid and positive tests for the oxime grouping with iron (III) were obtained for the copper complex. Original tests with the -O- methyl ether ($C_6H_5\overset{O}{\overset{\|}{C}}-\overset{OCH_3}{\overset{|}{N}}-C_6H_5$) derivative indicated that displacement of hydrogen did not take place, but extended investigation has shown that precipitation does not occur with stannic or stannous tin. Attempts to prove reduction by testing for stannous tin and examination of filtrate for oxidized products of the reagents were unsuccessful. Consideration of the oxidizing and reducing properties of these reagents and the corresponding oxidation potentials shown in Table III suggests that tin is reacting in the stannic state.

TABLE III

System	Standard potentials
$V^{+2} \rightarrow V^{+3} + e^-$	0.20
$Ti^{+3} + H_2O \rightarrow TiO^{+2} + 2H^+ + e^-$	−0.1
$Sn^{+2} \rightarrow Sn^{+4} + 2e^-$	−0.15
$H_2O + V^{+3} \rightarrow VO^{+2} + 2H^+ + e^-$	−0.31
$VO^{+2} + 3H_2O \rightarrow VO_4^{-3} + 6H^+ + e^-$	−1.00
$C_6H_5NH_3^+ + H_2O \rightarrow C_6H_5NH_2OH^+ + 2H^+ + 2e^-$	−1.20
$Cr^{+3} + 7H_2O \rightarrow Cr_2O_7^{-2} + 14H^+ + 6e^-$	−1.36
$Mn^{+2} + 4H_2O \rightarrow MnO_4^- + 8H^+ + 5e^-$	−1.52

In Table III the strong oxidizing agents have high negative potentials, and the couple with the more positive potential will be oxidized more readily. On the basis of the oxidation–reduction reactions that these compounds enter into, their oxidation potentials are quite similar to the phenylhydroxylamine–aniline couple (−1.20 volts). The co-ordination number of stannic tin combined with the oxidation potentials of the reagents favor the formation of the following complex.



The N-benzoyl derivative gave complete precipitation in solutions as high as 8% in concentrated hydrochloric acid. The naphthoyl-,2,4-dichlorbenzoyl-phenylhydroxylamine and the benzoylnaphthylhydroxylamine gave complete precipitation in solutions 1% in concentrated hydrochloric acid, whereas the remainder, O-ethoxybenzoyl, O-iodobenzoyl-, furoyl, and the 3,5-dinitrobenzoyl derivatives gave incomplete precipitation in such solutions. The effect on the tin reaction is more marked than that with copper; this is evident from a comparison of the tin and copper reactions with N-benzoylphenylhydroxylamine and O-ethoxybenzoylphenylhydroxylamine.

CONCLUSIONS

In the preparation of a more acidic reagent in which co-ordination occurs as well as substitution, it is insufficient to consider only the effect of the substituent on the acid grouping of the reagent; it is also necessary to consider the effect on the donor ability of the group which forms the co-ordinate bond. The use of substituents on the ring of the benzoyl group of N-benzoylphenylhydroxylamine failed to improve on this reagent as a precipitant, rather it destroyed the favorable property of being able to precipitate tin from a fairly acid medium.

The formation of the ammonium salt of N-furoylphenylhydroxylamine may prove advantageous for the determination of copper, iron, aluminum, titanium, vanadium, and zirconium as it is readily soluble in water.

An investigation into the effect of substituents on the ring of the phenylhydroxylamine group may be profitable. Substituents on this ring should have more effect on the acidity and less effect on the donor ability because of the increase in distance from the carbonyl although a comparison of the reactions of N-naphthoylphenylhydroxylamine and N-benzoylnaphthylhydroxylamine with copper is not in agreement with this hypothesis. Such a compound might also form a stable ammonium salt.

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ESTIMATION OF IMPURITIES IN LIQUID CHLORINE BY INFRARED ABSORPTION SPECTROPHOTOMETRY[1]

By A. W. Pross

ABSTRACT

Commercial chlorine may contain small amounts of chlorinated organic impurities, some of which have been estimated by infrared absorption spectrophotometry. Liquid chlorine has no infrared absorption spectrum up to 1180 cm^{-1}. This has enabled long path lengths to be used to increase the sensitivity to low concentrations of organic compounds. A 5 cm. tantalum-clad steel pressure cell fitted with calcium fluoride windows was used, and spectra were recorded on a single beam instrument fitted with a calcium fluoride prism. Using extinction coefficients, estimations were made to a few parts per million on impurities such as chloroform, methylene chloride, phosgene, and hexachlorobenzene. The method was checked by known additions to pure liquid chlorine. The estimation of moisture in liquid chlorine is discussed.

Commercial chlorine from the electrolysis of brine in either diaphragm or mercury cells contains small amounts of chlorinated organic impurities. Although such contaminants are present in only a few parts per million, a knowledge of their concentration is of importance to the manufacturer. The impurities appear to be predominantly C_1 and C_2 hydrocarbons such as carbon tetrachloride, chloroform, methylene chloride, and hexachloroethane with, in certain cases, more complex compounds such as hexachlorobenzene. The estimation of these impurities has been difficult, since the analytical methods available were time consuming and required several liters of sample. The most reliable method has been the distillation of approximately 10 liters of liquid chlorine through a fractionating column as described by Hedgepath and Riggs (3) and modified by Matthews and Warren (4). However, distillation methods are at a disadvantage because the chemical nature of the impurity may change during distillation; chloroform for example may chlorinate further to carbon tetrachloride. This disadvantage is absent in a spectrometric method.

Chlorine consists of the molecules Cl_2^{35-35}, Cl_2^{37-37}, and the heterotope Cl_2^{35-37}. The former, in common with other isotopically homogeneous molecules, are transparent to infrared radiation. The molecular heterotope, however, would be expected to absorb, and since its concentration is normally 36.6% this absorption cannot be ignored (2). The fundamental band has been calculated to be at 554 cm.$^{-1}$ in the gas phase, with first and second overtones at 1100 cm.$^{-1}$ and 1638 cm.$^{-1}$ respectively. In liquid chlorine the absorption frequencies of these bands would be lowered by about one half of one per cent (1). The fundamental and the first overtone are beyond the range of calcium fluoride transmission. No band at around 1640 cm.$^{-1}$ corresponding to the second overtone has been detected.

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Contribution from Canadian Industries Limited, Central Research Laboratory, McMasterville, Que.

EXPERIMENTAL

Wright and Smith employed a 1-in. tantalum-clad brass pressure cell with quartz windows for the estimation of moisture at 3700 cm.$^{-1}$ (7). This cell was limited by the cutoff of quartz at 2850 cm^{-1}. For the following work a 5.25 cm. tantalum-clad steel cell was used with calcium fluoride windows which are transparent in the infrared as far as 1180 cm^{-1}. The extreme transparency of liquid chlorine in the infrared has enabled the use of a path length which is approximately two thousand times greater than is usual for most organic liquids. This path length has caused the method to be sensitive to concentrations of absorbing substances of the order of a few parts per million. This cell was designed and made by the Perkin–Elmer Corporation (5).

A section of the cell is shown in Fig. 1. It consists of a 1$\frac{3}{4}$ in. diameter steel cylinder 2 in. long, clad with tantalum which is resistant to liquid chlorine (*A*). The windows are $\frac{1}{4}$ in. thick calcium fluoride (*B*). "Teflon" U-Section gaskets are used with neoprene O-ring inserts (*C*). The windows are secured by means of caps which are drawn against them. They are protected by $\frac{1}{8}$ in. diameter keys which prevent the caps from turning. The cell is designed for a pressure of 200 p.s.i. The vapor pressure of chlorine at 25°C. is 105 p.s.i. gauge.

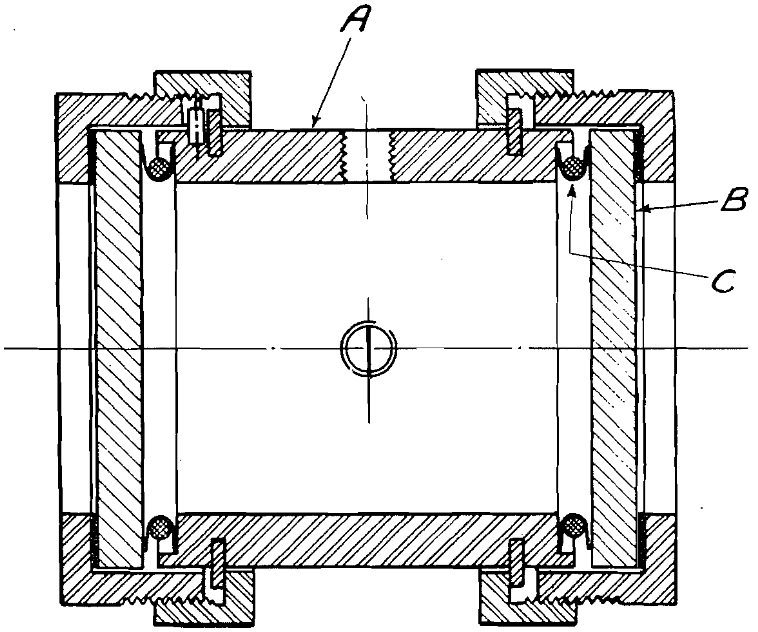

FIG. 1. Section of the Perkin–Elmer 5 cm. tantalum-clad steel cell.
A. Tantalum-clad steel cylinder.
B. Calcium fluoride window.
C. Rubber gasket in "Teflon" envelope.

The cell was fitted to a stainless steel reservoir and a valve system consisting of $\frac{1}{8}$ in. stainless steel "Hoke" needle valves. This makes possible the filling of the cell with liquid chlorine directly from an inverted commercial cylinder without cooling. Alternatively, by placing the reservoir in a Dewar flask packed with dry ice, liquid chlorine could be introduced from a flask as shown in the line diagram Fig. 2. As a precautionary measure the nitrogen inlet tube at *A* was held in place by hand so that it could be instantly released should excessive back pressure develop because some part of the system was insufficiently cooled. After the reservoir had been filled, the dry ice packing around the inlet tube was removed. Valves *B* and *C* were then closed, and the reservoir was removed from the Dewar. Before the reservoir was inverted, the system was brought to room temperature with the help of lukewarm water. This avoided possible fracture of the windows which might have resulted if cold chlorine were allowed to enter the cell. When filled, the reservoir and cell were supported in front of the entrance slit of the spectrometer.

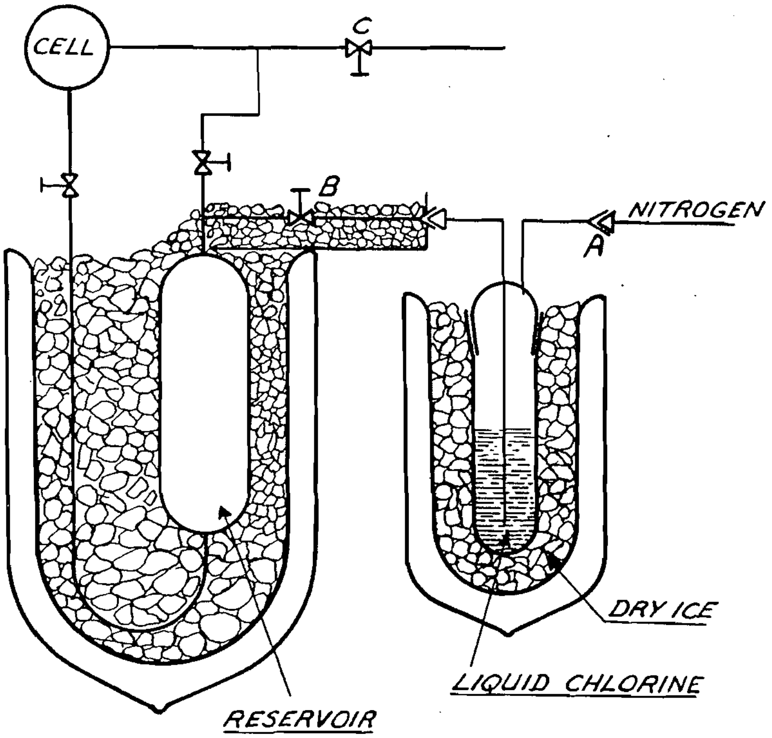

FIG. 2. Diagram to show method of filling reservoir.

Spectra were recorded on a Perkin–Elmer Model 12C single beam instrument using a calcium fluoride prism. The increased resolution afforded by a calcium fluoride over a rock-salt prism is an advantage in this work.

The specific extinction coefficient E_ν is given by the Lambert-Beer relationship:

$$E_\nu = \frac{1}{cl}\log\left(\frac{I_0}{I}\right)_\nu \max \qquad [1]$$

where c = concentration in gm. per ml.,
l = path length in cm.,
I_0 = intensity of incident radiation,
I = intensity of absorbed radiation.

In this work band intensities are a function of the experimental conditions. Apparent specific coefficients E_ν^a have therefore been quoted, following the example set by Ramsay (6). The incident and absorbed radiation intensities were taken as proportional to the background and band peaks respectively. Finite slit width and scatter corrections were dispensed with. Band intensities thus measured gave estimations of impurities which were accurate to between 10% and 20%.

Formula (1) was rearranged and parameters were substituted to give concentrations in parts per million from a constant multiplied by the optical density. The method was tested by addition of known quantities to liquid chlorine. The liquid chlorine used in these experiments was purified by distillation using a column packed with "Fenske" rings having a performance equivalent to approximately eight theoretical plates and a reflux to product ratio of 2: 1. A spectrum was first recorded to ensure the absence of impurities, after which the chlorine was distilled back into the flask surrounded by dry-ice. Volatile compounds such as chloroform and methylene chloride were added from a weighing pipette, and solids were added as such with subsequent agitation until dissolved. Recording time for the spectrum over the range 4000 cm.$^{-1}$ to 1180 cm.$^{-1}$ was approximately 30 min.

Table I summarizes the analytical results obtained with this technique. The frequencies of the analytical bands are those observed for the compounds in liquid chlorine as solvent. Further analytical bands of interest, with their frequencies and apparent extinction coefficients, are given in Table II. For concentrations that may be encountered in practice no suitable bands are

TABLE I
SUMMARY OF ANALYTICAL RESULTS

Compound	ν, cm.$^{-1}$	E_ν^a	Concentration in p.p.m.	
			Added	Found
$CHCl_3$	1216	900 ± 75	61	56
			106	100
CH_2Cl_2	1259	1320 ± 30	57	46
C_6Cl_6	1348	4900 ± 600	10	11
			20	18

TABLE II
ANALYTICAL ABSORPTION BANDS AND APPARENT EXTINCTION COEFFICIENTS

Compound	ν, cm.$^{-1}$	E_ν^a
$CH_2ClCOCl$	1821	4400 ± 100
$COCl_2$	1810	6080 ± 110
H_2O	1640	1010 ± 20

present in the range 400 cm.$^{-1}$ to 1180 cm.$^{-1}$ for carbon tetrachloride or hexachloroethane. Analysis for these compounds will depend on finding a suitable cell window material that will transmit further into the infrared.

WATER

Analytical estimations by this method are under investigation. The absorption band at 1640 cm.$^{-1}$ has an advantage over the 3700 cm.$^{-1}$ band used by Wright and Smith as there is no correction required for carbon dioxide. Any interference in the 1640 cm.$^{-1}$ region would be from amide-carbonyl and C=C unsaturation; and neither would be expected in liquid chlorine. The vaporizing of sufficient liquid chlorine into a gas cell as a means of correction for carbon dioxide is open to criticism as carbon dioxide boils off first resulting in a false value for this correction.

ACKNOWLEDGMENTS

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THE QUENCHING OF POTASSIUM RESONANCE RADIATION BY HYDROGEN AND DEUTERIUM[1]

BY W. M. SMITH, J. A. STEWART,[2] AND G. W. TAYLOR[3]

ABSTRACT

The quenching of the resonance radiation of potassium by hydrogen and deuterium has been studied over the temperature range 71°C. to 83°C. The quenching cross sections at 76°C. were found to be 1.56×10^{-16} cm.^{2} and 1.10×10^{-16} cm.^{2} respectively.

INTRODUCTION

Among the simplest processes involving quenching of excited atoms are those involving the various alkali metals in their lowest ^{2}P state and molecular hydrogen as quencher. Experimental studies have been restricted in the past to sodium. We have attempted to obtain cross sections for the quenching of excited potassium, $4^2P\rightarrow4^2S$, by hydrogen and by deuterium with a view to obtaining further data relating to systems relatively amenable to theoretical examination.

METHOD

The experimental method resembled that used by Steacie and LeRoy (8). Two resonance vessels containing potassium were housed together in a furnace and irradiated by a beam with a substantial portion of the radiation consisting of the doublet λ7665 Å and λ7699 Å. Quenching gas was added to one vessel; the other vessel served as a reference. The relative intensities of the resonance radiation emitted from the two vessels at right angles to the irradiating beam were estimated with a photoelectric photometer. Measurements made in the absence and in the presence of quenching gas yielded the quenching ratio, Q, which is defined as the ratio of the intensity of resonance radiation in the presence of quenching gas to the intensity of resonance radiation in the absence of quenching. The quenching cross section, σ^2, in cm.^{2} may be calculated from the slope, S_Q, of the plot of $1/Q$ against p (in mm. Hg) using the relation (5),

$$\sigma^2 = S_Q/2666.4\tau\left[\frac{2\pi N}{kT}\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right]^{\frac{1}{2}}$$

where τ is the mean life of the potassium atom in the 4^2P state which we have taken to be 2.71×10^{-8} seconds (9), N is Avogadro's number, k is the gas constant in ergs per molecule per degree, and M_1 and M_2 are the gram molecular weights.

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The two resonance vessels were constructed of tubing $2\frac{1}{2}$ cm. in diameter and were about 13 cm. long. They were of the usual light trap type with two plane windows meeting at right angles to facilitate entry of the irradiating beam and exit of a portion of the fluorescent radiation at right angles to the beam. The vessels were centrally mounted one above the other in a furnace about 28 cm. long containing double windows placed appropriately for entry and exit of the radiation referred to above. The interior of the furnace was blackened as were also the masks within the furnace which were used to demarcate the irradiating and fluorescent radiation. The resonance vessels used during the initial measurements were of quartz, during the final measurements of pyrex. The quenching vessel was connected via a stopcock outside the furnace to a wide bore mercury manometer, storage bulbs, MacLeod gauge, and pumping system. A cathetometer was used to read the levels of the manometer. A magnetic cutoff operating within the furnace in the line connecting the quenching vessel to the rest of the vacuum system was incorporated in the apparatus during the early measurements but was omitted in the later measurements. The reference vessel was permanently sealed. The portion of the vessel containing the windows was free of potassium deposit but that portion immediately adjacent was covered with a deposit around the entire inner circumference. Inspection of the vessels, with local heating if necessary, was carried out every few days to ensure that this distribution of potassium was maintained. Temperature differences of the order of 1°C. existed within the furnace. However the difference in temperature between the region containing the resonating vapor under observation and the site of potassium probably did not exceed 1/3°. The region of the vessel containing the windows and the resonating vapor under observation was at the highest temperature. The temperature was held constant during a run to within 0.1°C.

The source of the irradiating beam was a K-1 General Electric potassium lamp. The radiation from the lamp passed through a rectangular slit in a blackened mask, through a Corning filter number 2600 and a system of lenses which formed an image of the slit in the front portion of the resonance vessels. The beam was further restricted by a blackened mask containing two rectangular holes which was placed immediately in front of the resonance vessels. To check approximately the changes in intensity of the irradiating beam and so permit estimates to be made of the variation in intensity of the reflected radiation associated with the fluorescent beam, a Weston photronic cell was mounted so that it could be swung into the path of the irradiating beam. Although the sensitivity of the photronic cell to the radiation in the beam is very low, sizable deflections were obtained with a galvanometer in series with the photronic cell. Measurements of this sort were required only because of the relatively appreciable magnitude of the reflected radiation accompanying the fluorescent radiation and were used only when estimating the magnitude of the reflected radiation.

The fluorescent radiation emerging from openings in a mask covering the exit windows of the resonance vessels was focused on the sensitive surface of a RCA 917 phototube. As the eye is relatively insensitive to wave lengths around

7700 Å, a small flash light bulb was mounted under the resonance vessels, and was turned on during initial focusing operations. The phototube and the associated circuit, which was that devised by Gabus and Pool (2), was enclosed in a brass tube fitted with a shutter which permitted the focused fluorescent radiation from either resonance vessel to fall separately on the phototube. The amplified photocurrent was determined with a Rubicon galvanometer No. 3403. In subsequent paragraphs the setup involving phototube, amplifier, and galvanometer is called the detector. The correlation between light intensity and response of the detector was determined at intervals throughout the runs with calibrated neutral filters and invariably the detector showed response linear with light intensity. As a dark room was not available the entire optical system was housed in blackened boxes and all measurements were carried out at night.

The resonance radiation from the resonance vessels was examined spectrographically and only the 7699–7665 doublet appeared on the photographic plate.

MATERIALS

Hydrogen and deuterium were prepared by the action of light or heavy water on potassium. Distilled water, deaerated by several cycles of freezing, melting, and pumping off *in vacuo*, was distilled into an evacuated bulb of about 300 cc. capacity containing purified potassium and fitted with a mercury manometer of the blowoff type. The gas from the reaction bulb was passed slowly through two traps refrigerated with liquid air, and was then stored for a minimum of 24 hr. in a flask containing a film of potassium on the walls.

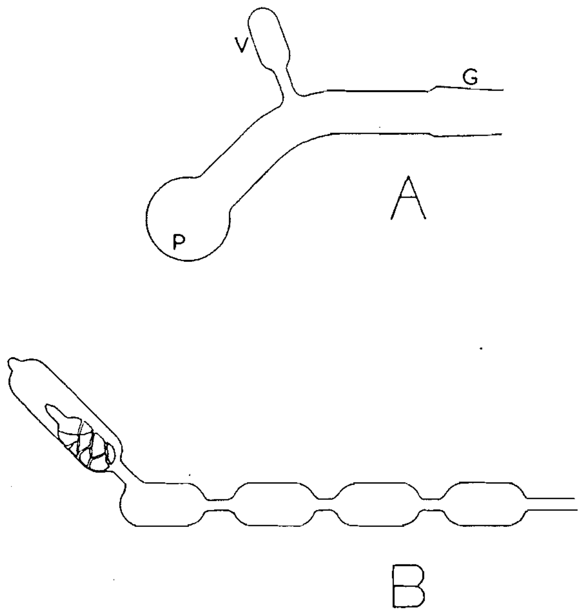

FIG. 1. Apparatus for purification of potassium.

The 99.6% heavy water was obtained from Atomic Energy of Canada Ltd.

The potassium was purified as follows. The surface film was cut off B.D.H. lump potassium, the metal was blotted dry with filter paper and then introduced into the unit indicated in Fig. 1A. This consisted essentially of a wide diameter tube bent to an angle of about 135° and connected horizontally to the vacuum system and traps via the ground joint *G*. One or two small vials *V* were connected to the larger tube at the bend and roughly in the same plane as the large bent tube. With potassium resting in the bottom of the tube at *P* the unit was connected to the vacuum system and evacuated. The potassium was then heated with refluxing until there was no evidence of gas evolution. The unit was then rotated and liquid potassium flowed into the vials at *V*. These were sealed off. Potassium from these vials was introduced into the vacuum apparatus where and when required by the technique of Dunoyer (1). This involved crushing the vial and quickly sealing it in the end bulb of a series of bulbs connected by short yet thick walled tubes, the whole series leading to the final site. These are illustrated in Fig. 1B. The end bulb was placed at a slant to facilitate the separation of potassium from the crushed vial and its entry into the second bulb without distillation. After entry of potassium into the second bulb *in vacuo*, the end bulb was sealed off and potassium was distilled *in vacuo* from one bulb into the next, the end bulb containing some residue of potassium being sealed off before the next distillation in the chain was carried out.

PROCEDURE

After the quenching vessel had been evacuated and the potassium lamp had been operating for more than one hour, measurements of the intensities of the radiation from quenching and reference vessels were made with the detector. Quenching gas was then added in steps and withdrawn in steps. Measurements of the pressure of gas in the quenching vessel and of the intensities of the radiation from each of the resonance vessels were made after each addition or removal of gas. It was found that there were no significant changes in intensity of radiation from the resonance vessel after about three minutes after addition of gas. In practice periods of 5 and 10 min. were allowed to elapse between addition of gas and taking of measurements. The quenching ratios obtained on addition and removal of gas were not significantly different.

At the conclusion of a quenching run the furnace was allowed to cool to room temperature and with the potassium lamp operating under steady conditions detector measurements were made of the intensities of the reflected radiation from the quenching vessel. As the vapor pressure of potassium at 36.4°C. is about 0.03 of the vapor pressure at 71°C. and as the intensity of the radiation from the resonance vessels was not detectably dependent on temperature at temperature less than 35°C. it is legitimate to conclude that the intensity of resonance radiation at room temperature relative to that at 76° (the mean temperature during the experiments) is negligible. These measurements indicated that the reflected radiation constituted from 5 to 20%

of the radiation emitted from the resonance vessel, the higher figure applying to the earlier measurements involving the quartz vessel. Measurements of the intensity of the irradiating beam were also made with the photronic cell inserted directly into the beam so that sizable variations in beam intensity and therefore in reflected radiation between hot and cold runs could be detected and allowed for. In fact the effect of such corrections on the allowance for reflected light was negligible.

Variations in the intensity of the irradiating beam or small variations in the concentration of potassium vapor due to change in furnace temperature would change the detector reading for radiation from reference and quenching vessel proportionally. Consequently the readings of intensity for radiation from the quenching vessel during a single run were corrected by dividing by a factor proportional to the reference vessel reading. The readings obtained in the initial stages of a run were arbitrarily chosen as standard to which the other readings were adjusted. From these adjusted values, the intensity of reflected radiation (determined in the cold run and adjusted on a proportional basis for variation in intensity of irradiating beam between the cold run and the initial measurements of the hot run) was subtracted. From these final values for fluorescent intensity the quenching ratios were obtained by dividing the intensity applying for a given pressure of added gas by the intensity applying for no added gas.

EXPERIMENTAL RESULTS

Considerable difficulty was encountered in obtaining quenching curves which were reproducible and independent of the position in the quenching vessel of the volume of potassium vapor which yielded the radiation which was measured. It was found essential to have the deposit of potassium within the body of the resonance vessel. Moreover, with the quartz vessel, an approach to reproducibility could be obtained only when the fluorescent radiation came from a volume relatively near the source of potassium. When the resonance radiation came from a region close to the front face of the vessel and relatively distant from the source of potassium plots of the measured values of $1/Q$ against pressure, P, yielded curves bending away from the P axis. At temperatures above 90°C. this effect was observed regardless of the positions of the resonating potassium vapor yielding the radiation which was measured. The effect became more pronounced with use of the resonance vessel. Apparently the concentration of potassium vapor was being reduced below its equilibrium value by reactive processes and this reduction was leading to abnormal drops in the intensity of the resonance radiation.

On the other hand the results obtained with the pyrex vessel were reproducible and independent of thickness of the fluorescent beam over the range of temperature 71 to 80°C. No attempts were made to examine the behavior at temperatures in excess of 80°C. or at less than 71°C. The independence of quenching ratio on the vapor pressure of potassium over the 9 degree range and on the thickness of the fluorescent beam suggests that effects due to imprisonment are negligible.

The experimental results are given in Fig. 2 as plots of $1/Q$ against pressure. The results include data from all runs with the pyrex vessel except one which was omitted because of poor distribution of potassium in the vessel. There are included data from a small group of runs in the quartz vessel selected on the basis that they yielded the smallest $1/Q$ values. The thickness of the fluorescent beam under observation ranged from 2 to 5 mm. There appears to be no significant change in slope of $1/Q$ against pressure over the temperature range 71 to 83°C. However there should be a small dependence of $1/Q$ (for a

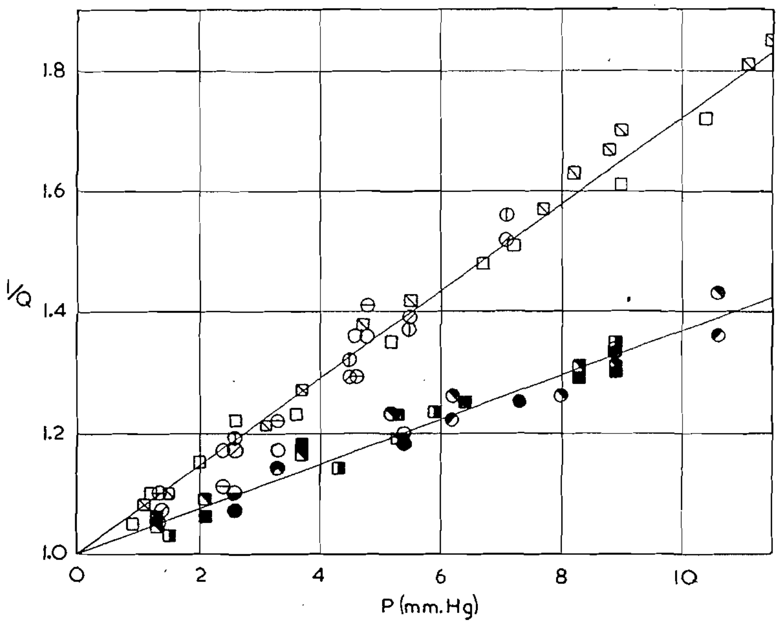

Fig. 2. $1/Q$ for various pressures of hydrogen and deuterium

Data for hydrogen			Data for deuterium		
	Quenching Vessel	Temperature °C.		Quenching Vessel	Temperature °C.
□	quartz	74	■	quartz	71
□	quartz	83	◩	quartz	71
○	pyrex	71	◨	quartz	76
⊖	pyrex	71	●	pyrex	71
⦶	pyrex	76	◒	pyrex	71
⊘	pyrex	76	◕	pyrex	80
			◑	pyrex	80

given pressure) on temperature if the cross section for quenching is independent of temperature because of the variation in concentration and molecular velocity with temperature. It is possible to correct the values of $1/Q$ to a common basis, that for T_{ref}, by multiplying each value of $(1/Q-1)$ by $(T/T_{\mathrm{ref}})^{\frac{1}{2}}$ where T is the absolute temperature at which the determination was made. However in view of the smallness of the corrections (less than one per cent) and the relatively low precision of our results we have not applied this correction. From the slope of the $1/Q$ vs. P plot of Fig. 2, 76°C. as the temperature, 2.71×10^{-8} seconds as the value of τ, we have determined that σ^2 for hydrogen is 1.56 Å^2 and σ^2 for deuterium is 1.10 Å^2.

DISCUSSION

The cross section for the quenching of excited sodium atoms by hydrogen is substantially larger than the cross section 1.56 Å^2 which we have found for the quenching of excited potassium. Norrish and Smith (6) found a cross section of 7.4 Å^2 at a temperature of 130°C. with sodium excited by the resonance method similar to that employed in the present work. Winans (10) using high velocity excited sodium atoms produced by the photodissociation of sodium iodide found that the cross section for quenching by hydrogen decreased with increasing velocity of the sodium atoms and attained a value of 5.7 Å^2 for the maximum velocity investigated which was about 10 times the mean velocity at 130°C.

Magee and Ri (4) and Laidler (3) have attempted theoretical calculations of the cross section for quenching of excited sodium by hydrogen. Both treatments describe the process in terms of the formation of a relatively stable complex of alkali metal and hydrogen and a transition to the ground state during the life of the complex with a probability close to unity. In Magee and Ri's treatment the critical state corresponds to the top of the rotational energy barrier for the formation of a complex involving excited alkali metal and hydrogen. In estimating the cross section it is assumed that complexes with rotational energy below a certain value have during their lifetime a probability of transition to the ground state (via an ionic state) near unity, but that the probability is zero if the rotational energy exceeds this value. In Laidler's treatment the cross section for quenching is identified with the square of the separation of centers of Na (^{2}P) and H_2 which, with the minimum potential energy, permits contact of the excited and the ionic (Na^+ H_2^-) potential energy surfaces. A slight extension of the H—H bond which nevertheless involves insignificant activation energy must be assumed and the critical separation for contact of the surfaces is identified with that corresponding to the minimum in the potential energy curve for the ionic state (Na^+ H_2^-) where the H—H separation is constrained to the slightly extended value. This configuration permits formation of an ionic complex and it is assumed that the probability of transition to the ground state is very much greater than the probability of decomposition of the complex so that once the ionic complex is formed the probability of internal quenching is close to unity.

Magee and Ri indicate that the cross section for quenching of excited potassium should be less than that for sodium. Laidler's treatment suggests the converse since the greater diameter of the potassium ion should lead to a slightly greater critical separation for alkali metal and hydrogen. Our results appear to contradict Laidler's treatment. However an energy of activation for the attainance of the critical state or a probability of transition to the ground state during the life of the complex of appreciably less than unity could lead to a reduced cross section for the quenching of excited potassium. It is impossible, by the technique used in this work, to determine experimentally the activation energy for quenching processes involving potassium. However, the work of Smith and Southam (7) indicated no appreciable activation energy for the quenching of excited sodium with methane, a process with very small cross section, and as far as we can determine there appears to be no evidence for any quenching process which does have an activation energy. The probability of internal quenching during the life of the complex depends on the life time of the complex, the availability of those configurations of the ionic complex from which transitions to the ground state can occur and on the probabilities of the transitions. This appears to be a problem for theoretical rather than experimental examination.

Our data indicate a cross section for quenching by deuterium which is less than that for hydrogen. This cannot be attributed to a difference in potential energy relations, nor does it appear that the difference in zero point energies of critical complex and "reactants" would favor the formation of the complex of hydrogen and potassium above that of the more massive deuterium–potassium complex. The difference in cross sections would appear then to be attributable to differences in the probability of transition between states during the life time of the complex.

ACKNOWLEDGMENTS

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KINETICS OF THE HOMOGENEOUS REACTION BETWEEN CUPRIC ACETATE AND MOLECULAR HYDROGEN IN AQUEOUS SOLUTION[1]

BY R. G. DAKERS[2] AND J. HALPERN

ABSTRACT

Cupric acetate was found to react homogeneously with molecular hydrogen in aqueous solution according to the following equation:

$$2Cu(OAc)_2+H_2+H_2O \rightarrow Cu_2O+4HOAc.$$

The paper describes a kinetic study of this reaction. Rates were determined at temperatures between 80 and 140°C. and hydrogen partial pressures between 6.8 and 34.0 atm. The reaction was found to be of second order, the rate being proportional to the concentrations of cupric acetate and molecular hydrogen. It was established that the rate was independent of the surface of the reaction vessel, the cuprous oxide product and of the concentrations of sodium acetate and acetic acid in the solution. The reaction has an activation energy of 24200 cal. per mole. The kinetic results are discussed and a mechanism is proposed. This appears to be one of the few known homogeneous reactions of molecular hydrogen in solution.

INTRODUCTION

Molecular hydrogen is a relatively unreactive gas. Its homogeneous reactions are often characterized by large activation barriers which reflect the high dissociation energy of the H—H bond and the repulsion forces associated with the closed shell configuration of the H_2 molecule in its ground state.

Many substances are known which lower the activation energies of hydrogenation reactions and thus function effectively as catalysts for these reactions. With few exceptions such catalysts are solids, common examples being the group of metals which includes Ni, Co, Pt, and Pd and certain metallic oxides such as CuO, Cr_2O_3, ZnO, and their mixtures (3). The action of these catalysts has been widely studied particularly with reference to organic hydrogenation reactions some of which are of great industrial importance. Nevertheless the detailed mechanism by which they operate is still not fully understood. It is generally believed that the primary function of the catalyst is to activate the hydrogen through chemisorption (3, 19). The catalyzed reaction then occurs heterogeneously. In some cases the catalyst may also serve to activate the reactant undergoing hydrogenation. Theories have been advanced which relate the activity of hydrogenation catalysts to their lattice spacing (1, 2) and to the character of their electronic bands (6, 21). These theories generally imply that catalytic activity, associated with the ability to activate molecular hydrogen, is confined to solids.

Recently there has been increasing interest in inorganic hydrogenation reactions involving the reduction of metallic ions in aqueous solutions. Reactions of this type have found important metallurgical application as methods of recovering metals from leach solutions (7, 8). The reduction of ions such as

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Ni^{++}, Co^{++} (14), UO_2^{++} (8), and VO_3^- (16) has been examined kinetically. All these reactions were shown to proceed heterogeneously and to require the presence of hydrogenation catalysts of the usual type such as finely divided metallic nickel or cobalt.

Of special interest is the reduction of cupric acetate in aqueous solution. Ipatieff and Werchowsky (11) first observed this reaction and reported that cuprous oxide was formed as the product under certain conditions. Recent work in this laboratory has confirmed that this reaction takes place at relatively low temperatures and hydrogen partial pressures and that unlike most hydrogenation reactions it does not require an added catalyst but proceeds homogeneously in solution (10). The present paper describes a kinetic study of this reaction, undertaken with a view to establishing its mechanism and determining the nature of the process through which the hydrogen becomes activated.

Only two other systems involving homogeneous hydrogenation reactions in solution appear to have been studied. Calvin (4, 5) found that cuprous acetate, dissolved in quinoline, catalyzed the homogeneous hydrogenation of compounds such as quinone. It has been suggested (5, 24) that in this system the hydrogen becomes activated through homogeneous interaction with a dimeric complex of cuprous acetate. The solvent appears to play an important role in this process since the reaction is confined to a narrow group of nitrogen containing solvents.

Recently Wender and his co-workers (17, 25) have reported that dicobalt octacarbonyl, $Co_2(CO)_8$, which is formed when metallic cobalt is treated with carbon monoxide at high pressures, also activates hydrogen and thus functions as a homogeneous catalyst in a variety of hydrogenation reactions. The activity of this catalyst like that of cuprous acetate has been observed only in certain organic solvents. The reduction of cupric acetate, described in this paper, appears to be the first instance of a homogeneous hydrogenation reaction reported to occur in aqueous solution.

EXPERIMENTAL

Materials

Cupric acetate, sodium acetate, ammonium acetate, and acetic acid, all of Reagent Grade, were supplied by Nichols Chemical Co. The solutions were prepared by dissolving weighed quantities of these chemicals in distilled water. Commercial hydrogen gas, supplied in cylinders by Canadian Liquid Air Co., was used without further purification.

Apparatus

The experiments were conducted in an autoclave manufactured by Autoclave Engineers Inc. and constructed entirely of No. 316 stainless steel which proved inert to the solutions used. The vessel had a capacity of 1 gal. and was designed for working pressures of up to 1200 lb. per square inch. A stirrer shaft, thermocouple well, cooling coil, and sampling tube extending below the surface of the solution, were connected through the lid of the autoclave. The solution was stirred with an impeller of 2.5 in. diameter which rotated at 900 r.p.m. The sampling tube was fitted with a stainless steel filter of fine porosity so that samples of solution withdrawn for analysis were free of cuprous oxide product. The partial pressure of hydrogen above the solution was controlled by a standard gas regulator. The autoclave was heated with a gas ring burner, the temperature of the solution being maintained to within ±0.5° C. with a Leeds and Northrup Micromax recording controller.

Procedure

Three liters of solution of desired composition was placed in the autoclave which was then sealed, flushed with nitrogen, and heated to temperature. Hydrogen was introduced and maintained at a desired partial pressure. Samples of the solution were withdrawn periodically and the concentration of unreacted cupric acetate determined with a Beckman DU Spectrophotometer using the blue cupric ammine color developed by addition of ammonia. The experiments were generally continued until about 98% of the cupric acetate had reacted. The charge was then removed from the autoclave and the cuprous oxide product separated by filtration, washed, and analyzed.

RESULTS

Stoichiometry of the Reaction

The solutions of cupric acetate used in these experiments generally contained about 0.5 M./liter of acetic acid and 0.5 M./liter of either sodium or ammonium acetate, added to buffer the pH of the solutions at a value between 4 and 5. Attempts to study the reaction in the region of higher pH were complicated by hydrolysis of cupric acetate and precipitation of basic cupric salts when the solutions were heated to the reaction temperature.

On introduction of hydrogen into the autoclave, a visible precipitate of cuprous oxide was immediately formed. As the reaction proceeded the cupric acetate concentration and the pH of the solution both decreased progressively, reflecting the formation of cuprous oxide and acetic acid as the reaction products. The reaction proceeded in every instance until the amount of copper remaining in solution was less than 0.003 M./liter, which corresponds to about 1 or 2% of the original cupric acetate concentration. Because of the buffering action of the acetate the pH drop during an experiment was usually less than 0.5 units.

The cuprous oxide product was identified by chemical analysis (Cu: found, 88.5 ± 0.3%; theoretical, 88.8%) and by X-ray diffraction measurements (lattice constant: found, 4.25 ± 0.01Å; given (13), 4.255Å). In no experiment could any reduction products of cupric acetate, other than cuprous oxide, be detected.

An observation of some interest was that the appearance of the cuprous oxide product differed, depending on whether the solution contained sodium acetate or ammonium acetate. If the solution contained sodium acetate, the product was bright red while if it contained ammonium acetate, the color ranged from dark purple to black. Both products were crystalline solids apparently identical in chemical composition and crystal structure. The difference in color was presumably due to differences in grain size. Reference has recently been made (12) to similar variations in the appearance of cuprous oxide prepared by other methods.

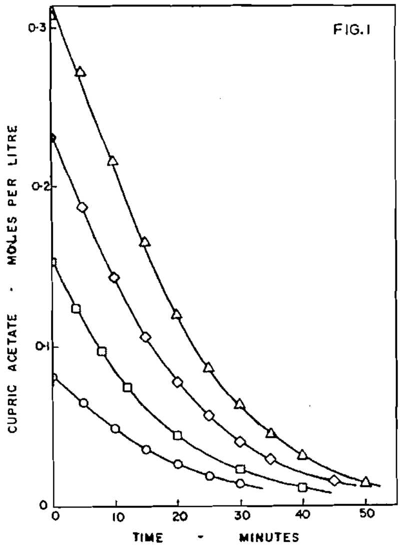
The stoichiometry of the reaction appears to be represented by the following equation:

$$2Cu(OAc)_2 + H_2 + H_2O \rightarrow Cu_2O + 4HOAc. \qquad [1]$$

When hydrogen was present in excess this reaction always went essentially to completion. The solubility of the cuprous oxide product was negligible.

Kinetics of the Reaction

Rate curves depicting the course of some typical experiments, throughout which the temperature and hydrogen partial pressure were held constant, are shown in Fig. 1. The cupric acetate concentration always fell off according to a first order kinetic law, illustrated by the linear plots of log $[Cu(OAc)_2]$ against time in Fig. 2. First order rate constants, k_1, calculated from the slopes of these plots were generally reproducible to within ±5%.



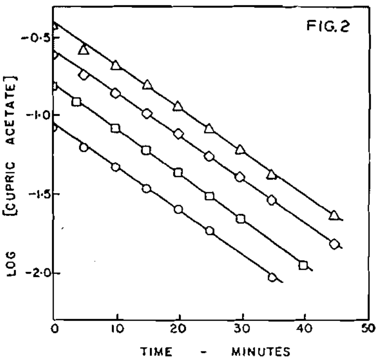


Fig. 1. Typical rate curves for the reaction of cupric acetate with hydrogen. Temperature, 130°C. H_2 partial pressure, 13.6 atm.

Fig. 2. Typical first order rate plots showing effect of varying initial cupric acetate concentration.

Further indication of first order kinetic behavior is provided by data in Table I which show that values of k_1 determined in this way are independent of the initial cupric acetate concentration. The rates were also found to be independent of the volume of solution and of the speed of rotation of the stirrer above 500 r.p.m.

Data are also provided in Table I which show that the rate of reaction remained essentially constant when the pH of the solution and the concentrations

TABLE I

EFFECT OF VARYING THE COMPOSITION OF SOLUTION ON THE RATE OF REACTION BETWEEN CUPRIC ACETATE AND HYDROGEN

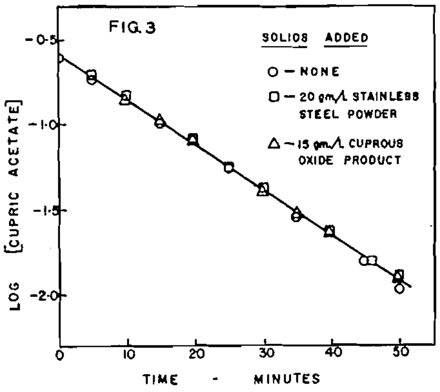
Temperature, 130°C.
H_2 partial pressure, 13.6 atm.

$Cu(OAc)_2$, M./liter	NH_4OAc, M./liter	NaOAc, M./liter	HOAc, M./liter	pH		k_1, min.$^{-1}$
				Initial	Final	
0.08	0	0.25	0.31	4.6	4.5	0.0614
0.16	0	0.25	0.38	4.5	4.1	0.0668
0.24	0	0.25	0.44	4.5	4.1	0.0643
0.32	0	0.25	0.40	4.5	4.1	0.0632
0.24	0	0.43	0.64	4.5	4.2	0.0629
0.24	0.25	0	0.10	5.1	4.3	0.0613
0.24	0.50	0	0.18	5.1	4.6	0.0617
0.24	0.75	0	0.26	5.1	4.7	0.0617
0.24	0	0.25	0.29	4.8	4.3	0.0631
0.24	0	0.25	0.44	4.5	4.1	0.0643
0.24	0	0.25	1.17	4.0	3.8	0.0691
0.24	0	0.25	2.35	3.7	3.6	0.0696

of sodium acetate and ammonium acetate were varied over a considerable range. On the basis of these results it can be assumed that the rates were not influenced by the much smaller changes in pH which occurred during the course of each experiment as a result of the formation of acetic acid as one of the reaction products. It may also be concluded that neither acetic acid nor acetate ion participates explicitly in the rate controlling step of the reaction.

Homogeneous Character of the Reaction

It was considered of particular importance to establish that the surface of the stainless steel autoclave was without catalytic effect on the reaction. An experiment was therefore made in which 20 gm. per liter of similar stainless steel, in the form of powder, was added to the solution. The surface area of this powder was estimated to be about 100 sq. cm. per gm. The total area of the added powder was thus at least five times as great as the surface area of



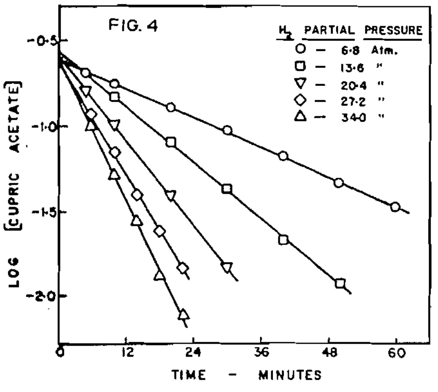


FIG. 3. Effect of surface on the rate.

FIG. 4. First order rate plots at different partial pressures of hydrogen. NaOAc, 0.25 M./liter. HOAc, 0.44 M./liter. Temperature, 130°C.

the autoclave normally in contact with the solution. Fig. 3 shows that, within experimental accuracy, the addition of this powder had no effect on the rate.

The results of a similar experiment in which 15 gm. per liter of cuprous oxide powder, the product from an earlier run, was added to the solution, are also depicted in Fig. 3. Again no effect on the rate could be detected.

These results provide direct confirmation of the homogeneous character of the reaction.

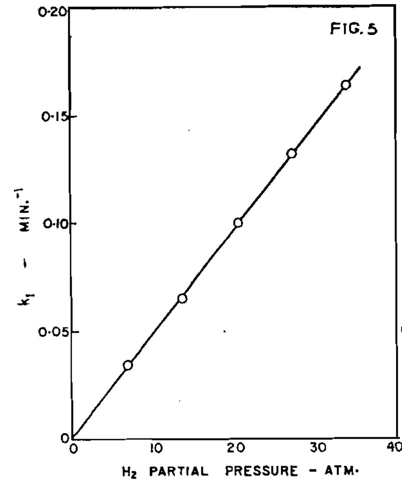
Effect of Hydrogen Partial Pressure

Fig. 4 shows the rate curves for a series of experiments in which the partial pressure of hydrogen was varied from 6.8 to 34.0 atm. The results are summarized in Fig. 5 where the rate is plotted against the hydrogen partial pressure. It is seen that the first order rate constant, k_1, is directly proportional to the partial pressure, P_{H_2}. Since the solubility of hydrogen in most aqueous solutions obeys Henry's law over this range of pressures (22), this relation also implies that k_1 is proportional to the concentration of molecular hydrogen in solution, $[H_2]$.

A new bimolecular rate constant, k_2, which is independent of the concentrations of both cupric acetate and hydrogen may thus be defined by the relation,

$$k_1 = k_2[H_2] = k_2 \alpha P_{H_2} \qquad [2]$$

where α is Henry's constant, denoting the solubility of H_2.



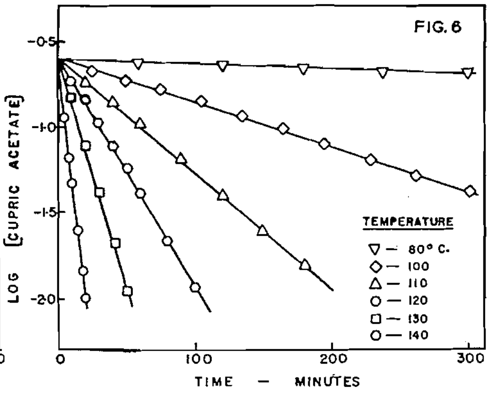


FIG. 5. Dependence of the rate on hydrogen partial pressure at 130°C.

FIG. 6. First order plots at different temperatures. NaOAc, 0.25 M./liter. HOAc, 0.44 M./liter. H_2 partial pressure, 13.6 atm.

The rate of reaction of cupric acetate can be expressed in terms of k_2 as follows:

$$-d[Cu(OAc)_2]/dt = k_2[Cu(OAc)_2]\,[H_2]\,. \qquad [3]$$

Values of α have not been determined for cupric acetate solutions, but the corresponding value of α denoting the solubility of H_2 in pure water is known to be 7.14×10^{-4} moles atm.$^{-1}$ liter^{-1} and to remain nearly constant with temperature over the range 60° to 100° C. where some of these experiments were conducted (22). Such determinations as have been made of the effect of acetic acid and various salts on the solubility of hydrogen in water (22) suggest that for solutions of the composition used in these experiments (i.e., approximately 0.5 M HOAc and 0.5 M NaOAc or NH_4OAc), α would be about 10% lower than for pure water or approximately 6.4×10^{-4} moles atm.$^{-1}$ liter^{-1}. It is believed that negligible error is introduced by assuming this value for the purpose of the present calculations.

Dependence of the Rate on Temperature

Rate curves for a series of experiments at temperatures ranging from 80° to 140° C. are given in Fig. 6. A good Arrhenius plot, shown in Fig. 7, was obtained when log k_1 was plotted against $1/T$. The activation energy, E, estimated from the slope of this plot using the Arrhenius relation, is 24200 ± 800 cal. per mole.

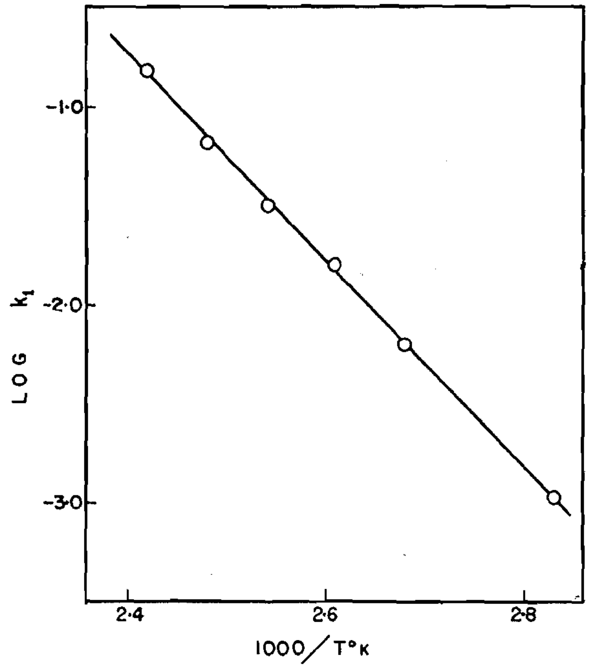


FIG. 7. Arrhenius plot for the reaction between cupric acetate and hydrogen. H_2 partial pressure, 13.6 atm.

If the solubility of hydrogen is taken to be independent of temperature, this activation energy can also be associated with the bimolecular rate constant, k_2. Assuming α to have the value, 6.4×10^{-4} moles atm.$^{-1}$ liter^{-1}, k_2 is given by:

$$k_2 = 9.6 \times 10^{13} \exp\left[\frac{-24200}{RT}\right] \text{liter mole}^{-1} \text{min.}^{-1} \qquad [4]$$

DISCUSSION

Mechanism of the Reaction

The kinetic results suggest that the rate determining step of the reaction is a bimolecular process involving one molecule of cupric acetate and one molecule of hydrogen. This step must lead to the formation of a complex in which the hydrogen has become activated so that its subsequent dissociation or reaction with another molecule of cupric acetate to give the observed reaction products is rapid. Such a sequence of steps may be represented as follows:

$$1.\ \mathrm{Cu(OAc)_2} + \mathrm{H_2} \xrightarrow[\text{slow}]{k} \mathrm{Cu(OAc)_2.H_2}. \qquad [5]$$

$$2.\ \mathrm{Cu(OAc)_2.H_2} + \mathrm{Cu(OAc)_2} + \mathrm{H_2O} \xrightarrow[\text{fast}]{} \mathrm{Cu_2O} + 4\ \mathrm{HOAc}. \qquad [6]$$

$$\text{Over-all reaction: } 2\mathrm{Cu(OAc)_2} + \mathrm{H_2} + \mathrm{H_2O} \xrightarrow{k_2} \mathrm{Cu_2O} + 4\ \mathrm{HOAc}$$

The first step in this sequence is considered to be rate determining. The rate constant for this step, k, is related to that for the over-all reaction, k_2, as follows:

$$2k = k_2. \qquad [7]$$

The factor, 2, in this expression reflects the fact that only one molecule of cupric acetate is involved in the rate determining step while two molecules are involved in the equation from the over-all reaction.

Combining equations [4] and [7] gives the following expression for k:

$$k = 4.8 \times 10^{13} \exp\left[\frac{-24200}{RT}\right] \text{liter mole}^{-1}\ \text{min.}^{-1} \qquad [8]$$

The value 4.8×10^{13} liter mole^{-1} min.$^{-1}$ for the Arrhenius frequency factor in this equation corresponds to an activation entropy, $\Delta S_c^{\ddagger}$, of -6.5 e.u. at 100° C. (9). These values are normal (15, 20) for a simple bimolecular reaction in solution, such as that represented by Equation [5]. This provides further support for the mechanism and rate determining steps which have been postulated above.

Nature of the Reactive Species

In the preceding discussion the reaction has been represented as involving undissociated $\mathrm{Cu(OAc)_2}$ molecules rather than simple cupric ions or other cupric complexes. This appears to be consistent with the kinetic results taken in conjunction with independent measurements of the dissociation constants of cupric acetate (18). These measurements indicate that in solutions of the composition used in these experiments, cupric acetate is predominantly undissociated. The degree of dissociation to $\mathrm{CuOAc^+}$ ranges from about 10% at the highest NaOAc concentration of 0.75 M./liter to about 25% at the lowest concentration of 0.25 M./liter. The dissociation to $\mathrm{Cu^{++}}$ is negligible. The insensitiveness of the rate to the concentration of acetate ion within this range and the magnitude of the frequency factor then provide fairly strong indication that the observed reaction is due predominantly to the undissociated cupric acetate molecules, with other cupric species making only a minor contribution. The low concentrations of these species and the limited accuracy of the measurements make it difficult to evaluate this contribution quantitatively.

Similar considerations discourage the suggestion that cuprous acetate, which may be formed as an intermediate, has an appreciable catalytic influence on the reaction. Cuprous acetate is unstable in aqueous solution where it is hydrolyzed and precipitated quantitatively as cuprous oxide (23). This was found to be the case for the solutions used in the present study and it may be concluded that only trace concentrations of cuprous acetate were present in these solutions during reaction. Such limiting concentrations would be highly variable, and particularly sensitive to the pH and acetate ion content of the solution. Any reaction mechanism in which an important catalytic influence is attributed to cuprous acetate would thus appear to be inconsistent with the observed kinetics. This is of interest in view of earlier work which indicated that cuprous acetate activates hydrogen homogeneously in quinoline solution (4, 5, 24). The two systems appear to be unrelated.

It is of further interest that the reaction does not appear to involve a dimeric complex incorporating two copper atoms. There has previously been evidence for only two other homogeneous hydrogenation reactions, in each of which the effective catalyst was apparently a dimeric molecule containing two metal atoms, i.e., $Cu_2(OAc)_2$ and $Co_2(CO)_8$. It has been suggested that, in order to be capable of activating molecular hydrogen homogeneously, a molecule must possess such a dimeric configuration which allows the two hydrogen atoms to become simultaneously bonded to metal atoms (24). However, the results of the present study fail to support this view.

CONCLUSIONS

Cupric acetate is reduced homogeneously by hydrogen in aqueous solution. The kinetic data which were obtained in this investigation have permitted only the general features of the mechanism and the sequence of steps involved in this reaction to be deduced. The detailed configuration of the complex formed by interaction of hydrogen and cupric acetate and the nature of the forces which stabilize this complex and thus contribute to the activation of the hydrogen remain to be elucidated.

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CHLORINE ISOTOPE EFFECT IN REACTIONS OF *TERT*-BUTYL CHLORIDE[1]

By Rosalie M. Bartholomew, F. Brown, and M. Lounsbury

ABSTRACT

When *tert*-butyl chloride reacts with either alcoholic silver nitrate or aqueous alcoholic sodium hydroxide the Cl^{35} compound reacts faster than the Cl^{37} compound. The ratio of the rates of reaction is $1.008^{+0.002}_{-0.001}$.

INTRODUCTION

A previous publication (1) has summarized some experiments showing that when *tert*-butyl chloride reacts with ethyl alcoholic silver nitrate solution, the Cl^{35} compound reacts faster than the Cl^{37} compound. This paper describes these experiments in more detail, together with some further experiments in which the chloride was allowed to react with aqueous alcoholic sodium hydroxide solution.

The reaction being studied is essentially the same in both series of experiments. The rate controlling step is the reaction:

$$C_4H_9Cl \rightleftharpoons C_4H_9^+ + Cl^-.$$

In the presence of silver nitrate the back reaction is prevented because the chloride ion is removed as silver chloride; the $C_4H_9^+$ ion reacts rapidly with the solvent to produce *tert*-butyl-ethyl-ether:

$$C_4H_9^+ + C_2H_5OH \longrightarrow C_4H_9OC_2H_5 + H^+.$$

When aqueous alcoholic sodium hydroxide is the medium, the $C_4H_9^+$ ion again reacts with the solvent or with the hydroxyl or ethoxide ions so that *tert*-butyl alcohol or *tert*-butyl-ethyl-ether is produced. The back reaction is prevented by the basic nature of the solution, since neither *tert*-butyl alcohol nor *tert*-butyl-ethyl-ether react with chloride ion in the absence of acid. For a summary of the mechanism of the reactions of alkyl chlorides, see Reference 4.

In the first series of experiments (1) the *tert*-butyl chloride was allowed to react with alcoholic silver nitrate solution ($M/10$) at room temperature. By means of three separate experiments the silver chloride arising from reaction of (*a*) the *first* 35%, (*b*) the *last* 5%, and (*c*) the whole of the *tert*-butyl chloride was isolated. The isotopic composition of the chlorine in these samples was determined mass spectrometrically after conversion of the silver chloride to chlorine gas. In the second series of experiments the *tert*-butyl chloride was allowed to react with 50% aqueous alcoholic sodium hydroxide ($M/10$) at room temperature. Once again the chloride ion formed by reaction of (*a*) the *first* 10% and (*b*) the *last* 7.5% was isolated and the isotopic composition determined.

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In all cases the extent of the reaction was measured by gravimetric analysis. By comparing the Cl^{35}/Cl^{37} ratios in the various samples with that in the original *tert*-butyl chloride (obtained from the experiment in which all of the chloride was allowed to react with silver nitrate) the relative rates of reaction k^{35}/k^{37} were obtained.

EXPERIMENTAL

The *tert*-butyl chloride used was obtained from commercial stock of boiling point 49.5–50.5°C. and redistilled before use. The portion used had a boiling point which was constant within ±0.25°C. The alcoholic silver nitrate was $M/10$ in 98% ethyl alcohol. The aqueous alcoholic sodium hydroxide was $M/10$ in a mixture of equal volumes of water and 98% ethyl alcohol.

Reactions with Silver Nitrate Solution

The "35%" reaction.—*Tert*-butyl chloride (2.0 ml., 1.69 gm.) was added to alcoholic silver nitrate solution ($M/10$, 200 ml.) at room temperature (about 20°C.) and the solution shaken until the precipitated silver chloride just coagulated (about five minutes). It was then filtered as rapidly as possible through a "Buckner" funnel and the precipitate washed with alcohol. This precipitate was dissolved in strong ammonia solution and reprecipitated by adding nitric acid. The precipitate was then collected in a weighed sintered glass crucible, dried at 110°C., and weighed. It was found that 34.8% of the *tert*-butyl chloride had reacted. It would have been better to have had a much smaller percentage reaction but five minutes was the minimum time required for the precipitate to coagulate sufficiently for effective filtration.

The "last 5%" reaction.—The reaction mixture was as above; the reaction was allowed to proceed for one hour, then the precipitate was filtered off and discarded. The filtered reaction mixture was then allowed to continue reacting overnight and the silver chloride produced was isolated and weighed as before. This silver chloride corresponded to 5.2% reaction of the *tert*-butyl chloride, i.e. 94.8% had reacted when the initial precipitate was rejected.

The "100%" reaction.—The above experiments were repeated except that the mixture was allowed to react for several hours, which is sufficient to bring about complete reaction and the *whole* of the precipitate was isolated as described above.

The Reactions with Aqueous Alcoholic Sodium Hydroxide Solution

The "10%" reaction.—*Tert*-butyl chloride (2.0 ml., 1.69 gm.) was added to aqueous alcoholic sodium hydroxide ($M/10$, 200 ml.) at room temperature (about 20°C.) and the solution left for 10 min. The solution was then extracted three times with benzene, and the benzene layer was rejected (to remove unreacted *tert*-butyl chloride). The aqueous alcohol phase was diluted with an equal volume of water and extracted with benzene again (the benzene being rejected). The aqueous phase now contained the sodium chloride formed by partial reaction of the *tert*-butyl chloride. The solution was acidified with nitric acid and the chloride determined as silver chloride; 10.2% of the *tert*-butyl chloride had reacted.

The "last 7.5%" reaction.—The reactants were as above. After two and one half hours' reaction the solution was extracted twice with benzene, and the aqueous alcohol phase rejected. The benzene layer (containing the unreacted *tert*-butyl chloride) was washed quickly with ice-cold water (with rejection of the aqueous washings) and then boiled under reflux with 50 ml. of $M/10$ aqueous sodium hydroxide for several hours. The resulting mixture was then cooled and the benzene layer was rejected. The aqueous solution now contained the chloride ion (as sodium chloride) corresponding to the *tert*-butyl chloride which had been unreacted at the time of the original benzene extraction. This chloride ion was converted to silver chloride by the standard procedure of gravimetric analysis and weighed. It corresponded to 7.53% of the original *tert*-butyl chloride, i.e. 92.47% had reacted at the time of the initial benzene extraction.

Conversion of Silver Chloride to Chlorine Gas

The various samples of silver chloride obtained as above were converted to chlorine gas for mass spectrometric analysis. The silver chloride was dissolved in strong ammonia solution and the silver removed by precipitation with hydrogen sulphide. The solution was evaporated just to dryness (with the occasional addition of a few drops of ammonia solution) leaving a residue of ammonium chloride. The dried ammonium chloride was heated with concentrated sulphuric acid and, by means of a stream of nitrogen, the hydrogen chloride thus evolved was swept through a bubbler containing a little cold water. The aqueous hydrochloric acid was converted to chlorine gas by persulphate oxidation (2) in a stream of helium. The chlorine gas was frozen from the helium stream into a trap cooled in liquid nitrogen and transferred to a vacuum line where the helium was removed. The chlorine was dried over phosphorus pentoxide for 15 min. and transferred to the mass spectrometer sampling bulbs.

Mass Spectrometry

A 90°-deflection, 6-in. radius mass spectrometer (3) was used for the isotopic analysis of the chlorine gas. A silicone oil diffuson pump was used in the gas inlet system, and apiezon high vacuum grease was used for stopcocks and ground joints. The fore-leak pressure was adjusted by means of an evacuated expansion bulb. The mass spectrum was scanned magnetically and recorded with a Leeds and Northrup Speedomax Type G.

The mass spectrometer can exhibit a memory effect in the analysis of chlorine gas. However, if the samples are not widely different in their isotopic abundances, as is the case here, then the error arising from memory effect is small.

The two stable isotopes of chlorine combine to form the following molecular species:

Mass	Composition
70	$Cl^{35}Cl^{35}$
72	$Cl^{35}Cl^{37}$
74	$Cl^{37}Cl^{37}$

The isotopic abundance ratio is given by:

$$\frac{\mathrm{Cl}^{35}}{\mathrm{Cl}^{37}} = \frac{2(70)+(72)}{2(74)+(72)}$$

where (70) is the height of the mass 70 peak, and similarly for the others.

RESULTS

The relative rates of reaction for *tert*-butyl chloride Cl^{35} and Cl^{37} can be calculated from the results in two ways:

A. The isotopic composition of the chloride ion obtained by partial reaction of the *tert*-butyl chloride, i.e. that from the "first" portion of the reaction, can be compared with the isotopic composition of the chlorine in the original *tert*-butyl chloride.

B. Alternatively, the chlorine in the *tert*-butyl chloride which remains after partial reaction, i.e. that from the "last" portion, can be compared with the original. The isotope effect is calculated by treating the two isotopically distinguishable *tert*-butyl chlorides as two species undergoing separate first order reactions under identical reaction conditions.

The corresponding formulae are:—

$$[A] \qquad \frac{k^{35}}{k^{37}} = \frac{\ln[F_1{}^{35}/(F_1{}^{35}-pF_2{}^{35})]}{\ln[F_1{}^{37}/(F_1{}^{37}-pF_2{}^{37})]}$$

where:

k^{35}/k^{37} is the ratio of the rate constants;

$F_1{}^{35}$ and $F_1{}^{37}$ are the fractions of Cl^{35} and Cl^{37} in the chlorine of the original *tert*-butyl chloride—so that, if $\mathrm{Cl}^{35}/\mathrm{Cl}^{37}$ is the measured ratio of isotopic abundances, then:

$$F_1{}^{35} = \frac{\mathrm{Cl}^{35}/\mathrm{Cl}^{37}}{1+\mathrm{Cl}^{35}/\mathrm{Cl}^{37}} \text{ and } F_1{}^{37} = \frac{1}{1+\mathrm{Cl}^{35}/\mathrm{Cl}^{37}}\,;$$

$F_2{}^{35}$ and $F_2{}^{37}$ are the similar quantities for the chloride ion *produced* by partial reaction;

and p is the fraction of the *tert*-butyl chloride reacted.

$$[B] \qquad \frac{k^{35}}{k^{37}} = \frac{\ln[F_1{}^{35}/(1-p)F_3{}^{35}]}{\ln[F_1{}^{37}/(1-p)F_3{}^{37}]}$$

where:

$F_3{}^{35}$ and $F_3{}^{37}$ are for the chlorine in the *tert*-butyl chloride which *remains* after partial reaction;

and $(1-p)$ is the fraction remaining unreacted.

The results and calculated isotope effects are summarized in Table I.

In each case, the error shown for the isotopic abundance ratio $\mathrm{Cl}^{35}/\mathrm{Cl}^{37}$ is the standard deviation of the individual spectrograms from their mean. The errors shown for the ratios of rate constants k^{35}/k^{37} are calculated on the basis of the errors in $\mathrm{Cl}^{35}/\mathrm{Cl}^{37}$ ratios. Errors arising from the mass spectrometer memory effect are equivalent to a cross contamination of samples which is certainly less than 10% and is probably in the order of 2%. Any cross con-

TABLE I
SUMMARY OF RESULTS

	Cl^{35}/Cl^{37}	k^{35}/k^{37}
Reaction between C_4H_9Cl and $AgNO_3$ in alcohol		
(1) Chlorine from first 34.8% reaction	3.104±0.003	1.007±0.003
(2) Chlorine from 100% reaction	3.087±0.003	
(3) Chlorine from last 5.2% reaction	3.019±0.005	1.008±0.001
Reaction between C_4H_9Cl and NaOH in aqueous alcohol		
(4) Chlorine from first 10.2% reaction	3.113±0.003	1.009±0.002
(5) Chlorine from 100% reaction (taken to be same as (2) above)	3.087±0.003	
(6) Chlorine from last 7.53% reaction	3.035±0.004	1.007±0.001

tamination of sample tends to lessen the measured isotope effect because it makes the isotopic compositions of the various samples appear to be more nearly identical than they in fact are. A cross contamination of 10% would cause the observed k^{35}/k^{37} ratio be to be about 0.001 low. Allowing for this possibility the isotope effect may therefore be taken as $k^{35}/k^{37} = 1.008^{+0.002}_{-0.001}$.

CONCLUSION

The isotope effect is small but significant and is in the expected direction i.e., the heavier isotope of chlorine is bound more firmly to the carbon atom than is the lighter isotope and consequently undergoes bond breaking reactions less rapidly. There is no measurable difference in the effect for the two sets of reaction conditions.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS

I. CODEINE MONOHYDRATE, CODEINE (ANHYDROUS), DIHYDROCODEINONE[1]

BY W. H. BARNES AND W. J. FORSYTH*

This is the first of a series of short notes on the unit cell constants, space groups, and indexed X-ray diffraction powder data for a number of narcotics (largely opium alkaloids and some of their salts). The determinations were made to authenticate a few of the powder patterns obtained in a recent survey of 83 narcotics (3) and as a preliminary step in the choice of suitable compounds for detailed structure investigation.

The unit cell and space group data were collected by the Buerger precession method (4), films were measured with the standard measuring device (5), and corrections for film shrinkage (2) were applied. Unless specifically stated otherwise, all precession photographs were taken with either Cu K_α radiation (λ = 1.5418 Å) or Co K_α radiation (λ = 1.7902 Å). Densities were determined by flotation of clear crystals in binary solutions of carbon tetrachloride or methylene iodide with acetone or benzene, as dictated by the particular compound involved, and all measurements were made at a temperature of 21–23° C.

The techniques employed for the powder photographs have been described in detail elsewhere (1, 3) where the complete powder data will be found. In the present notes, only those values of the observed spacings (generally for $d > 3$ Å) are repeated for which it seems useful to record the indices of the corresponding planes. Although indexing was continued to lower values of d than the smallest appearing in the present Tables of powder data, coincidence of reflections becomes too numerous at the higher 2θ angles to make the inclusion of the indices of any value. In all cases, Co K_α radiation (λ = 1.790 Å) was employed for the powder photographs and the apparatus "cut-off" was 20 Å; film shrinkage corrections were not significant, and, therefore, were not applied. After indexing, the powder films were re-examined on the powder-film measuring device and an estimate was made of the reflections that might reasonably be expected to have contributed to a given line on the photograph; such reflections are bracketed in the columns of d(Calc.) in the tables of powder data. Reflections probably present, but with $I/I_1 < 1$, are indicated by an asterisk in the columns of d(Obs.). Lines which appeared to be broader than the general average for a given pattern are designated B (broad) and BB (very broad) in the columns of I/I_1.

Unless otherwise acknowledged, all substances (some of commercial and some of laboratory origin) which are the subject of the present series of notes

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TABLE I
SINGLE CRYSTAL DATA FOR CODEINE MONOHYDRATE, CODEINE (ANHYDROUS), AND DIHYDROCODEINONE

	Codeine monohydrate	Codeine (anhydrous)	Dihydrocodeinone
a	12.15 Å	13.68 Å	14.02 Å
b	12.63 Å	14.72 Å	14.64 Å
c	10.51 Å	7.48_7 Å	7.23_5 Å
S.G.	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Z	4 molecules/cell	4 molecules/cell	4 molecules/cell
ρ (calc.)	1.307 gm./ml.	1.318 gm./ml.	1.338 gm./ml.
ρ (obs.)	1.295 gm./ml.	1.310 gm./ml.	1.342 gm./ml.

TABLE II
INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.00$ Å) FOR CODEINE MONOHYDRATE

I/I_1	*d*(Å)		*hkl*	I/I_1	*d*(Å)		*hkl*
	Obs.	Calc.			Obs.	Calc.	
90	8.76	8.75	110	—	—	3.79	212
20	8.11	8.08	011			3.78	301
	*	7.95	101	30	3.72	3.72	131
50	6.73	6.73	111		*	3.62	311
20	6.32	6.31	020	1	3.44	3.46	230
—	—	6.07	200	30	3.36	3.41	320
25	5.59	5.60	120			3.38	013
	*	5.47	210			3.37	103
		5.41	021			3.36	222
40	5.25	5.26	002, 201	15	3.30	3.29	032, 231
100	4.85	4.94	121		*	3.25	113
		4.85	012, 211			3.24	321
		4.82	102		*	3.21	302
1	4.52	4.51	112			3.17	132
8	4.37	4.38	220			3.16	040
20	4.05	4.04	022, 221	2B	3.05	3.11	312
10	3.96	3.98	130			3.06	023
		3.97	202			3.05	140
	*	3.91	031			3.04	400, 203
15	3.85	3.86	310			3.02	041
		3.83	122				

TABLE III

INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.00$ Å) FOR CODEINE (ANHYDROUS) AND DIHYDROCODEINONE

Codeine (anhydrous)			
I/I_1	d(Å)		*hkl*
	Obs.	Calc.	
15	10.1	10.0	110
3	7.34	7.36	020
30	6.85	6.84	200
10B	6.63	6.67	011
		6.57	101
100	6.47	6.48	120
20	6.20	6.20	210
15	6.00	6.00	111
40	5.23	5.25	021
40	5.04	5.05	201
		5.01	220
60	4.89	4.90	121
30	4.77	4.78	211
	*	4.62	130
	*	4.36	310
5B	4.12	4.16	221
		4.10	031
—	—	3.99	230
45	3.88	3.93	131
		3.89	301
		3.88	320
75	3.77	3.76	311
		3.74	002
10	3.67	3.68	040
		3.63	012
—	—	3.61	102
15B	3.52	3.55	140
		3.52	231
		3.51	112
15	3.44	3.44	321
		3.42	400
5	3.34	3.34	022, 330
		3.33	410
—	—	3.30	041
		3.28	202
25B	3.23	3.24	122, 240
		3.21	141, 212
1	3.10	3.11	401
		3.10	420
20	3.05	3.05	331
		3.04	411

Dihydrocodeinone			
I/I_1	d(Å)		*hkl*
	Obs.	Calc.	
15	10.1	10.1	110
3	7.33	7.32	020
25	7.02	7.01	200
100	6.49	6.49	011, 120
3	6.38	6.43	101
		6.32	210
10	5.87	5.89	111
25	5.14	5.15	021
25	5.02	5.06	220
		5.03	201
40	4.83	4.83	121
3	4.76	4.76	211
—	—	4.61	130
	*	4.45	310
3	4.15	4.15	221
5	4.04	4.05	031
—	—	4.01	230
15	3.90	3.94	320
		3.93	301
		3.89	131
75	3.78	3.79	311
5B	3.64	3.66	040
		3.62	002
10	3.53	3.54	140
		3.51	012, 400
		3.50	102, 231
—	—	3.46	321
20	3.40	3.41	112, 410
		3.38	330
1	3.25	3.27	041
		3.25	240
		3.24	022
	*	3.22	202
18	3.16	3.18	141
		3.16	122, 420
		3.15	401
		3.14	212
10	3.07	3.08	411
		3.06	331

were kindly supplied by Dr. C. G. Farmilo. Their authentication has been discussed elsewhere (8).

Data for codeine monohydrate, $C_{18}H_{21}O_3N \cdot H_2O$, codeine (anhydrous free base), $C_{18}H_{21}O_3N$, and dihydrocodeinone (dicodide), $C_{18}H_{21}O_3N$, are presented in Tables I, II, and III. Codeine was crystallized from water as the monohydrate, and from absolute ethanol as the anhydrous base. Crystals of the hydrate gave a positive piezoelectric test. They are efflorescent and gradually become opaque, even in a closed vial, without losing their external form; such individual pseudomorphs give excellent powder patterns of anhydrous codeine without crushing. Specimens of codeine, therefore, sometimes represent mixtures of the hydrated and the anhydrous forms and this fact should be borne in mind when X-ray diffraction powder patterns are employed for the identification of codeine base. In the present investigation the monohydrate and the anhydrous phase were differentiated initially on the basis of the axial ratios deduced from the single-crystal data (Table I), thus, $a:b:c$ = 0.9621 : 1 : 0.8326 (compare, 0.9595 : 1 : 0.8346) (9, No. 2060) for codeine monohydrate, and $a:b:c$ = 0.9291 : 1 : 0.5085 (compare, 0.9298 : 1 : 0.5087) (9, No. 2059) for anhydrous codeine.

The ring to which the alcoholic OH is attached in codeine (morphine methyl ether), $CH_3O \cdot C_{17}H_{17}ON \cdot OH$, contains one double bond; in dihydrocodeinone, $CH_3O \cdot C_{17}H_{18}ON \cdot O$, this ring is fully saturated and a keto-oxygen replaces the OH; otherwise the structural formulae of the two compounds are identical. The crystal structures of both, therefore, may be expected to be very similar and this is supported by the single-crystal data of Table I and the powder data of Table II.

Castelliz and Halla (6) have reported the space group of codeine and of "β-methyl-morphimetin" (β-methylmorphimethine (10)) as $P2_12_12$. For codeine they found a = 27.70, b = 29.80, c = 7.59 Å (probably kX units). That the material they examined really was codeine (anhydrous free base), and that their unit cell orientation is the same as that on which the present data are based, is indicated (1) by the axial ratio calculated from their cell dimensions, thus, $a:b:c$ = 0.9295 : 1 : 0.2547 (i.e., 0.5094/2), (2) by the fact that if their values for a and b are each divided by 2, the three axial lengths are similar (actually 1% higher in each case) to the corresponding ones obtained in the present study (see Table I), and (3) their observed density is 1.3068 compared with the present value (observed) of 1.310. Why they should have doubled the lengths of both a and b and missed the screw-axis along c is not clear. The fact that they found 16 molecules per cell, thus requiring (as they realized) four sets of general fourfold positions, should have suggested that the cell as measured probably was too large to be the true one. It is unfortunate that some of these data for codeine and for β-methylmorphimethine should have found their way into *Crystal Data* (7), particularly since there has been some confusion in the listings. Thus the prefix "beta-" has somehow become attached to "Codeine" in the Name Index (7, p. 677) and (under space group D_2^3—$P2_12_12$) in the Main Table (7, p. 27); this is particularly misleading because "β-codeine" is an alternative name for an isomer of codeine, namely, neopine. Apart from this, the numerical data of Castelliz and Halla (6) for codeine are not included in the Determinative Tables. On the other hand, β-methylmorphimethine appears as "beta-Methyl-moryhimetin" [*sic*] not only in the Name Index (7, p. 697) but also, with the complete data of Castelliz and Halla (6), in the Determinative Tables (7, p. 287). These data probably are no more reliable than are those for codeine; in fact, the number of molecules per cell is given in the original note (6) as "16 ($\sim$ 17)". Finally, β-methylmorphimethine does not appear with codeine in the Main Table (7, p. 27).

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS

II. *dl*-METHADONE HYDROCHLORIDE, *dl*-METHADONE HYDROBROMIDE[1]

By W. H. Barnes and W. J. Forsyth*

The unit cell constants, space group, and X-ray diffraction powder data for *dl*-methadone (amidone: 6-dimethyl-4,4-diphenyl-3-heptanone) hydrochloride and for *dl*-methadone hydrobromide were determined by the methods outlined in Part I of this series of notes (1); the results are shown in Tables I and II.

Both salts were recrystallized from distilled water. Some difficulty was experienced with one laboratory preparation of the hydrobromide (2) apparently because of mixed crystal formation with a significant proportion of the hydrochloride as contaminant. The purity of the crystals used for the X-ray diffraction data reported, however, was established by converting the salt to the free base with concentrated ammonia solution and obtaining the powder

TABLE I

Single crystal data for *dl*-methadone hydrochloride and for *dl*-methadone hydrobromide

	dl-Methadone hydrochloride	*dl* Methadone hydrobromide
a	16.26 Å	16.44 Å
b	9.76 Å	9.81 Å
c	25.74 Å	26.29 Å
β	106°05′	106°52′
S.G.	*Cc* or *C*2/*c*	*Cc* or *C*2/*c*
Z	8 molecules/cell	8 molecules/cell
ρ (calc.)	1.171 gm./ml.	1.278 gm./ml.
ρ (obs.)	1.178 gm./ml.	1.287 gm./ml.

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TABLE II
INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.60$ Å) FOR *dl*-METHADONE HYDROCHLORIDE AND *dl*-METHADONE HYDROBROMIDE

dl-Methadone hydrochloride				*dl*-Methadone hydrobromide			
I/I_1	d(Å)		*hkl*	I/I_1	d(Å)		*hkl*
	Obs.	Calc.			Obs.	Calc.	
25	12.4	12.4	002	30	12.6	12.6	002
10	8.25	8.28	110	25	8.27	8.33	110
		8.22	$11\bar{1}$			8.29	$11\bar{1}$
5	7.87	7.81	200		*	7.87	200
90	7.50	7.63	$20\bar{2}$	2	7.75	7.76	$20\bar{2}$
		7.52	111	90	7.53	7.56	111
		7.40	$11\bar{2}$			7.49	$11\bar{2}$
70	6.48	6.46	112	80	6.48	6.50	112
	*	6.32	$11\bar{3}$			6.42	$11\bar{3}$
1	6.20	6.18	004	1	6.25	6.29	004
20	5.92	5.91	202	10	5.90	5.94	202
5	5.70	5.67	$20\bar{4}$	20	5.80	5.81	$20\bar{4}$
	*	5.46	113	20	5.47	5.50	113
—	—	5.34	$11\bar{4}$			5.44	$11\bar{4}$
	*	4.88	020	—	—	4.91	020
30	4.72	4.79	021	—	—	4.81	021
		4.73	$31\bar{1}$	50	4.76	4.77	$31\bar{1}$
		4.70	$31\bar{2}$			4.75	$31\bar{2}$
—	—	4.64	114	—	—	4.68	114
100	4.57	4.60	310	100	4.60	4.63	310, $11\bar{5}$
		4.55	$11\bar{5}$			4.58	$31\bar{3}$
		4.54	022			4.57	022
		4.51	$31\bar{3}$	45	4.34	4.36	311
40	4.34	4.33	311			4.34	204
		4.30	204		*	4.29	$31\bar{4}$
3	4.20	4.21	314		*	4.25	$20\bar{6}$
		4.20	023	20	4.17	4.23	023
		4.18	$22\bar{1}$			4.21	$22\bar{1}$
20	4.14	4.15	$20\bar{6}$			4.19	006
		4.14	220			4.16	220
		4.12	006			4.15	$22\bar{2}$
		4.11	$22\bar{2}$		*	4.11	$40\bar{2}$
20	4.00	4.06	$40\bar{2}$	40B	3.98	4.04	115
		4.00	115, 312			4.02	312
		3.99	221			4.01	221
	*	3.94	$22\bar{3}$			4.00	$11\bar{6}$
		3.93	$11\bar{6}$			3.98	$22\bar{3}$
20	3.87	3.91	400			3.95	$31\bar{5}$
		3.87	$31\bar{5}$			3.93	400
		3.83	024	—	—	3.88	$40\bar{4}$
5BB	3.71	3.81	$40\bar{4}$			3.87	024
		3.76	222	5	3.77	3.78	222
		3.70	$22\bar{4}$			3.75	$22\bar{4}$
		3.65	313	5	3.67	3.67	313

pattern of the liberated ammonium salt. The latter showed excellent agreement with precision data (4) for NH_4Br. The density calculated on the basis of the single-crystal data (assuming pure methadone hydrochloride) also was in satisfactory agreement with that measured experimentally for these crystals.

A curious anomaly was encountered in the case of the hydrochloride. Independent determinations of the unit cell constants on separate crystals were in agreement to better than 0.2%, and the calculated density (assuming pure methadone hydrochloride) was 1.171 gm./ml. Three independent measurements by different individuals on separate groups of crystals from the same preparation, however, while in satisfactory mutual agreement, gave an average density of 1.207 gm./ml. The difference could be explained by replacement of approximately one third of the Cl atoms with Br atoms, or by the presence of $\frac{1}{2}$ mole H_2O per mole anhydrous salt. The first possibility is most unlikely because the powder pattern of the ammonium salt obtained by the action of ammonia (2) was in excellent agreement with precision data (4) for NH_4Cl. The second possibility is eliminated by a water-determination carried out by Mrs. P. M. Oestreicher (3). Finally, a density of 1.178 gm./ml. (mean of eight measurements) was observed for crystals from a different preparation, while the powder data from both specimens were the same within the limits of experimental error. It seems probable, therefore, that the higher density found for the first lot of crystals is real, but may be due simply to surface contamination. On the other hand, further study of the density of *dl*-methadone hydrochloride crystals from different preparations might be of interest.

Hubach and Jones (5) obtained some Weissenberg photographs of *dl*-methadone hydrochloride but do not report any values for the axial lengths of the unit cell. The monoclinic angle was measured with the rotating stage of the microscope as 74° (i.e., $\beta = 106°$). They found those space group extinctions which are consistent with either *Cc* or *C*2/*c* but ruled out the twofold axis on the basis of the morphology of the crystals, thus concluding that the space group is uniquely established as *Cc*. On the other hand, the presence of eight molecules per cell (Table I) favors *C*2/*c* unless, of course, the structural unit comprises two molecules.

The powder data of Hubach and Jones (5) (obtained with Cu K_α radiation) for *dl*-methadone hydrochloride are in very good agreement with those of Table II with the exception of a line of $d = 5.04$ Å (very weak) which cannot be a K_α line because it does not index on the basis of the single-crystal data of Table I; it agrees, however, with a K_β reflection corresponding to their strongest line of $d = 4.55$ Å. With the exception of a line of $d = 5.65$ Å (medium weak), their pattern does not contain those lines for which $I/I_1 \leqq 5$ in the present photographs, although their line of $d = 5.38$ Å (very weak), which could be indexed as $11\bar{4}$ (d(Calc.) $= 5.34$ Å), does not appear on the present films.

Finally, in connection with the data of Table II, it may be mentioned that the very broad line of $d = 3.71$ Å is resolved on some films into two lines of $d = 3.76$ Å and $d = 3.68$ Å, respectively.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION DATA FOR CERTAIN NARCOTICS

III. *dl*-ALPHAPRODINE HYDROCHLORIDE, *dl*-BETAPRODINE HYDROCHLORIDE[1]

By W. H. Barnes and W. J. Forsyth*

The unit cell constants, space group, and X-ray diffraction powder data for *dl*-alphaprodine (nisentil^{R}; α-1,3-dimethyl-4-phenyl-4-propionoxypiperidine) hydrochloride, $C_{16}H_{23}NO_2 \cdot HCl$, and for *dl*-betaprodine hydrochloride were determined by methods previously outlined (1); the results are shown in Tables I and II.

No difficulty was experienced with the specimen of the alpha-form but that of betaprodine hydrochloride was found to consist of crystal fragments of two different types. The larger crystals were slightly elongated along *b* and were tabular on {100}. The best-developed forms were the three pinacoids so that, with β differing from 90° by 17° only, the crystals had the superficial appearance of rectangular plates under low magnification. This constituent was identified as the α-form by direct comparison of its powder pattern with that of the specimen of *dl*-alphaprodine hydrochloride. The smaller crystals also were monoclinic but were tabular on {001} with other forms so developed as to give a somewhat elongated, pseudohexagonal outline under low magnification. They were present in larger proportion in the mixture and were accepted as representing the β-form. It was not difficult, therefore, to select reasonably good individual crystals of both the α- and β-forms from the partially or wholly anhedral fragments comprising the bulk of the specimen of *dl*-betaprodine hydrochloride.

According to the method of Ziering and Lee (2), *dl*-alphaprodine hydrochloride and *dl*-betaprodine hydrochloride are separated by first crystallizing out the α-form from a solution of the two in about 600 cc. of acetone containing a little methanol. Concentrating the filtrate to 250 cc. and allowing it to stand in the ice-box overnight then gives a second crop of crystals (supposedly the

TABLE I

Single crystal data for *dl*-alphaprodine hydrochloride and for *dl*-betaprodine hydrochloride

	dl-Alphaprodine hydrochloride	*dl*-Betaprodine hydrochloride
a	15.77 Å	12.09 Å
b	8.15 Å	11.84 Å
c	13.95 Å	12.31 Å
β	107°00′	112°35′
S.G.	$P2_1/c$	$P2_1/c$
Z	4 molecules/cell	4 molecules/cell
ρ (calc.)	1.154 gm./ml.	1.216 gm./ml.
ρ (obs.)	1.167 gm./ml.	1.214 gm./ml.

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[1] *Issued as N.R.C. No. 3362.*

**Now with the Aluminum Company of Canada, Arvida, Que.*

TABLE II

INDEXED X-RAY DIFFRACTION POWDER DATA ($d > 3.50$ Å) FOR *dl*-ALPHAPRODINE HYDROCHLORIDE AND *dl*-BETAPRODINE HYDROCHLORIDE

dl-Alphaprodine hydrochloride

I/I_1	d(Å) Obs.	d(Å) Calc.	*hkl*
50	15.1	15.1	100
5	7.50	7.54	200
100	7.14	7.17	110
—	—	6.96	011
1	6.87	6.89	$10\bar{2}$
70	6.69	6.72	$11\bar{1}$
		6.67	002
80	5.96	5.98	111
		5.93	$20\bar{2}$
10	5.52	5.55	$21\bar{1}$
		5.54	210
		5.53	102
—	—	5.26	$11\bar{2}$
60	5.16	5.16	012
10	5.01	5.03	300
30	4.74	4.79	$21\bar{2}$
		4.76	211
		4.73	$30\bar{2}$
30	4.56	4.58	112
5	4.39	4.40	202, $31\bar{1}$
25	4.27	4.28	310
20	4.06	4.09	$31\bar{2}$
		4.08	020
		4.04	$11\bar{3}$
20	3.88	3.94	120
		3.90	013, 021 $21\bar{3}$
		3.87	212
		3.86	$12\bar{1}$
30	3.78	3.81	311
		3.79	$40\bar{2}$
		3.77	400
—	—	3.70	121
60	3.58	3.59	220, $22\bar{1}$
		3.56	113, $31\bar{3}$
		3.55	302, $41\bar{1}$
—	—	3.51	$12\bar{2}$

dl-Betaprodine hydrochloride

I/I_1	d(Å) Obs.	d(Å) Calc.	*hkl*
20	11.2	11.2	100
100	8.13	8.20	011
		8.12	110
	*	7.70	$11\bar{1}$
25	6.08	6.10	$10\bar{2}$
70	5.87	5.92	020
		5.88	111
	*	5.68	002
	*	5.58	200
20	5.39	5.42	$11\bar{2}$
		5.36	$21\bar{1}$
15	5.24	5.25	021
		5.23	120
70	5.10	5.12	012
		5.11	$12\bar{1}$
—	—	5.07	$20\bar{2}$
		5.05	210
5	4.63	4.66	$21\bar{2}$
15	4.41	4.46	121
		4.42	102
40	4.23	4.25	$12\bar{2}$
		4.22	$22\bar{1}$
40	4.08	4.14	112
		4.11	211
		4.10	022
		4.06	220
40B	3.82	3.87	$11\bar{3}$, $30\bar{2}$
		3.85	$22\bar{2}$
		3.81	$31\bar{1}$
40B	3.69	3.73	031
		3.72	130, 300
		3.71	$21\bar{3}$
		3.68	$13\bar{1}$, $31\bar{2}$
	*	3.61	013
25	3.52	3.55	310
		3.54	122
		3.52	221

β-form) which is finally recrystallized three times from acetone. If the two specimens of prodine hydrochloride available for the present investigation were separated in this way, it is perhaps not surprising that the one labelled β-prodine hydrochloride should contain some of the α-isomer; this possibility should be considered in problems of identification involving prodine hydrochloride.

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DIVISION OF PHYSICS,
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OTTAWA, CANADA.

UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS
IV. PROTOPINE[1]

By W. H. Barnes and W. J. Forsyth*

The unit cell constants, space group, and X-ray diffraction powder data for protopine, $C_{20}H_{15}O_5N$, were determined by methods outlined previously (1).

Three samples were examined. The first (A), from a commercial supplier, was found (2) to be a mixture of two substances of which the coarser-grained proved to be protopine. The second constituent, however, was not identified but presumably it represents another alkaloid that was not separated from the protopine during the course of the procedure employed to isolate the latter; it is not cryptopine, nor any of the other narcotics for which powder data were readily available (2) for comparison.

The other two samples (B, C) were kindly provided by Dr. L. Marion. One of these (B), in the form of a relatively fine-grained powder, had come from the same commercial source as A. The second (C), comprising good single crystals and crystal aggregates, had been extracted from *Adlumia fungosa* and authenticated as protopine by Dr. Marion.

Powder patterns from B and from crushed fragments of C were identical with each other and with the coarser-grained material of A which was responsible for the appearance of markedly spotty lines on some of the powder photographs of the mixture. Confirmation was obtained from photographs of a few of the larger fragments from mixture A which were selected and

TABLE I
Indexed X-ray diffraction powder data ($d > 4.00$ Å) for protopine

I/I_1	d(Å)		*hkl*
	Obs.	Calc.	
20	10.7	10.7	011
35	8.74	8.72	020
—	—	7.33	021
25	6.77	6.76	002
5	6.57	6.58	$10\bar{2}$
		6.54	$11\bar{1}$
30	6.31	6.30	012
—	—	6.16	$11\bar{2}$
90	5.96	5.98	100
—	—	5.66	110
5	5.51	5.49	$12\bar{1}$
30B	5.30	5.34	022, 031
		5.25	$12\bar{2}$
35	4.97	4.98	$11\bar{3}$
		4.93	120
100	4.47	4.49	$13\bar{1}$
		4.47	111
		4.46	$12\bar{3}$
—	—	4.41	032
80	4.36	4.36	013, 040 $13\bar{2}$
25	4.16	4.17	130
		4.15	041
—	—	4.08	121
80	4.01	4.02	$10\bar{4}$
		4.00	023

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removed under the stereoscopic microscope and then reduced to a powder.

Precession photographs also were taken of a single clear fragment from A and of a small crystal from C. This completely established the identity of the larger particles of A as protopine and furnished data for the determination of the unit cell constants and space group.

The space group of protopine is $P\,2_1/c$; $a = 7.10_9$ Å, $b = 17.44$ Å, $c = 16.08$ Å (c chosen $>a$ to give protopine the standard (3) orientation for $C_{2h}{}^5$, unique axis b), $\beta = 122°45'$; the number of molecules per cell (Z) = 4; $\rho_{\mathrm{calc.}} = 1.399$ gm./ml., $\rho_{\mathrm{obs.}} = 1.393$ gm./ml.

On the basis of a morphological study by Schwantke of protopine crystals from *Chelidonium majus*, Schmidt (4) gives the axial ratio $a:b:c = 0.8992:1:?$ and $\beta = 57°19'$ (i.e., 122°41′), the latter in excellent agreement with the present value. If the a and c of Schwantke be interchanged, his axial ratio may be compared directly with the present $a:b:c = 0.4076:1:0.9219$.

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UNIT CELL, SPACE GROUP, AND INDEXED X-RAY DIFFRACTION POWDER DATA FOR CERTAIN NARCOTICS
V. PAPAVERINE, PAPAVERINE HYDROCHLORIDE[1]

By W. H. Barnes

During the compilation of X-ray diffraction powder data for the identification of a number of narcotics (3), no difficulties were encountered in obtaining reproducible photographs from papaverine (6:7-dimethoxy-1-[3′:4′-dimethoxy-benzyl] isoquinoline), $C_{20}H_{21}O_4N$, or from papaverine hydrochloride. In fact the base was selected for a demonstration of the effect of radiation wave-length on the appearance of powder photographs (1). At the time of the narcotics survey, therefore, it was not deemed essential to authenticate the powder data for either the free base or the hydrochloride from single-crystal data. During the preparation of the present series of notes (2), however, unit cell and space group data have become available (4) for both papaverine and papaverine hydrochloride and thus it now becomes of interest to index the powder patterns. The results are shown in Table I.

Van Hulle, Amelinckx, and Dekeyser (4) give the space group of papaverine as $P2_12_12_1$ with $a = 9.50$ Å, $b = 29.22$ Å, $c = 6.35$ Å, and that of papaverine hydrochloride as $P2_1/c$ with $a = 13.10$ Å, $b = 15.80$ Å, $c = 9.22$ Å, $\beta = 92°36'$. The cell dimensions were obtained from rotation and Weissenberg photographs and β (for the hydrochloride) from goniometric measurements and b-axis

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[1] *Issued as N.R.C. No. 3364.*

removed under the stereoscopic microscope and then reduced to a powder.

Precession photographs also were taken of a single clear fragment from A and of a small crystal from C. This completely established the identity of the larger particles of A as protopine and furnished data for the determination of the unit cell constants and space group.

The space group of protopine is $P\ 2_1/c$; $a = 7.10_9$ Å, $b = 17.44$ Å, $c = 16.08$ Å (c chosen $>a$ to give protopine the standard (3) orientation for C_{2h}^5, unique axis b), $\beta = 122°45'$; the number of molecules per cell (Z) = 4; $\rho_{\text{calc.}} = 1.399$ gm./ml., $\rho_{\text{obs.}} = 1.393$ gm./ml.

On the basis of a morphological study by Schwantke of protopine crystals from *Chelidonium majus*, Schmidt (4) gives the axial ratio $a:b:c = 0.8992:1:?$ and $\beta = 57°19'$ (i.e., 122°41′), the latter in excellent agreement with the present value. If the a and c of Schwantke be interchanged, his axial ratio may be compared directly with the present $a:b:c = 0.4076:1:0.9219$.

1. Barnes, W. H. and Forsyth, W. J. Can. J. Chem. 32: 984. 1954.
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zero-level Weissenberg films. The radiation employed was Cu K_α. The values for d(Calc.) in Table I are derived from these constants.

TABLE I
INDEXED X-RAY DIFFRACTION POWDER DATA FOR PAPAVERINE ($d > 3.25$Å) AND PAPAVERINE HYDROCHLORIDE ($d > 3.65$Å)

Papaverine			
I/I_1	d(Å)		hkl
	Obs.	Calc.	
10	14.8	14.6	020
12	8.90	9.03	110
3	7.89	7.96	120
—	—	7.31	040
—	—	6.80	130
	*	6.21	011
100	5.79	5.82	021
		5.79	140
	*	5.32	031
		5.28	101
25	5.21	5.20	111
30	4.93	4.98	150
		4.96	121
		4.87	060
30	4.77	4.79	041
		4.75	200
—	—	4.69	210
40	4.61	4.64	131
20	4.48	4.52	220
2	4.38	4.33	160
	*	4.30	051
25	4.26	4.28	141
		4.27	230
—	—	3.98	240
—	—	3.92	151
85	3.87	3.86	061
		3.82	170
—	—	3.80	201
90	3.73	3.77	211
		3.69	250
		3.68	221
5	3.65	3.65	080
5	3.57	3.58	161
		3.54	231
15	3.51	3.49	071
—	—	3.41	180
		3.40	260
2	3.35	3.37	241
40	3.28	3.27	171

Papaverine hydrochloride			
I/I_1	d(Å)		hkl
	Obs.	Calc.	
	*	13.1	100
20	10.1	10.1	110
20	7.87	7.96	011
		7.90	020
40	6.85	6.92	$11\bar{1}$
		6.76	120
5	6.59	6.68	111
		6.54	200
15	5.93	6.05	210
		6.00	021
—	—	5.51	$12\bar{1}$
40	5.35	5.39	121
75	5.12	5.15	$21\bar{1}$
		5.04	220
	*	4.96	211
		4.89	130
100	4.56	4.61	002
		4.57	031
70	4.44	4.49	$22\bar{1}$
		4.42	012
		4.41	$10\bar{2}$
3	4.32	4.36	221, 300
		4.35	$13\bar{1}$
		4.29	131
		4.28	102
	*	4.24	$11\bar{2}$
3	4.20	4.20	310
	*	4.13	112
25	4.08	4.10	230
—	—	3.98	022
		3.95	040
—	—	3.89	$31\bar{1}$
		3.85	$20\bar{2}$, $12\bar{2}$
20	3.79	3.82	320
		3.79	$23\bar{1}$
		3.78	140
		3.77	122
		3.76	311
60	3.68	3.74	$21\bar{2}$
		3.71	231
		3.69	202

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THE EFFECT OF MEMBRANE THICKNESS IN DIALYSIS

By J. H. E. Herbst

In another investigation it was suspected that under certain conditions the thickness of the membranes in the Webcell Continuous Dialyzer, Laboratory Model (Brosites Machine Company, New York) was not a rate-controlling factor. No information on the effect of membrane thickness in continuous dialysis was found in the literature. To investigate this phenomenon further, aqueous sodium chloride and sucrose solutions (100 gm./liter) were dialyzed at various feed rates with No. 300 and No. 450 P.T. cellophane membranes. The thickness of the dry membranes was 0.00088 in. and 0.0012 in., respectively. The water feed rate was 200 ml./min. In addition, batch dialyses were carried out with the same solutions and membranes. The solutions were stirred vigorously, and the water feed rates were sufficient to render the concentration of solute in the effluent diffusate negligible. The temperature was 10–15° in all experiments. Pertinent information is given in Table I.

TABLE I
Results of dialyses

Type of dialysis	Solute	Membrane	Solution feed rate, ml./min.	Dialysis rate coefficient*
Continuous	Sodium chloride	300	12	4.3
			28	4.2
			40	4.6
		450	4	3.6
			12	4.8
			15	4.2
			41	3.9
	Sucrose	300	3	0.96
			4	0.82
			6	0.92
		450	4	0.59
			5	0.73
Batch	Sodium chloride	300		4.9
				4.9
		450		3.9
				3.9
	Sucrose	300		0.78
				0.91
		450		0.69
				0.71

Grams of solute transferred per square meter of membrane per hour per gram per liter concentration difference (geometric mean).

The usual statistical tests† indicated that there was no correlation between the solution feed rate and the dialysis rate coefficient; that, for the continuous

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†*Kindly applied by Dr. D. B. DeLury.*

dialysis of sodium chloride, there was no significant difference between the dialysis rate coefficients for the two membranes; and that, for the batch dialysis of sodium chloride and the batch and continuous dialysis of sucrose, there was a significant difference between the dialysis rate coefficients for the two membranes.

Fick's law is obeyed fairly well in the batch dialysis of sodium chloride and the batch and continuous dialysis of sucrose (the ratio of the thicknesses of the dry membranes is 1.4, while the ratio of the dialysis rate coefficients is 1.4 for the continuous dialysis of sucrose, 1.3 for the batch dialysis of sodium chloride, and 1.2 for the batch dialysis of sucrose). Thus, the results indicate that in the continuous dialysis of sodium chloride, transfer to the membrane was a rate-controlling process, while, in the batch dialysis of sodium chloride and the batch and continuous dialysis of sucrose, transfer through the membrane was a rate-controlling process.

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A POLYSACCHARIDE FROM THE BLUE-GREEN ALGA, *ANABAENA CYLINDRICA*[1]

BY C. T. BISHOP, G. A. ADAMS, AND E. O. HUGHES

ABSTRACT

A complex polysaccharide has been isolated from the fresh-water alga, *Anabaena cylindrica*, grown in a synthetic culture medium. Prolonged acid hydrolysis yielded glucose, xylose, glucuronic acid, galactose, rhamnose, and arabinose in a molar ratio of 5 : 4 : 4 : 1 : 1 : 1. Chemical fractionations of the polysaccharide material from solution in cupriethylenediamine, and of its acetate from organic solvents indicated chemical homogeneity.

Except for the work of Hough, Jones, and Wadman (5) on *Oscillatoria* and *Nostoc*, little is known of the carbohydrate constituents of blue-green algae. In the gelatinous nodules of *Nostoc*, these authors found a complex polysaccharide containing six different sugars. The observation in this laboratory of agar-like gels formed by old partly evaporated cultures of *Anabaena*, a genus closely related to *Nostoc*, suggested that a similar carbohydrate might be present. Preliminary examination of this material showed that six sugars were present and further study indicated that they were components of one complex polysaccharide. In a recent study, Fogg (3) has described the production of a polypeptide and a pentose by the same organism. The present paper reports the properties and composition of its polysaccharide component.

Anabaena cylindrica Lemm. (Class Myxophyceae; Order Nostocales; Family, Nostocaceae) was grown in a liquid inorganic medium with or without supplementary carbon dioxide and under low or high light intensity. The same polysaccharide was found under all four conditions of growth.

The polysaccharide was isolated from the cultures after removal of non-carbohydrate material by treatment with hot dilute alkali. Examination of the acid-hydrolysis products of the polysaccharide material by qualitative and quantitative paper chromatography showed glucose, xylose, galactose, rhamnose, and arabinose in approximate molar ratios of 5 : 4 : 1 : 1 : 1. Thermal decarboxylation (10) indicated the presence of 4 moles of uronic acid. The five neutral sugars were identified by their optical rotations and by isolation of crystalline specimens. When examined on paper chromatograms the uronic acid and its methyl ester gave spots corresponding to glucurone and glucuronic

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acid methyl ester. Thus the uronic acid was tentatively identified as glucuronic acid.

Chemical fractionations of the polysaccharide material from cupriethylenediamine, and of its acetate from organic solvents, yielded no chemically different portions. Stepwise acidification of a cupriethylenediamine solution of the polysaccharide yielded four fractions with the same composition and optical rotation ($[\alpha]_D^{23}$ $-12°$). The acetate was insoluble in all organic solvents except dioxane in which it was soluble to the extent of only 0.1%. The soluble and insoluble fractions had the same compositions as the original acetate. Graded hydrolysis revealed no structural characteristics of the polysaccharide. Three hours' heating with 0.025 N sulphuric acid partially liberated all six components while more dilute acid had no effect.

From the evidence obtained it appears that the polysaccharide produced by *Anabaena cylindrica* is a complex, chemically homogeneous polysaccharide. Any fractionation obtained must have been on a basis of molecular weight. No confirmation of this possibility could be made because of the insolubility of all fractions in solvents suitable for molecular weight estimation.

The chemical composition of the *Anabaena* polysaccharide appeared to be similar to that of the complex acidic polysaccharide isolated from *Nostoc* by Hough *et al.* (5). The monosaccharide units, glucose, galactose, xylose, rhamnose, and glucuronic acid were present in each and, in addition, the polysaccharide of *Anabaena* contained arabinose while that of *Nostoc* contained galacturonic acid and an unknown sugar. Both polysaccharides showed a marked resistance to acid hydrolysis. Poor solubility properties and gel formation made purification difficult.

When the cell-free medium and cellular residue of *Anabaena* cultures were examined separately, polysaccharide material having the same chemical composition was found in each portion. Microscopic examination of the alga mounted in India ink showed that many of the filaments were enclosed in a mucilaginous material which was readily sloughed off into the medium. These observations suggest that the polysaccharide may be derived from the mucilaginous envelopes surrounding the trichomes.

EXPERIMENTAL

Paper strip chromatograms were run at room temperature (22–26°C.) on Whatman No. 1 using the following solvent systems: (*a*) pyridine : ethyl acetate : water, 1 : 2 : 2 (7); (*b*) butanol : pyridine : water, 6 : 4 : 3 (6); (*c*) butanol : pyridine : water, 10 : 3 : 3 (8).

Culturing of Anabaena cylindrica

A stock culture of *Anabaena cylindrica* Lemm. 1403–2 was obtained from the Cambridge Culture Collection of Algae and Protozoa.

Transfers were made to modified Chu No. 10 Solution (2) with nitrate concentration doubled and 1 ml. 4% Hoagland's solution added per liter. Presterilization pH was adjusted to 9.0 with dilute sodium hydroxide. Cultures were grown on a shaker under fluorescent daylight lamps (100–125 ft. candles) at 28°C. Although most of the material examined was grown under the above conditions, some cultures were supplied with 6% carbon dioxide in air (about 30 ml. per min. per liter) and others exposed to a higher light intensity (900 ft. candles) with or without supplementary carbon dioxide. For cultures on which yields are reported a 100 ml. suspension of *Anabaena* (dry weight of cells, about 1.4 mgm.) was used to inoculate each 900 ml. of medium in a 2 liter Erlenmeyer flask. Dry weights were determined periodically on cellular residues and supernatants obtained by centrifuging 50 ml. aliquots at 27,000 r.p.m. for 10 min. Cellular residues and supernatants were evaporated to dryness under reduced pressure at 40°C.

At low light intensity no significant difference was found in the total dry weight yields (*ca.* 110 mgm. per 100 ml.) of eight-week-old cultures with or without added carbon dioxide. At high light intensity, cultures with or without added carbon dioxide became yellowish-brown in a few days and the experiment was discontinued in two weeks. At this time, however, dry weight yields from the carbon dioxide cultures (113 mgm. per 100 ml.) were already equivalent to those obtained in eight weeks at low light intensity and almost twice as high as those obtained from the controls (61 mgm. per 100 ml.). At both light intensities, the percentage dry weight contributed by the cellular residue was much greater in the carbon dioxide cultures (45–70%) than in the controls (10–30%).

Isolation of Polysaccharide Material

In a typical experiment a culture of *Anabaena cylindrica* was made alkaline by addition of solid sodium hydroxide to a concentration of 4%. The mixture was boiled under reflux for six hours, filtered through sintered glass, acidified (pH 4) with hydrochloric acid, and dialyzed in cellophane bags against distilled water for three days. The non-dialyzable material was isolated by freeze drying. The cream-colored product (2.39 gm. from 16 liters of a seven-week-old culture) contained 10% ash, 0.27% nitrogen, and was insoluble in water or strong alkali. Hydrolysis of a small amount (10 mgm.), by heating with 2.5% sulphuric acid (5 ml.), and examination of the hydrolyzate by paper strip chomatography (solvents (*a*), (*b*), and (*c*)) indicated the presence of rhamnose, xylose, arabinose, glucose, galactose, and an uronic acid. In a separate experiment a culture of *A. cylindrica* was centrifuged to separate cells from medium. The polysaccharide materials, isolated from both the cells and the medium, were examined by hydrolysis and paper chromatography as just described. Both materials contained the same sugars in approximately the same proportions. The same polysaccharide was found in cultures grown at low and high light intensities and with or without added carbon dioxide.

Quantitative Estimation of Component Sugars

Preliminary experiments using different acid strengths showed that the polysaccharide was very resistant to acid hydrolysis as indicated by changes in reducing power. A sample (50 mgm.) of the polysaccharide material was hydrolyzed by heating at 97°C. for 24 hr. with 2.5% sulphuric acid (10 ml.). The hydrolyzate was neutralized with barium carbonate, filtered, and individual sugars in the filtrate were estimated by quantitative paper strip chromatography using solvent (*a*) and the phenol – sulphuric acid method of Dubois *et al.* (1). Uronic acid in the original polysaccharide was estimated by thermal decarboxylation (10). Calculated on a mole per cent basis the results showed the polysaccharide to be composed of five parts glucose, four parts each of uronic acid and xylose, and one part each of galactose, rhamnose, and arabinose. These figures are regarded as only approximate because the drastic conditions required for hydrolysis would almost certainly lead to some destruction of the sugars, particularly the pentoses.

Identification of Component Sugars

The hydrolyzate of 1 gm. of polysaccharide material was neutralized with Dowex-2 (carbonate form) and the filtrate evaporated to a syrup which was fractionated on a cellulose column (4) using butanol saturated with water as the mobile phase. The eluate from the column was collected in 5 ml. portions by an automatic fraction collector which changed the receiver every half hour. Every fifth fraction was examined by paper strip chromatography (solvent (*a*)) and appropriate portions of the eluate were combined to yield pure samples of the following sugars which were crystallized from methanol:

	m.p.		
L-Rhamnose	91– 92°C.	$[\alpha]_D^{25}$ + 8.58	(*c*, 1.4% in water)
D-Xylose	144–145°C.	$[\alpha]_D^{25}$ + 18.2	(*c*, 0.8% in water)
L-Arabinose	159–160°C.	$[\alpha]_D^{25}$ +101.0	(*c*, 1.4% in water)
D-Glucose	145-146°C.	$[\alpha]_D^{25}$ + 50.1	(*c*, 0.7% in water)
D-Galactose	170–171°C.	$[\alpha]_D^{25}$ + 78.4	(*c*, 1.27% in water)

Examination of Uronic Acid

No uronic acid could be recovered from the Dowex-2 used to neutralize the polysaccharide hydrolyzate. The hydrochloric acid hydrolyzate of 250 mgm. of the polysaccharide was neutralized with silver carbonate and excess silver ion was removed with hydrogen sulphide. The silver-free filtrate was evaporated to a syrup which was taken up in hot methanol and filtered. Paper strip chromatography of this solution (solvent (*a*)) showed the five sugars identified above and two other spots, one corresponding to glucuronic or galacturonic acid, the other corresponding to glucurone which is always associated with glucuronic acid (9).

The methanolic solution of the hydrolyzate was neutralized with ethereal diazomethane and the neutral solution was evaporated to a thin syrup. After paper strip chromatography of this syrup in solvent (*a*) for seven hours there was a spot having the same R_f value as glucuronic acid methyl ester (R_f 0.813) and situated between two spots given by galacturonic acid methyl ester (R_f 0.723, 0.833).

Attempted Fractionation from Cupriethylenediamine

The polysaccharide material (1.02 gm.) was dissolved in freshly filtered 1.0 *M* cupriethylenediamine (100 ml.) and fractionally precipitated by stepwise acidification with concentrated hydrochloric acid. Fractions were obtained at pH values of 8.9 (0.241 gm.), 5.2 (0.012 gm.), and 4.5 (0.480 gm.). A fourth fraction (0.140 gm.), soluble in the final acid solution, was isolated by alcohol precipitation after removal of inorganic ions by dialysis. By prolonged (48 hr.) shaking it was possible to obtain 1% solutions of the above fractions in 5% sodium hydroxide. Optical rotations of these solutions were the same, $[\alpha]_D^{23} = -12.0 \pm 1°$. Samples from each fraction were hydrolyzed by heating at 97°C. for 24 hr. with 2.5% sulphuric acid. Paper strip chromatograms (solvent (*a*)) of the neutralized hydrolyzates were identical with those obtained from hydrolyzates of the original polysaccharide material.

Acetylation and Attempted Fractionation

The polysaccharide material (0.500 gm.) was added in small quantities, with stirring, to 10 ml. of formamide. The mixture was heated at 65°C. for one hour, pyridine (10 ml.) was added, and the mixture kept at 65°C. for a further 15 min. Acetic anhydride (3.2 ml.) was added in 1/4 portions to the cooled mixture which was then stirred at room temperature for 18 hr. The reaction mixture was poured with stirring into ice water (200 ml.) and the precipitate, removed by centrifuging, was washed three times with water before it was dried *in vacuo* over phosphoric anhydride. After another acetylation by the same procedure the acetate was obtained as a white powder (0.407 gm.), insoluble in chloroform, acetone, or pyridine and only 0.1% soluble in dioxane. This solution gave no optical rotation, undoubtedly because of the low concentration. The portions of the acetate soluble and insoluble in dioxane were separately deacetylated by 4% alcoholic sodium hydroxide, and hydrolyzed with 2.5% sulphuric acid. Paper strip chromatograms (solvent (*a*)) of the neutralized hydrolyzates were identical with those given by hydrolyzates of the original polysaccharide material.

Graded Hydrolysis

Samples (50 mgm.) of the polysaccharide material were heated separately at 97°C. with 5 ml. of each of the following acid solutions: 0.02 *N* oxalic, 0.02 *N* sulphuric, and 0.025 *N* sulphuric. At one hour intervals samples were removed for examination by paper strip chromatography. Neither 0.02 *N* oxalic or 0.02 *N* sulphuric acid had any effect on the polysaccharide in seven hours. Three hours' heating with 0.025 *N* sulphuric acid released small amounts of all six component sugars. Complete hydrolysis of the polysaccharide, as determined by reducing power, required more drastic hydrolytic conditions (2.5% sulphuric acid, 97°C. for 24 hr.).

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REARRANGEMENT STUDIES WITH C^{14}

II. THE PREPARATION OF 2-PHENYLETHYL HALIDES[1]

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

ABSTRACT

The 2-phenylethyl halides were prepared from the treatment of 2-phenylethanol-1-C^{14} with thionyl chloride alone, thionyl chloride in pyridine, 48% hydrobromic acid, 55% hydroiodic acid, or phosphorus and iodine. Except for the reaction with thionyl chloride in pyridine, these reactions gave rise to some rearrangement of the C^{14} activity from the C-1 to the C-2 position. It appears probable that these rearrangements resulted from reactions having the S_N1 type of mechanism with the phenylethyl cation as reaction intermediate. The fact that the thionyl chloride in pyridine treatment leads to a product without rearrangement is of interest in that this method may have further applications in synthetic tracer chemistry.

INTRODUCTION

Among the most common methods for the preparation of an alkyl halide is the replacement of the hydroxyl group of an alcohol by a halogen through the reaction of the alcohol with a hydrohalic acid or a halide of sulphur or phosphorus. That the mechanism of such a replacement reaction may be bimolecular involving Walden inversion (S_N2) or unimolecular with a carbonium ion as intermediate (S_N1) has been pointed out by Hughes, Ingold, and co-workers (1). If the S_N1 mechanism were involved, typical carbonium ion-type rearrangements (2*b*) would be observed if conditions were favorable for rearrangement. For example, extensive structural changes occurred when pinacolyl alcohol was treated with hydrochloric acid (15) while less pronounced rearrangements were observed when *n*-amyl alcohol or pentanol-2 were heated with $ZnCl_2$ and HCl (13, 14).

It has previously been pointed out that the use of C^{14} as a tracer makes possible studies of rearrangements otherwise unobservable (5). In an attempt to convert cyclopentanol-1-C^{14} to cyclopentyl bromide with phosphorus tribromide, Loftfield (6) found that 20% of the total radioactivity had become rearranged to positions other than C-1. He pointed out that this reaction likely involved a carbonium ion "sufficiently free" to permit a "hydride ion" migration. On the other hand, Roberts *et al.* (10) observed no rearrangement of the C^{14} activity when 2-methyl-2-propanol-2-C^{14}, 2-methyl-2-butanol-1-C^{14}, and 2-methyl-2-butanol-2-C^{14} were converted to the corresponding chlorides by treatment with concentrated hydrochloric acid. In these cases, rearrangement of the C^{14} activity is unlikely because it would require the transformation of tertiary carbonium ions to the energetically less favorable secondary and/or primary carbonium ions. In the present paper, rearrangements observed in the preparation of 2-phenylethyl halides from the reaction between 2-phenylethanol-1-C^{14} and thionyl chloride, hydrobromic acid, hydroiodic acid, or phosphorus and iodine are reported.

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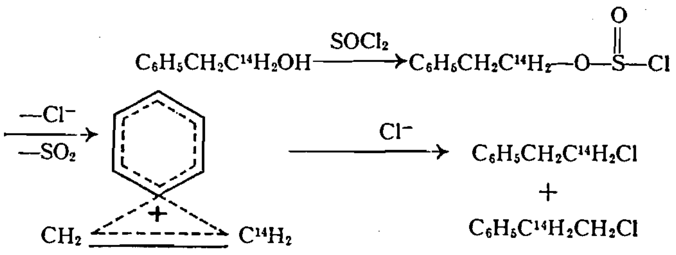
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask. For Paper I, see Reference 5.

RESULTS AND DISCUSSION

The degrees of rearrangement in the various preparations of 2-phenylethyl halides studied are summarized in Table I. The labeled 2-phenylethanol was synthesized by the lithium aluminum hydride reduction of phenylacetic acid carboxyl-C^{14} (8) obtained from carbonation, with $C^{14}O_2$, of the corresponding Grignard (5). That all the radioactivity was in the C-1 position was shown by oxidation of the labeled alcohol to non-radioactive benzoic acid. All the samples of 2-phenylethyl halides obtained were treated with magnesium in dry ether and then reacted with dry ice to give crystalline hydrocinnamic acid for radioactivity determination.

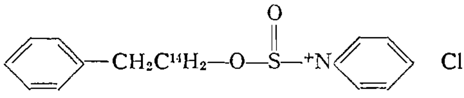
Subsequent oxidation of the hydrocinnamic acid to benzoic acid and measurement of its activity gave the amount of rearrangement from the C-1 to the C-2 position. It may be noted that the direct oxidation of the 2-phenylethyl halides to benzoic acid is also possible. Trials with inactive materials, however, showed that the conditions required to effect such an oxidation are quite drastic, and the yields attainable are low compared to that obtained from the oxidation of hydrocinnamic acid. Consequently, only one active sample of 2-phenylethyl iodide was oxidized directly, and the degree of rearrangement observed agreed very well with that found by the oxidation of hydrocinnamic acid derived from the same sample.

Except for the reaction of 2-phenylethanol-1-C^{14} with thionyl chloride in pyridine, all reactions studied gave rise to some rearrangement of the C^{14} activity from the C-1 to the C-2 position. Most probably, these rearrangements resulted from reactions having the S_N1 type of mechanism with the phenylethyl cation as reaction intermediate. The possible nature of the phenylethyl cation and how it might cause the rearrangement of C^{14} from C-1 to C-2 has previously been discussed (5, 11). It is noteworthy that in the treatment of the labeled alcohol with thionyl chloride alone, the resulting 2-phenylethyl chloride has its C^{14} activity practically equally distributed in the C-1 and C-2 positions. Such a finding is as would be expected if the phenylethyl cation has the symmetrical "non-classical" structure I.



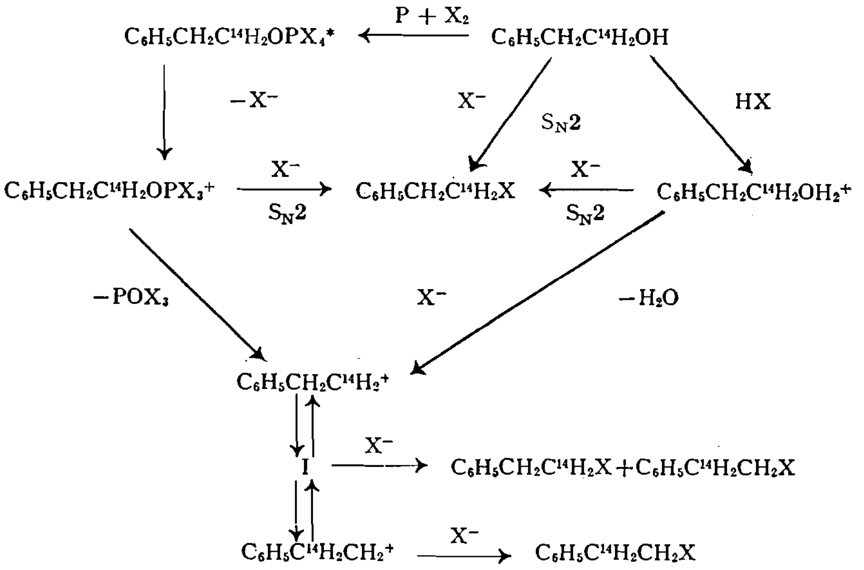
I

When the reaction with thionyl chloride is carried out in pyridine, a pyridinium chloride complex, II, (4) may be formed which, on decomposition, gives 2-phenylethyl-1-C^{14} chloride without rearrangement since no carbonium ion intermediate is likely to be formed with the organic base, pyridine, as solvent.



II

The degree of rearrangement found in the 2-phenylethyl bromide or iodide prepared from the treatment of the labeled alcohol with 48% hydrobromic acid, 55% hydroiodic acid, or phosphorus and iodine ranged from 2.5 to 7.4%. (Table I). In these instances, only a fraction of the reaction proceeds through the unimolecular mechanism involving rearrangement of the intermediate phenylethyl cation. The major portion of the reaction follows a process or processes which lead to no rearrangement. Such a process may be of the S_N2 type, or it may involve the rapid interaction between the unrearranged phenylethyl cation and the conjugate base of the reaction medium as previously suggested (5, 11).



It is of interest to note that the reaction of 2-phenylethanol-1-C^{14} with hydrobromic acid resulted in a greater degree of rearrangement than the corresponding reaction of the labeled alcohol with hydroiodic acid. Apparently the protonating power of 48% hydrobromic acid, as measured by Hammett's acidity function, H_0 (2*a*), is greater than that of 55% hydroiodic acid. That such a deduction is a reasonable one is further supported by the fact that the electron affinity of bromine is greater than that of iodine (9).

**Complex $ROPX_4$ has been suggested by Kenyon and co-workers (4) as intermediate in the reaction between ROH and PX_5. No attempt was made in the present study to definitely establish the structure of complex $C_6H_5CH_2CH_2OPX_4$. Another possible intermediate may be $C_6H_5CH_2CH_2OPX_2$.*

In view of the finding that the reagents frequently employed for the preparation of alkyl halides may give rise to rearranged products, it is of utmost importance that in the syntheses of C^{14}-labeled compounds, whenever the use of alkyl halides is involved, the positions of the labeled atoms in the final products be unequivocally established. In order to obtain a cyclopentyl-1-C^{14} halide for further synthetic applications, Loftfield (6) prepared the *p*-bromobenzenesulphonate of cyclopentanol-1-C^{14} and then treated this sulphonate with sodium iodide in acetone, a typical S_N2 reaction, to give the iodide without rearrangement. The observation that the replacement of a hydroxyl group with chlorine effected by thionyl chloride in pyridine eliminated the possibility of rearrangement (14) is here extended and shown to be applicable for C^{14}-labeled 2-phenylethanol. It is our belief that the thionyl chloride in pyridine method is much less time consuming and likely to give higher over-all yields than the sulphonate – sodium iodide in acetone method for the preparation of unrearranged alkyl halides, though both of these methods will most likely find further applications in the syntheses of C^{14}-labeled compounds.

TABLE I

REARRANGEMENTS IN 2-PHENYLETHYL HALIDES FROM 2-PHENYLETHANOL-1-C^{14}

Reagents used	Compound counted†	Specific activity, counts/min./mM. Run I	Specific activity, counts/min./mM. Run II	% rearrangement Run I	% rearrangement Run II
	Phenylurethan of 2-phenylethanol-1-C^{14}	1133 ±16			
	Benzoic acid‡	0.6± 3.6		0.0	
$SOCl_2$ alone	Hydrocinnamic acid	902 ±12	1134 ±13		
	Benzoic acid	453 ± 7	551 ±10	50.3	48.6
$SOCl_2$ in pyridine	Hydrocinnamic acid	1152 ±14	1132 ±13		
	Benzoic acid	−0.1± 3.2	−0.2± 3.2	0.0	0.0
48% HBr	Hydrocinnamic acid	1170 ±14	1143 ±13		
	Benzoic acid	82.0± 3.2	60.6± 2.5	7.0	5.3
55% HI	Hydrocinnamic acid	1158 ±13	1190 ±14		
	Benzoic acid	28.3± 2.5	32.7± 3.0	2.5	2.7
	Benzoic acid§	32.3± 3.0		2.8	
$P+I_2$	Hydrocinnamic acid	702 ±10	715 ±10		
	Benzoic acid	38.3± 3.6	531 ± 4.5	5.5	7.4

†*As "infinitely thick" samples of constant geometry in a windowless Q-gas counter.*
‡*From oxidation of 2-phenylethanol-1-C^{14}.*
§*From direct oxidation of active 2-phenylethyl iodide.*

EXPERIMENTAL

Reaction with Thionyl Chloride

In a 100 ml. round-bottomed flask, cooled in an ice bath and fitted with a reflux condenser, was placed 5.00 gm. of 2-phenylethanol-1-C^{14}. Fifteen milliliters of thionyl chloride was added slowly. The mixture was removed from the ice bath and refluxed gently for one half hour. The excess thionyl chloride was distilled off and the residue fractionated under reduced pressure. The yields of 2-phenylethyl chloride, b.p. 85–87°C. at 17 mm. (lit.(16) b.p. 81–84°C. at 14 mm.), for the duplicate runs were 4.64 and 4.40 gm. (81 and 77%, respectively).

Reaction with Thionyl Chloride in Pyridine

To a solution of 5.00 gm. of 2-phenylethanol-1-C^{14} in 20 ml. of pyridine in a 250 ml. Erlenmeyer flask cooled in an ice-bath was added portionwise 10 ml. of thionyl chloride. When the mixture was shaken and then heated on a steam bath for about five minutes (prolonged heating will cause extensive decomposition) a black solution resulted. The mixture was then allowed to stand at room temperature for one half hour before it was poured into ice water. The product was extracted with ether, the extract being washed successively with distilled water, dilute hydrochloric acid, 10% sodium bicarbonate solution, and distilled water. After the extract was dried over anhydrous sodium sulphate, the ether was removed from the extract and the residue distilled under reduced pressure. The yields of 2-phenylethyl chloride for the duplicate runs were 3.72 and 3.86 gm. (65 and 67%, respectively).

Reaction with Hydrobromic Acid

A mixture of 5.00 gm. of 2-phenylethanol-1-C^{14} and 28 gm. of 48% hydrobromic acid was heated under reflux, with occasional shaking, for two hours. After the resulting mixture was cooled to room temperature, it was poured into ice water and extracted with ether. The extract was washed with water and 10% sodium bicarbonate solution and dried over anhydrous sodium sulphate. The ether was evaporated off and the residue distilled under reduced pressure. The yields of 2-phenylethyl bromide, b.p. 110–113°C. at 17 mm. (lit.(7) b.p. 108–112°C. at 17 mm.), for the duplicate runs were 6.30 and 6.05 gm. (83 and 80%, respectively).

Reaction with Hydroiodic Acid

2-Phenylethanol-1-C^{14} (5.00 gm.) and 55% hydroiodic acid (38 gm.) were refluxed for two hours. The resulting mixture was worked up as described in the reaction with hydrobromic acid. The yield of 2-phenylethyl iodide, b.p. 115–118°C. at 14 mm. (lit.(12) b.p. 114–116°C. at 12 mm.), was 8.75 gm. (92%). In a duplicate preparation using 4.00 gm. of the labeled alcohol, the yield of the iodide was 6.88 gm. (90%).

Reaction with Phosphorus and Iodine

To a mixture of 4.00 gm. of 2-phenylethanol-1-C^{14} and 0.35 gm. of red phosphorus in a 100 ml. round-bottomed flask fitted with a reflux condenser was added 4.40 gm. of iodine in small portions with shaking at room temperature. A slight warming up of the reaction mixture resulted. After the addition of iodine had been completed, the mixture was heated over a steam bath for one hour. After the mixture was cooled, ether was introduced to dissolve the product. The ether solution was filtered through glass wool, washed with dilute sodium hydroxide solution and distilled water, dried over anhydrous sodium sulphate, and evaporated over a steam bath to give a residue which on fractionation under reduced pressure gave 2-phenylethyl iodide, b.p. 115–118°C. at 14 mm. The yields for duplicate runs were 6.14 and 6.46 gm. (81 and 85%, respectively).

Hydrocinnamic Acid from 2-Phenylethyl Halides

The phenylethylmagnesium halide was prepared in the conventional way and treated with excess solid carbon dioxide. The resulting reaction mixture was acidified and extracted with ether. After the solvent was evaporated off from the ethereal extract, the residue was taken up in dilute sodium hydroxide solution and washed with ether to remove any unreacted organic halide. The product was then precipitated by acidifying the washed sodium hydroxide solution and again recovered by extraction with ether. After the extract was dried over anhydrous sodium sulphate, the ether was removed from this final extract and the residue was crystallized from petroleum ether (b.p. 40–60°C.). Colorless needles of hydrocinnamic acid were obtained which melted alone, or on admixture with an authentic sample, at 48–49°C. (lit.(3) m.p. 48.6°C.). The yields based on the various samples of 2-phenylethyl halides used ranged from 70 to 80%.

Oxidation to Benzoic Acid

2-Phenylethanol-1-C^{14} or hydrocinnamic acid was oxidized to benzoic acid with potassium permanganate in sodium hydroxide solution according to a method previously described (5). The yields obtained generally exceeded 80%.

The oxidation of 2-phenylethyl iodide to benzoic acid was effected as follows. Three grams of 2-phenylethyl iodide was heated under reflux until it was nearly boiling. A saturated aqueous solution of potassium permanganate was added gradually whereby a very vigorous reaction took place. After a total of about 10 gm. of potassium permanganate, as a saturated solution, was added, the reaction mixture was allowed to reflux for one half hour. The product was worked up as previously described (5). It was further purified by dissolution in sodium hydroxide and washed with ether as indicated in the preparation of hydrocinnamic acid. The final yield of benzoic acid, crystallized from water, was 0.54 gm. (34%).

ACKNOWLEDGMENT

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AMINO ACIDS

I. PREPARATION AND PROPERTIES OF GLYCOCYAMIDINE[1]

By A. F. McKay,[2] R. O. Braun, and W. G. Hatton

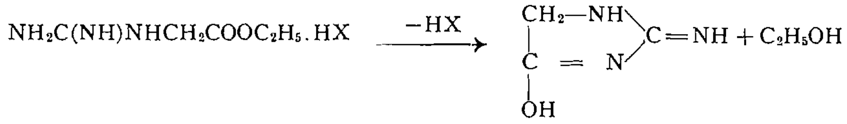
ABSTRACT

Attempts to prepare glycocyamidine by the cyclization of ethyl guanidoacetate in aqueous solutions gave mixtures of guanidoacetic acid and glycocyamidine. The properties of a sample of pure glycocyamidine, which was obtained from the reaction of guanidine with ethyl glycinate, are described.

Glycocyamidine hydrochloride (5) and glycocyamidine sulphate (1) have been prepared in good yields by heating guanidoacetic acid in concentrated hydrochloric acid solution and in normal sulphuric acid solution respectively. However no good methods are available for the preparation of the free base glycocyamidine. Several methods of preparing free glycocyamidine were investigated and the authors found that glycocyamidine could be obtained free from guanidoacetic acid only when the glycocyamidine was prepared under anhydrous conditions.

Glycocyamidine was obtained in 39% yield by treatment of guanidine with ethyl glycinate in absolute alcohol. The other product of this reaction was an oil which gave a picrate melting at 336.5°C. with decomposition. This oil appeared to be a polymer and it has not been further identified. The glycocyamidine prepared in this manner was shown to be free from guanidoacetic acid by paper chromatography. A sample of this glycocyamidine in a nitration medium of nitric acid – acetic anhydride gave glycocyamidine nitrate.

An attempt to prepare glycocyamidine by heating a mixture of guanidine carbonate and glycine gave guanidoacetic acid in agreement with the observations of Nencki and Sieber (7). Finally several experiments designed to prepare glycocyamidine (II) by the removal of acid from ethyl guanidoacetate salts (I) in aqueous solutions always gave a mixture of guanidoacetic acid (glycocyamine) and glycocyamidine. Hydrochloric acid was removed from an aqueous solution of ethyl guanidoacetate hydrochloride by passage of this solution through a bed of IRA-400 resin. On concentration of the aqueous eluate first guanidoacetic acid and then a mixture of guanidoacetic acid and glycocyamidine were obtained. These two crops of crystals were examined by



$$\mathrm{NH_2C(NH)NHCH_2COOC_2H_5.HX} \xrightarrow{-\mathrm{HX}} \begin{matrix}\mathrm{CH_2—NH} \\ | \qquad\quad \\ \mathrm{C} = \mathrm{N} \\ | \qquad\quad \\ \mathrm{OH} \qquad\end{matrix}\!\!\!>\!\mathrm{C{=}NH} + \mathrm{C_2H_5OH}$$

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[2] Monsanto Canada Ltd., Ville La Salle, Quebec.

paper chromatography. A similar result was obtained when an aqueous solution of the picrate of ethyl guanidoacetate was passed through a column of IRA-400 resin.

EXPERIMENTAL[3]

Ethyl Glycinate

Ethyl glycinate (b.p.$_{18}$ 59.5–61°) was prepared in 96.1% yield by the method of Viscontini (9).

Glycocyamidine

Guanidine carbonate (10 gm.) was converted into free guanidine by the method of Morrell and Bellars (6). This guanidine solution was evaporated at 20–25° *in vacuo* (15 mm.) to remove the water. The residual oil was dissolved in 50 cc. of absolute ethanol and the remaining insoluble guanidine carbonate removed by filtration. The filtrate was made up to 100 cc. in a volumetric flask and a 2 cc. aliquot was used for guanidine estimation by precipitation as guanidine picrate. This procedure gave ethanolic solutions containing 4.07–4.42 gm. (62.7–68%) of free guanidine.

When an ethanolic solution of free guanidine was added to an ethanolic solution of ethyl glycinate according to the procedure of Traube and Asher (8), a 24–29% yield of glycocyamidine was obtained. The remaining product was an oil which gave a picrate melting at 336.5°C. Anal. Calc. for $(C_{12}H_{13}N_{10}O_{11})_n$: C, 30.45; H, 2.74; N, 29.58. Found: C, 30.24; H, 2.84; N, 29.68.

The yield of glycocyamidine was increased slightly by the following modification in procedure. Absolute ethanol (50 cc.) was placed in a 500 cc. RB-5-necked flask fitted with two addition funnels, a stirrer, a condenser, and a nitrogen lead-in. An ethanolic solution of guanidine (4.0 gm., 0.068 mole of guanidine in 98 cc. of absolute ethanol) and a solution of ethyl glycinate (7.5 gm., 0.072 mole of ethyl glycinate in 100 cc. of absolute ethanol) were added simultaneously over a period of one hour to the refluxing ethanol. This reaction was carried out under an atmosphere of nitrogen. After removal of the ethanol at reduced pressure, a semisolid remained, yield 8.73 gm. This material was triturated with 10 cc. of ethanol and then it was filtered. The insoluble material did not melt up to 300° and it gave a picrate melting at 208–209°C. Two crystallizations from water raised the melting point to 214–215°C. This picrate was identified as glycocyamidine picrate by mixed melting point determination with an authentic sample. The yield of glycocyamidine was 2.35 gm. (35%). The ethanol filtrate from the glycocyamidine on removal of the ethanol by evaporation gave 5.98 gm. of viscous oil. This oil gave the picrate described above as melting at 336.5°C.

Guanidoacetic Acid

Method A

A mixture of 25 gm. (0.277 mole) of guanidine carbonate, 20.6 gm. (0.275 mole) of glycine, and 1 gm. of ammonium chloride were mixed in a porcelain

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[3] *All melting points are uncorrected. The microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill.*

evaporating dish. This mixture was heated at 100–160°C. with stirring for one hour and 40 min. During this time there was a strong evolution of ammonia. The cooled solid was triturated with water (127 cc.) and filtered to give 15.8 gm. (55.5%) of insoluble material which did not melt up to 300°C. This material was crystallized twice from water (23 cc./gm.) for analysis. Calc. for $C_3H_7N_3O_2$: C, 30.79; H, 5.99; N, 35.90. Found: C, 31.15; H, 5.80; N, 35.80.

An aliquot (27 cc.) of the original filtrate was treated with a saturated aqueous picric acid solution. This gave 1.5 gm. of a picrate (m.p. > 350°C.) which was identified as guanidine picrate by analysis. Thus 8.8% of the original guanidine carbonate remained unchanged. There was no evidence of the presence of glycocyamidine in the filtrate from the guanidoacetic acid. Calc. for $C_7H_8N_6O_7$: C, 29.18; H, 2.77; N, 29.18. Found: C, 29.58; H, 2.78; N, 29.62.

Method B

Guanidoacetic acid was prepared also from glycine and methyl isothiourea sulphate in 81% yield by the method of Brand and Brand (3).

Ethyl Guanidoacetate Hydrochloride

Guanidoacetic acid (36.0 gm., 0.308 mole) was dissolved in 200 cc. of absolute ethanol containing 34 gm. (0.924 mole) of anhydrous hydrogen chloride by refluxing for two hours. Then 100 cc. of the ethanol was removed by distillation and 210 cc. of benzene was added. This solution was distilled using a 12 in. Vigreux column to remove the benzene–ethanol–water and benzene – ethanol azeotropes. Finally the remaining ethanol solution was concentrated *in vacuo* to remove the last traces of ethanol. A heavy viscous sirup was obtained, yield 55.4 gm. (99.3%). A small sample of this product was converted to the picrate in the usual manner. It melted at 189.5–190.5°C., yield 85%. Anal. Calc. for $C_{11}H_{14}N_6O_9$: C, 35.30; H, 3.77; N, 22.45. Found: C, 35.30; H, 3.97; N, 22.27.

Preparation of Glycocyamidine from Ethyl Guanidoacetate

Method A

A 7% aqueous solution of ethyl guanidoacetate hydrochloride (71.8 gm., 0.395 mole) was passed through a bed of IRA-400 resin (885 ml. of IRA-400 resin with a cross sectional area of 28.5 cm.^{2}) at a rate of 25 cc. per minute. Then the column was washed. The total volume of effluent and washings was 16 liters. After removal of the water under vacuum, a total of 35.3 gm. of solid was obtained. The first crop (17.6 gm.) was shown by paper chromatography to be pure guanidoacetic acid while the second crop (17.7 gm.) was found to consist of a mixture of glycocyamidine and guanidoacetic acid. A sample of the second crop was converted to a picrate in the usual manner, yield 79.3%. Two crystallizations from water raised the melting point to 214.5–215.5°C. Anal. Calc. for $C_9H_7N_6O_8$: C, 32.93; H, 2.45; N, 25.62. Found: C, 32.94; H, 2.81; N, 25.25.

Method B

Ethyl guanidoacetate picrate (6.80 gm., 0.018 mole) was dissolved in 2500 cc. of cold water and then passed through a 50 cc. bed of IRA-400 resin (cross sectional area, 2.27 cm.^{2}). The resin column was then washed with a further 1000 cc. of water. The effluent and washings were combined and concentrated to a volume of 25 cc. *in vacuo*. This solution was then poured into 10 volumes of acetone and the precipitate removed by filtration, yield 1.01 gm. (55.5%). This product was identified as glycocyamidine by a comparison of its infrared spectrum with that of an authentic sample of glycocyamidine. On treatment with a saturated aqueous solution of picric acid, it gave glycocyamidine picrate (m.p. 213–215°C.). Found: C, 32.78; H, 2.66; N, 25.72%.

Glycocyamidine Nitrate

The nitrating medium was prepared by adding 8.4 cc. (0.2 mole) of absolute nitric acid (sp. gr. 1.5) to 20 cc. of acetic anhydride in the cold (0°C.). To this solution, 2 gm. (0.02 mole) of glycocyamidine was added and the mixture held at 0–12°C. for one hour and 30 min. This mixture was poured onto 200 gm. of crushed ice and the aqueous solution, after the ice had melted, was extracted with ether (2 × 100 cc.). The aqueous fraction was evaporated *in vacuo* and the residue treated with 25 cc. of absolute alcohol. Then the alcohol was removed *in vacuo* and the residue again treated with 25 cc. of absolute alcohol. After the alcohol was removed once more *in vacuo*, a white solid (m.p. 133°C. dec.) was obtained, yield 0.785 gm. (24%). Two crystallizations from absolute ethanol (25.5 cc./gm.) raised the melting point to a constant value of 145°C. with dec., yield 0.52 gm. Anal. Calc. for $C_3H_6N_4O_4$: C, 22.22; H, 3.70; N, 34.56%. Found: C, 22.33; H, 3.69; N, 34.55%.

This compound gave a positive test for the nitrate ion with Nitron reagent (4).

Paper Chromatography

In all cases 0.013 cc. of the 2% solutions were spotted at the zero point on No. 4 Watmann Chromatography paper. The chromatogram was developed with the upper layer of a mixture of 250 cc. of *n*-butanol, 250 cc. of water, and 60 cc. of glacial acetic acid and the chromatogram was sprayed with the Sakaguchi reagents as outlined by Block, LeStrange, and Zweig (2). In Fig. 1, columns I and II represent chromatograms of pure guanidoacetic acid and glycocyamidine respectively. Columns III and IV are chromatograms of samples from the first and second crops obtained from the eluate from passing ethyl guanidoacetate hydrochloride through a bed of IRA-400 resin. The first crop appears as pure guanidoacetic acid while the second crop is shown to be a mixture of glycocyamidine and guanidoacetic acid. Finally Column V is a chromatogram of the solid obtained from the eluate from the passage of ethyl guanidoacetate picrate through a bed of IRA-400 resin. The R_f values for pure guanidoacetic acid and glycocyamidine were 0.31 and 0.45 respectively when the above solvent mixture was used.

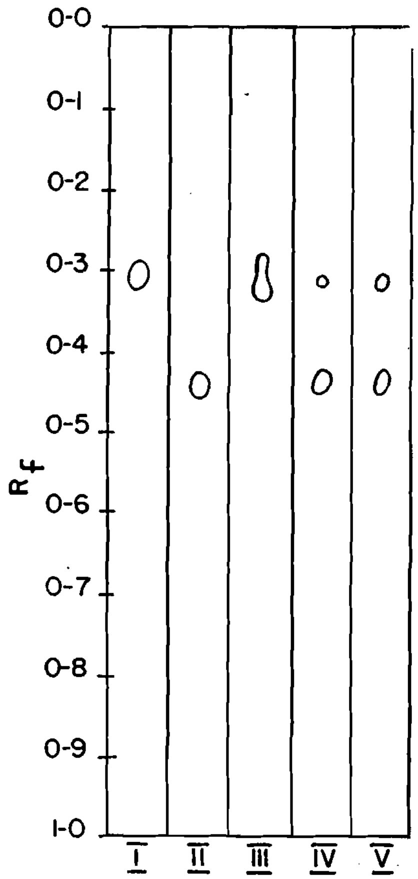

FIG. 1. Chromatograms.

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DETERMINATION OF THE ABSOLUTE FISSION YIELD OF Ba^{140} IN THERMAL NEUTRON FISSION OF U^{235} [1]

By L. Yaffe,[2] H. G. Thode,[3] W. F. Merritt, R. C. Hawkings, F. Brown, and Rosalie M. Bartholomew

ABSTRACT

The absolute fission yield of Ba^{140} in the thermal neutron fission of U^{235} has been determined to be $(6.32 \pm 0.24)\%$. The reaction $B^{10}(n, \alpha)Li^7$ was used as a neutron monitor and the B^{10}/B^{11} ratio determined mass spectrometrically before and after neutron bombardment. The Ba^{140} disintegration rate was determined using 4π counting techniques. The half-life of La^{140} has been found to be 40.31 ± 0.06 hr.

INTRODUCTION

Absolute fission yields were first determined by Anderson *et al.* (2). Uranyl sulphate and later manganese sulphate were irradiated in the same position in a neutron beam obtained from a cyclotron. The nuclear reaction $Mn^{55}(n, \gamma)Mn^{56} \xrightarrow{\beta}$ was used as a monitor of the neutron flux. The Ba^{140} was separated radiochemically. The value obtained for the fission yield of Ba^{140} was 8.4%.

Accurate values of the fission and capture cross sections of uranium and manganese respectively and good absolute disintegration rate determination techniques are necessary for this method to yield accurate results. Since no indication is given by Anderson *et al.* of the cross-section values used, their result cannot be recalculated in terms of more recent values for those constants.

To avoid the difficulties due to reproducibility of neutron flux caused by positioning and variations due to the fact that the neutron monitor was irradiated at a time different from the sample itself, Grummitt *et al.* (18) irradiated natural uranium and used the reaction $U^{238}(n, \gamma)U^{239} \xrightarrow{\beta}$ as an internal monitor.

Then

$$N_{U^{239}}/N_{Ba^{140}} = \sigma_c/\sigma_f . Y_f$$

where $N_{U^{239}}$ and $N_{Ba^{140}}$ are the 'steady state' activities of U^{239} and Ba^{140}, σ_c and σ_f are the capture and fission cross sections of natural uranium respectively and Y_f is the fission yield. Again accurate cross-section data and accurate absolute disintegration rate determination methods are essential. The value obtained was 5.6%.

Using more recent values for the capture cross section of U^{238} ($\sigma_c = 2.80 \times 10^{-24}$ cm.^{2} for 2200 meters/sec. neutrons (9)) and for the thermal neutron fission cross section of natural uranium due to U^{235} ($\sigma_f = 3.95 \times 10^{-24}$ cm.^{2} (3, 9)), this result for the absolute fission yield of Ba^{140} becomes 6.0%.

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Absolute fission yield experiments are described by Freedman and Steinberg (16) in a paper summarizing work done by themselves and colleagues in the Manhattan Project. The technique used was to irradiate simultaneously in the same neutron flux a thick and a thin piece of uranium. Fissions from the thin sample were counted in a pulse ionization chamber. Radiochemical analyses were performed on the thick piece.

Using the above method, Engelkemeir *et al.* (13) obtained a value of 5.8% for the fission yield of Ba^{140}. They used a value of 12.5 days for the half-life rather than the presently accepted value of 12.8 days (12). Use of the latter value would give a slightly higher yield. Freedman and Engelkemeir (15) using the same equipment, but improved techniques, obtained a value of $6.15 \pm 0.13\%$ for the absolute fission yield of Ba^{140}.

The chief error in this experiment lies in the determination of the absolute disintegration rate of Ba^{140}. Using the best available absorption and scattering data for Ba^{140}, Steinberg (23) corrected the results of Freedman and Engelkemeir yielding a value of 6.17. In a private communication Steinberg (22) has given us a reassessed value of 6.32 ± 0.6 as the best value for this experiment.

In the above experiment several sources of error are possible. First, in the fission counter, where the "geometry" is assumed to be 50%, corrections have to be made for coincidences, pulse height selection, and fission background of the chamber. These corrections can be made to ±2% according to Steinberg. Secondly, one assumes that the fission rate per U atom in the thick and thin samples is identical. Thirdly, the following corrections have to be made to the experimentally determined counting rate of Ba^{140} to transform it into an absolute disintegration rate.

(*a*) Self-scattering and self-absorption.

(*b*) Back-scattering.

(*c*) Absorption in counter window of Geiger counter and air gap between the sample and counter window.

(*d*) Geometrical efficiency of the counter.

All of these corrections, some of which are not negligible, have caused Steinberg to put an error of ±10% on the absolute measurement of Ba^{140}.

We have measured the absolute fission yield of Ba^{140}. Instead of the fission chamber arrangement we have used the change in the ratio of B^{10}/B^{11} before and after irradiation as a neutron flux monitor. One eventually has to turn to a fission chamber determination to obtain a value for the fission cross-section σ_f. However, this can be done very accurately in an experiment designed specifically to obtain this result.

By the use of a 4π type of counter (7, 19) we have avoided the necessity of using the correction factors previously described; thus there resulted better accuracy in the determination of the Ba^{140} disintegration rate.

EXPERIMENTAL

(i) *Irradiation*

A purified sample of boron trifluoride was divided into two parts, each sealed into a quartz tube at a pressure of about 30 cm. of mercury. One was irradiated with the uranium metal, the other was kept for later reference.

The accurately weighed sample of uranium metal (about 600 mgm.) was placed in a 'self-serve' irradiation container along with the sample of boron trifluoride. The irradiation container was evacuated and the container sealed *in vacuo* using the cold welding technique (1). The uranium metal, after irradiation, showed no signs of oxidation testifying to the efficacy of the cold-weld sealing technique. The sample showed a loss of weight of only 0.0006 gm. after the irradiation period of 36 days in the NRX reactor.

(ii) *Mass Spectrometry*

A conventional 180° direction focusing mass spectrometer with vibrating reed d-c. amplifier and speedomax recorder was used to compare the isotopic ratios of the irradiated and unirradiated part of the boron trifluoride sample.

The ratio of B^{10}/B^{11} before irradiation to that after irradiation for the sample in question was found to be 1.029 ± 0.001. An accuracy of 0.1% is about the best obtainable at the present time when single ion collection methods are used, particularly where fluorides are involved. However, the samples have been retained and isotopic ratios can be redetermined later using the simultaneous collection system of ion measurement. A simultaneous collection instrument used for the rapid comparison of isotopic ratios is now being adapted for use with boron.

(iii) *Chemical Separation*

The uranium metal was dissolved in nitric acid to which 50 mgm. barium nitrate carrier had been added. Barium was separated from the mixture using a method previously described (17). It consisted of chloride, chromate, and nitrate separations with the addition of appropriate holdback carriers. The final barium nitrate precipitate was dissolved in water and made up to a constant volume. From this, small aliquots were taken with calibrated micropipettes for measurement purposes. The chemical yield, determined gravimetrically by the precipitation of barium as barium sulphate from the remainder of the solution, was 72.9%.

(iv) *Counting*

The disintegration rate of $Ba^{140}+La^{140}$ was determined using the 4π counting technique (19). Counting samples were prepared by the evaporation, under an infrared lamp, of known aliquots of the barium nitrate solution on a thin (100 μgm./cm.^{2}) polystyrene film which had a conducting film of gold (25 μgm./cm.^{2}) on each side. Self-absorption in the source material (i.e. barium nitrate) was largely eliminated by the technique of successive dilutions and by taking care to spread the material as uniformly as possible. The small self-absorption loss due to the finite size of the crystals constituting the source cannot be eliminated in this manner but is considered negligible in this case (i.e. $<1\%$).

Corrections were made for absorption of beta particles in the thin plastic film and for coincidence losses in the counting apparatus. The total correction required for the above losses was usually less than two per cent.

Corrections were also made to the counting data for growth and decay in the Ba^{140}–La^{140} system during the time interval between the last separation of Ba^{140} from its daughter La^{140} and the time of counting. This correction is discussed in detail in the following section.

(v) *Growth and Decay Correction*

If one assumed a steady build-up of Ba^{140} the saturation factor for the irradiation period used would have been 85.8%. One must, however, take into account neutron flux variations which occurred during the course of the irradiation. Conditions during this experiment were such that one could, with a maximum error of ±0.5%, assume that the reactor power was proportional to the neutron flux. An analogue computer, designed by Bayly (5), was used to establish the "effective" saturation factor as (58.0 ± 0.3)%. The samples were of such a size that no correction for perturbation of the neutron beam had to be made (21).

The half-life of La^{140} is given by Weimer *et al.* (25) as 40.0 ± 0.3 hr. over 11 half-lives from neutron bombardment of spec-pure lanthanum oxide. Bothe (8) observed a period of 39.5 ± 0.5 hr. with thermal neutrons on La^{139}. Cork *et al.* (10) followed the decay of La^{140} prepared by (n, γ) reaction of pile neutrons on specially purified La^{139} through eight half-lives to get a half-life of 41.4 hr. Ballou *et al.* (4) irradiated two samples of lanthanum nitrate with neutrons from cyclotron deuterons on beryllium. The first sample gave 39.5 hr. over 8 half-lives, and the second 40.3 hr. over about 13 half-lives for an average of 40.0 ± 0.5 hr. Bishop *et al.* (6) observed a half-life of 40.0 ± 0.1 hr. Using the 4π counter, we have followed the decay of a sample of La^{140} produced by thermal neutron bombardment of spectroscopically pure La_2O_3 for 14 half-lives. A least squares analysis of the counting data gave the half-life of La^{140} as 40.31 ± 0.06 hr. This is in excellent agreement with the value of 40.3 hr. obtained by Ballou over a corresponding interval.

Cork *et al.* (11) report a half-life of 13.4 days for Ba^{140}. Engelkemeir *et al.* (12) have followed the decay of Ba^{140} for periods up to about 12 half-lives and obtained a value of 12.8 days. We have used 12.8 days as the half-life for Ba^{140} in all our calculations. This value has been found to give a good fit to our experimental data followed over periods of up to five half-lives of Ba^{140}.

The total disintegration rate of the separated Ba^{140} was found to be $5.395 \pm 0.067 \times 10^8$ dis./sec. corrected to the end of the irradiation. From this must be subtracted a fast fission contribution (21) of $(0.8^{+0.6}_{-0.3})\%$. The loss of Ba^{140} by recoil of the fission fragments from the unwrapped uranium is estimated to be $(0.3^{+0.0}_{-0.1})\%$. The other experimental values pertinent to a calculation of a value for the fission yield of Ba^{140} are tabulated below:

Weight of uranium metal = 646.5 mgm.
Effective saturation factor = (58.0 ± 0.3)%.
Chemical yield (barium separation) = (72.9 ± 0.4)%.
Ratio of B^{10}/B^{11} before irradiation to B^{10}/B^{11} after irradiation = 1.029 ± 0.001.
Actual running time of reactor (t) = 2.429×10^6 sec.

The effective flux of thermal neutrons may be calculated from the experimental data as follows:

[1] $$dN/dt = -N(\rho v)_{\mathrm{th}}\sigma_{\mathrm{B}}$$

or,

[2] $$N = N_0 \exp[-(\rho v)_{\mathrm{th}}\sigma_{\mathrm{B}}t].$$

N = number of B^{10} atoms present at any time t,
$(\rho v)_{\mathrm{th}}$ = effective thermal neutron flux,
σ_{B} = thermal neutron capture cross section of B^{10},
N_0 = number of B^{10} atoms present when $t = 0$.

The thermal neutron absorption cross section of B^{10} is usually attributed to the reaction $B^{10}(n, \alpha)Li^7$. Since we have used the change in the ratio of B^{10}/B^{11} as a measure of the integrated thermal neutron flux any reaction other than the (n, α) reaction which affects this ratio may constitute a source of error. The reaction $B^{11}(n, \gamma)B^{12}$ will not affect the results since the B^{11} capture cross section is known to be small relative to that of B^{10} ($1:10^5$). On the other hand, no experimental evidence exists as to the cross section for the reaction $B^{10}(n, \gamma)B^{11}$.

For the conditions of this experiment calculations show that a cross section for this reaction of approximately 80 barns would result in an error equal to the limit of the error in the mass spectrometer analysis. A cross section of approximately 20 barns would be completely negligible insofar as this experiment is concerned. We have assumed, therefore, that the cross section for the reaction $B^{10}(n, \gamma)B^{11}$ does not exceed 20 barns so that the change in the ratio of B^{10}/B^{11} as measured mass spectrometrically gives the change in the number of B^{10} atoms as a result of the irradiation and the error given for the mass spectrometric analysis represents the analytical error.

Thus,

[3] $$\frac{N_0}{N_0\exp[-(\rho v)_{\mathrm{th}}\sigma_{\mathrm{B}}t]} = 1.029$$

or,

$$\exp[(\rho v)_{\mathrm{th}}\sigma_{\mathrm{B}}t] = 1.029$$

whence

$$(\rho v)_{\mathrm{th}}\sigma_{\mathrm{B}}t = 0.0286$$

and

[3a] $$(\rho v)_{\mathrm{th}} = 0.0286/\sigma_{\mathrm{B}}t.$$

The rate of depletion of U^{235} may be expressed by

[4] $$dU/dt = -U(\rho v)_{\mathrm{th}}\sigma_{\mathrm{abs}}$$

or,

[4a] $$U = U_0\exp[-(\rho v)_{\mathrm{th}}\sigma_{\mathrm{abs}}t]$$

where U = number of U^{235} atoms present at time t,
U_0 = number of U^{235} atoms when $t = 0$,
$(\rho v)_{\mathrm{th}}$ = effective thermal neutron flux,
σ_{abs} = thermal neutron absorption cross section of U^{235}.

In terms of the U^{235} present initially, the fission rate is therefore

[5] $$[dU/dt]_{\mathrm{fission}} = -\{U_0\exp[-(\rho v)_{\mathrm{th}}\sigma_{\mathrm{abs}}t]\}(\rho v)_{\mathrm{th}}\sigma_f$$

$$= -[U_0(\rho v)_{\text{th}}\sigma_f]\exp[-(\rho v)_{\text{th}}\sigma_{\text{abs}}t]$$

where σ_f = thermal neutron cross section for fission of U^{235}.

We may then write for the net rate of formation of Ba^{140} at any time t during the irradiation,

$$dX/dt = -Y_f[dU/dt]_{\text{fission}} - \lambda X \tag{6}$$

where

X = number of atoms of Ba^{140} at any time t,
Y_f = thermal neutron fission yield for Ba^{140},
λ = disintegration constant for Ba^{140}.

From equations [5] and [6] we have

$$dX/dt = Y_f[U_0(\rho v)_{\text{th}}\sigma_f]\exp[-(\rho v)_{\text{th}}\sigma_{\text{abs}}t] - \lambda X. \tag{7}$$

Integrating and multiplying through by λ, equation [7] becomes

$$X\lambda = \frac{\lambda Y_f[U_0(\rho v)_{\text{th}}\sigma_f]}{\lambda - (\rho v)_{\text{th}}\sigma_{\text{abs}}}\{\exp[-(\rho v)_{\text{th}}\sigma_{\text{abs}}t] - \exp(-\lambda t)\}. \tag{8}$$

Substituting for $(\rho v)_{\text{th}}$ from equation [3*a*] we may write for the disintegration rate of Ba^{140}

$$X\lambda = \frac{\lambda Y_f[(0.0286/t)U_0(\sigma_f/\sigma_B)]}{\lambda - (0.0286/t)(\sigma_{\text{abs}}/\sigma_B)}[\exp(-0.0286\sigma_{\text{abs}}/\sigma_B) - \exp(-\lambda t)]. \tag{9}$$

Investigations into the natural abundance of the boron isotopes have been carried out by Inghram (20) who obtained a B^{11}/B^{10} ratio of 4.31 (i.e. 18.83% B^{10}). Thode *et al.* (24) showed that a variation of about four per cent occurred in the natural abundance depending on the geographical location from which the boron had been obtained. However the actual boron samples used gave an abundance ratio identical with that found by Inghram for American borax.

Thus,

$$\sigma_{\text{abs}}/\sigma_B = 0.90 \times 0.1883 = 0.169$$

where 0.90 has been taken as the value for the ratio of the absorption cross section of U^{235} (σ_{abs}) to the capture cross section of natural boron, under the conditions of the experiment (i.e. a Maxwellian distribution of neutrons at 57°C).

Evaluating the terms of equation [9] which involve $\sigma_{\text{abs}}/\sigma_B$ we find

$$\lambda - (0.0286/t)(\sigma_{\text{abs}}/\sigma_B) = 6.27 \times 10^{-7} - 1.99 \times 10^{-9} = 6.25 \times 10^{-7}$$

and

$$\exp(-0.0286\,\sigma_{\text{abs}}/\sigma_B) = 0.995.$$

It is obvious that even a large change in the value of $\sigma_{\text{abs}}/\sigma_B$ will not appreciably affect the final result.

The ratio σ_f/σ_B is a quantity which is usually determined experimentally. Since the ultimate value of Y_f is critically dependent on this ratio it was thought desirable to use it as a standard rather than the independent values of the two constants. Thus the value for Y_f may be easily adjusted in accordance with any subsequent revisions in the value of the ratio σ_f/σ_B.

We have used a ratio of 0.773 for σ_f/σ_B for natural boron having an isotopic composition identical with that used in our experiment. The ratio already takes into account the fact that our irradiation occurred in a beam of neutrons having a Maxwellian distribution corresponding to a temperature of 57°C.

For B^{10}

$$\sigma_f/\sigma_B = 0.1883 \times 0.773 = 0.1456.$$

From equation [9]

$$Y_f = \frac{X\lambda[\lambda - (0.0286/t)(\sigma_{abs}/\sigma_B)]}{\lambda[(0.0286/t)\cdot U_0(\sigma_f/\sigma_B)]\{\exp(-0.0286\ \sigma_{abs}/\sigma_B) - \exp(-\lambda t)\}}.$$

Evaluating the remaining factors in the above equation we find the value for

$$X\lambda = \frac{5.395 \times 10^8 \times 0.992}{0.729 \times 0.997} = 7.363 \times 10^8 \text{ dis./sec.}$$

where 0.992 is the correction factor to bring the result to that resulting from thermal neutron fission alone, 0.729 is the correction for chemical recovery, and 0.997 is the correction for recoil loss.

$$\lambda = \frac{0.6932}{12.8 \times 3600 \times 24} = 6.27 \times 10^{-7}\text{sec.}^{-1},$$

$$t = 2.429 \times 10^6\text{sec.},$$

and

$$U_0 = \frac{0.6465 \times 6.025 \times 10^{23} \times 0.00719}{238.07} = 1.176 \times 10^{19} \text{ atoms}$$

where 0.00719 is the value for the natural abundance of U^{235}(14) and $\exp(-\lambda t) = 1 - \text{effective saturation factor} = 1 - 0.580 = 0.420$. Therefore,

$$Y_f = \frac{7.363 \times 10^8}{6.27 \times 10^{-7}} \cdot \frac{6.27 \times 10^{-7} - 2.01 \times 10^{-9}}{1.178 \times 10^{19} \cdot 1.177 \times 10^{-8} \cdot (\sigma_f/\sigma_B)} \cdot \frac{1}{0.995 - 0.420}$$

$$= \frac{9.206 \times 10^{-3}}{\sigma_f/\sigma_B}$$

$$Y_f = \frac{9.206 \times 10^{-3}}{0.1456} = 6.32\%.$$

The errors involved in our measurement are:

(*a*) disintegration rate (standard)	1.2%
(*b*) mass spectrometer analysis (average deviation)	3.4%
(*c*) chemical yield (average deviation of three results)	0.5%
(*d*) fast fission contribution (estimated maximum)	0.6%
(*e*) saturation factor (estimated maximum)	0.5%
(*f*) fission recoil loss (estimated maximum)	0.1%.

Errors not associated with the measurement but which occur in the calculation are:

(*g*) abundance of U^{235} in natural uranium,
(*h*) abundance of the boron isotopes,
(*i*) the ratio σ_f/σ_B.

The errors in (*g*) and (*h*) are small. No error is included for the value of σ_f/σ_B chosen. Should a better value be available our result need be corrected only by the ratio of the new value to the old.

Treating the errors listed ((*a*)–(*f*)) as standard errors the thermal neutron fission yield of Ba^{140} is $(6.32 \pm 0.24)\%$.

ACKNOWLEDGMENTS

The authors wish to thank Dr. D. G. Hurst for valuable discussions and Dr. W. B. Lewis for many helpful suggestions during the preparation of this manuscript.

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THE POLAROGRAPHIC REDUCTION OF AMARANTH[1]

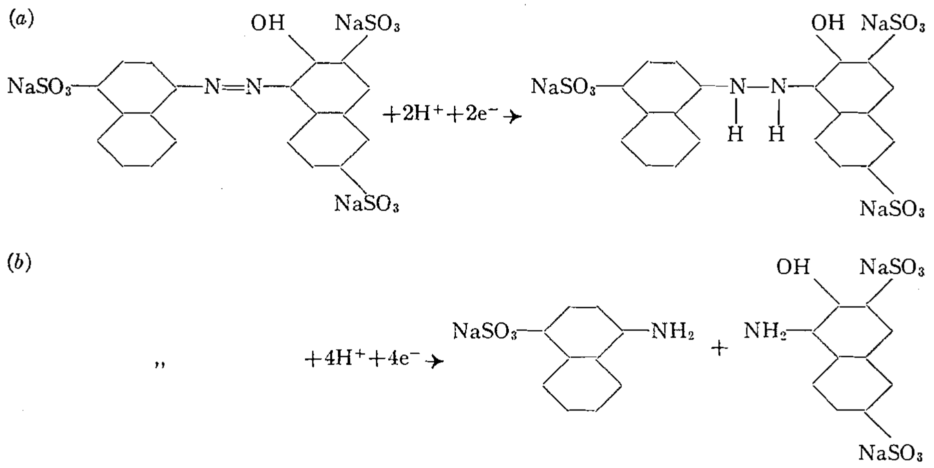
By G. G. McKeown and J. L. Thomson

ABSTRACT

Amaranth, a food color, has been studied polarographically over a pH range of 2.0 to 10.0 in aqueous solution and was found to give a well-defined wave, diffusion controlled and suitable for quantitative work. Irreversibility was indicated by the behavior of the half-wave potential to changes in pH and concentration. With pH, a direct relationship of −0.080 v. per pH unit held between pH 2.0 and 7.0, while with concentration, the half-wave potential was found to apparently vary directly with the logarithm of concentration. Using a coefficient of diffusion value obtained by conductance measurements the value of *n* for the reaction was calculated to be 4, which corresponds to a rupture of the azo group to yield the corresponding amines.

In connection with the work of this laboratory, a study of the polarographic behavior of the artificial food colors was begun with the object of determining the possible value for qualitative and quantitative analysis. This paper is the first of a series and describes the reduction of amaranth at the dropping mercury electrode.

A consideration of the formula of amaranth reveals that two likely possibilities for reduction exist: (*a*) the azo group accepts two hydrogen atoms to form an hydrazo group, and (*b*) the azo group accepts four hydrogen atoms to yield the corresponding amines.



Polarographic work on several compounds similar to amaranth suggests that the former reaction should take place. The azo-hydrazo reaction has been shown to occur with azobenzene and its derivatives (5, 6), although some doubt still exists as to the reversibility of the reaction (7). The azo dyes, orange II and metanil yellow, are claimed to follow a two electron reduction

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Contribution from the Food and Drug Laboratory, Department of National Health and Welfare, Ottawa, Ont.

on the basis of an n value calculated from the wave slope (2). However, this claim would seem to be somewhat doubtful as the wave included an unsuppressed maximum and the behavior of the half-wave potential with changes in pH and concentration indicated the reaction to be irreversible.

On the other hand, amaranth has long been known to undergo a four electron reduction under the influence of chemical reducing reagents. The reaction forms the basis of the quantitative determination of amaranth and similar azo colors by titanium trichloride reduction (4).

EXPERIMENTAL

All current–voltage curves were obtained on a Leeds and Northrup Type E recording polarograph using a polarizing range of 0.0 to -1.0 v., a current range of 20 μa. and damped at position 1 on the instrument. Half-wave potentials were obtained by first determining the diffusion current then manually adjusting the polarizing voltage to give the half value. The characteristics of the capillary of the dropping mercury electrode as determined at a potential of -0.5 v. and a mercury head of 60.0 cm. were $m = 1.90$ mgm./sec., $t = 3.66$ sec., and $m^{2/3}\ t^{1/6} = 1.90$ mgm.$^{2/3}$ sec$^{-1/2}$.

The usual H-type cell was employed containing a saturated calomel electrode as reference anode separated from the electrolysis compartment by a sintered glass disk and an agar plug. The cell was equipped with inlets to admit gas for the deoxygenation of test solutions. All experiments were carried out with the temperature of the cell controlled at 25.0°C.

A commercial sample of amaranth, manufactured by H. Kohnstamm and Co., Inc., New York, was purified by repeated recrystallization from aqueous solutions of sodium acetate. The product was washed with boiling ethanol and dried *in vacuo*. A stock solution of the purified dye in water was prepared and standardized by titanium trichloride titration.

Solutions of the Universal Buffer Mixture of Prideaux and Ward (1) were prepared from reagent grade chemicals for pH values from 2.0 to 10.0. These were checked on a Beckman Model G pH meter.

Gelatin supplied by the British Drug Houses (Canada) was used to suppress maxima.

Tank nitrogen, purified by passage through an acid solution of chromous sulphate, was used to deoxygenate all solutions.

Amaranth was polarographed in aqueous solutions that contained by volume 80% buffer solution and were 0.5 M in potassium chloride as supporting electrolyte. Gelatin, when used to suppress maxima, was present in the amount of 0.01%.

Conductivity measurements were made using a Leeds and Northrup medium conductivity cell equipped with platinum black coated electrodes. All measurements were carried out with the temperature of the cell controlled at 25.0°C.

RESULTS

Preliminary experiments showed amaranth to give a well-defined wave over a wide pH range provided that the solutions were well buffered and contained a liberal concentration of supporting electrolyte. A maximum appeared on the wave which was readily suppressed by gelatin.

Influence of pH

Polarograms were run of 0.5 m*M* amaranth buffered at pH values from 2.0 to 10.0. These were done in duplicate, with and without gelatin, to note its effect on the wave. Some typical curves are shown in Fig. 1. Half-wave potentials and diffusion currents are listed in Table I.

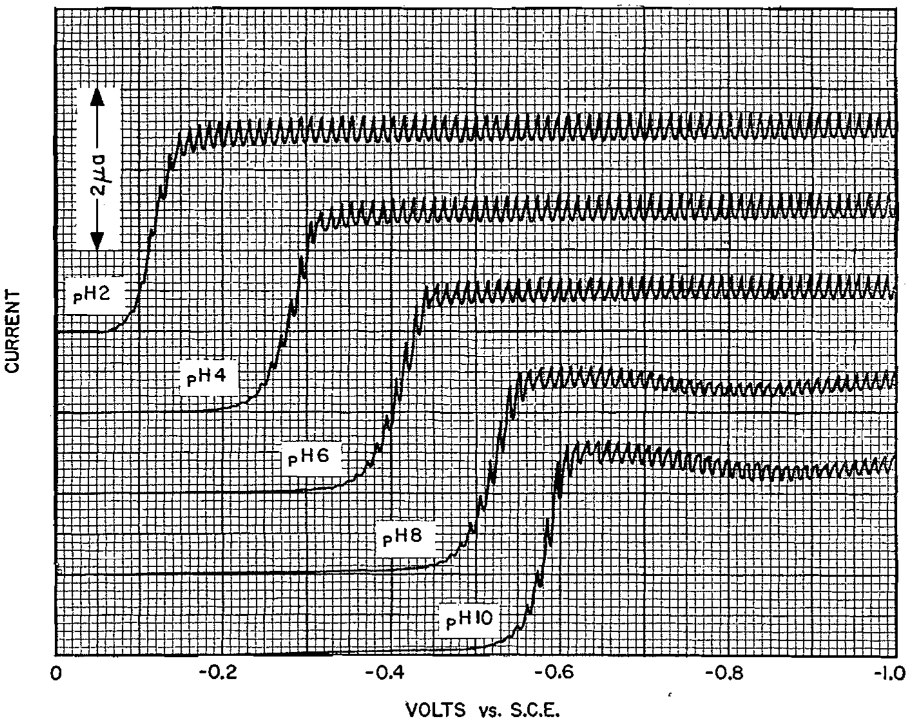

FIG. 1. Current-voltage curves of 0.5 m*M* amaranth at various pH's. Solutions contained 0.01% gelatin.

TABLE I
HALF-WAVE POTENTIALS (VS. S.C.E.) AND DIFFUSION CURRENTS OF 0.5 m*M* AMARANTH AT VARIOUS pH VALUES

pH	$-E_{\frac{1}{2}}$ (v.)		i_d (μa.)	
2.0	.118	.110*	5.0	4.9*
3.0	.207	.203*	5.0	4.9*
4.0	.281	.275*	5.0	4.9*
5.0	.368	.348*	5.0	4.9*
6.0	.443	.405*	5.0	4.9*
7.0	.521	.462*	5.0	4.9*
8.0	.579	.516*	5.0	4.9*
9.0	.611	.549*	5.0	4.9*
10.0	.647	.579*	5.0	4.9*

**Solutions were 0.01% in gelatin.*

The maximum appearing in the polarograms of unsuppressed solutions was not sufficiently pronounced to interfere with the measurement of half-wave potentials and diffusion currents. The addition of gelatin, on the other hand, besides suppressing the maximum, caused a slight decrease in the height of the wave and tended to shift the half-wave potential to more positive values, the effect being very noticeable at high pH values.

The half-wave potential was found to vary with the pH in a manner suggesting an irreversible, organic reaction. Between pH 2.0 and 7.0, the relationship was linear with a shift of −0.080 v. per pH unit. Beyond pH 7.0, however, the variation with pH was found to steadily diminish. The results are illustrated in Fig. 2.

The height of the wave was found to be independent of pH.

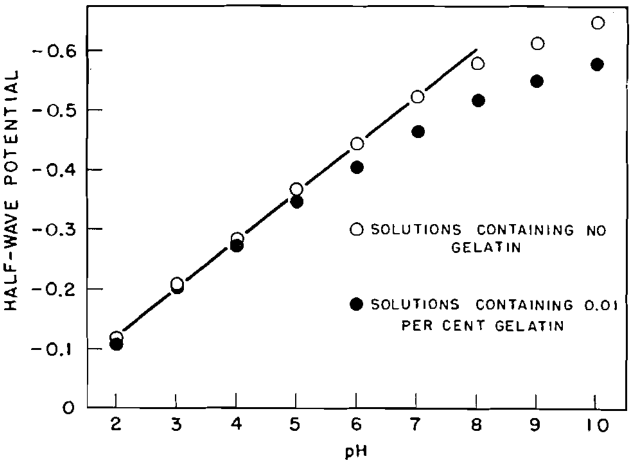

FIG. 2. Effect of pH on the half-wave potential of 0.5 mM amaranth.

Influence of Concentration

Polarograms were run of solutions containing amaranth in concentrations ranging from 0.05 to 1.00 mM. These were done in duplicate, with and without

TABLE II
HALF-WAVE POTENTIALS (VS. S.C.E.) AND DIFFUSION CURRENTS OF AMARANTH IN VARIOUS CONCENTRATIONS

Concentration (mM.)	$-E_{\frac{1}{2}}$ (v.)						i_d (μa.)					
	pH 4.0		pH 6.0		pH 8.0		pH 4.0		pH 6.0		pH 8.0	
1.00	.311	.302*	.475	.432*	.612	.541*	9.6	9.5*	9.6	9.6*	9.6	9.5*
0.75	.302	.291*	.462	.421*	.602	.531*	7.2	7.2*	7.2	7.1*	7.3	7.2*
0.50	.289	.278*	.444	.406*	.583	.519*	5.0	5.0*	5.0	4.9*	5.0	5.0*
0.25	.270	.260*	.418	.385*	.551	.498*	2.6	2.6*	2.6	2.6*	2.6	2.5*
0.10	.234	.231*	.372	.361*	.505	.477*	1.2	1.2*	1.2	1.2*	1.2	1.2*
0.05	.214	.215*	.346	.342*	.475	.460*	0.6	0.6*	0.6	0.6*	0.6	0.6*

Solutions were 0.01% in gelatin.

gelatin, at pH values of 4.0, 6.0, and 8.0. Some typical curves are shown in Fig. 3. Half-wave potentials and diffusion currents are listed in Table II.

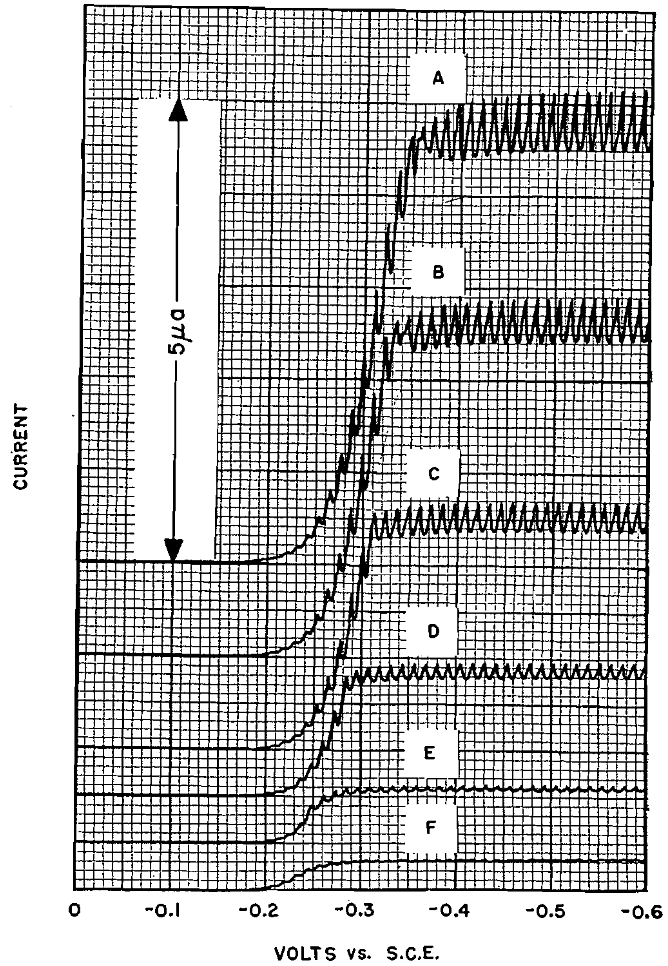

FIG. 3. Current–voltage curves of amaranth in various concentrations—*A*, *B*, *C*, *D*, *E*, and *F* were 1.00, 0.75, 0.50, 0.25, 0.10, and 0.05 m*M* respectively. All solutions contained 0.01% gelatin and were buffered at pH 4.

These results also indicate the reaction to be irreversible. The half-wave potential was found not to remain constant but to shift to more negative values with increasing concentration. This behavior occurred at all three pH values and, as illustrated in Fig. 4, a direct relationship appears to exist between the logarithm of concentration and the half-wave potential for the unsuppressed solutions. In the presence of gelatin, the half-wave potential also varies with concentration but in a non-linear manner. The effect of gelatin becomes almost negligible at low concentrations.

The height of the wave was found to vary directly with the concentration.

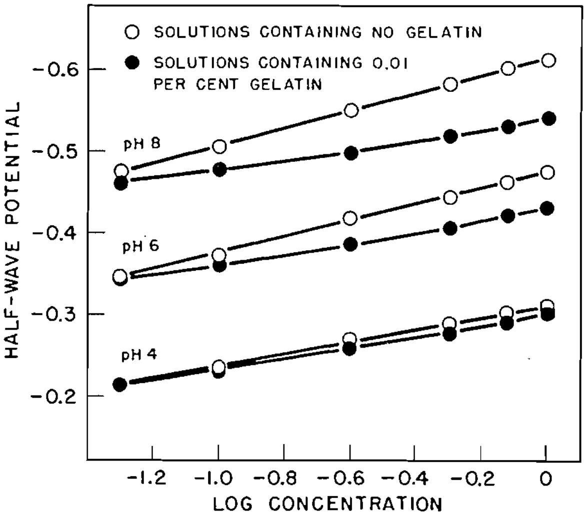

FIG. 4. Effect of concentration on the half-wave potential of amaranth.

Effect of the Mercury Pressure on the Height of the Wave

Wave heights were determined on a 0.5 m*M* amaranth solution at various pressures on the dropping mercury electrode. The results are shown in Table III.

TABLE III
EFFECT OF MERCURY PRESSURE ON WAVE HEIGHT

Pressure (cm. Hg)	Droptime (sec.)	Pressure (corrected)	Current(i) (μa.)	$i/p^{\frac{1}{2}}$
60	3.66	58.4	5.01	.655
55	4.01	53.4	4.78	.654
50	4.48	48.5	4.55	.654
45	5.08	43.5	4.31	.653
40	5.67	38.6	4.06	.653
35	6.49	33.7	3.80	.655
30	7.55	28.7	3.50	.653

It will be seen that the height of the wave is proportional to the square root of the mercury pressure which thus proves the reaction to be diffusion controlled.

Determination of the Diffusion Coefficient of the Amaranthate Ion

In order to calculate the number of electrons involved in a polarographic reaction, the coefficient of diffusion of the ion or molecule being reduced must be known. In this case, amaranth being the trisodium salt of an organic ion, one is concerned with the diffusion coefficient of that ion. While it is difficult to determine the coefficient of diffusion of an ion under the exact experimental conditions of a polarographic reaction, a value at infinite dilution can be readily obtained from conductivity measurements. With low electron numbers, such values are always sufficiently close to the true values to give the correct solutions.

Electrical conductivities of pure amaranth were determined at 25.0°C. for concentrations ranging from 0.005 to 0.00025 equivalents. By extrapolation, the equivalent conductance at infinite dilution was obtained:

$$\Lambda_{0\mathrm{Am}} = 127.5 \text{ ohms}^{-1} \text{ cm.}^2$$

Applying the equation

$$\Lambda_0 = \lambda^+ + \lambda^-,$$

where the equivalent conductance is equal to the sum of the ionic conductances, and substituting the known value for the sodium ion

$$\lambda^+_{0\mathrm{Na}+} = 50.1 \text{ ohms}^{-1} \text{ cm.}^2$$

the equivalent ionic conductance of the amaranthate ion is obtained:

$$\lambda^-{}_{0\,\frac{1}{3}\mathrm{Am}---} = 77.4 \text{ ohms}^{-1} \text{ cm}^2.$$

Substituting this value into the equation

$$D_0 = 2.67 \times 10^{-7}\, \lambda_0/Z \text{ cm.}^2 \text{ sec.}^{-1} \text{ (Ref. 3)}$$

where the ionic charge Z is equal to 3, the coefficient of diffusion of the amaranthate ion is obtained:

$$D_{0\mathrm{Am}---} = 6.9 \times 10^{-6} \text{ cm.}^2 \text{ sec}^{-1}.$$

CONCLUSIONS

The wave given by amaranth has been shown to be diffusion controlled since its height is proportional to concentration, independent of pH, and varies with the square root of the mercury pressure on the dropping electrode. As the wave is well-defined, producible over a wide pH range, and free from excessive distortion by maxima, it is well suited for quantitative work. The dye may be readily detected in concentration as low as 5 mgm./liter (8.3 μM.) which gives a current of approximately 0.1 μa.

The behavior of the half-wave potential has indicated the reaction to be irreversible. While the half-wave potential is dependent upon the pH as one would expect for an organic reaction, the shift per pH unit exceeds the theoretical values predicted for reversible reactions. In addition, the half-wave potential is not independent of concentration, but apparently varies with its logarithmic value. Provided that proper attention is given to the factors of pH, concentration, the effect of gelatin, etc. on the half-wave potential, the wave could be of value for qualitative identification.

To determine the number of electrons involved in the reaction, the figures from above, $i_d = 1.2$, $C = 0.1$, $D = 6.9 \times 10^{-6}$, and $m^{2/3}\, t^{1/6} = 1.90$, are substituted into the Ilković equation

$$i_d = 607\, n\, CD^{1/2}\, m^{2/3}\, t^{1/6}$$

to give

$$n = 4.0.$$

A transfer of four electrons is in agreement with the second equation as presented above in which the azo group is completely reduced to yield the corresponding amines. This conclusion is substantiated by the fact that the process was found to be irreversible as such a reaction would certainly be.

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n-EICOSENOIC ACID IN SOME NATURAL GLYCERIDE OILS[1]

By C. Y. Hopkins and Mary J. Chisholm

ABSTRACT

n-Eicosenoic acid (as acid or ester) was isolated from the following oils: rutabaga seed (*Brassica napobrassica* Mill.), frenchweed seed (*Thlaspi arvense* L.), dogfish liver (*Squalus acanthias* L.), and the blubber oil of the beluga or white whale (*Delphinapterus leucas* [Pallas]).

The eicosenoic acid from each of these materials was found to have the unsaturation in the 11,12 position. The content of eicosenoic acid in the four oils is estimated as follows (% of the total fatty acids): rutabaga 6, frenchweed 7, dogfish liver 11, beluga 4. The best sources, in respect to yield and purity, were frenchweed seed and rutabaga seed.

The frenchweed oil had the following fatty acid composition (% total fatty acid): saturated acids 3, oleic 16, linoleic 25, linolenic 12, eicosenoic 7, erucic 37.

9-Hexadecenoic acid was identified as a constituent of dogfish liver oil and beluga oil.

INTRODUCTION

n-Eicosenoic acid is available from the seed wax of jojoba (*Simmondsia californica* Nuttall) but the wax alcohols interfere to some extent with the isolation of the acid. Neither the seed nor the wax is offered through ordinary commercial channels. Accordingly an effort has been made to find a glyceride oil having a relatively large content of eicosenoic acid, so as to provide a more convenient source.

The materials chosen for the present work were (*a*) two members of the Cruciferae family, rutabaga and frenchweed, and (*b*) two examples of marine fauna, dogfish and beluga. Certain Cruciferae seed oils have already been shown to contain appreciable amounts of eicosenoic acid (1, 4, 7). The oils of most fish livers and marine mammals have a good proportion of C_{20} acids, although mainly polyenoic. Their value as a practical source of eicosenoic acid has not been determined hitherto.

EXPERIMENTAL

A. Rutabaga Seed Oil

Rutabaga seed (*Brassica napobrassica* Mill.) was supplied by the Canadian Department of Agriculture under the common name "Acadia Swede Seed". The oil content was 31%. It had iodine value 106.7, saponification value 178.4, and unsaponifiable matter 1.8%. The methyl esters were prepared by methanolysis and distilled at a pressure of 0.1 mm. or less in two lots, totalling 595 gm.

Distillation data for one lot are given in Table I.

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TABLE I
DISTILLATION OF METHYL ESTERS OF RUTABAGA SEED OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	-115	14.8	68.7
2	115-117	23.5	127.9
3	117-120	35.8	145.1
4	120-123	39.5	141.1
5	123-130	30.4	137.8
6	130-141	8.6	102.9
7	141-145	10.0	82.4
8	145-148	3.5	82.7
9	148-151	17.8	81.3
10	151-162	28.0	75.3
11	162-165	32.0	73.0
R	Residue	43.5	
		287.4	

Fraction 9, judged to be mainly esters of C_{20} acids, was crystallized from acetone and gave the following fractions:

Fraction	Temp. of cryst'n, °C.	Yield, gm.	Iodine value
91	−25	1.4	(Solid)
92	−32	9.2	77.5
93	−50	4.6	79.6
94	Filtrate	2.3	120.9

Fraction 92 was hydroxylated by alkaline permanganate and gave dihydroxyeicosanoic acid readily, m.p. 129–130°, equivalent weight 344.6 (theory 344.5). Fraction 93 was saponified and gave eicosenoic acid, melting after one crystallization at 21° (accepted m.p. 23–24°).

The dihydroxyeicosanoic acid from fraction 92 was subjected to oxidative cleavage by periodate and gave nonaldehyde (semicarbazone, m.p. 99–100°) and 10-aldehydodecanoic acid (semicarbazone, m.p. 159–160°). These products were identified by mixed melting points with authentic specimens. The original acid is therefore *n*-11-eicosenoic acid.

The content of eicosenoic acid is estimated to be about six per cent of the total fatty acids of the oil. Acids higher than C_{20} make up about 35% of the total and the remainder is chiefly C_{18} acids.

B. Frenchweed Seed Oil

Seed of frenchweed (*Thlaspi arvense* L.), also called penny cress, stinkweed, and fanweed, was separated mechanically from the screenings from wheat grown in Western Canada.* The oil, obtained by solvent extraction, had I.V. 119.7, sap. value 176, and unsaponifiable matter 1.7%. Distillation of the methyl esters was carried out at about 0.1 mm. pressure, (Table II).

**Kindly furnished by Alberta Seed Growers' Co-operative Ltd.*

TABLE II
DISTILLATION OF METHYL ESTERS OF FRENCHWEED SEED OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	100–132	82.7	153
2	132–136	39.7	165
3	136–147	7.6	108
4	147–153	23.0	94.1
5	153–162	12.6	81.8
6	162–165	68.4	73.5
R	Residue	40.0	
		274.0	

Fraction 4 was crystallized from acetone, taking fractions at −30° and −45°. The crystals deposited at −45° were crystallized once more and gave 7.5 gm. of methyl eicosenoate, I.V. 78.7 (theory 78.2). This product was converted to eicosenoic acid, m.p. 23.6°, I.V. 81.0, equiv. wt. 311 (theory 310.5). The acid was hydroxylated by performic acid, giving the low-melting isomer of 11,12-dihydroxyeicosanoic acid, m.p. 96–97°, equiv. wt. 343 (theory 344.5). The melting point was unchanged in admixture with an authentic sample.

The position of the double bond was confirmed by carrying out a cleavage of the dihydroxy acid by periodate. Nonaldehyde (semicarbazone, m.p. 99–100°) and 10-aldehydodecanoic acid (semicarbazone, m.p. 159–160°) were the products. Mixed melting points with pure semicarbazones showed no change.

A second lot of esters was distilled and certain of the C_{18} and C_{22} fractions were examined by low-temperature crystallization. Erucic acid, m.p. 32–34°, was isolated. Esters of saturated acids (C_{16} and C_{18}) were deposited from acetone at −30°. There was little saturated acid in the higher fractions. Dienoic and trienoic acids were determined by ultraviolet spectrophotometry.

The content of eicosenoic acid in the oil is calculated to be about seven per cent of the total fatty acids. Other component acids are estimated as follows: oleic 16, linoleic 25, linolenic 12, erucic 37, saturated acids (mainly palmitic and stearic) 3%.

C. *Dogfish Liver Oil*

A sample of dogfish liver oil was kindly furnished by the Fisheries Research Board (Canada). It was obtained from dogfish (*Squalus acanthias* L.) taken off the eastern Canadian coast. The oil had I.V. 126, sap. value 165.6, and unsaponifiable matter 13.3%.

It was saponified by potassium hydroxide–ethanol and the unsaponifiable matter was removed by extracting the dried soaps repeatedly with acetone. The soaps were converted to acids and the acids were washed, dried, and esterified. The methyl esters were distilled at reduced pressure (Table III).

Fraction 8, judged to consist mainly of the esters of C_{20} acids, was subjected to repeated crystallization from acetone at temperatures from −30° to −60°. Head and tail fractions were discarded. The purified ester had I.V.

TABLE III
DISTILLATION OF METHYL ESTERS OF DOGFISH LIVER OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1	110–120	17.3	25.9
2	120–123	19.8	43.9
3	123–127	46.5	44.3
4	127–131	29.6	70.2
5	131–135	38.6	92.8
6	135–137	10.7	94.5
7	137–149	17.0	96.5
8	149–154	26.2	107.6
9	154–162	26.2	109.7
10	162–172	30.0	109.7
R	Residue	55.0	
		316.9	

78.9 (methyl eicosenoate 78.2) and $n_D^{25°}$ 1.4530. It was hydroxylated by performic acid, giving dihydroxyeicosanoic acid (low-melting isomer), m.p. 94–95°, equiv. wt. 345 (theory 344.5). The melting point was not depressed by mixing with authentic 11,12-dihydroxyeicosanoic acid. The content of eicosenoic acid is estimated to be 11% of the total fatty acids.

The lower-boiling esters of dogfish liver oil were examined for hexadecenoic acid. Fraction 1 (Table III), I.V. 25.9, was dissolved in acetone and cooled to −55° to precipitate saturated acids. The filtrate gave 3.0 gm. of esters of I.V. 55.0. This portion was hydroxylated by permanganate and gave an acid of m.p. 123–124°. It did not depress the melting point of a sample of 9,10-dihydroxyhexadecanoic acid, m.p. 124°, prepared in the same way from cod liver oil. The structure of the cod liver oil acid was determined by periodate cleavage and identification of the two fragments.

D. Beluga Oil

A sample of oil from the blubber of the beluga or Hudson Bay white whale (*Delphinapterus leucas* [Pallas]) was obtained from the extraction plant at Churchill, Man.*

The oil had I.V. 116.5, sap. value 210, and unsaponifiable matter 1.4%. It was converted to methyl esters (480 gm.) and distilled at reduced pressure (Table IV). Some low-boiling material, probably methyl isovalerate, was lost at the beginning of the distillation.

It was judged from the course of the distillation that fractions 9 and 10 consisted chiefly of esters of C_{20} acids. They were crystallized three times from acetone, the saturated and polyenoic esters being discarded each time. Two lots of methyl eicosenoate were thus obtained, 4.6 gm. of I.V. 77.9 and 6.7 gm. of I.V. 78.0 (theory 78.2). On saponification and hydroxylation, this material gave dihydroxyeicosanoic acid, m.p. 93–94° (by performic acid) and 128–129° (by alkaline permanganate). These melting points were not

Kindly furnished by W. J. Ward, President, Adanac Whale and Fish Products Ltd.

TABLE IV
DISTILLATION OF METHYL ESTERS OF BELUGA OIL

Fraction	Vapor temp., °C. (approx.)	Wt. of fraction (gm.)	Iodine value
1–4	83–129	225.8	
5	129–132	28.9	95.6
6	132–136	34.0	111.6
7	136–140	38.5	122.2
8	140–146	8.6	139.6
9	146–153	43.3	170
10	153–156	25.3	194
11	156–160	18.6	208
12	160–166	18.3	234
R	Residue	22.3	
		463.6	

depressed on admixture with the low- and high-melting isomers, respectively, of 11,12-dihydroxyeicosanoic acid.

Oxidative cleavage of the dihydroxy acid by sodium periodate gave nonaldehyde (semicarbazone m.p. 94–95°) and 10-aldehydodecanoic acid (semicarbazone m.p. 159–160.5°). Mixed melting points with pure semicarbazones showed no depression.

The quantity of eicosenoic acid originally present in the oil is estimated at 4% of the total fatty acids.

The lower-boiling esters of beluga oil were examined for hexadecenoic acid. Fraction 3 (Table IV), I.V. 82.9, was crystallized from acetone, giving a monoenoic fraction of I.V. 94.5 (methyl hexadecenoate, I.V. 94.6). The yield was poor. It was hydroxylated by permanganate to give dihydroxypalmitic acid, m.p. 123–124°. The melting point was unchanged in admixture with 9,10-dihydroxypalmitic acid made from cod liver oil. The hexadecenoic acid from beluga oil was also converted to the low-melting isomer of 9,10-dihydroxypalmitic acid, m.p. 87–88°.

The data are not sufficient to calculate the content of acids other than eicosenoic. However, the time:temperature distillation curve indicates approximately the following fatty acid groups: below C_{16}, 15%; C_{16}, 40%; C_{18}, 20%; C_{20}, 15%; above C_{20}, 10%.

DISCUSSION

A. Rutabaga seed fatty acids have not been studied hitherto. The constants of the oil and the distillation data show that it is a typical Cruciferae oil, resembling rapeseed oil in composition. The content of eicosenoic acid is similar to that of other Cruciferae.

B. Frenchweed seed fatty acids (*Thlaspi arvense* L.) were described in 1944 in papers by Schrader (5) and by Clopton and Triebold (2). The principal acids were oleic, linoleic, and erucic. The present work shows that there is also an appreciable content of eicosenoic acid. The isolation and purification of 11-eicosenoic acid from this oil was relatively easy.

C. Dogfish liver oil (from *Squalus acanthias* L.) was shown by earlier workers (3) to have a large proportion of C_{20} acids and a lower content of polyenoic acids than many fish oils. These authors did not isolate the individual acids. However, it is assumed that eicosenoic acid is present in oils of this type. The content of C_{20} acids in our sample of dogfish liver oil is less than the 29% found by Guha and co-workers. The yield of eicosenoic acid was also less than expected. It was difficult to purify, apparently because of the more highly unsaturated acids that accompany it. There was also some difficulty in purifying the derivative, dihydroxyeicosanoic acid, indicating that more than one isomer of eicosenoic acid may be present. This trouble was not encountered in studying the vegetable oils.

D. Beluga oil was examined by Williams and Maslov (6), who analyzed the jaw, head, and body oils separately. They did not report the individual monoenoic acids. The present work shows that 11-eicosenoic acid is present in the oil although in rather small amount, viz. 4% of the total acids. 9-Hexadecenoic acid was also identified and is apparently present in substantial amount.

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THE MASS SPECTRUM OF TITANIUM TETRACHLORIDE[1]

By J. E. Hogg

ABSTRACT

An investigation of the mass spectrum of titanium tetrachloride prepared from both commercial titanium dioxide and titanium minerals has been carried out, using a 180° Nier-type mass spectrometer. Values for the relative abundances of the titanium and chlorine isotopes have been found. Measurements of the singly ionized trichloride group show that any variation in the relative abundances of the isotopes of titanium contained in these samples must be less than one per cent.

INTRODUCTION

Naturally occurring variations have been found in the relative abundances of the non-radiogenic isotopes of many elements, including carbon, oxygen, sulphur, boron, and silicon. The investigations of these variations have been summarized by Thode (6, 7) and Ingerson (3).

Titanium consists of five isotopes of mass numbers 46 to 50. The relatively large mass difference between the lightest and the heaviest of these isotopes might allow natural processes to introduce some fractionation, for it is known from general chemical and physical considerations that the extent of isotopic fractionation is highly dependent on mass differences.

In order to try to detect any major variation in the isotopic abundances of this element, measurements were carried out on samples prepared from commercial titanium dioxide and also from several titanium bearing minerals. These are described in Table I.

TABLE I
Descriptions of samples analyzed

Sample No.	Mineral	Remarks	Location	Source
1	Ilmenite	Beach sand	Melbourne, Florida	Ward's Natural Science Establishment
2	Ilmenite	Massive	Kragero, Norway	Ward's Natural Science Establishment
3	Rutile	Massive	Kragero, Norway	Ward's Natural Science Establishment
4	Rutile	Crystals in feldspar	Pine Creek, N. Carolina	Dr. D. H. Gorman, University of Toronto
5	Rutile	Massive	Unknown	Dr. D. H. Gorman, University of Toronto

The mass spectrometer used in this project was a 180° direction focusing Nier-type instrument with a resolution of 1 mass unit in 300. It has been described in detail by Collins (1). Titanium tetrachloride, a liquid at normal

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temperatures with a high vapor pressure, has suitable properties for analysis by such a spectrometer. A study of the mass spectrum of titanium chloride showed the singly ionized trichloride group to be the most satisfactory for this investigation because it is very abundant, and falls in a mass range which is completely free from any residual hydrocarbon background.

EXPERIMENTAL PROCEDURE

For the production of titanium tetrachloride, a modification of the Dumas method, described by Walton (8), was used. This method involves passing chlorine over an intimate mixture of titanium dioxide and carbon at red heat. The chloride is formed by the reaction:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2.$$

Great care was taken to exclude all moisture from the reaction line, for titanium tetrachloride will react with water vapor. Dissolved chlorine was removed by refluxing in a current of nitrogen. Very high yields can be obtained with the above reaction.

In the preparation of standard samples, C.P. titanium dioxide was used. The mineral samples used included ilmenite ($FeTiO_3$) and rutile (TiO_2) from various mineral associations and from deposits of different ages. Attempts to produce pure titanium tetrachloride from samples of sphene ($CaTiSiO_5$) and pseudobrookite (Fe_2TiO_5) have been unsuccessful.

The first two samples run on the mass spectrometer were prepared from commercial titanium dioxide. These were then mixed together to serve as the standard during the remainder of the runs. A third sample, prepared in the same manner, was run as a check and then discarded.

It was found during preliminary analyses that both the singly and doubly charged ion groups of the tetrachloride, dichloride, and monochloride were formed, as well as singly charged titanium ions. The low mass region of the doubly charged titanium ions was obscured by the spectrometer background, which rises when halogens are introduced through the sample line. The $TiCl_2^{++}$ and $TiCl_4^+$ groups were found to be the least abundant. Most abundant were the Ti^+ and $TiCl_3^+$ groups. Because the mass range was slightly obscured up to nearly mass 50, the singly ionized trichloride group was considered to be the most satisfactory for the analyses. An investigation of the mass discrimination introduced by the spectrometer in this range showed it to be much smaller than the precision of the measurements.

The various chlorine and titanium isotopes combine in the formation of titanium trichloride in such a manner as to form ions of 11 masses, from 151 to 161 inclusive. The relative abundances of these were measured with the mass spectrometer. Thus, 11 equations were obtained and solved for the seven unknowns (the abundances of the five isotopes of titanium and the two isotopes of chlorine).

RESULTS

The measured abundances of the components of the $TiCl_3^+$ group for each sample analyzed are shown in Table II. Using five of the equations mentioned

TABLE II

PEAK HEIGHTS OF THE TITANIUM TRICHLORIDE GROUP FROM ANALYSES OF SAMPLES AND STANDARDS

Sample	Peak heights of masses observed										
	151	152	153	154	155	156	157	158	159	160	161
Std. A	3.40	3.13	35.05	5.43	34.37	3.31	12.46	0.858	1.819	0.080	0.080
Std. B	3.40	3.14	35.09	5.43	34.35	3.30	12.45	0.856	1.820	0.081	0.080
Std. C	3.43	3.14	35.16	5.45	34.30	3.30	12.40	0.855	1.812	0.078	0.076
Std. A+B	3.40	3.13	35.05	5.42	34.39	3.31	12.46	0.864	1.816	0.076	0.077
No. 4	3.42	3.14	35.11	5.41	34.41	3.29	12.45	0.850	1.808	0.074	0.072
No. 4	3.41	3.12	35.12	5.42	34.37	3.30	12.45	0.851	1.818	0.074	0.074
No. 2	3.40	3.14	35.11	5.42	34.37	3.29	12.45	0.849	1.817	0.074	0.074
Std. A+B	3.43	3.14	35.16	5.45	34.30	3.30	12.43	0.848	1.810	0.072	0.073
No. 3	3.42	3.13	35.10	5.44	34.33	3.30	12.46	0.851	1.820	0.076	0.077
No. 1	3.42	3.15	35.14	5.43	34.36	3.32	12.41	0.854	1.813	0.072	0.072
Std. A+B	3.41	3.15	35.12	5.44	34.34	3.31	12.43	0.849	1.818	0.072	0.071
Std. A+B	3.42	3.14	35.14	5.45	34.35	3.29	12.41	0.850	1.805	0.074	0.075
No. 2	3.41	3.13	35.11	5.40	34.41	3.31	12.43	0.853	1.803	0.074	0.073
No. 5	3.42	3.14	35.13	5.41	34.41	3.29	12.42	0.848	1.803	0.071	0.073
No. 1	3.40	3.12	35.10	5.42	34.41	3.30	12.44	0.849	1.815	0.072	0.071
Std. A+B	3.42	3.13	35.11	5.43	34.41	3.29	12.41	0.847	1.807	0.073	0.073
Std. A+B	3.40	3.12	35.16	5.43	34.41	3.29	12.38	0.852	1.814	0.080	0.079
No. 3	3.40	3.14	35.17	5.39	34.38	3.28	12.43	0.848	1.807	0.077	0.073
No. 5	3.42	3.14	35.11	5.40	34.35	3.30	12.46	0.852	1.813	0.075	0.075
Std. A+B	3.42	3.13	35.11	5.43	34.41	3.29	12.41	0.847	1.807	0.073	0.073
Std. A+B	3.40	3.12	35.15	5.42	34.41	3.28	12.42	0.849	1.803	0.074	0.075

Note: The analyses are listed in the order in which they were made.

TABLE III

ISOTOPIC ABUNDANCES OF TITANIUM SAMPLES

Sample	Per cent abundance				
	Ti^{46}	Ti^{47}	Ti^{48}	Ti^{49}	Ti^{50}
Std. A	7.96	7.31	73.89	5.50	5.34
Std. B	7.96	7.33	73.91	5.47	5.32
Std. C	8.03	7.34	73.93	5.48	5.22
Std. A+B	7.96	7.30	73.93	5.50	5.32
No. 4	8.00	7.33	74.03	5.43	5.25
No. 4	7.98	7.29	73.98	5.47	5.29
No. 2	7.96	7.33	73.99	5.44	5.29
Std. A+B	8.03	7.34	73.95	5.46	5.23
No. 3	8.01	7.32	73.88	5.47	5.33
No. 1	8.00	7.34	73.99	5.47	5.23
Std. A+B	7.98	7.36	73.95	5.46	5.27
Std. A+B	8.00	7.34	74.01	5.45	5.20
No. 2	7.98	7.30	74.06	5.47	5.21
No. 5	8.00	7.33	74.07	5.43	5.20
No. 1	7.96	7.29	74.03	5.46	5.27
Std. A+B	8.00	7.32	74.03	5.44	5.22
Std. A+B	7.96	7.29	74.05	5.47	5.23
No. 3	7.96	7.33	74.11	5.41	5.20
No. 5	8.00	7.32	73.94	5.45	5.28
Std. A+B	8.00	7.32	74.02	5.44	5.23
Std. A+B	7.96	7.29	74.13	5.44	5.18
Average	7.99	7.32	73.99	5.46	5.25
Std. Deviation	0.02	0.02	0.07	0.02	0.05

Note: The analyses are listed in the order in which they were made.

above, values for the relative abundances of the titanium isotopes were obtained by assuming various values for the Cl^{37}/Cl^{35} ratio. These values were then substituted in the six remaining equations in order to calculate the corresponding $TiCl_3^+$ abundances. By comparison of these values with the measured ones, it was found that $Cl^{37}/Cl^{35} = 246/754$, the values obtained by Nier (5), gave the best result, values one per cent on either side of this giving large discrepancies between the observed and the calculated $TiCl_3$ peak heights.

Using this value for the relative abundances of the chlorine isotopes, the 11 equations were solved by a method of least squares for the abundances of the five titanium isotopes. The results are shown in Table III.

CONCLUSIONS

Among the samples analyzed no significant variations in the relative abundances of the titanium isotopes were found. Small systematic errors were too small to be significant. The average of these abundances is given in Table IV, along with the values obtained by Nier (4) and Hibbs (2). It is seen that the author's determinations result in a slightly greater abundance of Ti^{48} than that obtained by Nier or Hibbs. No explanation has been found for this difference.

TABLE IV
SUMMARY OF THE RELATIVE ABUNDANCES OF THE TITANIUM ISOTOPES

	Author	Nier	Hibbs
Ti^{46}	7.99	7.95	8.22
Ti^{47}	7.32	7.75	7.42
Ti^{48}	73.99	73.45	73.38
Ti^{49}	5.46	5.51	5.56
Ti^{50}	5.25	5.34	5.41

In order to study the isotopes of titanium with a gas source mass spectrometer, the sample must be introduced as a halide. Using titanium tetrachloride, it was found that HCl was unavoidably produced in the spectrometer, and that this compound can only be removed from the spectrometer tube by very long periods of baking out at high temperatures. Solid compounds, which formed a coating on the inside of the tube, were also produced. In addition, it is possible that the chemical procedures carried out may have introduced isotopic fractionation, since the use of volatile compounds was involved. The properties of titanium tetrafluoride and tetrabromide are such as to render these compounds even less satisfactory for mass spectrometeric analysis.

Because of these disadvantages in the use of the halides of titanium, a solid source mass spectrometer might give measurements of the relative abundances of the titanium isotopes of greater precision than those reported here. With this type of instrument, the samples might be introduced as titanium dioxide, the form in which the element usually occurs in nature.

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NOTE

THE RAMAN SPECTRA OF TRICHLOROETHYLENE: C_2HCl_3 AND C_2DCl_3*

By G. Allen† and H. J. Bernstein

The infrared spectra of light and heavy trichloroethylene have been reported by Bernstein (1) together with a summary of previous Raman investigations on the light compound. The assignment for $CHCl{=}CCl_2$ has since been revised on the basis of the sum rule for vibrational frequencies (2), but no depolarization data were available to confirm the new assignment.. No Raman spectrum has been reported for $CDCl{=}CCl_2$. In this investigation the Raman spectra and depolarization data have been obtained for both compounds and the revised assignment (2) for $CHCl{=}CCl_2$ has been confirmed. The assignment for $CDCl{=}CCl_2$ has also been revised.

EXPERIMENTAL

The Raman spectra of pure $CHCl{=}CCl_2$ and $CDCl{=}CCl_2$ diluted with CCl_4 have been obtained on a photoelectrically recording spectrometer (5).

TABLE I
Raman spectra[a]

		$CHCl{=}CCl_2$		$CDCl{=}CCl_2$	
	Approx. character	Wave numbers	Depolarization ratio	Wave numbers	Depolarization ratio
ν_1	ν CH	3080(s)	0.31	2302(s)	0.36
ν_2	ν C=C	1589(s)	0.40	1589(m) 1561(s) [b]	0.46 0.40
ν_3	δ CH	1242(m)	0.56	1014(m)	0.51
ν_4	ν CCl	932(w)	0.65	876(w)	P?
ν_5	ν CCl	840(w)	0.24	792(m)	0.35
ν_6	ν CCl	628(s)	0.16	618(s)	0.27
ν_7	↑	381(s)	0.35	381(s)	0.33
ν_8	δ skeletal	274(s)	0.77	274(s)	0.80
ν_9	↓	172(s)	0.60	172(s)	0.60
ν_{10}	δ CH	780(m)	0.87	630(m)	0.87
ν_{11}	↑	450(m)	0.87	427(m)	0.87
ν_{12}	δ skeletal ↓	211(m)	0.87	213(m)	0.87
$2 \times \nu_{11}$		907(v.w.)			
$2 \times \nu_8$		530(v.w.)		530(v.w.)	

[a] *Although the numbering of fundamentals (ν_1 etc.) is still identified with the schematic representation of the vibrational modes given by Bernstein (Fig. 5, Ref. 1), the assignment is different from that given in Table I of Ref. 1.*

[b] *Resonance doublet, with fundamental in the region* ∽*1570 cm*$^{-1}$.

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†National Research Council Postdoctorate Fellow 1952–54.

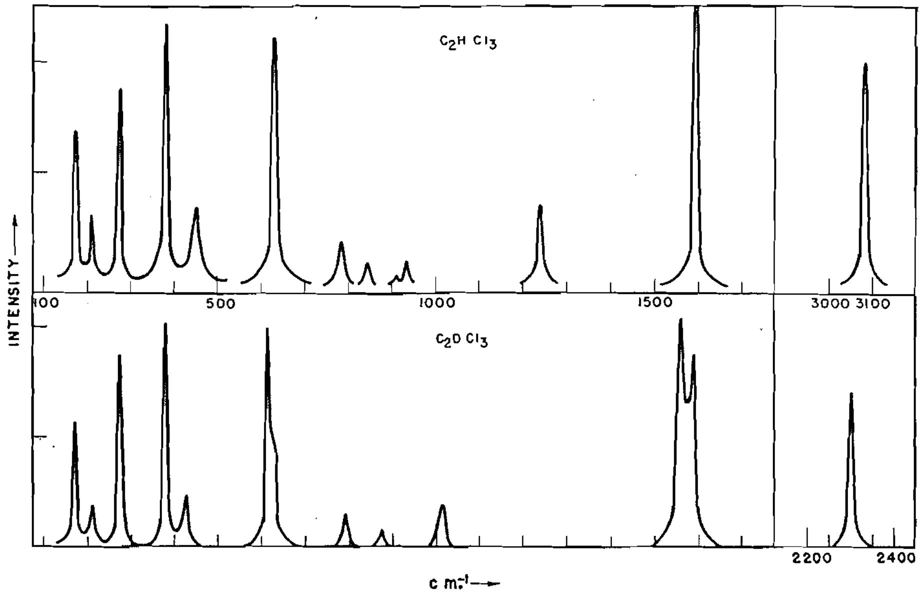

FIG. 1

Depolarization ratios were obtained by the method of Edsall and Wilson (3) and corrected for convergence (4). The results are given in Table I and Fig. 1.

DISCUSSION

Since three antisymmetrical out-of-plane vibrational modes are expected, these are assigned to the three depolarized bands in each spectrum. The in-plane or symmetrical modes can then be assigned as shown in Table I. The assignment for $CHCl{=}Cl_2$ is now identical with the one indicated by the sum rule (2); the major difference between the present and original (1) assignments is that the band at 932 cm.$^{-1}$ is now assigned as an in-plane mode whereas the band at 450 cm.$^{-1}$ is now assigned as an out-of-plane mode. The assignment for $CDCl{=}CCl_2$ has been revised in a similar manner to make it consistent with that for the light compound.

The two assignments are consistent with the Bernstein–Pullin (2) sum rule for isotopic substitution. The rule predicts

$$\sum^{\text{out-of-plane}} \nu C_2HCl_3 - \sum^{\text{out-of-plane}} \nu C_2DCl_3 = 173 \text{ cm.}^{-1}$$

$$\sum^{\text{in-plane}} \nu C_2HCl_3 - \sum^{\text{in-plane}} \nu C_2DCl_3 = 1095 \text{ cm.}^{-1}$$

and the observed differences are 173 and 1105 cm.$^{-1}$ respectively.

Thermodynamic Functions

The functions given in Table II were calculated for $CHCl{=}CCl_2$ by the usual statistical methods using the wave numbers of fundamentals as given in Table I. The following structural parameters were used to calculate the

TABLE II
THERMODYNAMIC FUNCTIONS FOR $CHCl{=}CCl_2$
(Units cal. deg.$^{-1}$ mole^{-1})

T, °K.	$C°_p$	$\frac{H° - E°_0}{T}$	$\frac{-F° - E°_0}{T}$	$S°$
298.16	19.172	13.333	64.296	77.629
300	19.245	13.370	64.377	77.747
400	21.795	15.172	68.476	83.648
500	23.669	16.693	72.031	88.724
600	25.063	17.978	75.191	93.169
700	26.115	19.066	78.042	97.108
800	26.942	20.001	80.650	100.651
900	27.605	20.812	83.062	103.874
1000	28.145	21.519	85.284	106.803
1100	28.594	22.144	87.376	109.520
1200	28.964	22.692	89.311	112.003
1300	29.283	23.191	91.155	114.346
1400	29.551	23.633	92.884	116.517
1500	29.783	24.040	94.544	118.584

product of the principal moments of inertia:

$$C{-}H = 1.08\ \text{Å}, \qquad C{=}C = 1.36\ \text{Å}, \qquad C{-}Cl = 1.72\ \text{Å};$$
$$\angle CCH = 120°, \qquad \angle HCCl = 116°, \qquad \angle ClCCl = 117°.$$

The product of the three principal moments is calculated to be 9.05×10^{-113} c.g.s. units.

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ON THE DRYING OF DIALYZED LIGNINSULPHONIC ACID[1]

BY ALAN G. NEWCOMBE

ABSTRACT

To evaluate the effect of drying temperature on the composition of high molecular weight ligninsulphonic acids, samples of a dialyzed ligninsulphonic acid solution were dried in several ways. Analyses showed that heating the solution to 70°C. for 16 hr. did not give an anhydrous material. When this material was heated for an additional period of 22 hr. at 90°C., it became anhydrous and also lost part of its sulphur content. Air drying of either the free acid or the calcium salt, followed by grinding and drying *in vacuo* to constant weight, produced materials with essentially the same elemental composition after allowance was made for the calcium content, and because of this it is concluded that no decomposition of the free acid occurred during this drying process. Elementary analyses were in good agreement with those reported by other workers. The hydroxyl content found for the free acid was lower, and the oxygen content was higher, than the corresponding values reported by Erdtman, Lindgren, and Pettersson or those reported by Freudenberg, Lautsch, and Piazolo.

INTRODUCTION

The determination of the total solids content of aqueous solutions of free ligninsulphonic acid has presented some difficulties since dehydration or decomposition reactions appear to take place at temperatures greater than 70°C. Since it is known that ligninsulphonic acids are relatively strong acids, and that many organic compounds undergo alteration in an environment which is strongly acidic and especially at elevated temperature, it would seem desirable for total solids determinations to convert ligninsulphonic acids to neutral salts and to dry and weigh these neutral salts. It was of interest to us, however, to determine the effect of different methods of drying on the composition of the free acid and this effect has therefore been investigated.

The method for determining the total solids in waste sulphite liquor published by Yorston (7), and by Partansky and Benson (4), involves heating an aliquot of the solution for 24 hr. at 105°C. Freudenberg *et al.* (2) have presented analytical values for ligninsulphonic acid dried *in vacuo* at 55°C.; Peniston and McCarthy (5) have obtained analytical values on a sodium ligninsulphonate dried *in vacuo* at a temperature less than 60°C.

Wald *et al.* (6) have found that the composition of Klason lignin varies with the length of time that the material is dried at 105°C., and suggested that a thermal decomposition was involved, since the same phenomenon was observed when the drying was conducted under pure nitrogen.

[1] *Manuscript received May 27, 1954.*
Contribution from the Department of Chemistry, Ontario Research Foundation, Toronto, Ont.

Since ligninsulphonic acid (LSA) becomes insoluble on heating at elevated temperatures, it seemed probable that it would be similar to Klason lignin, in that it would also require mild drying conditions in order to minimize decomposition. It was therefore decided to dry LSA at room temperature and at two elevated temperatures, and then to compare the analytical values obtained for these materials.

EXPERIMENTAL

The fermented waste sulphite liquor used in this investigation was kindly supplied by the Ontario Paper Company. It was subjected to exhaustive dialysis in a cellophane tube to remove low molecular weight materials and then decationized by passage through a column containing a cation exchange resin (Amberlite IR-120) on the hydrogen cycle.

A sample of the dialyzed, decationized LSA was allowed to stand in a tared dish at room temperature and pressure until a solid, brittle residue was obtained; it was then finely ground in an agate mortar and dried *in vacuo*[2] over P_2O_5 at room temperature to constant weight (Sample I).

A second sample of this LSA solution was converted into the calcium salt by the addition of an excess of calcium carbonate, and, after filtration through a fine porosity sintered glass crucible, was dried as above (Sample II).

A further sample (10.0 ml.) (11.8% solids) of this LSA solution was placed in a weighing dish (diameter = $2\frac{3}{8}$ in.) and heated in an oven at 70°C. for 16 hr. (Sample III). The material was then finely ground and a portion of it was heated at 90°C. for a further 22 hr. (Sample IV).

The carbon, hydrogen, sulphur, and methoxyl contents of Samples I to IV were then determined and the oxygen content calculated by difference. The hydroxyl content of the free acid, dried *in vacuo*, was determined by the method of Erdtman *et al.* (1). The sulphur dioxide which distills over simultaneously with the acetic acid was, however, not determined by their procedure, but by titration with standard (0.01 *N*) iodine solution.

The analytical results are shown in Table I; from these analytical figures the formulas shown in Table II were calculated on the basis of nine carbon atoms.

DISCUSSION OF RESULTS

There were no large differences between the C_9 formulas for the free acid

TABLE I
ANALYSES OF DIALYZED, DECALCIFIED, LIGNINSULPHONIC ACID DRIED UNDER DIFFERENT CONDITIONS

Sample No.	Drying temp., °C.	%C	%H	%O	%S	%Ca	%OH	$\%OCH_3$
I	RT	54.4	5.6	33.7	6.29	—	3.18	13.2
II	RT (Ca salt)	52.6	5.0	31.3	6.64	4.35	—	12.2
III	70	51.5	5.6	36.9	6.02	—	—	12.1
IV	90	57.5	5.4	32.3	4.80	—	—	13.9

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[2] *In all cases where the phrase "in vacuo" appears a water pump was used to lower the pressure.*

TABLE II

FORMULAS, ON A C_9 BASIS, FOR DIALYZED, DECALCIFIED, LIGNINSULPHONIC ACID DRIED UNDER DIFFERENT CONDITIONS

Sample No.	Drying temp., °C.	C	H	O	SO_3H	OCH_3	Ca	Weight of the C_9 group
I	RT	9	9.0	2.40	0.43	0.93	—	219.3
II	RT (Ca salt)	9	8.2	2.13	0.47†	0.89	0.25†	
			8.7*				0.00*	216.6*
III	70	9	9.8	3.13	0.43	0.90	—	230.9
IV	90	9	9.8	2.33	0.31	0.93	—	209.2

**After allowance was made for the amount of calcium present.*

† $\frac{SO_3H}{Ca} = \frac{1.9}{1}$.

dried at room temperature *in vacuo* and the calcium salt dried under the same conditions.

The materials dried at room temperature and that heated for 16 hr. at 70°C. showed large differences not in the SO_3H or OCH_3 contents, but in the hydrogen and oxygen contents, presumably due to the presence of water. The higher C_9 reacting weight (230.9) of the material heated at 70°C. as compared with that dried at room temperature (216.6–219.3) also suggested the presence of water in the former material.

The oxygen content of the material dried at 90°C. is similar to that of the materials dried at room temperature and it seemed probable, therefore, that the material heated at 90°C. was anhydrous. The higher hydrogen content could be due to a slight error in the hydrogen analysis. Although the material appears to be anhydrous it has been partially desulphonated.

The insolubility in water of the materials dried at 70°C. and 90°C. indicated that they were chemically changed by the higher temperatures. The lack of change in the methoxyl content of a C_9 unit indicated that the methoxyl groups were unaffected by the conditions of drying.

TABLE III

C_9 FORMULAS FOR PARENT LIGNINS

Substance dried	Drying conditions, Temp., °C.	Pressure	C	H	O	OCH_3	OH	Weight of the C_9 group
Ba salt of LSA (1)	—	—	9	8.2	2.5	0.94	—	185.5
				6.7	1.0		1.45–1.53	
Acid (LSA) (2)*	55	Reduced	9	8.6	2.36	0.91	—	182.8
				7.0	0.78		1.58	
Lignothioglycollic acid (3)	—	—	9	8.9	2.85	0.92	—	191.2
Na salt of LSA (5)	<60	Reduced	9	7.2	2.75	0.94	—	188.5
			9	7.0	2.84	0.95	—	190.1
Free acid	RT	Reduced	9	9.4	2.80	0.93	—	191.2
				8.6	1.96		0.84	
Ca salt	RT	Reduced	9	9.1	2.60	0.89	—	186.5

**The values shown were calculated by Erdtman et al. from the analytical results of Freudenberg.*

Assuming that sulphonation of the lignin involved the replacement of one hydroxyl group by one sulphonic acid group, the formula for the parent lignin has been calculated, and the results are compared, in Table III, with those of other workers.

The C, H, O, OCH_3 formulas in Table III are in general agreement, although the hydrogen content reported by the author is higher than that of other workers.

The elementary analyses of the materials for which hydroxyl values were available were essentially the same before the exclusion of the methoxyl and hydroxyl groups; after allowance was made for these groups it was found that the free acid, dried at room temperature, had a higher oxygen content and a lower hydroxyl content per C_9 unit than the other two materials.

Since the free ligninsulphonic acid dried *in vacuo* at room temperature gave the same analytical results as the calcium salt dried under the same conditions it is concluded that no decomposition of the free acid occurred.

ACKNOWLEDGMENTS

Carbon, hydrogen, and sulphur analyses were done by the Micro-Tech Laboratories, Skokie, Ill., and their assistance is appreciated.

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THE ELECTRICAL CONDUCTANCES OF AQUEOUS SOLUTIONS OF SILVER NITRATE AND OF AMMONIUM NITRATE AT THE TEMPERATURES 221.7°C. AND 180.0°C., RESPECTIVELY[1]

BY A. N. CAMPBELL, E. M. KARTZMARK, M. E. BEDNAS,[2] AND J. T. HERRON[3]

ABSTRACT

The specific and equivalent conductances (which also involve the densities) of aqueous solutions of silver nitrate and of ammonium nitrate, ranging in concentration from 0.1 *M* to that of the pure molten salt, have been determined at temperatures of 221.7°C. and 180.0°C., respectively. It has been found that when the equivalent conductance is plotted against logarithm of the concentration, a straight line is obtained in the region of concentrations greater than about 6 *M* or less. Hence the equivalent conductance can be calculated from the relation

$$\Lambda_C = \Lambda_a - D[\log C_a - \log C]$$

where D = the slope and Λ_a = equivalent conductance at the limiting experimental concentration, C_a (in the molten state).

In continuation of the work which has been going on in this laboratory for the past five years (2, 3), the specific and equivalent conductances of aqueous solutions of silver nitrate and of ammonium nitrate, ranging in concentration from 0.1 *M* to that of the pure molten salt, have now been determined at temperatures above the melting points of the salts, viz. 221.7°C. for silver nitrate (m.p. 212°) and 180.0°C. for ammonium nitrate (m.p. 169.6°). In order to obtain equivalent conductance it was also necessary to determine the densities of all solutions at the temperatures of determination of conductance. In this way we have been able to attack the problem experimentally, almost for the first time, of what happens to the conductance of a molten salt when a little water is added. The viscosities were not determined but it is planned to do these as a separate undertaking, if a suitable technique can be developed.

EXPERIMENTAL

Since the vapor pressure of water at 220°C. is of the order of 25 atm., all work had to be done in a sealed bomb. A standard steel bomb was obtained from the American Instrument Company and electrical leads introduced. These were rendered gas-tight, in the manner recommended by the Company, by crushing soapstone cones together under pressure. We were never troubled by gas leaks but occasional electrical shorts were traced to faulty insulation. This was remedied by enclosing the conducting wire in Teflon tubing before screwing down the soapstone cones.

Fig. 1 shows the type of cell used, in position in the bomb. If used for dilute solutions, such a cell would show a pronounced Parker effect, but this effect is negligible with concentrated solutions. The cell was provided with ground-

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Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Man.
[2] *Holder of a National Research Council Bursary, 1952–53.*
[3] *Cominco Fellow, 1953–54.*

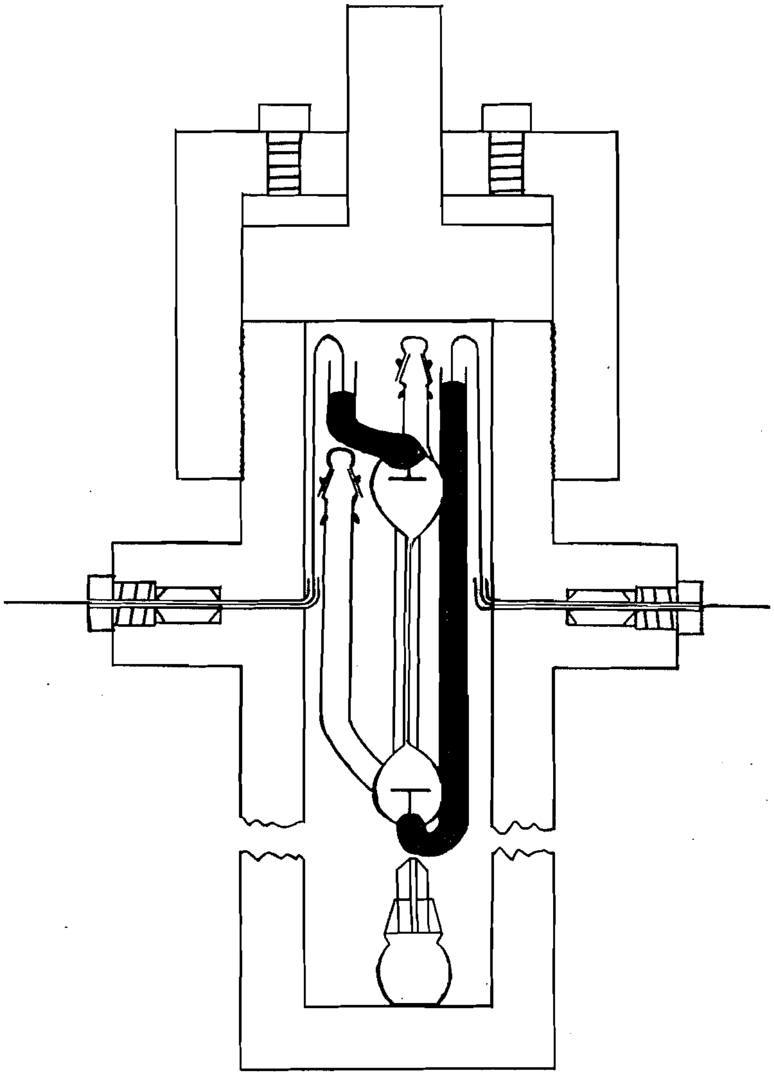

FIG. 1. Diagram of the cell in the bomb.

glass caps but these were perforated to equalize the pressure inside and outside of the cell. A very high cell constant is necessary in this work for accurate determinations of resistance, and this was achieved by the use of a fine capillary.

Densities were determined in a small specific gravity bottle of 10 ml. capacity, the usual precautions being taken, but in view of the smallness of the bottle and the difficulty of operating at these high temperatures, we have not expressed densities beyond the third decimal. The density bottle, after being filled, was placed at the bottom of the bomb and the charged conductance cell on top; in this way density and conductance were always determined at the same temperature. Since the specific gravity bottle of necessity overflowed as a consequence of rising temperature, this had the desirable effect of having solution both outside and inside the conductance cell so that distillation effects in the cell were avoided.

Constancy of temperature within ±0.05° was attained in the thermostat. This temperature variation introduces an uncertainty of about 0.1% into our conductance measurements. Such an error would be intolerable in work on dilute solutions, but it is of no great consequence here where the dilution factor is so small. In any case, the temperature control was good for the high temperature involved. The thermostat consisted of a rectangular copper tank, of capacity about 8 gal. As thermostat fluid we used "Sturbinol No. 65" from Imperial Oil. This is good for about 30 days' continuous running. This oil fumes rather badly but the escape of fumes into the laboratory was minimized by having the thermostat enclosed in a wooden cabinet with a glass cover and exhaust draught. Stirring was provided by two large stirrers of the Archimedean screw type placed at opposite corners of the thermostat and driven by flexible leads. A mercury-in-glass control with large reservoir was used.

Temperature was measured on a Beckmann which was calibrated frequently against a standard platinum resistance thermometer. To guard against possible sudden fluctuation of the Beckmann calibration, a direct reading thermometer, graduated in 1/5°, was also kept in the bath. The space (about 2 in. all round) between the thermostat and the containing cabinet was packed with powdered asbestos.

Electrical measurements were made with the Campbell–Shackelton bridge, previously described (2, 3). Cell constants were determined in a separate thermostat, at 25.00°C.; it has been shown previously, by calculation, that the effect of temperature on the cell constant is negligible.

Reference to the solubility isotherms of silver nitrate (1) and of ammonium nitrate (6) shows that water is saturated with these salts at a concentration of about 60% by weight at room temperature. Therefore, only up to this concentration can solutions be made up by direct weighing. For higher concentrations, the procedure was adopted of weighing out approximate quantities of salt and water and raising the temperature, with constant stirring, to a temperature somewhat above that at which the mixture becomes homogeneous. The conductance cell and specific gravity bottle were then filled and a sample removed for analysis, as nearly simultaneously as possible; slight fall in temperature was unimportant so long as the solution remained unsaturated. Analysis was made by determining the specific conductance at 25°C. (after dilution with a weighed quantity of water and after a weighed aliquot was taken). By this method, concentrations up to 88% or 90% could be prepared. There remained a gap between 90 and 100% salt by weight but, since the change of equivalent conductances with concentration is so slight in this region, this is not serious. For the anhydrous salts a somewhat different procedure had to be adopted and for this purpose the apparatus of Fig. 2 was constructed; it is practically self-explanatory. The whole apparatus was immersed in an oil bath at a temperature above the melting point of the

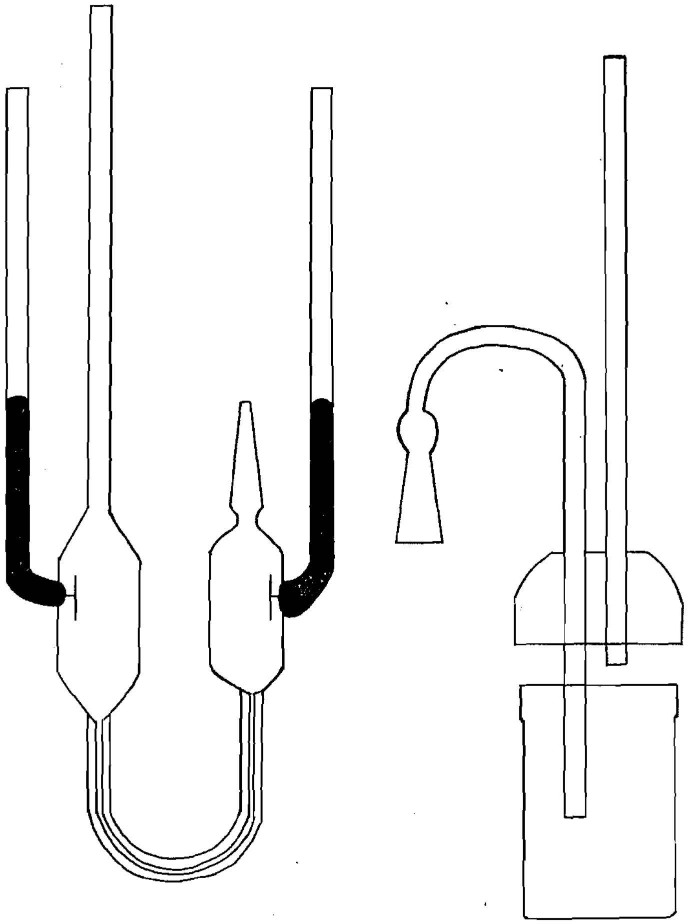

FIG. 2. Apparatus for molten salts.

salt. After fusion, the conductance cell was filled by pressure. The density of molten ammonium nitrate was determined in the usual way with a specific gravity bottle but that of silver nitrate could not be done in this way, since incipient decomposition caused the formation of gas bubbles, which could not be removed by agitation. For silver nitrate, therefore, we resorted to a simple U-tube immersed in an oil bath. The bend was filled with molten silver nitrate and one limb with a silicone; the heights of the columns were measured with a cathetometer. This relatively crude method gave a density which can only be quoted to the second decimal, but, so far as it goes, the figure is in agreement with the figure of Goodwin and Mailey (4) and with that interpolated from the work of Spooner and Wetmore (7); Jaeger's figure (5) seems to be erroneous.

RESULTS

Table I contains our results for specific and equivalent conductances and density.

TABLE I
CONDUCTANCES AND DENSITIES OF AQUEOUS NITRATE SOLUTIONS

Weight %	Specific conductance in mhos	Density, gm./ml.	Molarity	Equivalent conductance in mhos
Aqueous silver nitrate solutions at 221.7°C.				
1.954	0.05615	0.8393	0.0965	581.9
18.94	0.3639	1.003	1.119	325.2
28.56	0.5286	1.111	1.868	283.0
41.03	0.7110	1.296	3.130	227.2
48.65	—	1.413	4.047	—
48.84	0.8030	1.418	4.076	197.0
54.94	0.8809	1.515	4.900	179.8
59.27	0.9420	1.652	5.763	163.4
60.91	0.9698	1.718	6.159	157.5
65.84	1.023	1.831	7.097	144.2
69.63	1.053	1.982	8.124	129.6
75.40	1.105	2.199	9.761	113.2
81.56	1.135	2.495	11.98	94.78
85.92	1.122	2.832	14.32	78.34
88.91	1.084	3.059	16.01	67.71
92.06	1.019	3.268	17.71	57.54
100.00	0.719	3.94	23.19	31.00
Aqueous ammonium nitrate solutions at 180.0°C.				
0.7984	0.0474	0.8919	0.0890	532.3
8.5160	0.3752	0.9276	0.9868	380.2
16.077	0.6192	0.9571	1.922	322.2
24.028	0.8172	0.9935	2.982	274.0
24.028	0.8165	0.9955	2.988	273.3
32.141	0.9718	1.030	4.136	235.0
38.692	—	1.062	5.133	—
38.692	1.058	1.061	5.128	206.1
45.215	1.100	1.099	6.207	177.2
50.190	1.119	1.121	7.029	159.2
54.907	1.122	1.145	7.854	142.9
58.590	1.118	1.166	8.534	131.0
61.995	1.104	1.184	9.170	120.4
66.71	1.063	1.218	10.15	104.7
66.85	1.050	1.213	10.13	103.7
71.20	1.014	1.231	10.95	92.60
76.42	0.9338	1.272	12.14	76.92
78.84	0.8828	1.290	12.70	69.51
83.78	0.7881	1.322	13.84	56.94
85.15	0.7817	1.326	14.11	55.40
88.50	0.7003	1.355	14.98	46.75
100.00	0.433	1.44	18.0	24.1

DISCUSSION

As was found at 95°C. (3), the specific conductances of both salts pass through maxima with increasing concentration. The maximum specific conductance of silver nitrate, at 221.7°C., has the value 1.136 mhos at a concentration of 12.11 M; the value at 95°C. is 0.6068 at 10.7 M. That of ammonium nitrate at 180.0°C. is 1.122 at a concentration of 7.62 M; the value at 95°C. is 0.7868 at 7.28 M. Reference to our work at 95° and, in the case of ammonium nitrate at 25°, shows that the concentration corresponding to the maximum is shifting somewhat in the direction of higher concentration with rising temperature.

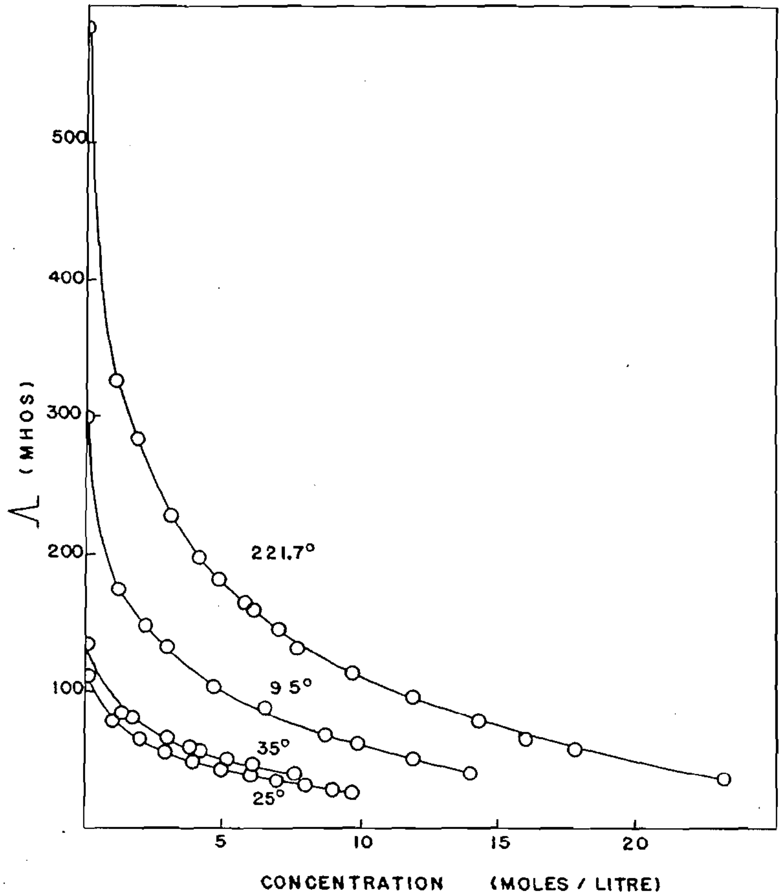

FIG. 3. Silver nitrate.

In Figs. 3 and 4, the equivalent conductances for all four temperatures of this work are plotted against concentration. The approach to straight line behavior is marked but, if our data are plotted on a large scale, it will be found that it is only an approach; absolute straight line behavior is never attained. On the other hand, one of us (J.T.H.) when plotting various functions at random discovered that if Λ be plotted against $\log_{10}C$ (or, of course, $\ln C$) a very exact straight line is obtained from concentrations of about 2 M ($AgNO_3$) and upwards, and 6 M (NH_4NO_3) and upwards. This is illustrated in Figs. 5 and 6. Since graphical representation on the small scale of a journal is no true indication of linearity, we have evaluated the slope from a large scale graph and used this to calculate Λ_C from the equation

$$\Lambda_C = \Lambda_a - D[\log_{10}C_a - \log_{10}C],$$

where Λ_a is the equivalent conductance at the limiting experimental concentration C_a, and in this way convinced ourselves of the straightness of the plot.

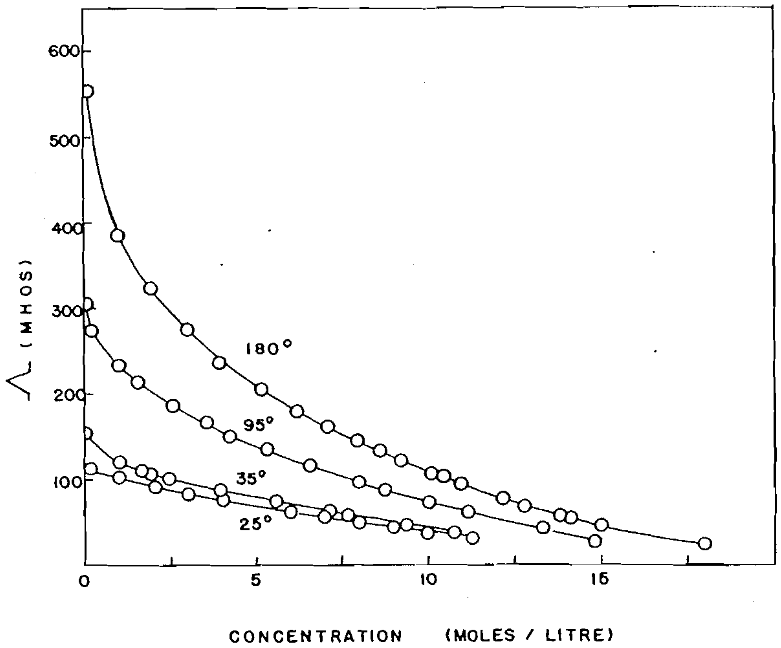

FIG. 4. Ammonium nitrate.

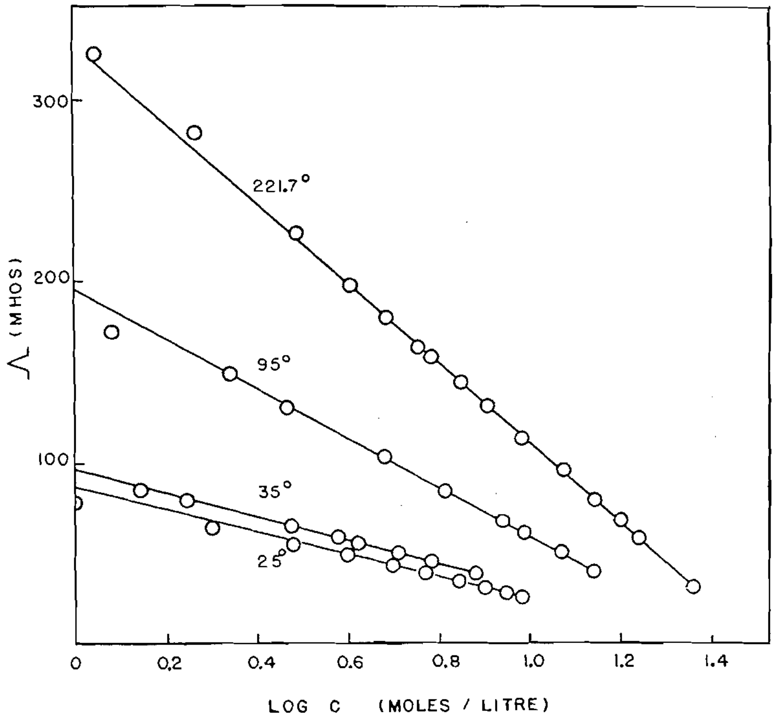

FIG. 5. Silver nitrate.

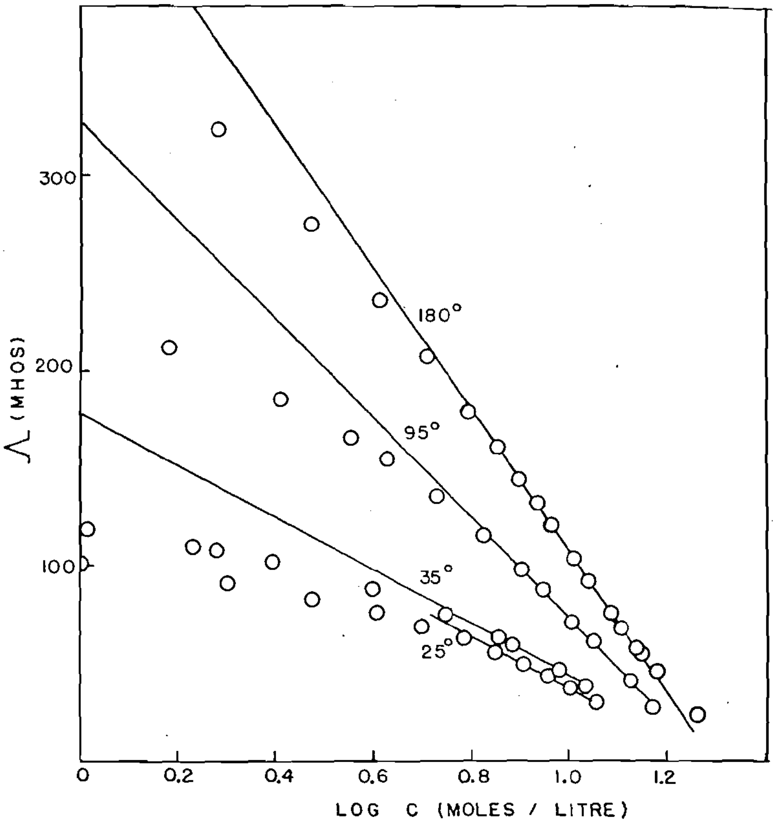

FIG. 6. Ammonium nitrate.

In previous communications (3) we pointed out that the plot of equivalent conductance (at equal concentrations) against temperature was a straight line (for silver nitrate and for ammonium nitrate) up to 95°C. although this

TABLE II

TEMPERATURE COEFFICIENTS OF CONDUCTANCE, BETWEEN 95° AND 221.7° ($AgNO_3$) AND BETWEEN 95° AND 180.0° (NH_4NO_3)

Concentration in moles/liter	Temperature coefficient	
	$AgNO_3$	NH_3NO_4
1	0.00626	0.00743
2	0.00642	0.00672
3	0.00627	0.00676
4	0.00599	0.00640
5	0.00606	0.00584
6	0.00619	0.00556
7	0.00620	0.00531
8	0.00634	0.00517
9	0.00645	0.00526
10	—	0.00509

straight line behavior could not be continued indefinitely; the conductance must (presumably) decrease before the critical temperature of water is reached. This is now found to be the case. Our complete results (for 25°, 35°, 95°, and 221.7° or 180°) are plotted in Figs. 7 and 8 (for interpolated molarities). In the absence of data from which to obtain the curvature, the curves are given as two straight lines; the slope is now decreasing beyond 95°. So-called temperature coefficients of conductances have been evaluated, between 95° and the higher temperature, from the equation

$$\Lambda_{t^\circ} = \Lambda_{95^\circ}[1+B(t-95)].$$

These figures are given in Table II, for integral molarities. They have no quantitative significance, since they assume straight line behavior, but they do show that the temperature coefficient is becoming smaller with rising temperature. A change in these coefficients is to be exepcted with increasing concentration, since, after a certain concentration is reached, the ion must begin to lose its sheath of water molecules. Some such effect might be attributed

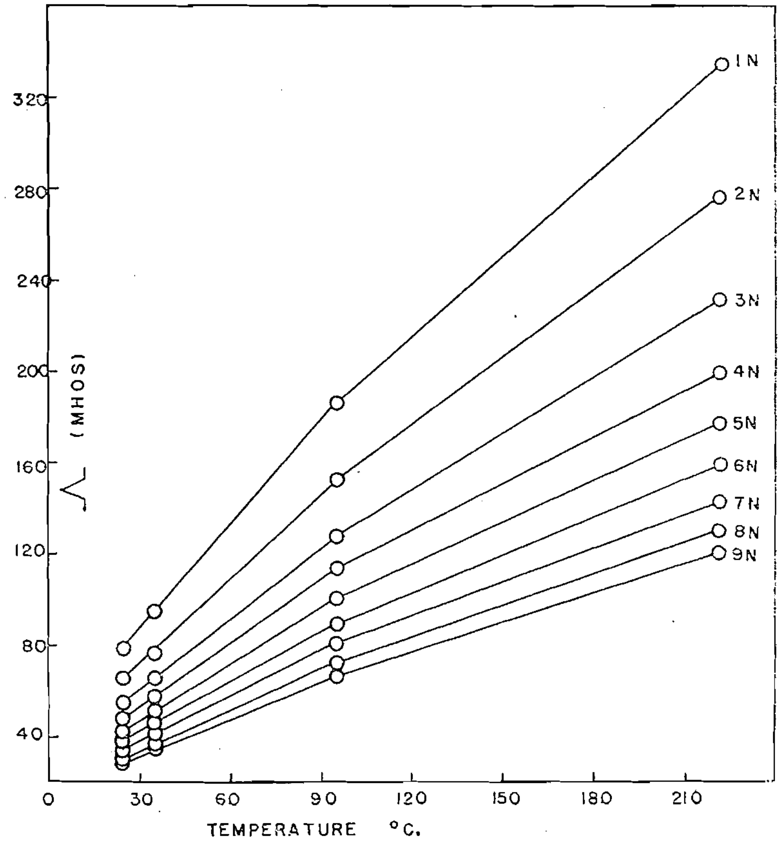

FIG. 7. Silver nitrate.

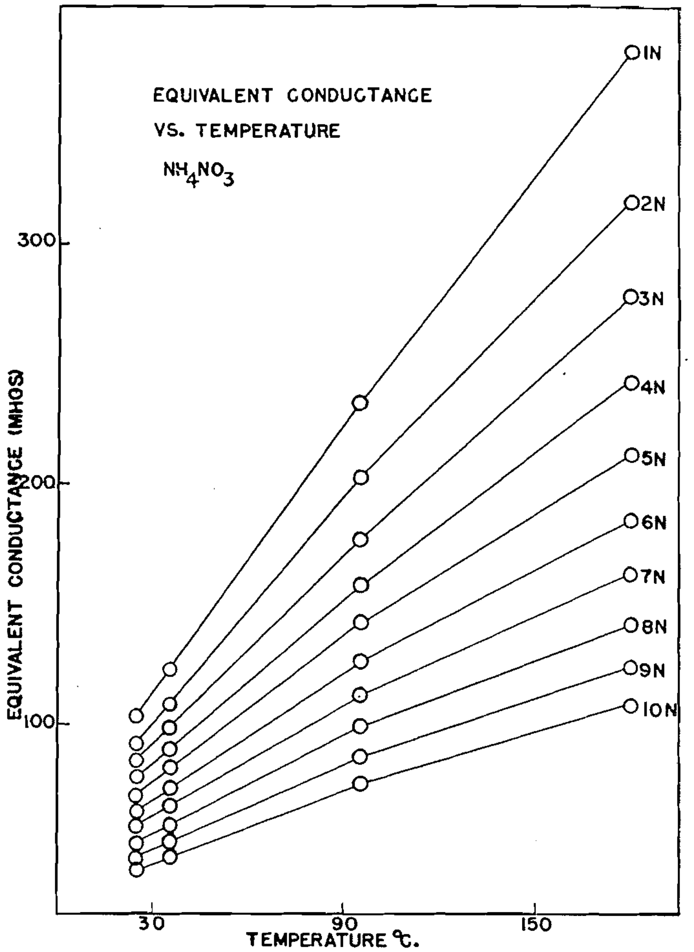

FIG. 8. Ammonium nitrate.

to the ammonium nitrate where the "coefficient" seems to level off as the anhydrous condition is approached, but the values for silver nitrate are quite sporadic. Possibly the method of calculation makes the values quite worthless and no conclusion should be drawn.

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THE PHOTOLYSIS OF 2,2′-AZO-BIS-ISOBUTYRONITRILE[1]

By R. Back[2] and C. Sivertz[3]

ABSTRACT

The photolysis of 2,2′-azo-bis-isobutyronitrile (AIN) has been studied in benzene solution through combined Corning filters 9863 and 5850 in the near ultraviolet, employing a General Electric UA-2B quartz Uviarc as a light source. An over-all quantum yield of 0.43 was found. The rate of decomposition of AIN in moles/liter seconds for this system is equal to 0.43 × [total light absorbed]. Twice this value may be taken as the rate of initiation when AIN is used as a photochemical initiator of polymerization.

INTRODUCTION

Thiele and Heuser (16) first synthesized the compound 2,2′-azo-bis-isobutyronitrile (AIN) in 1896. They showed it to be thermally unstable and identified its decomposition products as nitrogen and tetramethyl succinodinitrile (TSN). Dox (5) in 1925 extended this synthesis to several similar azo compounds.

The use of AIN as a thermal free-radical initiator was first reported in 1949 by Lewis and Matheson (9), who measured its rate of thermal decomposition by following nitrogen evolution and found the activation energy of decomposition. Overberger *et al.* (12) made similar measurements about the same time. A reliable first order decomposition rate that was practically independent of the solvent medium was found. It is this feature which makes AIN such an excellent initiator in the kinetic studies of free radical systems for which it has been widely used (4, 9, 12, 13, 17).

Lewis and Matheson (9), using a mercury arc source, first reported in 1949 the use of AIN as a photoinitiator in a free radical system. It has since been used in this role in the sector method (2, 11) and in the study of "unsteady state" kinetics (7, 10) and seems especially suited to it, producing a reliable rate which can be made constant for practical purposes. One parameter which must be evaluated in these studies is the rate of initiation. This may be done by the use of inhibitors (3) or by a comparison of rates with a thermally initiated system (15). Both these methods are open to criticism (3, 15). Bamford (2) evaluated his initiation rate by following AIN photolysis by the measurement of nitrogen evolved under standard reaction conditions, and assumed the rate of initiation to be equal to twice the rate of AIN disappearance.

The sector method has been used in recent kinetic studies in this laboratory (1) with AIN photoinitiation, and an accurate evaluation of the rate of initiation was desirable. Inhibitors could not be used as they were found ineffective in the systems under investigation, and nitrogen evolution could not be readily measured. A spectrophotometric method of following AIN

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disappearance was devised, using the characteristic azo absorption peak at 3450 Å. The photolysis was carried out in benzene solution in a quartz dilatometer, to duplicate reaction conditions. The absolute light intensity was determined by uranyl oxalate actinometry, and the quantum yield of AIN photolysis was calculated. From this data the rate of initiation may be evaluated for any system using AIN photoinitiation by merely measuring the light intensity and the AIN concentration, assuming that every radical is successful in initiating a chain.

MATERIALS

AIN was synthesized from acetone and hydrazine by the method of Overberger *et al.* (12). It was recrystallized twice from diethyl ether and had a melting point 101°–102°C.

Benzene was Merck Reagent Grade Thiophene-Free, used without further purification.

Oxalic acid was Baker and Adamson Reagent Grade Crystal $H_2C_2O_4 \cdot 2H_2O$, used without further purification.

Uranium acetate was Baker and Adamson Reagent Grade $(CH_3COO)_2UO_2 \cdot 2H_2O)$, used without further purification.

METHODS

All absorption spectra and optical densities were measured in 1 cm. quartz cuvettes in a Model DU Quartz Beckmann Spectrophotometer, using the ultraviolet phototube and the hydrogen lamp source.

The absorption spectrum of AIN in benzene was measured at a concentration of 0.0143 M./liter. Solutions of AIN in benzene from about 0.01 to 0.1 M./liter were made up gravimetrically, and their optical densities carefully measured at 3450 Å, using a 0.5 mm. slit width.

The decomposition product of AIN* in benzene was found to absorb slightly at this wave length, making a small correction for its absorption necessary. It was prepared by refluxing a benzene solution of AIN for 20 hr., was recrystallized from methanol, and its absorption spectrum was measured at a concentration of 1.41 gm./liter. The melting point (169°C.) coincided with that reported by Thiele and Heuser (16) for tetramethyl succino-dinitrile. The extinction coefficients for AIN and TSN are shown in Table I.

Photolysis was carried out in a cylindrical quartz cell mounted in front of a quartz window in a water bath thermostat held at 25°C. The plane faces of the cell were of optical quartz.

The light source was a General Electric UA-2B quartz Uviarc low pressure mercury vapor lamp, operated on a 58-G-284 25 cycle autotransformer, and mounted about 20 cm. from the cell. Corning filters 9863 and 5850 were mounted directly in front of the quartz window.

**It has since been reported by Dr. S. Bywater of the National Research Council of Canada and confirmed in this laboratory that the absorption reported here cannot be due to tetramethyl succinodinitrile but is due to a resonance form of the isobytronitrile radical, most probably combining with the normal form to give* $N{\equiv}C{-}C(CH_3)_2{-}N{=}C{=}C(CH_3)_2$. *This fact will not affect the general conclusions drawn in this paper.*

TABLE I
ULTRAVIOLET ABSORPTION DATA FOR AZO-BIS-ISOBUTYRONITRILE (AIN) AND TETRAMETHYL SUCCINO-DINITRILE (TSN) IN BENZENE

Wave length (Å)	Extinction coefficient AIN	Extinction coefficient TSN′
4000	0.85	0.29
3900	2.25	0.48
3800	4.58	0.67
3700	8.04	0.77
3600	11.85	0.96
3575	12.55	
3550	13.45	
3525	14.00	
3500	14.45	1.3
3475	14.65	
3450	14.65	1.6
3425	14.60	
3400	14.30	1.8
3375	13.85	
3350	13.25	
3300	11.55	2.3
3200	7.60	3.1
3100	4.35	3.9
3000	2.30	5.4
2900		7.0
2800		8.4

The cell was filled with a 0.0109 M solution of AIN in benzene and irradiated for periods ranging from 0 to 500 min. The solution was then removed, and its optical density at 3450 Å measured on the Beckmann, using a 0.5 mm. slit width.

The light intensity was measured by uranyl oxalate actinometry. Five milliliters each of 0.01M $UO_2(CH_3COO)_2 \cdot 2H_2O$ and 0.05 M $H_2C_2O_4 \cdot 2H_2O$ were added to the cell, which was then made up to volume (11.75 ml.) with water. Irradiation was carried out for periods ranging from 0 to 300 min., and the residual oxalate was determined by permanganate titration in hot acid solution. The absorption spectrum of the actinometry solution and the transmission characteristics of the filter combination were measured on the Beckmann, while the spectral energy distribution of the Uviarc was known from data supplied by the manufacturers (6). Knowing the over-all rate of oxalate disappearance, and using the quantum yield versus the wave length data of Leighton and Forbes (8), the absolute light intensity for each wave length band was evaluated.

From the absorption spectrum of the AIN solution, the per cent absorption in the cell was calculated for each wave length band, and the total light absorbed by the AIN was determined. Knowing this, and the over-all rate of AIN disappearance, the quantum yield of AIN photolysis was calculated as indicated in the next section.

TREATMENT OF RESULTS

In terms of the measured extinction coefficients at 3450 Å for AIN and decomposition product which will be symbolized by TSN′ (Table I), the optical density of a benzene solution of these in a 1 cm. cell will be

[1] $$\mathrm{OD} = 15.0\,C + 1.6\,C_2$$

where C = moles/liter AIN remaining
and C_2 = moles/liter TSN′.

Assuming that 1 M. of TSN′ formed for each mole of AIN decomposed, then

$$C_2 = C_0 - C \text{ where } C_0 = \text{original conc. AIN} = 0.0109 \text{ M./liter.}$$

In terms of these data it is apparent that the extent of photolysis can be expressed

[2] $$C_2 = C_0 - C = (0.164 - \mathrm{OD})/13.4.$$

A plot of equation [2] against time of irradiation gives a curve which is nearly linear, dropping off at high values of C_2. This is to be expected when the absorption falls because of decreasing AIN concentration. A correction for this can readily be made. The rate of photolysis will vary directly as the light absorbed;
thus

[3] $$-dc/dt = KI_0(1 - e^{-klc})$$

in which K = quantum yield,
I_0 = total incident light intensity,
C = moles/liter AIN remaining,
k = molar extinction coefficient × 2.303,
l = length of light path,
t = time.

Integrated between limits C_0 and C and $t = 0$ and t, equation [3] results in

[4] $$(C_0 - C) - 1/kl \ln(1 - e^{-klc}) = KI_0t + \text{constant}.$$

Using an effective mean value for the extinction coefficient of 9.16 calculated from Tables II and III, the left-hand side of equation [5] was evaluated for

TABLE II
CALCULATION OF TOTAL INCIDENT RADIANT FLUX

Wave length band (Å)	R_λ	A_λ	Φ	I_λ (einsteins/sec.)
2996–3047	0.0024	0.999	0.56	0.557×10^{-11}
3047–3103	0.0018	0.999	0.56	0.418×10^{-11}
3103–3163	0.2820	0.999	0.55	65.8×10^{-11}
3163–3223	0.0210	0.997	0.54	4.90×10^{-11}
3223–3288	0.358	0.984	0.53	8.34×10^{-11}
3288–3356	0.2448	0.946	0.53	56.8×10^{-11}
3356–3430	0.0814	0.810	0.51	19.0×10^{-11}
3430–3513	0.0598	0.634	0.50	13.9×10^{-11}
3513–3602	0.0605	0.420	0.48	14.1×10^{-11}
3602–3695	3.9060	0.271	0.47	918×10^{-11}
3695–3797	0.0724	0.198	0.48	17.0×10^{-11}
3797–3912	0.0379	0.151	0.49	8.83×10^{-11}
3912–3950	0.0289	0.167	0.50	6.75×10^{-11}
4028–4069	0.1189	0.228	0.52	27.8×10^{-11}
4153–4197	0.0014	0.406	0.53	3.27×10^{-11}
Total		$\Sigma I_\lambda = I_0$	=	1.17×10^{-8}

TABLE III
CALCULATION OF RADIANT FLUX ABSORBED BY AIN

λ (Å)	I_λ (einsteins/sec.)	A_λ (AIN)	$I_\lambda A_\lambda$	$100 I_\lambda A_\lambda / \Sigma I_\lambda A_\lambda$
2996–3047	0.557×10^{-11}	0.100	0.557×10^{-12}	—
3047–3103	0.418×10^{-11}	0.144	0.602×10^{-12}	—
3103–3163	65.8×10^{-11}	0.198	130×10^{-12}	3.5
3163–3223	4.90×10^{-11}	0.260	12.7×10^{-12}	0.3
3223–3288	8.34×10^{-11}	0.332	27.7×10^{-12}	0.8
3288–3356	56.8×10^{-11}	0.403	229×10^{-12}	6.2
3356–3430	19.0×10^{-11}	0.445	84.5×10^{-12}	2.3
3430–3513	13.9×10^{-11}	0.455	63.2×10^{-12}	1.7
3513–3602	14.1×10^{-11}	0.418	59.0×10^{-12}	1.6
3602–3695	918×10^{-11}	0.328	3010×10^{-12}	82.0
3695–3797	17.0×10^{-11}	0.229	38.9×10^{-12}	1.0
3797–3912	8.83×10^{-11}	0.126	11.1×10^{-12}	0.3
3912–3950	6.75×10^{-11}	0.067	4.52×10^{-12}	0.1
4028–4069	27.8×10^{-11}	0.020	5.56×10^{-12}	0.1
4153–4197	3.27×10^{-11}	0.006	0.196×10^{-12}	—
Total	1.17×10^{-8}		3.68×10^{-9}	99.9

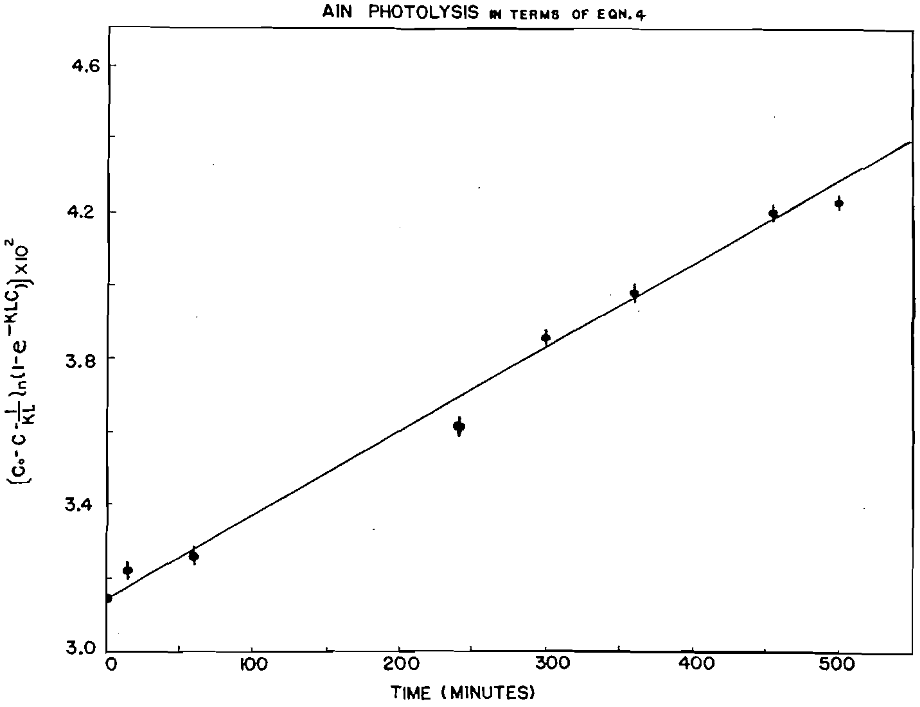

FIG. 1.

each experimental point and plotted against time as shown in Fig. 1. The slope of this straight line yielded a value of

$$KI_0 = 4.32 \times 10^{-7} \text{ M./liter}^{-1} \text{ sec}^{-1}.$$

Determination of the Light Intensity I_0

The rate of decomposition of uranyl oxalate was determined from a graph showing oxalate decomposed against time of irradiation. A linear relationship is obtained in this case as the absorption depends chiefly on the uranyl ion (8) which remains constant. A rate of disappearance of 2.11×10^{-9} M./sec. was found. Since the light used was not monochromatic and both the extinction coefficient of uranyl oxalate and the quantum yield vary considerably over the wave lengths used, the following treatment is required to calculate the total light intensity. It can be shown that the total incident radiant flux in a single wave length is

$$I_\lambda = (\text{rate of oxalate disappearance})\, R_\lambda / \overset{\lambda}{\Sigma}\, A_\lambda \phi_\lambda R_\lambda$$

where R_λ = relative radiant energy for wave length band λ,
A_λ = fractional absorption by oxalate solution over λ,
ϕ_λ = quantum yield for uranyl oxalate photolysis over wave length band λ.

Values of R_λ were obtained from a General Electric Bulletin (6) and the transmission characteristics of Corning filters 9863 and 5850. A_λ was obtained from the measured optical density of the actinometry solution and the cell dimensions. I_λ values were secured from the data of Leighton and Forbes for unstirred uranyl oxalate solution (8).

These calculations resulted in a total incident radiant flux

$\Sigma I_\lambda = I_0 = 1.17 \times 10^{-8}$ einsteins/sec. in the cell or 9.94×10^{-7} einsteins/liter sec. (see Table II).

Determination of the Quantum Yield K

Since KI_0 was determined above and also I_0 it is apparent that the quantum yield is

$$K = KI_0/I_0 = 4.32 \times 10^{-7}/9.94 \times 10^{-7} = 0.43.$$

DISCUSSION AND CONCLUSIONS

(1) The low value of the quantum yield is probably due to the fact that 82% of the light absorbed (see Table II) in the strong 3650 Å group of emission lines falls on the low energy side of the AIN absorption peak. This energy probably accounts for considerably less than 82% of the photolysis whereas the 3342 Å line (6.2%) and the 3132 Å line (3.5%) probably accounts for more than these percentages in photolysis.

(2) For the light source and filters described and on the assumption that there are two effective radicals per molecule of AIN, the rate of production of free radicals is given by equation [3] multiplied by two. Since any low pressure mercury arc should yield very closely the same distribution of energy the value of $2.303\,k = 9.16$ will hold. KI_0 may be readily evaluated by uranyl oxalate actinometry and calculations such as presented in Tables II and III.

(3) There appears to be some uncertainty that both of the radicals from AIN decomposition are effective in all reaction systems (4, 11, 14). However the use of inhibitors to determine rates of initiation does not dispel this un-

certainty. The method outlined yields results which are as dependable as any. For the application in this laboratory no inhibitor could be found which was effective. This situation will exist whenever the rate of the principal reaction is greater than or comparable with inhibitor rates of reaction.

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THE OXIDATION OF CARBON MONOXIDE BY SOLID PERMANGANATE REAGENTS

VII. THERMAL DECOMPOSITION OF SILVER PERMANGANATE[1]

BY G. A. GRANT AND MORRIS KATZ

ABSTRACT

The thermal decomposition in a vacuum at 100°C. of both whole and ground crystals of pure dry silver permanganate was followed by the measurements of increase in pressure and of loss in weight. The decomposition products were determined by analysis and calculations to be silver oxide, silver, manganese dioxide, silver permanganite, and oxygen. On the basis of chemical analysis the following mechanism of decomposition is proposed:

$$(1)\quad AgMnO_4 \longrightarrow AgMnO_3 + \tfrac{1}{2}O_2,$$
$$(2)\quad 2AgMnO_3 \longrightarrow Ag_2O + 2MnO_2 + \tfrac{1}{2}O_2,$$
$$(3)\quad Ag_2O \longrightarrow 2Ag + \tfrac{1}{2}O_2.$$

The reaction proposed in equation (1) goes to completion, while the reaction proposed in equation (2) goes to approximately 37.7% completion, and that in equation (3) goes to approximately 6.6% completion.

INTRODUCTION

In the investigations of the oxidation of carbon monoxide by solid silver permanganate – zinc oxide, it has been reported previously that the reaction may be partially catalytic (6). This view was supported in part by the fact that more carbon monoxide is found to be oxidized than can be accounted for by oxygen released by the proposed equation for the decomposition of silver permanganate (7). However, no attempts have been made previously either to identify the decomposition products or to verify the equation proposed for the reaction other than by analyses for silver, manganese, and active oxygen.

Heat distribution studies (4) indicate that temperatures as high as 100°C. are reached in a silver permanganate – zinc oxide reagent packed column. The temperature of the reagent depends on the concentration of carbon monoxide and on the space velocity of the influent air–gas mixture.

It is thought that at these reaction temperatures, the thermal decomposition of the silver permanganate may be an important factor influencing the amount of oxygen from the silver permanganate – zinc oxide reagent available for reaction with carbon monoxide.

Several studies have been made in efforts to elucidate the mechanism of thermal decomposition of silver permanganate and of other permanganate salts (3, 5, 9, 10, 13). Prout and Tompkins (9) suggested from kinetic evidence that the chemical nature of the decomposition is best represented by:

$$4AgMnO_4 \rightarrow 2AgO + 4MnO_2 + 3O_2.$$

Sieverts and Theberath (10) suggested the following equation:

$$2AgMnO_4 \rightarrow 2AgMnO_3 + O_2,$$

which was given some support by Prout and Tompkins (9).

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Various attempts, mostly by analyses for silver, manganese, and active oxygen, have been made to identify the end products. Gorgeu (3) and Sieverts and Theberath (10) suggested the existence of the compound $AgMnO_3 \cdot \frac{1}{2}H_2O$ and Hein (5) calculated the product of decomposition to be $8Ag_2O \cdot 15MnO_2 \cdot MnO_3 \cdot O$ for the dry salt and $8Ag_2O \cdot 15MnO_2 \cdot MnO_3 \cdot 60.8H_2O$ or $AgMnO_{2.94} \cdot \frac{1}{2}H_2O$ for the moist salt. The decomposition of silver permanganate when mixed with zinc oxide was studied by Katz *et al.* (7) and the decomposition product was expressed as a manganate–manganite of the composition $Ag_2O \cdot Mn_2O_5$ or $AgMnO_3$.

It is apparent that no clear-cut evidence has been put forward to support the existence of any of the compounds suggested. No method of analysis of the decomposition products has been used in which the various components were separated on the basis of their chemical or physical properties. In the present investigation the decomposition at 100°C. of pure whole crystals and ground crystals was followed by measurements of the increase in pressure in a vacuum system and of the loss in weight. The decomposition products have been analyzed by a scheme of analysis which provided for the separation of some of the decomposition products. On the basis of chemical analysis of the decomposition products a new mechanism of thermal decomposition of silver permanganate is proposed.

EXPERIMENTAL

Preparation of Silver Permanganate

Monoclinic crystals of silver permanganate approximately 1 to 5 mm. long were prepared by adding silver nitrate (C.P.) solution to potassium permanganate (C.P.) solution at 40°C. The solution was filtered through glass wool and the silver permanganate was allowed to crystallize in the dark. The material was crystallized twice from distilled water and dried in a desiccator. The pure crystals were stored in the dark until required.

The purity of the crystals was determined by analysis for active oxygen and silver content. The active oxygen was determined by dissolving the crystals in carbon dioxide free distilled water and filtering through a Gooch crucible packed with purified asbestos wool. An excess of a standard solution of sodium oxalate acidified with 5% sulphuric acid was added to the filtrate and the excess sodium oxalate titrated with standard potassium permanganate solution. The total silver was determined gravimetrically as silver chloride (2, pp. 821–23). The purity of the material was shown by the active oxygen method to be 99.3% and by the silver method to be 99.4%.

The term "whole crystals" refers to the crystals obtained from the last crystallization. Whole crystals ground gently in an agate mortar to reduce the size are referred to as "ground crystals". The variation in the size of crystals was determined by the use of a microscope.

Procedure and Apparatus

The rate of thermal decomposition at 100°C. was followed by measuring the increase in pressure in a vacuum system. The vacuum system was composed of a Hyvac and a mercury-diffusion pump, a calibrated McLeod gauge, a constant volume manometer (1) by which the pressure could be measured without a change in volume of the system, liquid air traps, a calibrated bulb, a manifold, and a reaction chamber containing a calibrated quartz spiral and a foil bucket. The rate of loss in weight and finally the loss in weight of the material were determined by means of the calibrated quartz spiral. A copper–constantan thermocouple was placed near the reaction bucket to measure the temperature of the reaction vessel.

In any one run, an accurately weighed sample of 0.3 to 0.4 gm. of silver permanganate was put in the foil bucket which was placed on the end of the quartz spiral. The glass reaction vessel was attached by means of a ground-glass joint to the system which was then evacuated to a pressure below 1×10^{-3} mm. and exhausted for 18 to 24 hr. to remove any moisture adsorbed on the crystals and in the system. When the constant temperature bath was raised to surround the reaction vessel, temperature equilibrium was established within a few minutes as indicated by the thermocouple in the reaction vessel.

Pressure measurements were made at intervals of 10 to 20 min. until no change in pressure occurred in 16 hr. The constant temperature bath was removed and the whole system was allowed to come to room temperature before the final pressure was measured. The loss in weight was followed by the change in length of the quartz spiral. The total loss in weight was obtained by removing the foil bucket from the apparatus and weighing it on an analytical balance.

Method of Analysis of Decomposition Products

Because of the conflicting evidence concerning the nature of the decomposition products present, some of the solid oxides of manganese and silver were considered as well as silver permanganate, silver permanganite, and elemental silver. The materials which were considered are listed below:
$AgMnO_4$, Ag, AgO, Ag_2O, MnO, MnO_2, Mn_2O_3, Mn_3O_4, $AgMnO_3$, MnO_3, Mn_2O_7. Of these materials, $AgMnO_4$, MnO_3, Mn_2O_7 are water soluble while only Ag_2O and AgO are soluble in ammonium hydroxide solution. The properties of $AgMnO_3$, if it exists, are unknown. On the basis of these solubility factors a scheme of analysis was designed. The analytical scheme was tested as far as possible. Preliminary experiments were made employing Ag_2O in the crucible used in the analysis, to determine the efficiency of leaching and weighing technique under the conditions employed in the proposed scheme of analysis. Recoveries were excellent. Thus the general leaching process and the general technique of the analysis were tested. No method could be devised to check the analysis of the hydroxide and water insoluble fraction. The increase in solubility product of silver chloride in concentrated hydrochloric acid was also considered and is not in the order of magnitude to introduce a serious error in the analysis for the purpose intended.

Approximately 80 to 100 mgm. of decomposed material was weighed into a 30 ml. beaker and 20 ml. of water was added. The mixture was stirred for 15 min. and heated gently on a hot plate for 20 min. After being allowed to stand overnight, the mixture was filtered through a weighed, sintered glass crucible. The crucible and contents were dried in alcohol and ether and placed in an oven at 100°C. for two hours and the water insoluble fraction weighed. The filtrate, containing the water soluble fraction, if any, was made up to a definite volume and portions were tested for silver and manganese ions. The weighed crucible was placed in a 50 ml. beaker and a solution of 14% ammonium hydroxide was allowed to percolate through the residue for 24 hr. at room temperature to dissolve any oxides of silver. The crucible was removed from the beaker, washed with 14% ammonium hydroxide, and then all the solution was filtered through the crucible. The crucible was washed with alcohol and ether, dried, and the ammonium hydroxide insoluble fraction weighed. The filtrate containing silver oxide was treated with dilute hydrochloric acid and the precipitated silver chloride was weighed. The remaining insoluble fraction was treated with concentrated hydrochloric acid in the crucible to dissolve the residual manganese oxides and silver permanganite and to form silver chloride.

After 18 hr. the solution was filtered through the crucible. The residue of silver chloride was dried and weighed. The filtrate containing manganese chloride was evaporated to dryness in a 100 ml. beaker, dissolved in water, and transferred to a small weighed beaker. The solution was again evaporated to dryness on a hot plate and then placed in an oven at 200°C. to remove the last trace of water and decompose the hydrated salts of manganese chlorides. The manganese content of the dried manganese chloride residue was determined as a manganous pyrophosphate ($Mn_2P_2O_7$) (2, pp. 560–61). Standard X-ray diffraction techniques were applied to the decomposition products.

RESULTS

The approximate size and weight of the crystals employed is given in Table I, as well as the weight loss of the crystals for each run.

TABLE I

Run No.	Crystal size	Initial crystal weight (mgm.)	Weight lost (mgm.)
2	Whole 1 to 5 mm.	303.5	27.4
3	Whole 1.0 to 5 mm.	303.5	26.1
4	Whole 1 to 5 mm.	303.4	27.3
5	Ground 0.1 to 0.001 mm.	303.4	27.3
6	Ground 0.1 to 0.001 mm.	302.3	27.2

The curve for the rate of decomposition of whole and ground crystals of silver permanganate is shown in Fig. 1. It is evident that in the case of the

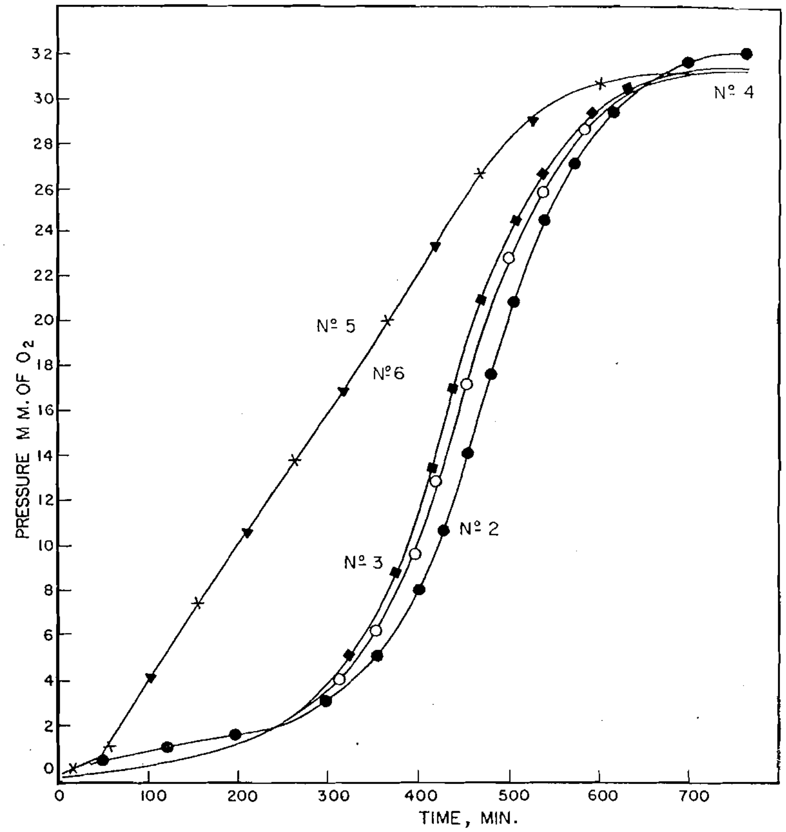

FIG. 1. The rate of decomposition of whole and ground crystals of silver permanganate.

whole crystals the reproducibility between runs is not as good as in the case of the ground crystals. The most striking observation was that after a short induction period the rate of decomposition of the ground crystals was linear, while the rate of decomposition of the whole crystals varied with time to produce a sigmoidal type of rate curve. This sigmoidal type of rate curve has been reported previously by other investigators (3, 10, 13) and indicates that more than one reaction rate may be involved in the decomposition. Attempts to fit experimental data to equations derived by Prout and Tompkins (9) in their studies of the decomposition of silver permanganate were unsatisfactory. From the observations of the effect of crystal size, it is unlikely that kinetic equations can be derived without considering the rate of reaction as a function of the initial particle size of the crystals. However, it appears that when the particle size reaches a certain minimum size a linear first order equation will fit the decomposition curve after allowance is made for a short induction period. This equation however has little significance in regard to the mechanism.

The decomposition rate curves obtained by following the loss in weight of the crystals were similar in shape to those obtained by measuring the increase of pressure of the enclosed system and are therefore omitted. The average loss of oxygen of 9.00% was calculated from the loss in weight rather than the final pressure measurement, as the value obtained by the pressure measurement was not reliable, because of variation in temperature of the apparatus. The results for the five runs are given in Table I. There was no significant difference in loss of weight between the ground and whole crystals and the agreement between runs was good, except for run 3.

Analysis of Decomposition Products

Chemical analyses were conducted on runs 3 and 4. Following the scheme of analysis devised, no water soluble fraction was obtained in any of the runs, as shown by negative tests for silver ion and manganese. Therefore, no silver permanganate was present in the heat treated sample. It was also evident from the fact that no X-ray powder diffraction patterns were obtained on X-ray analysis that the original silver permanganate crystals had undergone complete thermal decomposition.

The ammonium hydroxide soluble fraction corresponding to 14.8% of the solid decomposition products was analyzed for silver. The average silver content was 93.6%. From this analysis it is evident that the product was Ag_2O and not Ag_2O_2 or AgO. The ammonium hydroxide insoluble fraction contained 38.0 silver and 41.9% manganese dioxide. The silver could have been in the form of elemental silver or in the form of silver permanganite, $AgMnO_3$, while the manganese could have been in the form of manganese dioxide, MnO_2, or in the form of silver permanganite, $AgMnO_3$. The reason for not being able chemically to identify the form in which the silver and manganese dioxide occurred is that the silver permanganite decomposed in the presence of hydrochloric acid. The results of the chemical analyses are given in Table II.

TABLE II

Run No.	Ammonium hydroxide soluble fraction Ag_2O %	Ammonium hydroxide insoluble fraction Ag %	 MnO_2 %	 Oxygen released %
2	16*	—	—	9.03
3	12.6*	39.0*	42.7	—
4	14.8*	37.0	41.6	8.99
Average	14.8	38.0	41.9	9.00†

**Average of two values.*
†*Average of runs 2, 4, 5, 6.*

DISCUSSION

A number of possible paths for the decomposition of silver permanganate may be written. These are given below with the percentage of the decomposition products.

$$\begin{array}{lllll}
\mathrm{4AgMnO_4} \longrightarrow & \mathrm{2Ag_2O} & +\ \mathrm{4MnO_2} & +\ \mathrm{3O_2} & [1]\\
& 50.8\% & 38.3\% & 10.9\% & \\
& 57.1\% & 42.9\% & & \text{as percentage of weighed decomposition products.}
\end{array}$$

$$\begin{array}{lllll}
\mathrm{AgMnO_4} \longrightarrow & \mathrm{AgMnO_3} & +\ \tfrac{1}{2}\mathrm{O_2} & & [2]\\
& 92.96\% & 7.04\% & &
\end{array}$$

$$\begin{array}{lllll}
\mathrm{AgMnO_4} \longrightarrow & \mathrm{AgMnO_3} & +\ \tfrac{1}{2}\mathrm{O_2} & & [3a]\\
& 92.96\% & 7.04\% & & \\
\mathrm{2AgMnO_3} \longrightarrow & \mathrm{Ag_2O} & +\ \mathrm{2MnO_2} & +\ \tfrac{1}{2}\mathrm{O_2} & [3b]\\
& 54.9\% & 41.2\% & 3.9\% & \\
& 57.1\% & 42.9\% & & \text{as percentage of weighed decomposition products.}\\
\mathrm{Ag_2O} \longrightarrow & \mathrm{2Ag} & +\ \tfrac{1}{2}\mathrm{O_2} & & [3c]\\
& 93.1\% & 6.9\% & &
\end{array}$$

$$\begin{array}{lllll}
\mathrm{AgMnO_4} \longrightarrow & \mathrm{AgMnO_3} & +\ \tfrac{1}{2}\mathrm{O_2} & & [4a]\\
& 92.96\% & 7.04\% & & \\
\mathrm{AgMnO_3} \longrightarrow & \mathrm{Ag} & +\ \mathrm{MnO_2} & +\ \tfrac{1}{2}\mathrm{O_2} & [4b]\\
& 51.2\% & 41.2\% & 7.6\% & \\
& 55.5\% & 44.5\% & & \text{as percentage of weighed decomposition products.}
\end{array}$$

$$\begin{array}{lllll}
\mathrm{2AgMnO_4} \longrightarrow & \mathrm{Ag_2O} & +\ \mathrm{Mn_2O_3} & +\ \mathrm{2O_2} & [5]\\
& 51.09\% & 34.8\% & 14.1\% & \\
& 59.4\% & 40.6\% & & \text{as percentage of weighed decomposition products.}
\end{array}$$

$$\begin{array}{lllll}
\mathrm{AgnMO_4} \xrightarrow{100\%} & \mathrm{AgMnO_3} & +\ \tfrac{1}{2}\mathrm{O_2} & & [6a]\\
& 92.96\% & 7.04\% & & \\
\mathrm{2AgMnO_3} \xrightarrow{27.2\%} & \mathrm{Ag_2O} & +\ \mathrm{Mn_2O_3} & +\ \mathrm{O_2} & [6b]\\
& 54.6\% & 37.4\% & 8.0\% &
\end{array}$$

$$\begin{array}{lllll}
\mathrm{6AgMnO_4} \longrightarrow & \mathrm{3Ag_2O} & +\ \mathrm{2Mn_3O_4} & +\ 6\tfrac{1}{2}\mathrm{O_2} & [7]\\
& 51.09\% & 33.7\% & 15.21\% &
\end{array}$$

$$\begin{array}{lllll}
\mathrm{AgMnO_4} \xrightarrow{100\%} & \mathrm{AgMnO_3} & +\ \tfrac{1}{2}\mathrm{O_2} & & [8a]\\
& 92.96\% & 7.04\% & & \\
\mathrm{6AgMnO_3} \xrightarrow{26.9\%} & \mathrm{3Ag_2O} & +\ \mathrm{2Mn_3O_4} & +\ 3\tfrac{1}{2}\mathrm{O_2} & [8b]\\
& 55.0\% & 35.8\% & 9.2\% &
\end{array}$$

From the experimental evidence obtained a number of these equations can be ruled out. Equations [1], [5], and [7] can be neglected as they would yield 57.1, 59.4, and 51.09% silver oxide, respectively, while only 14.8% can be found experimentally. As previously stated, the silver found in the ammonium hydroxide insoluble fraction may have been derived from free silver or from the combined silver in silver permanganite, $AgMnO_3$. If all the silver were free, equation [4] would not be in agreement with the experimental results as a larger quantity of oxygen would be evolved, approximately 4% more than can be accounted for experimentally (9.00%). Equation [4] may also be neglected as Ag_2O was present in the ammonium hydroxide fraction. Equation [2] can be ruled out on the basis that the system only yields 7.04% oxygen and would not account for the 9.00% oxygen plus the silver oxide found.

The mechanism represented by equations [8*a* and *b*] may also be ruled out. Calculating the percentage that part *b* of equation [8] goes to completion based on the percentage Ag_2O found in the decomposition products, one finds that the equation would have to go to 26.9% of completion and this would produce 2.47% oxygen. Thus the total amount of oxygen evolved by the mechanism would be 9.51%, which is in excess of the 9.0% found experimentally.

Considering the mechanism represented by equations [6*a* and *b*] one can calculate, based on Ag_2O found experimentally, that equation [6*b*] would have to go to 27.2% of completion and this would give 2.17% oxygen. Therefore 9.21% oxygen would be evolved by the mechanism represented in equations [6*a* and *b*]. This is in slight excess of the 9.0% found experimentally; however the correct value could be obtained if only 13.6% Ag_2O had been found instead of the average 14.8%. The possibility of 13.6% Ag_2O occurring is good, as values obtained in different runs varied from 12.6% to 16.0%.

Therefore the mechanism proposed in equations [6*a* and *b*] cannot be ruled out on the basis of the oxygen and Ag_2O found and stoichiometric considerations.

Thus the possibility of the oxide of manganese Mn_2O_3 as a decomposition product has not been ruled out.

In postulating the existence of Mn_2O_3 as one of the decomposition products the problem of the mechanism of two manganese atoms becoming bonded must be approached. This may be best discussed by first studying the crystal and structure and lattice constants for $AgMnO_4$.

The crystal structure of silver permanganate has been studied by Sasvari (11) and the coordinates are given in Wyckoff (12, p. 25) for *hko* and *kol* projections.

The manganese and four oxygen atoms are arranged in a distorted tetrahedron and have Mn—O separation varying from 1.40 to 1.80 Å. Each silver atom has two oxygen neighbors calculated at approximately 2.21 Å and four more at distances between 2.58 to 2.72 Å. The shorter Ag—O bonds link the Mn tetrahedron in chains along the *b* axis and parallel to the *b*, *c* axis. The longer Ag—O bonds form the cross links between the chains of the Mn tetrahedron. It is evident from this structure that there is little bonding between the manganese atoms.

It is also evident from the study of bond length that two oxygen atoms are more closely bonded to the manganese atom than the remaining oxygen atoms. The fact that there is little manganese to manganese bonding in the crystal lattice and that two oxygen atoms are bonded significantly more closely to the manganese atoms suggests very strongly that MnO_2 would be one of the decomposition products rather than Mn_2O_3.

If Mn_2O_3 were one of the decomposition products then a mechanism must be postulated for the formation of the manganese to manganese bond. At the temperature condition of the experiments it is difficult to see how Mn_2O_3 could be formed from MnO_2.

Therefore it appears most likely that the mechanism proposed in equations [6*a*] and [6*b*] can be ruled out as it is unlikely that Mn_2O_3 is one of the decomposition products.

From the analyses of the decomposition products, it was evident that silver oxide, Ag_2O, is present. Considering equation [3], MnO_2 must then be present in the decomposition product. Thus it was assumed that the decomposition products were silver oxide, manganese dioxide, oxygen, silver permanganite, and possibly elemental silver. Considering equation [3], 7.04% oxygen is released by part [*a*] and 1.05% by part [*b*] providing equation [3*b*] goes to (14.8/54.9 × 100) or 27% completion. Thus parts [*a*] and [*b*] of equation [3] account for only about 8.1% of the oxygen released. The remaining amount of oxygen (0.9%) may be accounted for by part [*c*] of equation [3]. On the basis of the calculation of the percentage of oxygen and Ag_2O found experimentally, the following mechanism may be proposed:

$$AgMnO_4 \longrightarrow AgMnO_3 + \tfrac{1}{2}O_2, \qquad [3a]$$

$$2AgMnO_3 \longrightarrow 2AgO + 2MnO_2 + \tfrac{1}{2}O_2, \qquad [3b]$$

$$2AgO \longrightarrow Ag_2O + \tfrac{1}{2}O_2, \qquad [9]$$

$$Ag_2O \longrightarrow 2Ag + \tfrac{1}{2}O_2. \qquad [10]$$

Equation [3*a*] goes to completion and equation [3*b*] goes to approximately 37.5% completion, the Ag_2O and O_2 being formed by the decomposition of AgO according to equation [9]. Equation [10] indicates that the decomposition of Ag_2O goes to approximately 6.6% of completion. Further supporting evidence for the mechanism may be obtained from the analysis of silver and manganese in the ammonium hydroxide insoluble fraction.

Assuming the reaction mechanism to be that described above by equations [3*a*], [3*b*], [9], and [10], then the manganese dioxide found by analysis was derived from the thermal decomposition as represented in equation [3*b*] and from decomposition by the hydrochloric acid used in analyzing for silver permanganite. The experimental average value of 41.9% MnO_2, found by analysis, is in agreement with the calculated value of 41.8% MnO_2. The silver found in the ammonium hydroxide insoluble fraction was derived from silver permanganite and elemental silver. The value of 38.0% silver found experimentally is also in agreement with the calculated value of 38.0%.

The over-all agreement of experimental values with those calculated on the basis of the mechanism outlined above is good and it therefore appears that the proposed mechanism may be correct.

If the proposed mechanism is correct, then the amount of oxygen evolved in thermal decomposition will depend greatly on the temperature, as it is most likely that the rate and amount of completion of equations [3*b*] and [10] are temperature dependent. Equation [10] has been shown to be temperature dependent by previous workers (8) studying the thermal decomposition of silver oxide.

From the results of the over-all amount of oxygen evolved from the ground and whole crystals, it is evident that the decomposition rates are not the same for whole and ground crystals. A number of theories have been discussed in the literature concerning the path of the decomposition. Molecular chain theories involving degenerate branching have been proved improbable, as well as processes based on photochemical reduction. A mechanism based on differences in geometric forms and dimensions of the decomposition products is attractive; as MnO_2 is a centered tetragon cell and silver permanganate is monoclinic in a unit cell of four molecules. Thus one could propose, as has been done by Prout and Tompkins (9), that the surface array of decomposition product molecules produces lateral strain. However, it is difficult to reason that the decomposition can produce lateral strain as the decomposition products do not have any rigid geometric crystal form. This is evident from their amorphous nature as indicated by the absence of X-ray diffraction patterns.

In recent years studies of crystal structure have shown that there are many imperfections and vacant sites inside of crystal lattices. If one assumes that these imperfections and vacant sites may act as nuclei for the initiation of decomposition, then the molecules of oxygen released inside the crystals would be trapped until such time as decomposition from outer surfaces of the crystals weakened the inner lattice structure. This would allow the trapped gas from the inside to escape. Therefore, during a thermal decomposition of a crystal, initially the oxygen would be slowly liberated because of the decomposition of the outer surfaces. When a portion of the outer surface has been decomposed to such an extent as to expose inner unit cells already thermally decomposed, the accumulated oxygen will be liberated and thus the over-all rate will increase. In the case of small crystals (ground silver permanganate) there is less chance for oxygen to be trapped in the inner cells as decomposition from the outer surfaces immediately weakens the inner cellular units, and thus a uniform rate of release of oxygen is established.

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THE PHOTOINITIATED ADDITION OF BUTYL MERCAPTAN TO CONJUGATED AND UNCONJUGATED DOUBLE BONDS[1]

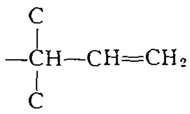
By R. Back,[2] G. Trick,[3] C. McDonald,[4] and C. Sivertz[5]

ABSTRACT

This study elucidates the details of a typical initiation encountered in polymerization. A kinetic mechanism for the photoinitiated addition of normal butyl mercaptan to single and conjugated double bonds is proposed, and the corresponding velocity constants namely the attack k_a, the transfer k_{ct}, and the termination k_t have been measured employing a sector method. For the concentrations employed in this work the over-all rate of addition to the double bond is determined by the transfer rate of the composite mercapto monomer radical, while the capture of initiating radicals depends on the rate of attack of the mercaptyl radicals on the double bonds. The transfer rate is about 1000 times faster for a pentenyl than for a conjugated styryl radical, while the attack step is estimated to be several hundred times faster for the conjugated monomer. These conclusions are shown to be consistent with results observed when conjugated and unconjugated monomers are in competition, and are in agreement with the quantum mechanical structure of the radicals and molecules involved. This work reports a general survey of the field, and subsequent papers will extend the observations.

INTRODUCTION

GR-S synthetic rubber is a copolymer of styrene and butadiene, produced by a free radical, emulsion polymerization. The butadiene may add to the growing polyradical in one of two ways (10): 1,2 addition results in a residual "side vinyl" double bond on the polymer chain, while 1,4 addition may result in either an 'internal' or 'crotyl' residual double bond.



$$\overset{\displaystyle C}{\underset{\displaystyle C}{-CH}}-CH{=}CH_2$$

Vinyl

$$-CH_2-CH{=}CH-CH_2-$$

Internal

$$-CH_2-CH{=}CH-CH_3$$

Crotyl

It is generally agreed that the reactions of these residual functional groups in the polymerization system lead to undesirable variations from a simple linear polymer.

These residual double bonds undergo two general types of reaction. These are addition, in which a free radical adds to the double bond, and dehydrogenation, in which a free radical abstracts a hydrogen atom from a carbon atom adjacent to the double bond. Addition results in both branching and cross linking between polymer chains, while dehydrogenation leads mainly to branching. This investigation concerns the addition reaction only.

Since a direct study of the polymer itself is impractical, because of low solubility, doubtful structure, low concentration of functional groups, and

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other experimental difficulties, a "model molecule" technique was employed. It has been shown (18) that vinyl double bonds are about 50 times more reactive than crotyl or internal double bonds, and hence are of primary interest in a study of the cross-linking problem. 1-Pentene was chosen as a model for the vinyl double bond. Admittedly, the behavior of a side vinyl double bond in a large polymer molecule will be considerably different from that of 1-pentene; however, its reactivity should be of the same order of magnitude, and the general features of the reaction similar in the two cases.

THEORETICAL

Since the cross-linking process goes on in the polymerization system which contains unreacted monomer, the addition of radicals to residual double bonds must compete with the normal propagation reaction. Hence it is the relative reactivity of the vinyl double bonds compared to that of the monomer which is of importance. In the present investigation the common attacking radical for this comparison is the mercaptyl radical. The free radical addition of mercaptan to olefins is known to take place through a chain mechanism of the following type (16).

$$\text{Initiation} \qquad \xrightarrow{k(\text{I})} \dot{\text{R}\text{S}} \qquad (1)$$

$$\text{Attack} \qquad \text{R}\dot{\text{S}}+\text{M} \xrightarrow{k_a} \dot{\text{A}} \qquad (2)$$

followed by

$$\text{Chain transfer} \qquad \dot{\text{A}}+\text{RSH} \xrightarrow{k_{ct}} \text{AH}+\text{R}\dot{\text{S}} \qquad (3)$$

the kinetic chain is broken by

$$\begin{aligned} \text{Termination} \qquad \text{R}\dot{\text{S}}+\text{R}\dot{\text{S}} &\xrightarrow{2k_{t_1}} \text{RSSR} \qquad (4)\\ \dot{\text{A}}+\dot{\text{A}} &\xrightarrow{2k_{t_2}} \text{A}_2\\ \dot{\text{A}}+\text{R}\dot{\text{S}} &\xrightarrow{k_{t_3}} \text{ASR} \end{aligned}$$

where M is $\text{R}'\text{—CH}{=}\text{CH}_2$
$\dot{\text{A}}$ is $\text{R}'\text{—}\dot{\text{C}}\text{H—CH}_2\text{—S—R}$ radical

Steps (2) and (3) are the chain-propagating ones, and, as will be shown later, kinetic chain lengths may be quite large, of the order of 10^3 or higher, permitting a simple kinetic treatment of the system, as initiation and termination reactions become negligible in the stoichiometric relationship.

A reaction competing with step (3) is, of course, propagation,

$$\dot{\text{A}}+\text{M} \xrightarrow{k_p} \dot{\text{A}}_2$$

where $\dot{\text{A}}_2$ is the dimerie radical. By the use of equimolar concentrations of mercaptan and monomer, propagation was minimized.

The free radical addition of *n*-butyl mercaptan to 1-pentene [model for vinyl double bond], also to styrene, and to isoprene was studied. Isoprene was used instead of the more volatile butadiene which is the other comonomer used in GR-S.

Reactions were carried out in benzene solution, using photochemical initiation either by direct photolysis of the mercaptan or by the use of 2,2 azo-bis-isobutyronitrile as a photoinitiator. Reaction rates were determined dilatometrically, and absolute rate constants were evaluated using the rotating sector method of intermittent illumination.

The sector method can be used to measure the concentration of an active species in any reaction system which can be initiated photochemically and where disappearance of the active species is second order. The theory of the sector method has been adequately described elsewhere (12, 13) and will be only briefly outlined here.

Consider a system containing any active radical species $\dot{\mathrm{A}}$. Then, assuming disappearance of $\dot{\mathrm{A}}$ by mutual termination only,

$$d(\dot{\mathrm{A}})/dt = k(\mathrm{I}) - 2k_t(\dot{\mathrm{A}})^2 \qquad [1]$$

where $k(\mathrm{I})$ is the rate of photochemical initiation and k_t is the rate constant for the mutual termination of two $\dot{\mathrm{A}}$ radicals.

Under steady state conditions, with continuous illuminations,

$$d(\dot{\mathrm{A}})dt = 0, \text{ and } (\dot{\mathrm{A}}_s) = \sqrt{k(\mathrm{I})/2k_t}. \qquad [2]$$

When the light is shut off ($k(\mathrm{I}) = 0$) the radical $\dot{\mathrm{A}}$ dies off with a half life

$$\lambda = 1/k_t(\dot{\mathrm{A}}_s). \qquad [3]$$

If $k(\mathrm{I})$ and λ are measurable, Equations [2] and [3] above can be solved, k_t and $(\dot{\mathrm{A}})$ being thus evaluated.

If $\dot{\mathrm{A}}$ is the active species in a chain process, so that the over-all rate is dependent on $(\dot{\mathrm{A}})$, the rate constant for the process can be determined.

To evaluate λ, reaction rates are measured using intermittent illumination over a range of values of t, the duration of the light flash. It can be shown that

$$\frac{R}{R_s} = \frac{1}{p-1}\left\{1+\frac{1}{m}\ln\left(1+\left[\frac{pmB}{B+1}\right]\right)\right\}, \qquad [4]$$

$$\text{where } B = \frac{pm\tanh m}{2(pm+\tanh m)}\left\{1+\sqrt{1+\frac{4}{pm\tanh m}+\frac{4}{p^2m^2}}\right\},$$

R = rate with intermittent illumination,

R_s = rate with steady illumination,

$p = \dfrac{\text{duration of dark period}}{\text{duration of light flash}}$,

$m = t/\lambda$.

By plotting $(R/R_s)\sqrt{(p+1)}$ against $\log m$, an S-shaped theoretical curve is obtained, asymptotic to unity for small m values, and to $1/\sqrt{(p+1)}$ for large m values.

Experimentally, $(R/R_s)\sqrt{(p+1)}$ values are plotted against $\log t$, and the theoretical curve is superimposed to give the best fit. At the value of $\log m = 0$, $m = 1$ and $t = \lambda$. Thus $\log m = 0$ on the theoretical curve will coincide with $\log t = \log \lambda$ on the experimental plot, and λ can be evaluated by comparison of the abscissa scales. Assuming the principal termination to be k_{t2} and that the transfer step is rate determining, a steady state analysis of the basic equations presented above yields

$$-dM/dt = -d\mathrm{RSH}/dt = k_{ct}\,\mathrm{RSH}\,\omega,$$

where $\omega = \sqrt{k(\mathrm{I})/2k_t}$. Consequently the reaction should be first order. The next paper makes a detailed analysis of how the rate determining step depends on concentration and in what way the two radicals involved take part in the termination.

EXPERIMENTAL

Materials

Phillips Research-grade 1-pentene was used without further purification. Styrene and isoprene were obtained from Polymer Corporation, Sarnia, and distilled through a short column to remove the inhibitor. *n*-Butyl mercaptan was obtained from Eastman Kodak and at first purified by distillation through a 100 cm. glass helices column. More often this reagent was prepared by precipitation as the lead salt followed by recovery of the mercaptan and subsequent distillation. Merck Reagent grade Thiophene-free benzene was used without further purification. AIN (2,2, azo-bis-isobutyronitrile) was prepared by the method of Overberger (15).

Irradiation Apparatus

All reactions were carried out in a cylindrical quartz dilatometer cell about 3 cm. in diameter and 2 cm. across, mounted in a water bath thermostat controlled to 0.02°C. The cell was irradiated through a quartz window.

Two light sources were used. The first was a General Electric medium pressure mercury UA-2B quartz Uviarc, powered by a General Electric 58-G-280 autotransformer, and operated on 110 v. a-c. Corning filters 9863 and 5850 were used in conjunction with this source. The light was not collimated. The other light source was a General Electric Photospot tungsten filament lamp, operated on 110 v. a-c. A 1-liter round-bottomed flask, filled with running water, was used to focus the light beam and to absorb some of the heat that was radiated.

The rotating sector was mounted close to the reaction vessel, to give a sharp transition from light to dark in the system. The sector was driven by a constant speed electric motor with a suitable set of gears and pulleys. Low speeds were measured by a mechanical counter mounted on the sector shaft, while a calibrated stroboscope was used at higher speeds. In the styrene system, a sector giving equal periods of light and dark ($p = 1$) was used. A sector having $p = 3$ was used in the other systems.

METHODS

In this preliminary study of reactions involving conjugated and unconjugated olefins with mercaptans a choice was made between:

(I) measuring a few constants with high precision by employing the usual technique of degassing under high vacuum with alternate freezing and melting or

(II) sacrificing some precision and surveying a much larger field of reactions by employing more rapid methods. Consequently observations of rates were made on solutions in which reagents (*a*) had not been degassed, (*b*) were degassed in reservoir flasks and then added by open transfer, (*c*) were degassed under high vacuum with alternate freezing and melting.

In the series of monomers studied such unconjugated monomers as 1-pentene showed maximum over-all rates in a typical observation of (*a*) 0.69, (*b*) 0.95, (*c*) 1.1 in dilotometer units of cm. min.$^{-1}$ with "inhibition" periods varying from six to one minute. It was found particularly difficult to reduce the induction period for fast reacting monolefins to zero. Rates of conjugated monomers and monomers such as cyclohexene, which are relatively slow in transferring compared to a peroxide radical, were found to be unaffected by the oxygen present when mercaptan is the transfer agent. A quantitative discussion of this point will be presented in a subsequent paper in the series. Fig. 1 shows some typical rates and brings out the very great difference in behavior between conjugated and unconjugated structures.

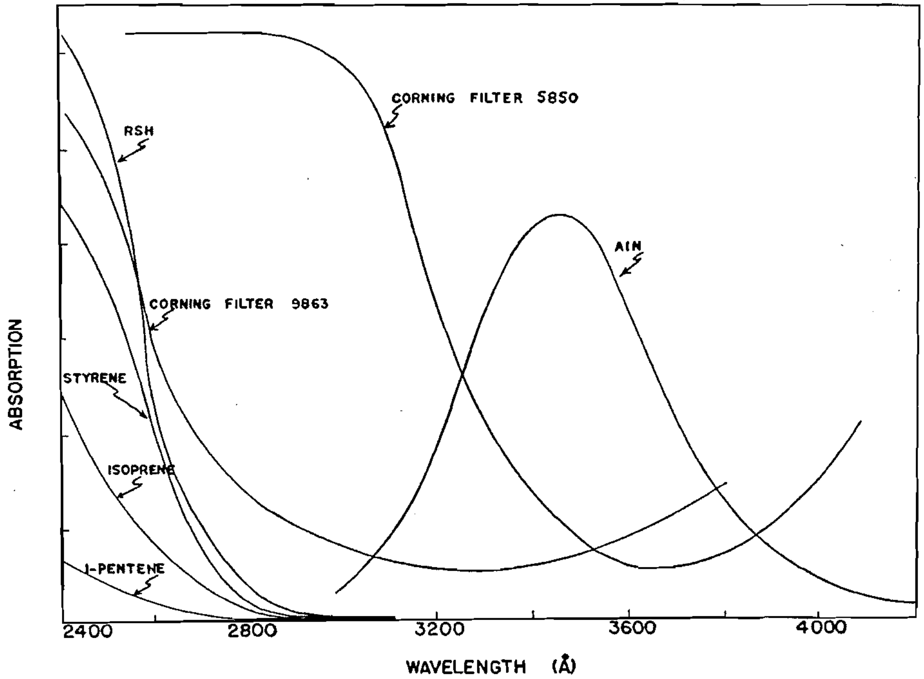

FIG. 1. Ultraviolet absorption spectra.

In summary the rate constants for conjugated and slow transferring olefins are without error owing to small amounts of oxygen, and those for monolefins are considered to be well within the precision desired for a survey of this family of reactions. Work is now under way to redetermine the constants for 1-pentene by exhaustive deaeration but such changes, while providing a better order of magnitude, will not affect the general conclusions arrived at in this paper.

Contraction of the reaction mixture during the reaction was followed by the observation of the meniscus in the dilatometer capillary with a cathetometer. Contraction was related to mercaptan disappearance for each monomer by the amperometric titration of residual mercaptan with silver nitrate by the method of Kolthoff and Harris (9). In this way, any contraction due to a propagation reaction will not affect the rate measurements.

Reaction rates were evaluated from the slope of contraction vs. time curves. With the styrene and isoprene systems, curves obtained were almost linear at the low conversions attained, and slopes were taken at zero time (Fig. 2).

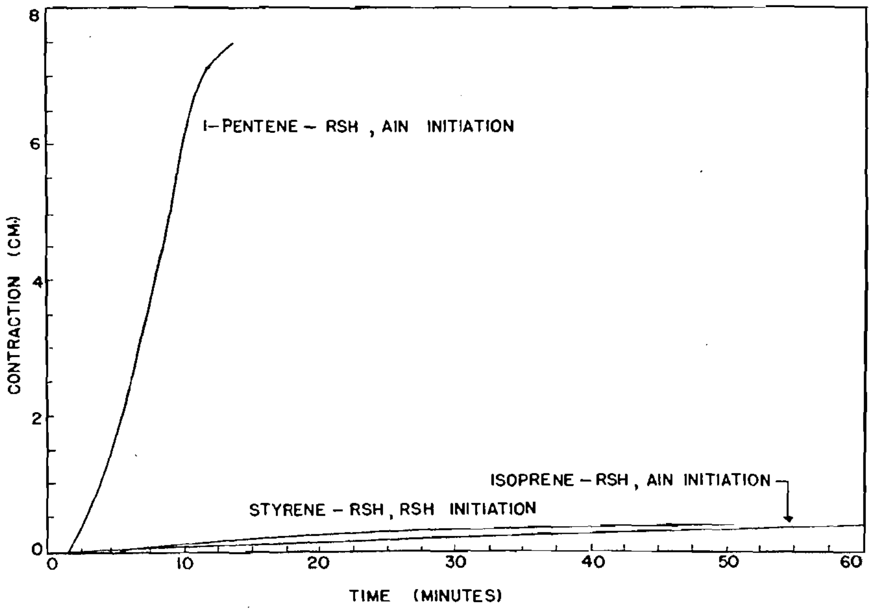

FIG. 2. Typical reaction curves.

In the 1-pentene system a slight S-curve showing a definite induction period was observed (Fig. 2). Maximum slopes were measured at the point of inflection, and concentrations were corrected to the value at this point in calculating the rate constants.

Two methods of photoinitiation were used. When the Uviarc source with Corning filter 9863 was employed and AIN omitted from the reaction system, initiation was by direct photolysis of the mercaptan (8).

$$RSH+h\nu \longrightarrow R\dot{S}+\dot{H}$$

The hydrogen atom may react with mercaptan, forming H_2 and $R\dot{S}$, or it may add to a double bond itself. Either way, two reaction chains are initiated by each mercaptan molecule photolyzed. Photoactivation of 1-pentene is prevented by the sharp cutoff of filter 9863: with styrene and isoprene, some activation may occur, but it will be only a small fraction of the total initiation (Fig. 1).

If Corning filters 9863 and 5850 are used and AIN is added to the system, initiation will be by AIN photolysis only, as the 5850 filter cuts off all radiation below 3100 Å, thus preventing activation of either the monomer or the mercaptan (Fig. 1).

The rate of initiation $k(\mathrm{I})$ was evaluated by two general methods. The photolysis of AIN has been studied previously in this laboratory and has been related to the absolute light intensity (2). Thus, by the use of light of the same spectral energy distribution (quartz Uviarc and Corning filters 9863 and 5850), the rate of AIN photolysis was evaluated simply by the measurement of the light intensity by uranyl oxalate actinometry. The rate of initiation was assumed to be twice the rate of AIN photolysis. The validity of this assumption in polymerization systems has been questioned (4, 20) although recent work by Overberger (14) seems to justify it. Certainly in the system used here, with relatively high mercaptan concentrations and long kinetic chain lengths, mutual termination by isobutyronitrile radicals should be negligible.

In systems using initiation by mercaptan photolysis, or AIN photolysis with the G.E. Photospot light source, rates of initiation could not be obtained directly. From Equation [2], it is seen that the radical concentration (A) and hence the reaction rate varies directly as the square root of $k(\mathrm{I})$. When this relationship is used, an unknown $k(\mathrm{I})$ can be evaluated by a comparison of known and unknown rates of initiation. Either AIN photoinitiation under standard irradiation conditions, or AIN thermal initiation, which has been accurately measured by several workers (11, 15), was used to give a known rate of initiation.

In all cases, absorption across the cell was less than 20%, assuring homogeneous initiation. A determination of $k(\mathrm{I})$ by the inhibitor method, often used in rotating sector measurements, was attempted, but no inhibitor could be found to give the sharp inhibition necessary. This can be explained by the inability of the ordinary free radical inhibitors to compete successfully with the extremely reactive mercaptan. This suggests the use of such mercaptan addition reactions to measure the efficiency of inhibitors. Work on this aspect of these reactions is under way.

Reaction rates with intermittent illumination were measured in the following systems at 25°C., and λ, the half life of the active species, was evaluated.

(1) *Isoprene-n-butyl Mercaptan*

0.040 M. isoprene, 0.037 M. mercaptan, 2.47×10^{-4} M. AIN.

Irradiation by Uviarc with Corning filters 9863 and 5850.

Initiation by AIN photolysis, with direct determination of $k(\mathrm{I})$ from light intensity measurement.

(2) *Styrene-n-butyl Mercaptan*

0.045 M. styrene, 0.045 M. mercaptan.

Irradiation by Uviarc with Corning filter 9863.

Initiation by mercaptan photolysis. $k(\mathrm{I})$ was determined by rate comparison with an AIN thermally initiated system.

(3) *1-Pentene-n-butyl Mercaptan*

0.0184 M. 1-pentene, 0.0185 M. mercaptan, 2.29×10^{-4} M. AIN.

Irradiation by G.E. Photospot, filtered through pyrex.

Initiation by AIN photolysis, with determination of $k(I)$ by rate comparison with system using standard AIN photolysis with Uviarc and Corning filters 9863 and 5850.

Experiments were also made in the 1-pentene-*n*-butyl mercaptan system with small quantities of styrene and isoprene added, using direct mercaptan photoinitiation.

Reaction rates in the 1-pentene-*n*-butyl mercaptan system and the styrene-*n*-butyl mercaptan system were measured over a range of temperature, and activation energies were evaluated.

RESULTS

Experimental data are tabulated in Table I. Typical reaction curves are shown in Figs. 2 and 3.

TABLE I
DATA FOR RATE CONSTANT DETERMINATION T. = 25°C.

System	Monomer, M. liter^{-1}	(RSH), M. liter^{-1}	Rate, M. liter^{-1} sec.$^{-1}$	$k(I)$, M. liter^{-1} sec.$^{-1}$	λ, seconds
(1) Isoprene–mercaptan	3.40	3.16	1.18×10^{-5}	4.5×10^{-7}	0.089
(2) Styrene–mercaptan	3.83	3.83	9.79×10^{-5}	1.0×10^{-7}	0.1
(3) 1-Pentene–mercaptan	0.975	0.975	2.11×10^{-3}	1.3×10^{-6}	0.00074

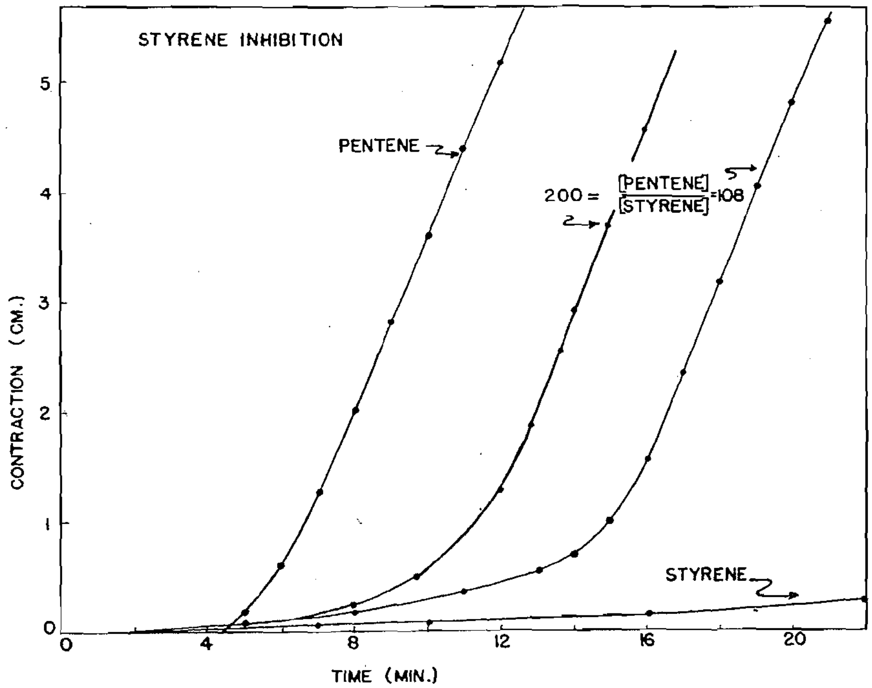

FIG. 3. Typical reaction curves.

Both styrene and isoprene reaction systems gave a reproducible curve which yielded a straight line with a first order plot. No measurable induction period was noted. Degassing had little or no effect on reaction rates or the shape of the curve.

The 1-pentene–mercaptan system, on the other hand, gave an S-shaped reaction curve with a definite inhibition period of about three minutes, followed by a sharp increase, and levelled off again after the depletion of the reagents. The over-all rate was strikingly rapid compared to that of the styrene and isoprene systems. It was suspected that oxygen was causing the observed inhibition: this was confirmed by subsequent degassing of the system. The inhibition period was reduced, but never completely eliminated, by repeated degassing. The reaction rate, taken as the slope at the point of inflection, was increased in the degassed system as pointed out above. However, it was found difficult to degas the system reproducibly (5).

The speed of the pentene reaction was somewhat unexpected from general concepts of double bond reactivities. The conjugated double bond of styrene has been reported as 50 times as reactive as the vinyl double bond (18).

The effect of small quantities of styrene or isoprene in the pentene–mercaptan system offers an explanation of this apparant anomaly. The series of curves in Fig. 3 illustrates the effect of styrene: similar curves were obtained with isoprene. It is seen that styrene acts as an inhibitor in the pentene–mercaptan system, suppressing the pentene reaction rather effectively until the styrene is expended. The relatively small concentrations of styrene involved should be noted. Thus, although the over-all rate of the pentene reaction is at least twenty times that of styrene, the latter apparently reacts preferentially in a pentene–styrene–mercaptan system.

Recalling that the reaction chain is perpetuated by two alternating consecutive steps, the attack of the mercaptyl radical on the double bond, followed by the transfer of the resultant radical with mercaptan, this retardation may be readily explained. With styrene, the competitive attack step must be much faster than with pentene, in order to produce the sharp inhibition which was observed. To account for the slower over-all rate of the styrene reaction, it must be concluded that the transfer step is rate controlling, and is much slower than in the pentene system. This explanation is in accordance with accepted principles of free-radical reactivity (22). The conjugated double bond of styrene or isoprene is much more susceptible to radical attack than is the isolated, unconjugated, 1-pentene double bond. The resultant radical, however, will be resonance stabilized, and will react relatively slowly with mercaptan. The pentyl–mercaptyl radical, on the other hand, has no resonance stabilization, and will react rapidly. The calculated rate constants for the three systems support this theory. A kinetic analysis of the competitive reaction between styrene and 1-pentene and a report on the various constants involved is in course of publication (7).

The values of λ shown in Table I for the isoprene and styrene systems are of the order of 0.1 sec., while that for the pentene system is more than a hundred times smaller.

Kistiakowsky (6) has shown that an a-c. light source can be used in sector measurements within the range $\lambda > 1/f$ where f is the frequency of the source variation. Using a 60 cycle a-c. source, with $f = 120$, both the styrene and the isoprene half lives fall well within this range. The pentene system does not fulfill this criterion. Successful measurements were finally made using a nonflicker tungsten filament source, as previously described.

Calculation of Rate Constants

In the proposed reaction mechanism, steps [2] and [3] are chain propagating, and either, or both, may be rate controlling.

In the isoprene and styrene systems, there is good evidence that the transfer step is rate controlling (Fig. 3): the reaction rate will be given by

$$[5] \qquad \frac{-d(\mathrm{RSH})}{dt} = \frac{-d(\mathrm{M})}{dt} = k_{ct}(\dot{\mathrm{A}})(\mathrm{RSH}) = k_{ct}\mathrm{RSH}(k(\mathrm{I})/k_t)^{\frac{1}{2}}.$$

This predicts a reaction rate first order in (RSH) and independent of (M) at the concentrations used. Reactions were carried out over a range of (M) and (RSH) values, and this was found to be true. A slow linear increase with increasing (M) at high monomer concentrations was attributed to propagation.

It also follows that $(\dot{\mathrm{A}}) \gg (\mathrm{R\dot{S}})$, hence the radical concentration as determined by the sector method will be approximately that of the $\dot{\mathrm{A}}$ radical. Chain termination will be almost entirely by $\dot{\mathrm{A}}$ radicals, and the k_t value found will be that of the $\dot{\mathrm{A}}$ radical, that is the stabilized composite styryl radical.

The picture is not quite so clear in the 1-pentene system. In this case, no definite conclusions may be drawn from the inhibition phenomena (Fig. 3) as to which step is rate controlling. Reaction rates were measured over a series of concentrations, and first order dependence on (RSH) was found, but the rate was also partially dependent on (M), approaching independence at higher concentrations. It appears evident that the transfer step is again the slower one, but is considerably faster than in the styrene and isoprene systems, and is approaching a velocity of the same order as that of the attack step. This is expected, as the pentene $\dot{\mathrm{A}}$ radical, having no resonance stabilization, will be much more reactive; also, the attack on the unconjugated double bond will be considerably slower.

The reaction rate in the 1-pentene reaction is still given by

$$[6] \qquad \frac{-d(\mathrm{RSH})}{dt} = \frac{-d(\mathrm{M})}{dt} = k_{ct}(\dot{\mathrm{A}})(\mathrm{RSH}).$$

Also $(\dot{\mathrm{A}}) > (\mathrm{R\dot{S}})$ but it is now questionable to assume that $(\dot{\mathrm{A}})$ is given by the sector method, which measures the *total* concentration of radicals in the system: i.e., $(\dot{\mathrm{A}})+(\mathrm{RS})$.

If $k_a \div 10 \times k_{ct}$, as appears likely, then $(\dot{\mathrm{A}}) \div 10 \times (\mathrm{RS})$, and the true value of $(\dot{\mathrm{A}})$ will be about 90% of that given by the sector determination.

The sector method will also yield a weighted mean value of k_t. The error involved here will be small, as the k_t values for the $\dot{\mathrm{A}}$ and $\mathrm{R\dot{S}}$ radicals are probably of the same order of magnitude.

In the following calculations, $(\dot{A})$ in the pentene system is assumed to be equal to that given by the sector determination. This approximation is probably valid considering the accuracy of the over-all treatment.

Knowing (RSH), $-d(\mathrm{RSH})/dt$, $k(\mathrm{I})$, and λ, (Table I) the rate constants of the system can be evaluated as below.

From Equations [2] and [3],

$$\dot{A} = k(\mathrm{I})\lambda$$

then $k_{ct} = [-d(\mathrm{RSH})/dt]/[(\dot{A})(\mathrm{RSH})]$ and $k_t = k(\mathrm{I})/2(\mathrm{A})^2$.

The kinetic chain length of the reaction, v_k, has the value

$$v_k = [-d(\mathrm{RSH})/dt]/k(\mathrm{I}).$$

The calculated values for the three systems are given in Table II. It should be noted that only k_{ct} and k_t are rate constants: v_k and (A) are parameters of the system dependent on $k(\mathrm{I})$ and (RSH). Using lower rates of initiation, kinetic chain lengths of over 10^4 were observed in the 1-pentene system. The values of v_k given in Table II are not comparable, as different values of $k(\mathrm{I})$ and (RSH) were used in different systems.

TABLE II
CALCULATED RATE CONSTANTS T. = 25°C.

System	(A), M. liter^{-1}	k_{ct}, liters M.$^{-1}$	k_t, seconds^{-1}	Chain length, v_k
(1) Isoprene–mercaptan	4.0×10^{-8}	93	1.4×10^8	26
(2) Styrene–mercaptan	1.0×10^{-8}	2.6×10^3	5×10^8	980
(3) 1-Pentene–mercaptan	9.6×10^{-10}	2.5×10^6	6×10^{11}	1600

Activation Energy

Activation energies of 6.2 and 2.4 kcal. were found for the styrene and 1-pentene systems respectively over temperature ranges 25° to 70° for the former and 15° to 30° for the latter. These should correspond to the energies of activation for the transfer steps less half those of the termination steps. Since Bamford and Dewar (3) find the activation energy of termination for macro styryl radical to be 2.8 kcal. and a corresponding k_t of 2.8×10^6 at 25°C. we may safely conclude that the activation energy for the more reactive mercapto styryl radicals (with a k_t of 5×10^8 (Table II)) is only a few hundred calories and considerably less for the mercapto pentenyl. Consequently we find k_{ct} (styryl) $= 7.9 \times 10^7 \exp(-6.2/RT)$: k_{ct}(pentene) $= 2 \times 10^8 \exp(-2.4/RT)$.

DISCUSSION

These results illustrate strikingly the difference in behavior of conjugated and unconjugated double bonds in a free radical system, and the dependence of free-radical reactivity on structure.

(1) The *magnitude of the attack constant* k_a of $R\dot{S}$ radical on a conjugated structure can be estimated from the "inhibition" by styrene shown in Fig. 3. In the pentene system k_a is somewhat greater than 2×10^6, yet the reaction is effectively suppressed by a styrene concentration of the order of 1% of the pentene. Hence a conservative estimate would give k_a (styrene) 1×10^8 l.M.$^{-1}$ sec^{-1}. This may be compared with the propagation constant for macro styryl radical on styrene of 18.7 at 25°C. (3) or approximately 10^7 times faster! The magnitude of k_a for $R\dot{S}$ on a conjugated system permits only a very small activation energy for this process. Indeed this rate is quite comparable with with certain radical combination rates. The principal conclusion here is that a very much larger rate is achieved when the attack results in the disappearance of a localized electron on $R\dot{S}$ and the formation of the relatively delocalized mercapto styryl electron.

(2) The *termination constants* found at 25°C. also reflect the difference in delocalization energy (used synonomously with resonance stabilization) of the mercapto styryl radical, $k_t = 5 \times 10^8$, and the corresponding pentenyl, $k_t \doteqdot 6 \times 10^{11}$, or a ratio of about 1000. In turn the former may be compared with the termination constant for macro styryl radical 2.8×10^6 (3).

(3) The *dehydrogenation* of mercaptan by these radicals also is consistent with their structure. Here again the ratio of k_{ct} pentenyl to styryl is $2.5 \times 10^6/2.6 \times 10^3$ or about 1000. Again it is interesting to compare the k_{ct} of 365 at 30°C. for *macro* styryl, measurements of which have been made here (19, 1), with the value of 2.6×10^3 for *mercapto* styryl. This presents unique confirmation of the inference drawn from entirely independent evidence reported from this laboratory (10) that the addition of butyl mercaptan to butadiene produced the 1,4 addition product only: the resonance accounting for the 1,2 product being largely suppressed and hence leading to less electron delocalization.

(4) The *activation energies*. From absolute rate theory the usual approximation of partition functions for a radical–mercaptan reaction will lead us to conclude that the A values in the Arrhenius equation will be approximately the same and hence we should expect to find the difference in reactivity reflected entirely in the exponential. This is found to be the case and hence the difference in stabilization energy of the radicals is some multiple of the difference $(6.2-2.4) = 3.8$ kcal. If we choose the fashionable value of about 4, the difference between pentenyl and styryl due to electron delocalization amounts to approximately 15 kcal., which is in good agreement with quantum mechanical estimates (17).

(5) The *vinyl double bonds* are apparently capable of much more rapid reaction with such radicals as mercaptyl than was previously suspected. Indeed, it is only the inhibition of their reaction by the conjugated monomer present in the system which prevents rapid and extensive cross linking throughout the system. Subsequent papers will deal with these conclusions in a quantitative way.

(6) The *complications introduced* into a GR-S polymer by cross linking are chiefly the result of a competitive reaction of the single double bonds in the

dead polymers and the conjugated monomer for the radicals thus:

$$\dot{A}_s + P_r \xrightarrow{k_x} \dot{A}_{r+s}$$
$$\dot{A}_s + M \xrightarrow{k_p} \dot{A}_{s+1}$$

It is the ratio k_x/k_p which determines the extent of cross linking. In this study we have concluded that when $\dot{A}_s = R\dot{S}$ this ratio is of the order 5×10^{-3}. We believe this is close to the value for k_x/k_p even when the common attacking radical is styryl.

(7) The *role of oxygen* in the reaction can be explained as follows. Definite inhibition by oxygen was observed in the pentene system, but not in the styrene or isoprene systems (Fig. 2). Oxygen is known to react readily with most free radicals, forming a peroxide radical. This undoubtedly occurs in all three systems: in the pentene system, the resulting peroxide radical is apparently more stable than the pentene $\dot{A}$ radical, and hence the reaction is retarded. In the styrene or isoprene systems, the peroxide radical is apparently of approximately the same or slightly greater reactivity than the $\dot{A}$ radical, hence its substitution in the kinetic chain does not affect the reaction rate in a measurable way. In other words we conclude that oxygen plays the same role in the pentene reaction as styrene does.

The oxygen in the pentene system undoubtedly lowers the observed value of $d(M)/dt$: this was shown by the increased rates observed in the degassed systems. Thus the true k_{ct} value for pentene is probably even higher than the one reported.

ACKNOWLEDGMENTS

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LIGHT-SCATTERING AND SEDIMENTATION STUDIES OF BOVINE SERUM ALBUMIN AT LOW pH[1]

By M. E. Reichmann[2] and P. A. Charlwood

ABSTRACT

Light-scattering measurements of bovine serum albumin made at pH 1.9 in 0.1 M–0.45 M potassium chloride show that the molecule is not dissociated, but has the same molecular weight as in neutral solution. At pH 1.9 in the absence of salt aggregation occurs, the extent increasing with time. The sedimentation constant at pH 1.9 increases from 3.2S in 0.1 M potassium chloride to 3.6 in the 0.5 M salt, compared with 4.3 in neutral solution. These differences are ascribed to changes of molecular shape.

INTRODUCTION

The kinetic unit of a protein dissolved in aqueous salt solutions is probably an ordered entity, and not merely a randomly coiled polypeptide chain. As Pauling and collaborators (16, 19) have pointed out, the stability of the structure may be ascribed largely to the cumulative strength of the hydrogen bonds between the carbonyl groups of some peptide links and the amino groups of others, although certain covalent cross-links may also make a contribution to the rigidity. Conditions which promote the breaking of hydrogen bonds could cause changes of size or shape, or even dissociation. The hemoglobin molecule has been shown to dissociate in urea solution (4) and that of insulin at acid pH (18).

Dissociation would be precluded for a protein molecule composed of a single polypeptide chain. End group determinations with bovine serum albumin have revealed a single α-amino terminal group per molecule (26, 27), suggesting a single chain. Recent viscosity and optical rotation studies (32) have been taken to indicate an isotropic swelling of the albumin molecule at acid pH, but no dissociation. On the other hand, Weber (29, 30) originally interpreted his results on the polarization of fluorescence of labelled molecules as demonstrating dissociation under acid (or alkaline) conditions. To decide between these conflicting views, the weight average molecular weight of bovine serum albumin at acid pH was determined by light-scattering observations at various salt concentrations, supplementary information being obtained from sedimentation measurements.

MATERIALS AND METHODS

The bovine serum albumin was supplied by Armour and Co. (Lot R370. 295B). The protein solutions were prepared by diluting aqueous solutions with the appropriate solvent, and dialyzing against several changes of solvent. Solvents were prepared by adding concentrated hydrochloric acid to salt solutions. The pH of both solvent and solution was checked in a Beckman

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[2] *National Research Council Postdoctorate Fellow, 1953–54.*

model G pH meter. The protein concentrations were calculated from measurements of optical density (at 2800 Å) in a Beckman model DU spectrophotometer, using the extinction coefficient 6.6/gm. albumin/100 ml./cm. in water at neutral pH (6).

A B.S. Light-Scattering Photometer, manufactured by the Phoenix Precision Instrument Co., Philadelphia, was used. The calibration of this type of photometer, to give reduced intensities in absolute units, has been reported by Brice *et al.* (3). All light-scattering measurements were made at 4370 Å. The refractive increment of the albumin (dn/dc) was taken as 0.195 (10), giving $2\pi^2 n_0^2\,(dn/dc)^2/N\lambda^4(=K)$ the value 6.2×10^{-7}. Because of the low pH, glass Erlenmeyer or cylindrical cells had to be substituted for the usual cemented square ones. Calibration of the cells was carried out as described by Doty and Bunce (8). Details of the technique of preparing dust-free solutions and of successively diluting them in the cell are to be found elsewhere (21).

Sedimentation measurements were made using the Spinco ultracentrifuge, in the usual way (5). Protein concentrations of 0.1% and 0.25% were used, at potassium chloride strengths ranging from 0.1–1.0 *M*. Both normal (12 mm.) and long (30 mm.) cells were used, some having metal, and others plastic centerpieces. The maximum rotor speeds which could be used with the normal and long cells were 59,780 and 50,740 r.p.m. respectively. The results did not appear to be influenced by these variations.

RESULTS

The molecular weight found for bovine serum albumin in 0.1 *M* sodium chloride (pH 5.4), 77,000–79,000, is in good agreement with values found in other light-scattering studies (9, 10, 13). In Fig. 1 is shown a plot of Kc/R_{90} against albumin concentration in a solution at pH 2.9 free from added salt.

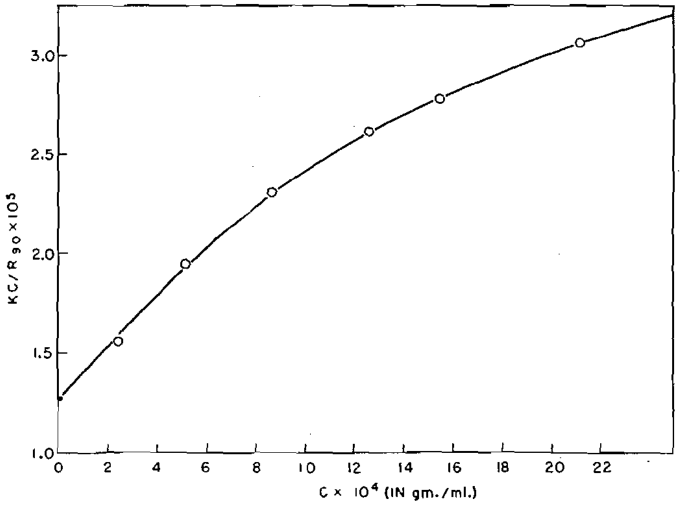

FIG. 1. The intensity of light scattered at 90° from a solution of bovine serum albumin in water, as a function of protein concentration, pH 2.9.

Here R_{90} is the reduced intensity of the light scattered at 90° and c is the protein concentration in gm./ml. In accordance with the basic equation $Kc/R_{90} = 1/M+2\ Bc$ (M = molecular weight, B = second virial coefficient), the intercept obtained by extrapolating to $c = 0$ is the reciprocal of the molecular weight, while the limiting slope is twice the second virial coefficient. The molecular weight given by the intercept in Fig. 1 is the same as in 0.1 M sodium chloride (pH 5.4). The high positive value of the second virial coefficient in Fig. 1 (about 1.5×10^{-2} ml.moles/gm.^{2}) is a measure of the repulsive coulombic forces between the albumin molecules, due to the high net charge at this pH. Both M and B at pH 2.9 are in excellent agreement with the data of Doty and Steiner at pH 3.3 (9).

Below pH 2.9, in the absence of salt, bovine serum albumin undergoes aggregation, followed by precipitation, as revealed by a marked opacity of the solution upon standing. That the precipitate consisted of protein, and not of fatty acid impurities, was demonstrated by a Kjeldahl nitrogen analysis. Since the extent of aggregation increased with time, no reproducible measurements of molecular weight could be made below pH 2.9 in the absence of salt. Thus measurements taken about four hours after the pH had reached 1.9 gave a molecular weight of about 120,000. This is illustrated by Fig. 2, which shows the relation between Kc/R_{90} and c at pH 1.9, in the absence of salt. Similar findings have been made by Goring (12), who followed the rate of growth of aggregates.

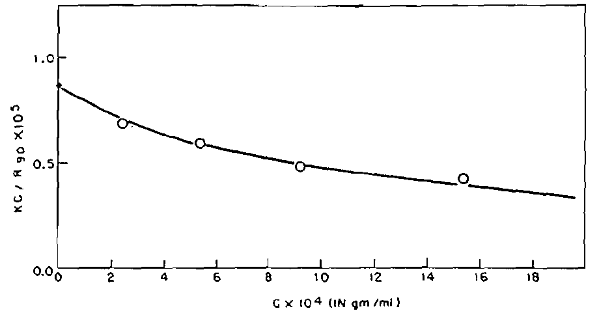

FIG. 2. The intensity of light scattered at 90° from a solution of bovine serum albumin in water, as a function of protein concentration, pH 1.9.

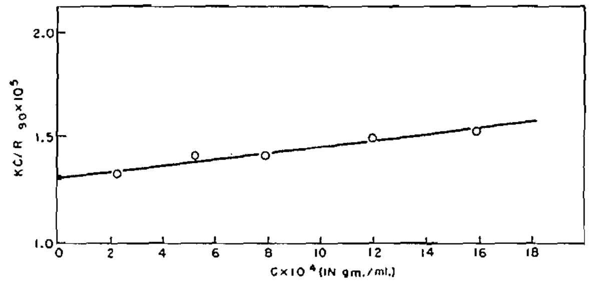

FIG. 3. The intensity of light scattered at 90° from a solution of bovine serum albumin in 0.1 M potassium chloride, as a function of protein concentration, pH 1.9.

Aggregation of bovine serum albumin at pH 1.9 is prevented by 0.1 *M* potassium chloride. Light-scattering measurements in this solvent (Fig. 3) lead to an intercept corresponding to a molecular weight of 77,000, the same as at neutral pH. The behavior at concentrations of 0.2 *M*, 0.35 *M*, and 0.45 *M* potassium chloride is shown in Fig. 4. Four light-scattering cells were used to obtain the results shown in Fig. 4. Each cell contained 0.2 *M* potassium chloride (pH 1.9) initially, but a different concentration of protein. When the scattering intensity at 90° had been measured, a concentrated solution of potassium chloride was added from a pipette to make the strength 0.35 *M* and the measurement was repeated. Similarly a further series was obtained in 0.45 *M* salt. It is clear that the molecular weight was not altered by this treatment. Moreover, repetition 24 hr. later of the measurements in the 0.45 *M* solution showed that no alteration occurred on standing.

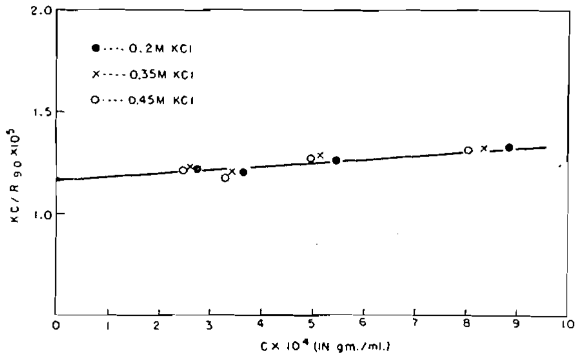

FIG. 4. The intensity of light scattered at 90° from bovine serum albumin solution at various salt concentrations, as a function of protein concentration, pH 1.9.

The variations in sedimentation constant (at pH 1.9) with increasing potassium chloride concentration are shown in Fig. 5. The figures, which are expressed in Svedberg units (S) have been corrected to water at 20°, assuming the normal partial specific volume, $\bar{v} = 0.734$ (7). Near neutrality, and at

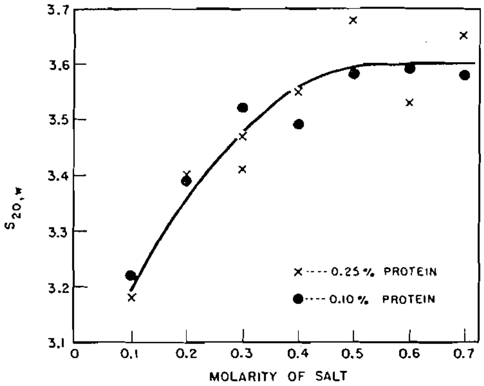

FIG. 5. Sedimentation constants of bovine serum albumin at pH 1.9 in potassium chloride solutions.

similar protein concentrations, the corrected sedimentation constant is about 4.3 (23). In 0.1 *M* potassium chloride, at pH 1.9, Fig. 5 indicates a value of 3.2. With increasing salt concentration this figure rises to about 3.6 at 0.5 *M* potassium chloride. Above 0.5 *M* the pattern becomes complicated as an increasing proportion of the material is aggregated. A little precipitates on dialysis, a portion sediments very rapidly, and some produces a second peak which gradually separates from the main peak (Fig. 6). The points in Fig. 5 at concentrations of potassium chloride greater than 0.5 *M* refer only to measurements made on the slowest peak when it is free from the influence of the aggregated fractions. At 0.6–0.7 *M* measurements become inaccurate and depend on the time of dialysis.

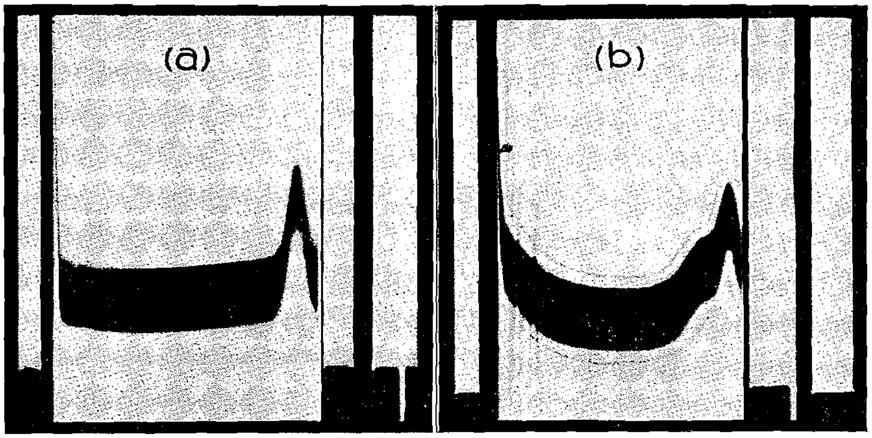

PLATE I

FIG. 6. Ultracentrifuge patterns of bovine serum albumin at pH 1.9 in (*a*) 0.2 *M* potassium chloride, (*b*) 0.8 *M* potassium chloride. Protein concentration 0.25%. Exposures 16 min. after reaching full speed (59,780 r.p.m.). Sedimentation is from right to left.

DISCUSSION

The light scattering results of Fig. 3 indicate clearly that the molecular weight of bovine serum albumin is the same (in 0.1 *M* potassium chloride) at pH 1.9 as at neutral pH. Weber originally suggested that the decrease in the polarization of fluorescence of conjugates of the albumin under similar conditions might be caused by dissociation (29, 30). Since light-scattering measurements preclude this possibility, an alternative interpretation must be found. An increase of internal degrees of freedom for the conjugate group is one possibility now entertained by Weber (31).

Evidence put forward in support of the concept of dissociation included a high diffusion constant ($D_{20,\mathrm{w}} = 6.85 \times 10^{-7}$ c.g.s. units) and a low sedimentation constant ($s_{20,\mathrm{w}} = 2.7$) at pH 1.8 (30). It seems probable that insufficient electrolyte was present in the diffusion experiments, and that the results are anomalously high. According to Dr. R. A. Kekwick (14), who carried out the sedimentation, the figure of 2.7 was not obtained by extrapolation to zero protein concentration, but refers to a 1% solution. Moreover, diffusion potentials would not be eliminated at the salt concentration used, so that the measured value of s is probably smaller than $s^0_{20,\mathrm{w}}$. An erroneous figure for the molecular weight is, therefore, obtained by the use of these sedimentation and diffusion values. It is interesting to add that at 0.4% protein (in a solution containing H_3PO_4 0.124 M, KH_2PO_4 0.206 M, pH 2.3) values of $s_{20,\mathrm{w}}$ and $D_{20,\mathrm{w}}$ of 3.68 and 4.49 respectively have been observed by Dr. Kekwick (14).

The earliest sedimentation measurements on albumin at low pH were made by Svedberg and Sjögren (24) using horse serum albumin. Their observations, made in a restricted range of potassium chloride concentration, showed low values of s. Subsequently von Mutzenbecher (17) confirmed this by measurements on the albumin peak in the pattern given by horse serum. Work on bovine serum albumin has been referred to by Pedersen (20), although no details were published.

In the present experiments, the value of s increases steadily (Fig. 5) as the salt content of the solution ranges from 0.1 M up to 0.5 M. Above this s remains constant, for unaggregated material, within the increasing experimental error. The light-scattering results of Fig. 4 show that the increase in s up to 0.45 M potassium chloride is not due to aggregation. As there is no evidence for a systematic variation of s between 0.1% and 0.25% protein, the increase is not to be ascribed to suppression of diffusion potentials.

The β function of Scheraga and Mandelkern (22) depends only on the axial ratio of the ellipsoid which is hydrodynamically equivalent to the protein molecule. This treatment has recently been criticized by Tanford and Buzzell (25). The maximum value of β which they could obtain from combination of sedimentation and viscosity data in neutral solution was 2.13. If all the sedimentation figures are too low by about two per cent, as now seems highly probable (1, 28), this figure becomes 2.17. Values below 2.12 are meaningless in the Scheraga–Mandelkern interpretation. Thus the axial ratio in neutral solution may be considered to lie between 3:1 (for a prolate ellipsoid) and unity. A comparison with acid solution can be made as follows: M is taken to be the same, because of the evidence from light-scattering. It is assumed that $\bar{v}$ is unaltered. The intrinsic viscosities (32) are 0.036 and 0.097 for neutral and acid solution respectively. Provided $s_{20,\mathrm{w}}$ (Fig. 5) in 0.1 M salt at pH 1.9 is equal to $s^0_{20,\mathrm{w}}$ within experimental error, and since $s^0_{20,\mathrm{w}}$ in neutral solution is known (23), the ratio of the β functions in acid and neutral solution can be calculated as 1.04 i.e. $\beta = 2.26–2.20$ in acid, corresponding to axial ratios of 5.5: 1–4: 1, and equivalent volumes about 50% greater than in neutral solution. The validity of these calculations depends, of course, on the assumptions underlying the Scheraga–Mandelkern theory (25). The axial ratios and equivalent volumes are highly sensitive to errors in the experimentally determined factors.

The increased viscosity of horse serum albumin at low pH was attributed by Björnholm *et al.* (2) to aggregation. The light-scattering results (Figs. 2, 3, and 4) indicate that this explanation is not applicable to bovine serum albumin in the presence of salt. Yang and Foster (32) suggested that the increase in viscosity was due to a large isotropic expansion of the albumin molecule. In their opinion, since no birefringence of flow was observed, significant unfolding was unlikely. The accuracy of this method is, however, low for a small molecule.

Hypotheses consistent with the observed results can be formulated in terms of the theories of Kuhn *et al.* (15) or Flory (11). At pH 1.9 in water there is an expansion of the molecule, due either to repulsive electrostatic forces (15), or to a Donnan effect between the intramolecular solution and that surrounding the molecule (11). The expansion is probably accompanied by unfolding, which exposes some sites for interactions between molecules, and results in the time-dependent aggregation (cf. Björnholm *et al.* (2)). The introduction of 0.1 M salt decreases the electrostatic intramolecular forces (15), or the Donnan term (11), reduces the extension of the molecule, and the sites of intermolecular action are no longer exposed. However, as the sedimentation constant is low, the size (volume), and shape are not the same as in neutral solution. Addition of potassium chloride, up to 0.5 M, results in further contraction of the molecule (and increase in s), in accordance with the theories (11, 15). Since solubility restrictions prevent accurate measurements above 0.5 M salt, it is not possible to say whether the molecule would attain its normal configuration under those conditions.

ACKNOWLEDGMENTS

The authors wish to thank Drs. W. H. Cook and J. R. Colvin for their interest, helpful suggestions, and encouragement. The technical assistance of Mr. D. Muirhead is gratefully acknowledged.

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THE ROLE OF WATER IN THE FORMATION OF SODIUM TRIPHOSPHATE BY CALCINATION[1]

By J. D. McGilvery[2] and A. E. Scott[3]

The formation of sodium triphosphate by calcination, below the sodium triphosphate fusion point, of various phosphate mixtures of over-all composition $5Na_2O.3P_2O_5.xH_2O$ was investigated. Water plays an important role, decreasing the amounts of pyrophosphate and high molecular weight polyphosphate impurities and increasing the reaction rate under certain conditions. It is suggested that water catalyzes the reactions by: (1) facilitating ionic diffusion, (2) hydrolyzing —P—O—P— linkages, and (3) assisting in the crystallization of sodium triphosphate. With ortho- and pyro-phosphate mixtures temperatures of about 300°C. and higher are necessary for the rapid formation of sodium triphosphate. With glasses of the composition $5Na_2O.3P_2O_5$ good yields may be obtained at temperatures as low as 250°C. when water is present.

INTRODUCTION

The thermal dehydration of hydrogen orthophosphates to form condensed phosphates has been the subject of numerous investigations since the phenomenon was first reported by Thomas Clark in 1827. However, most investigators have concerned themselves only with the nature of the final products and little thought has been given to the reaction mechanisms involved. It is only recently that a start has been made on these problems, notably by Audrieth and his co-workers (1, 3, 4) who have emphasized the acid–base nature of these high temperature reactions. Also an interesting attempt to elucidate the reaction mechanisms involved in the formation of sodium triphosphate from orthophosphates containing radioactive phosphorus has been reported by Herr and Meyer-Simon (2).

The present work is concerned primarily with the role which water plays in the formation of sodium triphosphate when various mixtures of sodium phosphates are calcined below their fusion points. Commercially the usual method of preparation of sodium triphosphate is by the calcination in a rotary kiln at 300 to 450°C. of an intimate mixture of disodium and monosodium orthophosphates in the mole ratio 2: 1. In spite of the commercial importance of this process no detailed study of the reactions involved or the effect of experimental conditions on them has been published. The present work was begun to remedy this situation and was extended to various other initial reactants when the importance of water to the reaction was realized. The approach to the problem was essentially a kinetic one.

EXPERIMENTAL

Materials

The intimate mixture of orthophosphates prepared commercially by flash evaporation on a drum-drier is often called ortho-mix. In the present experi-

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This paper was presented at the Annual Conference of The Chemical Institute of Canada at Windsor, Ont., on June 4, 1953.

[2,3] *Research Fellows, Ontario Research Foundation.*

ments a commercial ortho-mix sample containing slightly more than the theoretical amount of disodium orthophosphate was used. For this reason, the reaction was complete when the products consisted of about 96% sodium triphosphate and 4% sodium pyrophosphate.

Other phosphate mixtures used were:

pyro-mix—an intimate mixture of pyrophosphates obtained by heating ortho-mix at about 220°C. for several hours.

pyro-meta-mix—mechanical mixtures of $x\mathrm{Na_4P_2O_7} + (\mathrm{NaPO_3})_x$ (Maddrell's salt) or $3\mathrm{Na_4P_2O_7} + (\mathrm{NaPO_3})_3$.

tri-glass-mix—a glassy product obtained by quenching rapidly a melt of the composition $5\mathrm{Na_2O.3P_2O_5}$. The glass was quite opaque owing to the separation of sodium pyrophosphate crystallites.

Variables Studied

Four variables were investigated:

(1) the nature of the starting materials

(2) the calcination temperature

(3) the calcination time

(4) the partial water vapor pressure of the atmosphere surrounding the reaction mixture.

The general experimental pattern was to study the effects of water vapor pressure and calcination time at a series of fixed temperatures.

Apparatus

The kiln used in the calcination experiments is shown in Fig. 1. It is a copper block 10 in. × 3 in. × 2 in. wound with an electric heating element and lagged with asbestos. In the center of the block is a slot 8 in. × $\frac{3}{4}$ in. × $\frac{1}{8}$ in. into which is inserted a long dish made of platinum foil containing the sample

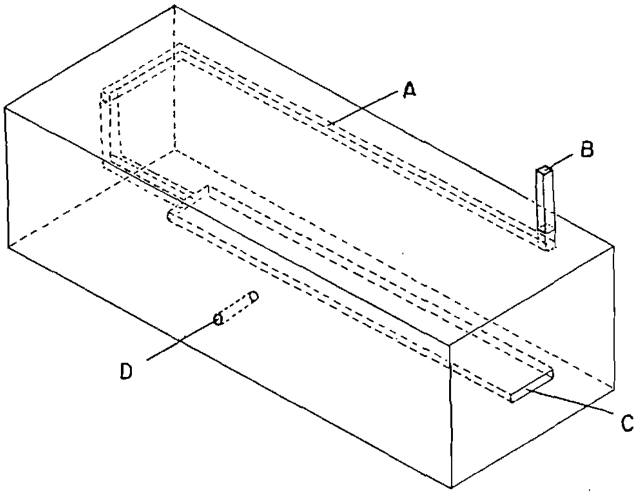


FIG. 1. Copper block kiln.
A—preheat channel
B—gas inlet
C—sample slot
D—thermocouple well

to be calcined. Further channels are cut in the block in such a manner that air injected into the block passes through about 28 in. of $\frac{1}{2}$ in. × $\frac{1}{8}$ in. channeling and exits over the sample. The humidity of the entering air is controlled by passage through two water bubbling towers maintained at the appropriate temperature to give the desired water vapor pressure. In 'anhydrous' experiments the air was dried by passage through a calcium chloride tower. To obtain 760 mm. water vapor pressure steam was passed through the block.

The temperature was measured using a chromel–alumel thermocouple embedded in the copper block about $\frac{1}{8}$ in. below the center of the sample slot. Preliminary tests indicated that the slot temperature at the sample position was within 2°C. of the block temperature and usually much closer than this.

The ortho-mix sample (0.5–1.0 gm.) was spread on the platinum dish in a layer less than 1 mm. in thickness to ensure a rapid approach to the desired operating temperature. Similarly at the end of the calcination time rapid quenching was obtained by pressing the dish onto a cold copper block.

Analysis

The use of filter paper chromatography for the separation and estimation of the various condensed phosphates greatly simplified the analytical work involved in this investigation. The general procedure was similar to that outlined by Westman, Scott, and Pedley (8) though the whole method has been considerably improved, for example, by the use of a commercial filter paper which does not require prewashing. This paper, Schleicher and Schuell's No. 589 Orange Ribbon, was used in most of the analyses.

Since linear polyphosphates greater in length than triphosphate were not well separated in the solvent systems used, they were lumped together for quantitative analysis and designated as 'high poly'. Cyclic metaphosphates such as trimetaphosphate were only observed in the pyro-meta-mix experiments. The analysis was thus reduced to a determination of ortho-, pyro-, tri-phosphate and high poly. No unknown compounds were detected on our chromatograms. The limit of detection was probably about 1% and the experimental error limits about ±5% in the early analyses. In subsequent work it was possible to determine the percentage of a constituent to ±1 by using the most recent techniques developed at the Foundation.

RESULTS

Effect of Temperature

The temperature regions in which the various condensation reactions occur were mapped out by obtaining the heating curve of ortho-mix from room temperature to about 400°C., and chromatographing samples of the mixture at various stages in the calcination. The heating curve is shown in Fig. 2. The inflections in the curve in the temperature range 50–150°C. (*A* and *B*) correspond to the removal of water of crystallization from the orthophosphates. The inflection at about 210°C. (*C*) corresponds to the formation of pyrophosphates and those at 290–330°C. (*D* and *E*) to the formation of triphosphates

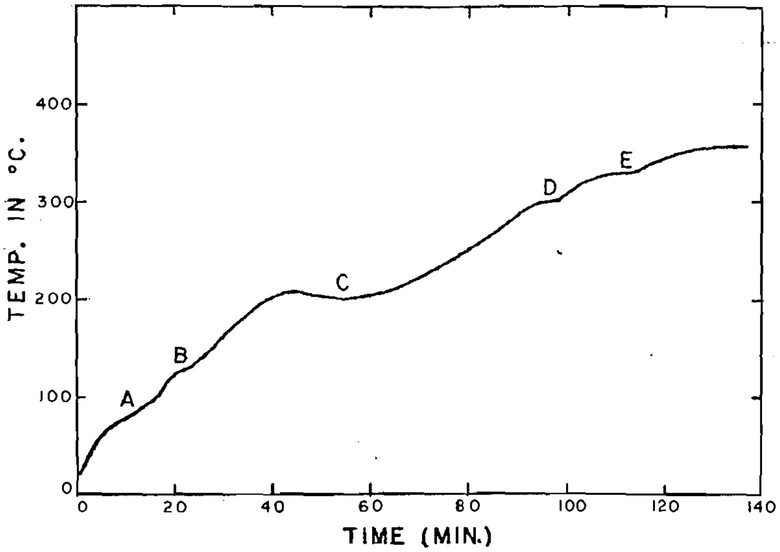


FIG. 2. Heating curve for the dehydration of ortho-mix.

and higher polyphosphates. It was evident from these preliminary experiments that temperatures of about 250°C. and higher were necessary to form triphosphate at an appreciable rate when the initial reactants were mixtures of ortho- or pyro-phosphates.

In Fig. 3 are shown the amounts of triphosphate formed in the calcination of ortho-mix as a function of the time at various temperatures. An atmosphere of water vapor was maintained over the reaction mixture in every case. It will be noted that the reaction proceeds at a rapid rate above about 300°C.

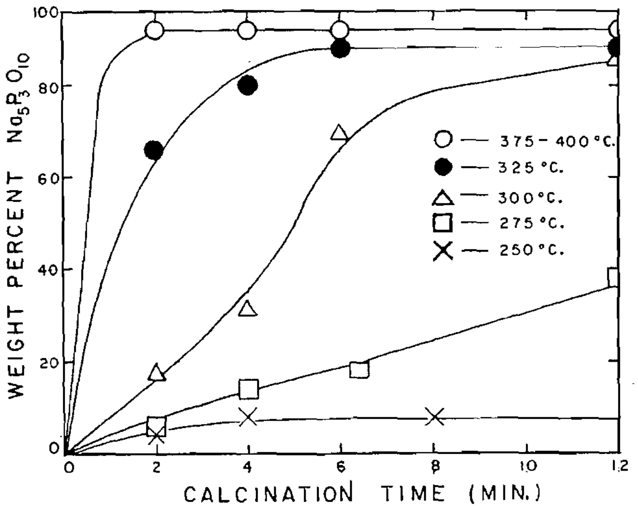


FIG. 3. The effect of temperature on the formation of sodium triphosphate by the calcination of ortho-mix in an atmosphere of water vapor.

Effect of Water Vapor Pressure

In studying the effect of water vapor pressure on the formation of triphosphate it must be kept in mind that in some of the systems studied, moisture was being evolved in the calcination process and this tended to confuse the effects of the water vapor added to the system. Thus when the initial reactants are orthophosphates or pyrophosphates, water of constitution will be evolved so that in the 0 mm. water vapor pressure experiments although the atmosphere over the reactants is essentially anhydrous the reacting mass itself will contain appreciable amounts of water for a portion of the time the sample is in the temperature region in which reaction can occur. On the other hand, the pyro-meta-mix and tri-glass-mix systems were truly anhydrous except for slight traces of water which such materials are known to retain even at high temperatures. Here one would expect the effects of water vapor to be most pronounced. This is indeed the case.

Mechanical mixtures of tetrasodium pyrophosphate and Maddrell's salt $(NaPO_3)_x$ in a 1: 1 molar ratio failed to react after 20 min. at 350°C. under an anhydrous atmosphere. Similar results were obtained with a mechanical mixture of tetrasodium pyrophosphate and sodium trimetaphosphate. However, if these mixtures are heated at the same temperature (i.e. 350°C.) in an atmosphere of water vapor, substantial amounts of triphosphate are formed. This is shown graphically in Fig. 4. It will be noted that the rate falls off long before the reaction is completed. This is believed to be associated with inadequate mixing rather than any inability of the components to react.

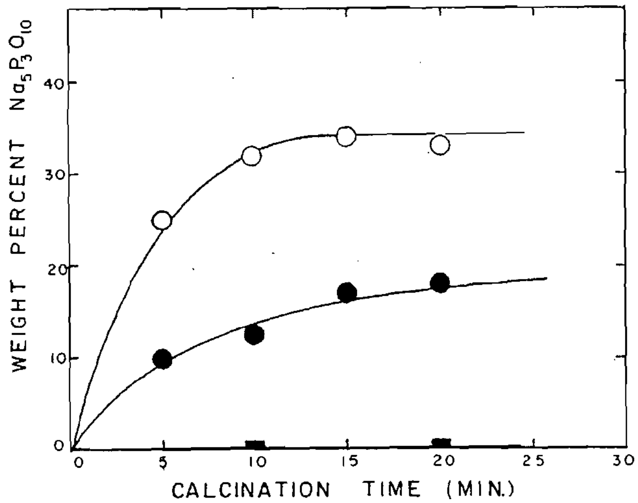


FIG. 4. The effect of water vapor on the formation of sodium triphosphate by calcination at 350°C. of mechanical mixtures of sodium phosphates which contain no water of constitution.
○—$(NaPO_3)_3+3Na_4P_2O_7$ at 760 mm. water vapor pressure.
●—$(NaPO_3)_x+xNa_4P_2O_7$ at 760 mm. water vapor pressure.
■—either mix at 0 mm. water vapor pressure.

Similar results are obtained at 350°C. when ortho- or pyro-mix is used as the starting material. Here, however, substantial amounts of triphosphate are formed at 0 mm. water vapor pressure presumably because of the water of constitution being evolved. Fig. 5 illustrates the effect of water vapor on the calcination of pyro-mix at 350°C. The situation thus disclosed is unusual, since ordinarily one would expect a condensation reaction in which water is formed to be retarded by the presence of water vapor.

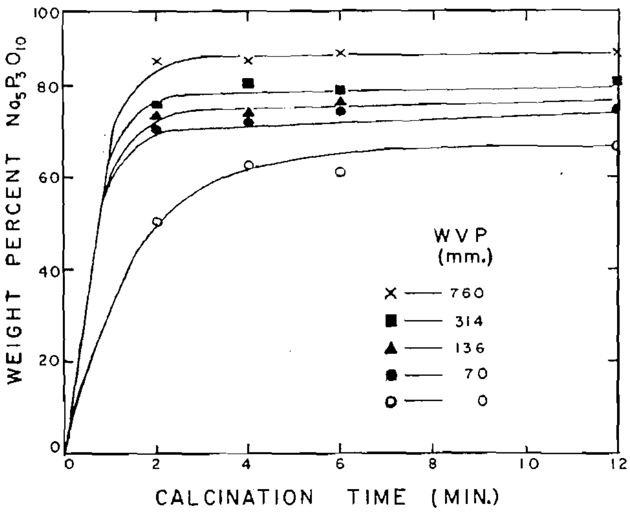


FIG. 5. The effect of water vapor on the formation of sodium triphosphate by calcination of pyro-mix at 350°C.

The foregoing examples of the effect of water vapor have all been in experiments at 350°C. The ortho-mix system has been studied more extensively than any of the others and it is found that at temperatures below about 300°C.

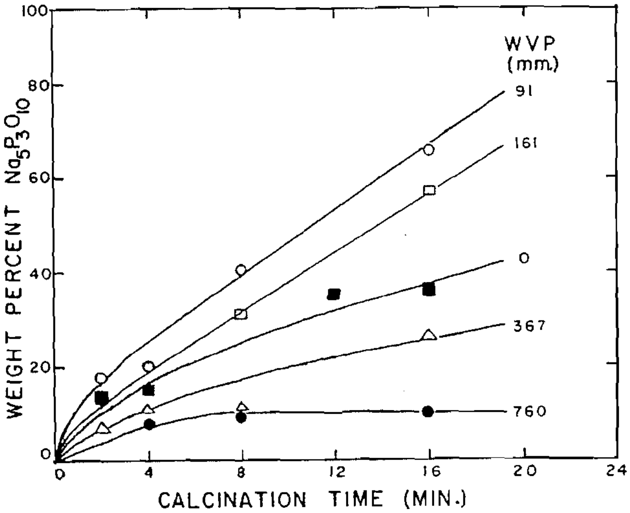


FIG. 6. The effect of water vapor pressure on the formation of sodium triphosphate by calcination of ortho-mix at 250°C.

the rate of formation of triphosphate goes through a maximum as the water vapor pressure is increased from 0 to 760 mm. Fig. 6 illustrates the effect at 250°C., the rate being a maximum in the neighborhood of 90 mm. water vapor pressure.

The tri-glass-mix system differs from the others in that a much more intimate mixture of reactants is present and they are in a noncrystalline form. This lack of crystallinity implies a higher energy system which will be metastable with respect to crystalline sodium triphosphate at temperatures below the melting point of sodium triphosphate (about 625°C.). Consequently it is not surprising that conversion to triphosphate is observed in this system at lower temperatures and even under supposedly anhydrous conditions. Indeed one method of manufacturing triphosphate is to rapidly cool a melt of the correct Na/P ratio and devitrify the glass obtained by tempering for long periods at temperatures in the range 500–600°C.

The present experiments show that this conversion of glass to crystalline triphosphate is greatly accelerated by the presence of water vapor and the extent of this conversion is increased, particuarly at lower temperatures. Fig. 7 illustrates the differences in conversion after six minutes at various temperatures under hydrous and anhydrous conditions. At temperatures of about 600°C. and higher in the presence of an atmosphere of water vapor a melt is obtained, the triphosphate content of which is only about 20 to 30%. Presumably the crystallization of sodium triphosphate does not occur under these conditions.

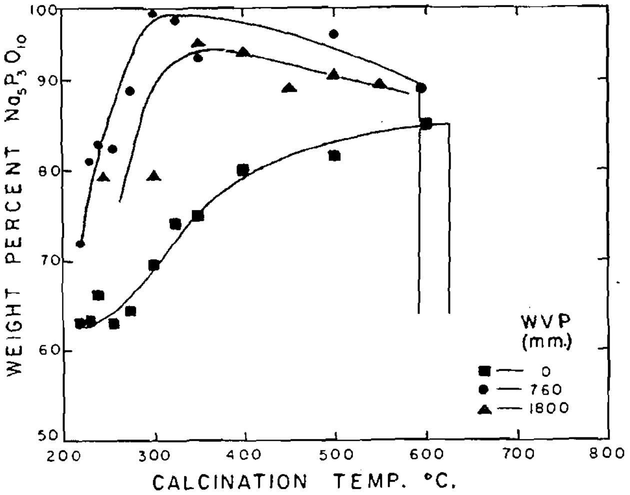


FIG. 7. The effect of water vapor on the formation of sodium triphosphate when a glass of composition $5Na_2O.3P_2O_5$ is calcined for six minutes at various temperatures.

Intermediates

It is of interest to consider now the appearance and disappearance of other constituents intermediate in the formation of triphosphate.

As we have noted earlier, cyclic metaphosphates were undetectable in any of the ortho-mix, pyro-mix, or tri-glass-mix experiments though trimetaphosphate was present in the pyro-meta-mix experiments as an initial reactant. It appears that in the more alkaline media the cyclic metaphosphates are not readily formed, the linear polyphosphates being favored. This is perhaps not surprising in view of the relative ease with which alkaline hydrolysis of cyclic metaphosphates occurs.

The usual products from ortho-, pyro-, and tri-glass-mix calcinations are pyrophosphate, triphosphate, and higher polyphosphates. In Fig. 8 is shown the change with time in the composition of an ortho-mix charge calcined at 250°C. and 161 mm. water vapor pressure. The general pattern is typical for ortho-mix calcinations, though the rates of appearance and disappearance of the various constituents and their relative proportions are dependent to a great extent upon temperature and water vapor pressure. This has already been discussed, with respect to triphosphate.

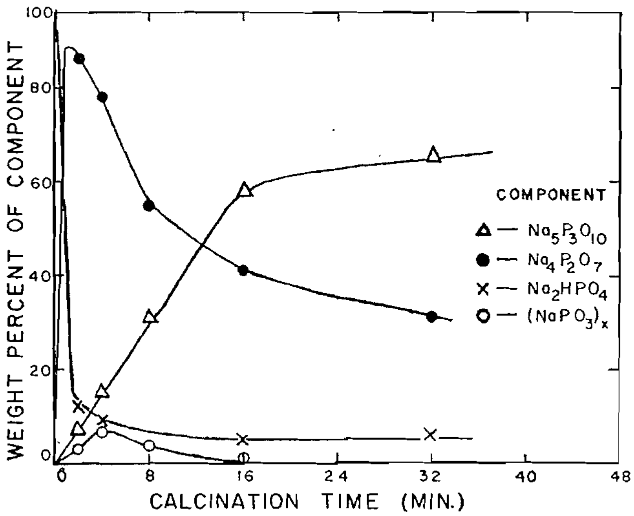


FIG. 8. The change in composition with calcination time of an ortho-mix sample calcined at 250°C. and 161 mm. water vapor pressure.

The appearance and nature of the higher polyphosphates is of some interest. The molecular weight of the higher polyphosphates increases with increasing temperature for a constant water vapor pressure. Thus at 250°C. and 161 mm. water vapor pressure significant amounts of tetraphosphate are present and all the material is soluble, whereas at 350°C. many of the higher polyphosphates are of such high molecular weight as to be insoluble. The effect of increasing the water vapor pressure at a constant temperature is to decrease the amount and the molecular weight of the higher polyphosphates formed. This decrease in the amount of high polyphosphate is demonstrated in a series of pyro-mix calcinations at 350°C. (see Fig. 9).

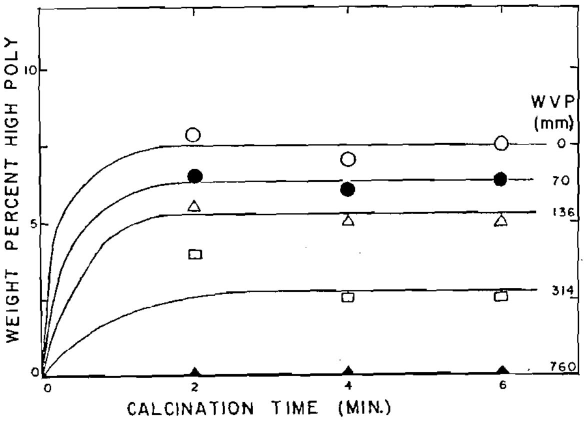


FIG. 9. The effect of water vapor pressure on the high molecular weight polyphosphate content of samples of pyro-mix calcined at 350°C.

DISCUSSION

It is evident from the foregoing results that moisture is almost as important as temperature in the formation of sodium triphosphate. To explain these observations we should like to suggest that the role played by water is threefold:

(1) it assists in ionic diffusion,

(2) it hydrolyzes —P—O—P— linkages,

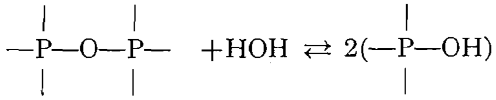
(3) it assists in the crystallization of $Na_5P_3O_{10}$.

Ionic Diffusion

In so far as the commercial preparation of ortho-mix on drum dryers is concerned it is doubtful whether a really intimate mixture can be obtained. There is little or no evidence of mixed crystals of di- and mono-sodium orthophosphate and so long as crystallization occurs we may expect discrete pockets of these compounds and their hydrates to be present. Therefore in the transformation of these materials to sodium triphosphate it is obvious that there must be a migration of Na^+ ions from those areas initially rich in Na^+ ion (i.e. where disodium orthophosphate crystals existed) to those areas initially poor in Na^+ ion (i.e. where monosodium orthophosphate crystals existed). If such a migration does not occur then dehydration will result in pockets of pyrophosphate and insoluble high molecular weight polyphosphates. This actually does occur to an increasing extent as the water vapor pressure is decreased. It seems reasonable to believe, therefore, that the presence of water vapor in the surrounding atmosphere assists in this ionic diffusion process. Whether the water vapor as such is effective in promoting diffusion or whether a liquid water phase is formed is not decided by our experiments.

Hydrolysis

As we have noted above, at low water vapor pressures the calcination of ortho- or pyro-mixes results in the formation of pyrophosphate and high molecular weight polyphosphates. Both pyro-meta-mix and the tri-glass-mix contain these components as initial reactants. For triphosphate formation to occur the higher polyphosphates must be degraded and the dimers (i.e. pyrophosphates) polymerized. It is suggested that the necessary scission of —P—O—P— linkages is effected very readily by water or water vapor at these temperatures. That thermal scission of these bonds does occur is suggested by the formation of triphosphate from tri-glass-mix under anhydrous conditions.[4] However, hydrolysis is probably much more effective, particularly at lower temperatures. In the presence of water vapor the —P—O—P— linkages are continually being broken and reformed so that an equilibrium of the type



$$-\text{P}-\text{O}-\text{P}- \;+\text{HOH} \rightleftarrows 2(-\text{P}-\text{OH})$$

is set up. Now if a Na^+ ion is exchanged for the H^+ ion in the terminal group further growth to form higher polyphosphates is blocked at this point. Conversely replacement of a Na^+ ion by a H^+ ion permits further growth at the point of replacement. Consequently, concurrent with the ionic diffusion already mentioned there are polymerization and degradation processes occurring, the products of which are to some extent stabilized by the distribution of Na^+ ions. If no crystallization occurred, the final equilibrium would be a nearly uniform distribution of Na^+ ion and an average phosphate chain length of three.

Crystallization

However, crystallization of $Na_5P_3O_{10}$ does occur and it is for this reason that nearly pure sodium triphosphate may be prepared by direct calcination. In a randomly organized system, although the average chain length may be three, the proportion of the trimer will be comparatively small (7). This situation is observed in the tri-glass-mixes. To get the high yields of triphosphate which are obtained, a breakdown of the random organization must occur—i.e. sodium triphosphate must crystallize out. It is suggested that this is facilitated by water vapor. Really this is simply another manifestation of the ability of water to promote diffusion, since crystallization will be dependent upon the diffusion of ions to the crystal surfaces.

The ability of a particular polyphosphate to crystallize is probably the criterion of whether or not that material may be produced in any purity by direct calcination. Thus the dimer (pyrophosphate), the trimer (triphosphate), and the very high molecular weight polymers such as Maddrell's salt are readily crystallizable and it is significant that these are the only species which have been prepared in a pure form without too much difficulty. It seems likely that the intermediate polyphosphates such as tetra-, penta-, hexaphosphate are not obtained in the pure form from melts of the appropriate Na/P ratios, not because of any inherent instability in these configurations but simply because they do not crystallize well.

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[4] *Although it is possible that traces of water in the glasses are responsible. These traces are very difficult to remove.*

Retardation of Rate

Thus far we have discussed the role of water vapor in assisting the formation of triphosphate and have ignored the fact that at lower temperatures in ortho-mix systems the rate goes through a maximum as the water vapor pressure is increased. However, this is quite compatible with the foregoing explanations.

It must be remembered that the hydrolysis of —P—O—P— linkages results in the degradation of triphosphate as well as higher and lower polyphosphates. Consequently the net rate of formation will be the difference between the trimer formed per unit time and the trimer hydrolyzed per unit time. At lower temperatures (<300°C.) in ortho-mix systems degradation by hydrolysis becomes the dominant effect of water vapor at water vapor pressures less than 1 atmosphere, and therefore a maximum occurs in the rate of formation of triphosphate. At higher temperatures (>300°C.) it seems probable that hydrolysis does not become a dominating process until water vapor pressures greatly in excess of 1 atmosphere are reached. Hence in our experiments at temperatures greater than 300°C. the rate always increased with increasing water vapor pressure.

Mechanism

Herr and Simon (2) conclude from their experiments with an ortho-pyro-mix that at 250–260°C. reaction occurs preferentially according to the equation

$$2Na_2HPO_4 + \tfrac{1}{2}Na_2H_2P_2O_7 \rightarrow Na_5P_3O_{10} + 1\tfrac{1}{2}H_2O$$

without the preliminary formation of pyrophosphate from the orthophosphate. However, the results of the present investigation show that the preferred first step in the polymerization process is the formation of pyrophosphate. Thus after two minutes calcination at 250°C. about 86% pyrophosphate is present (see Fig. 8) and even at 350°C. about 75% pyrophosphate is present after 0.5 min. calcination. That pyrophosphate should be the first product in the calcination process seems reasonable in view of the fact that dimerization occurs rapidly at about 220°C. while polymerization to higher polyphosphates does not occur with any rapidity even at 250°C. Furthermore, both tetrasodium and disodium dihydrogen pyrophosphate are readily crystallizable which is an important factor in determining calcination products.

The transition from the dimer to the trimer probably proceeds by many different paths, the common denominator being a process of formation of —P—O—P— linkages with the evolution of water and of destruction of —P—O—P— linkages by hydrolysis. Thus one path would probably be condensation of the dimer to the tetramer followed by hydrolysis to the trimer and the monomer:

$$2HP_2O_7^{3-} \rightarrow P_4O_{13}^{6-} + H_2O$$
$$P_4O_{13}^{6-} + HOH \rightarrow HP_3O_{10}^{4-} + HPO_4^{2-}$$

In support of this Westman, Scott, and Pedley (8) have found that hydrolysis of tetraphosphate does yield some triphosphate and orthophosphate, although the major product is pyrophosphate as Thilo (5) has observed.

The apparent absence of orthophosphate in most calcination products suggests that the reactions

$$HPO_4^{2-}+HP_nO_{3n+1}^{(n+2)-} \rightarrow P_{n+1}O_{3n+2}^{(n+3)-}+H_2O$$

occur with rapidity. When $n = 2$ the reaction suggested by Herr and Simon is obtained and this may well be an important reaction in the formation of triphosphate.

In the period between the breakdown of pyrophosphate crystalline structure and the formation of triphosphate crystalline structure the reaction mixture is probably an amorphous mass and it is in this period that the difficultly crystallizable higher polyphosphates (e.g. tetraphosphate, pentaphosphate) exist.

A somewhat similar conception of the dehydration mechanism, involving hydrogen ion migration, has been advanced by Thilo and Seemann (6). However they consider water evolution to occur when a proton encounters an —OH end-group. The course of the subsequent reaction is not discussed but presumably a tri-co-ordinated P atom is involved.

With tri-glass-mixes calcined under hydrous conditions the same mechanism is visualized, the only change being that the reactants are already in the amorphous condition noted above.

The formation of triphosphate by calcination of tri-glass-mix under anhydrous conditions presumably involves the breaking of —P—O—P— bonds by thermal scission* resulting in very reactive tri-co-ordinated terminal phosphorus atoms. Polymerization then occurs by the addition of these groups to the terminal oxygen atoms of phosphate chains. Sodium triphosphate separates by a crystallization process as in the hydrous calcinations.

ACKNOWLEDGMENTS

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**See footnote 4.*

AN ACCURATE METHOD OF ANALYSIS FOR SMALL QUANTITIES OF ETHYLENE[1]

BY A. SHEPP[2] AND K. O. KUTSCHKE

ABSTRACT

A procedure is described for the accurate analysis of ethylene in mixtures of ethane and ethylene by hydrogenation over a nickel–kieselguhr catalyst. Samples of ethylene as small as 0.03 cc. in mixtures of the order of 1.5 cc. of gas at N.T.P. can be determined to an accuracy of about one half per cent. Results are reported over a range of mixtures.

In photochemistry, the analysis of small quantities of ethylene is a common problem. In particular, when ethylene appears with ethane, a very accurate analysis is necessary if the difference between the two species is needed. In previous work in this laboratory such mixtures have been analyzed by either the Blacet–Leighton technique (4), or by the mass spectrometer. Accuracy of the order of 1 or 2% is achieved by these methods if samples of 0.2 cc. of gas at N.T.P. are supplied; this is sufficient for most work. The method of hydrogenation over a nickel–kieselguhr catalyst was developed to determine ethyene to better than one per cent on small samples of gas.

Much work has been done on the catalytic hydrogenation of ethylene*, but hydrogenation is usually not carried to completion and is not discussed as an analytical technique. Catalytic hydrogenation was used by Trenner *et al.* (6) to analyze accurately for rather large samples of ethylene. In photochemistry, the technique has been used before (2, 3, 5) but not to a high degree of accuracy, and a procedure has not been described. In this work, such a procedure is described, and a range of ethane–ethylene mixtures is studied.

In principle, the method is as follows. A known excess of hydrogen gas (H) is measured into the nickel catalyst chamber. A known sample of gas (W) containing ethylene (E) is then measured into the oven. When the reaction is over, the quantity of ethylene is given in terms of the final quantity of gas (F) by

$$E = H + W - F. \qquad [1]$$

If the condensable gas (or gases) is frozen in liquid nitrogen before the final reading is taken so that (T) is the final quantity of noncondensable gas, then ethylene is given by

$$E = H - T. \qquad [2]$$

APPARATUS

The catalyst chamber is a small glass bulb (about 4 cc.) maintained at 100 ± 2°C. by an oven. It leads through a capillary "U" tube trap through one stopcock to the high vacuum, or through another stopcock to the Toepler

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[2] *National Research Laboratories Postdoctorate Fellow 1953–.*

**See, for instance, papers by Beeck, O., Eley, D. O., Rideal, E. H., Twigg, C. H., etc., in Discussions Faraday Soc. 8. 1950.*

pump-burette (T-burette). The unthermostatted connecting tubing was kept as short as possible. The total volume of the T-burette, when the mercury is pulled down to a fixed mark, is about 350 cc. The large standard volume in this burette is 1.4356 cc., so that the intrinsic error in measuring gas samples (assuming 0.2 mm. uncertainty in the pressure reading) is about 0.0003 cc. of gas at N.T.P. Hydrogen could be pumped into the T-burette from a supply line, and sample bulbs of ethane and ethylene could be introduced through a tapered joint and stopcock.

MATERIALS

Commercial hydrogen was passed through a liquid nitrogen trap and passed slowly through a palladium thimble at 300°C. Ethylene and ethane were also commercial products and were degassed by bulb to bulb distillation. The nickel–kieselguhr catalyst was prepared according to the specifications of Adkins (1). (Kieselguhr is sold by Johns–Manville as "Filter-Cel". It is cleaned in nitric acid, and a water solution of nickel carbonate is ground into it. A solution of ammonium carbonate is mixed in, and the nickel carbonate – kieselguhr is filtered off. The product is put in an oven at 110°C. and 20 mgm. of the resulting nickel oxide – kieselguhr is pulverized and put in the catalyst chamber.) The catalyst is reduced as follows. About 100 mm. of hydrogen is put over the catalyst, and the chamber is kept at about 400°C. for three hours, with a solid carbon dioxide bath on the trap to condense the water. The hydrogen and water are then pumped off and the procedure repeated twice, for periods of several hours. The temperature of the oven is then lowered to 100°C. and 100 mm. of hydrogen is kept over the catalyst for a day. After this treatment, small samples of hydrogen can be recovered from the oven to an accuracy of 0.0003 cc. of gas at N.T.P.

As is well known* (6), hydrocarbons will crack over a nickel catalyst at temperatures of 200°C. or higher, but at 100° no cracking products are observed. Thus, 100°C. was used for hydrogenation. Because a hydrogen layer adsorbs on the nickel, the oven must be kept at this temperature at all times after the above treatment, and during actual hydrogenation the excess hydrogen must always be introduced into the oven first. It was observed that hydrogen has a vapor pressure over the nickel catalyst. By exposing the chamber to the open T-burette, a quantity of gas corresponding to a vapor pressure of about 10^{-3} mm. can be taken off. Since it takes several minutes for this equilibrium to be attained the results need not be corrected for this extra gas if readings are taken very quickly. Adsorption of ethane on the catalyst makes complete recovery by expansion into the T-burette impossible. Therefore equation [1] is not used, but at the conclusion of a run, the resulting ethane is frozen in liquid nitrogen, and equation [2] is used.

By taking rapid readings, the vapor of ethane at liquid nitrogen temperature does not have time to saturate the burette, so that again no correction for extra gas need be made. The hydrogen samples used were always in excess of

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See, for instance, papers by Beeck, O., Eley, D. O., Rideal, E. H., Twigg, C. H., etc., in Discussions Faraday Soc. 8. 1950.

the total hydrocarbon mixture, usually sufficiently in excess so that about 0.1 cc. of hydrogen gas remained. The method does not seem dependent on the ratio of hydrogen to ethylene (cf. Taylor *et al.* (3)).

PROCEDURE

The procedure was as follows. Samples of ethane and ethylene were measured into the T-burette and stored in a pump-down trap. A hydrogen sample was pumped in, measured, and expanded into the catalyst chamber. The hydrocarbons were then pumped back into the T-burette, remeasured as a check, and opened to the chamber. The gases were immediately mixed by expansion into the burette and compressed back to the chamber. Mixing was done again at intervals of one quarter, one half, one, and two hours, and thereafter as convenient. This mixing is very important. At each mixing the volume of the gas drawn into the burette was measured, and using equation [1], an estimate of the conversion was made. When these estimates consistently read 100% ethylene converted, the reaction could be stopped. At the conclusion of the run, condensables were carefully frozen by liquid nitrogen on the "U" tube trap, and the hydrogen in the chamber was determined as follows. The stopcock to the T-burette was opened, and the gas quickly expanded in by drawing down the mercury. With the stopcock closed, the gas was measured, and then pumped off. This procedure was repeated a second time. Since the ratio of these two gas quantities was about 0.012, and since the total sample size was of order 0.1 cc., all measurable material was obtained in these two samples. The catalyst chamber was then opened to the vacuum pumps, and the liquid nitrogen flask removed. After about ten minutes of pumping, the chamber was shut off until the next run. A few minutes' pumping always preceded the next introduction of a hydrogen sample.

RESULTS

Results are shown in Tables I and II. Runs *A*, *B*, and *C* are on samples of approximately 30%, 50%, and 70% ethylene; runs *D* are on 100% ethylene. Table I shows the approximate per cent reaction at the first three mixing time

TABLE I
PER CENT OF ETHYLENE REACTED

Run		Time			% C_2H_4	cc. at N.T.P. of C_2H_4
		15 min.	30 min.	1 hr.		
A	1	88	98	100	27.3	.0303
	2	86	96	98	33.8	.0414
	3	88	98	100	33.1	.0425
B	4	91	99	100	52.4	.0471
	5	98	100	100	49.4	.0451
C	6	86	97	98	69.1	.0798
	7	88	97	99	65.5	.0901
D	8	93	99	100	100	.1028
	9	96	100	100	100	.0651

intervals. The correlation between sample size and per cent of ethylene is interesting. Thus, runs *A* go slower than runs *B*, presumably because the large initial pressure of ethane hinders the ethylene in its diffusion to the catalyst surface during the first minutes. Runs *C* go at about the same speed as *A*, having more ethylene to react, but less ethane in the way. Runs *D* go about as fast as runs *B*, having more ethylene, but no ethane initially. Table II demonstrates the accuracy to be expected from this method and shows that on this size sample a reaction time of five hours should be sufficient to ensure complete hydrogenation.

TABLE II*

Run	C_2H_4	C_2H_6	% C_2H_4	H_2	Time	C_2H_4 determined	% C_2H_4 determined
A 1	.0303	.0807	27.3	.1258	2 hr.	.0301	27.1
2	.0414	.0809	33.9	.1321	5 hr.	.0407	33.3
3	.0425	.0857	33.2	.1425	12 hr.	.0423	33.0
B 4	.0471	.0427	52.4	.1336	2 hr.	.0468	52.1
5	.0451	.0461	49.5	.1391	5 hr.	.0452	49.6
C 6	.0798	.0356	69.2	.1616	2 hr.	.0800	69.3
7	.0901	.0474	65.5	.1546	5 hr.	.0904	65.7
D 8	.1028	0	100	.1429	5 hr.	.1025	99.7
9	.0651	0	100	.1387	5 hr.	.0655	100.6

**The unit of gas is cc. at N.T.P.*

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THE BIOGENESIS OF ALKALOIDS

XII. THE MODE OF FORMATION OF THE TROPINE BASE OF HYOSCYAMINE[1]

By Edward Leete[2], Léo Marion, and Ian D. Spenser[2]

ABSTRACT

Ornithine-2-C^{14} was fed to mature *Datura stramonium* plants and radioactive hyoscyamine was isolated from the whole plant, while the hyoscine obtained from the plant was inactive. Systematic degradation of the radioactive alkaloid indicated that all the activity was present in the 1 or 5, or both, positions of the tropine half of the alkaloid indicating that ornithine is a precursor of the ring system in tropine, but not of scopine, the base present in hyoscine.

INTRODUCTION

The biogenesis of the tropine molecule has received much discussion (3, 8, 18, 19), probably because of the facile *in vitro* synthesis of tropinone under "so-called physiological conditions" from succindialdehyde, methylamine, and acetone dicarboxylic acid (22). Ornithine has been suggested as the amino acid which acts as a precursor of the pyrrolidine ring in tropine. In support of this, ornithine has been detected in the pressed juice of *Atropa belladonna* sprouts (7) and acetyl ornithine has been found in various plants of the *Corydalis* species (13, 14). It was thus decided to feed radioactive ornithine labelled on the carbon atom carrying the carboxyl group to *D. stramonium* plants which produce hyoscyamine and hyoscine. These alkaloids were isolated from the plant after a suitable period of time and separated by paper chromatography and by partition chromatography on a celite column according to an established method (21). The hyoscine was inactive but the hyoscyamine was active. It was degraded according to the scheme in Fig. 1 to determine the positions of activity. The hyoscyamine (I) was hydrolyzed with dilute sodium hydroxide solution to give tropine (II) and tropic acid (III) (25). According to Liebermann (11) the action of chromic acid and sulphuric acid on tropine gave a mixture of tropinic and ecgonic acids. Later, Willstätter (24) showed that chromic acid on either of these acids produced N-methylsuccinimide (IV). In the present work prolonged oxidation of tropine with chromic and sulphuric acids gave, under the best conditions, a 10% yield of N-methylsuccinimide. The action of phenyl magnesium bromide on N-methylsuccinimide has been investigated by Lukeš and Prelog (12) who isolated from the reaction mixture 1-methyl-2,5-diphenylpyrrole (V) and 1-methyl-2-phenyl-2-hydroxy-5-oxo-tetrahydropyrrole. In the present work the former compound was obtained pure in 19% yield by prolonging the reaction time and using a large excess of the Grignard reagent. Oxidation of the pyrrole derivative with potassium permanganate caused fission of the double bonds to give a mixture of oxalic

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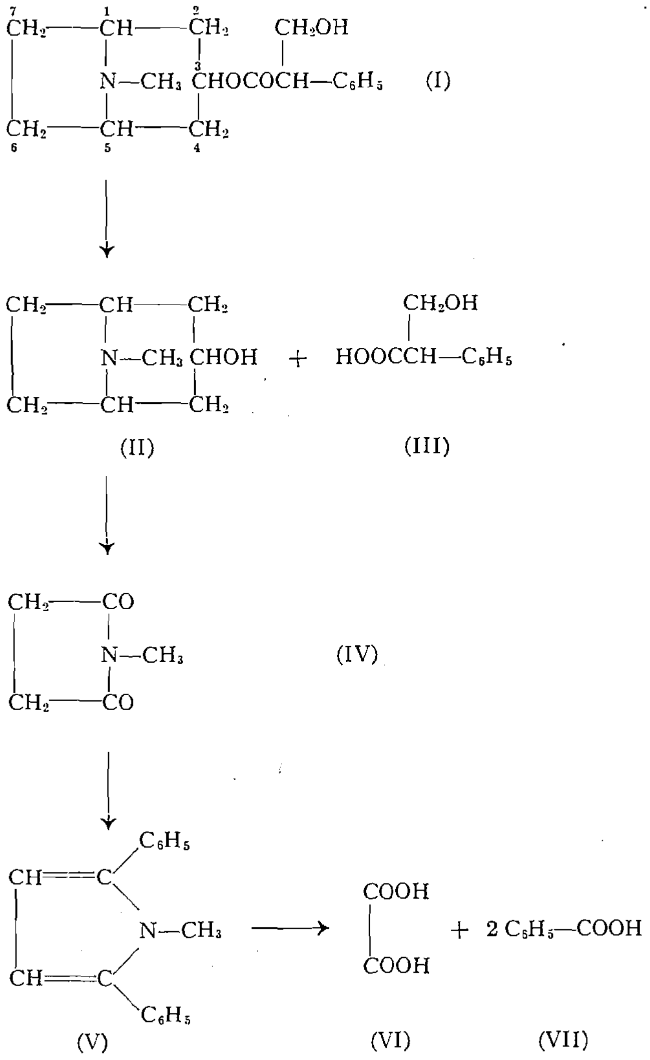

FIG. 1. Degradation of the hyoscyamine.

(VI) and benzoic acids (VII) which were separated by crystallization from water, the oxalic acid being finally isolated as the sparingly soluble calcium salt.

EXPERIMENTAL[3]

Synthesis of Radioactive Ornithine

C^{14}-methyl labelled sodium acetate was converted to ethyl cyanoacetate-2-C^{14} by the method previously described (9) and this was used to prepare DL-ornithine-2-C^{14} by the method of Fields *et al.* (5).

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[3] *All melting points are corrected.*

Administration of the Radioactive Ornithine and Isolation of the Alkaloids

D. stramonium seeds were germinated in soil and then allowed to grow in soil for four months with transplantations as required. The almost mature plants were then transferred to a hydroponics setup with the roots of each plant dipping into a beaker containing an aerated nutrient solution. The solution was kept in the dark while the upper part of the plant was in the light. The nutrient solution contained (per liter): KNO_3 (505 mgm.), $Ca(NO_3)_2 . 4H_2O$ (1180 mgm.), $MgSO_4 . 7H_2O$ (495 mgm.), KH_2PO_4 (272 mgm.), $FeSO_4 . 7H_2O$ (2 mgm.), plus traces of micronutrients (B, Mn, Zn, Mo, Cu). Each plant was furnished with about 500 cc. of nutrient solution which was changed once a week. New healthy roots were produced on the plants. After three weeks in the nutrient solution the plants were in various stages of development, some flowering and others already producing seed pods. At this stage radioactive DL-ornithine monohydrochloride (100 mgm. with an activity of 2.90×10^5 disintegrations per min. per mgm., or 4.8×10^7 disintegrations/min./mM.) was divided equally among 10 plants. The plants were allowed to remain in contact with the nutrient solution containing the active ornithine for seven days. The activity decreased each day, the total activity remaining in the nutrient solution of one plant was found to be: initially, 2.9×10^6, 1st day, 2.6×10^6, 2nd day, 1.6×10^6, 3rd day, 1.1×10^6, 4th day, 0.52×10^6, 5th day, 0.25×10^6, 6th day, 0.07×10^6, 7th day, 0.01×10^6 disintegrations per min. The plants were harvested on the seventh day, dried at 50–60°, and then ground in a Wiley mill. This ground material was extracted with methanol for three days in a soxhlet extractor, the methanol extract evaporated to dryness *in vacuo*, and the residue dissolved in 250 cc. of 2 *N* sulphuric acid. The solution was extracted with a chloroform–ether (4 : 1) mixture (Extract A) to remove fats and chlorophyll. The aqueous acid solution was made alkaline with ammonia and extracted with more of the same chloroform–ether mixture. Evaporation of this second extract gave the crude alkaloids containing hyoscyamine and hyoscine (Extract B). The residual aqueous alkaline solution (Solution C) contained the water soluble amino acids and its relatively high activity was probably due to free unchanged ornithine. The activities and weights of these various extracts are shown in Table I.

The crude alkaloid extract was subjected to paper chromatography, the best separation being achieved using Whatman No. 1 paper buffered with phosphate-citric acid buffer to pH 7 with a mixture of *n*-butanol (80 cc.) and water (15 cc.) as the developing solvent, when R_f values for hyoscyamine and hyoscine of 0.65 and 0.83 respectively were obtained. The alkaloids were detected by spraying with Dragendorff's reagent (17) which brought them out by coloring the spots a fairly permanent orange. The paper was assayed in 1 cm. strips as previously described (10) with the result shown in Fig. 2. This result suggested that all the activity was present in the hyoscyamine. The alkaloids were then separated on a larger scale on a column of celite ("Hy-Flo Filter cel") which was prepared by shaking celite (15 gm.) with chloroform (200 cc.) and *N* hydrochloric acid (4 cc.), the aqueous layer being absorbed on the celite. The crude alkaloids were dissolved in about 20 cc. of

TABLE I
EXTRACTS OF THE *D. stramonium* FED WITH DL-ORNITHINE-2-C^{14}

Fraction	Weight	Activity*
Fresh plant	277 gm.	
leaves		*ca.* 10 disint./min./mgm.
roots		*ca.* 3000 disint./min./mgm.
seeds		*ca.* 20 disint./min./mgm.
Dried plant	33.3 gm.	
Methanol extract of plant	9.94 gm.	6.96 × 10^5 disint./min. (total activity)
Plant after extraction with methanol	23.4 gm.	28.6 × 10^5 disint./min. (total activity)
Extract A		0.42 × 10^5 disint./min. (total activity)
Crude alkaloids (Extract B)	142.1 mgm.	0.78 × 10^5 disint./min. (total activity)
Residual alkaline solution (Extract C)		5.57 × 10^5 disint./min. (total activity)
Pure hyoscyamine aurichloride	13.6 mgm.	1.08 × 10^6 disint./min./mM.
Pure hyoscine aurichloride	11.0 mgm.	0

The activities were determined as thin samples with a Radiation Counters Laboratory "Nucleometer" making the usual corrections for self-absorption etc.

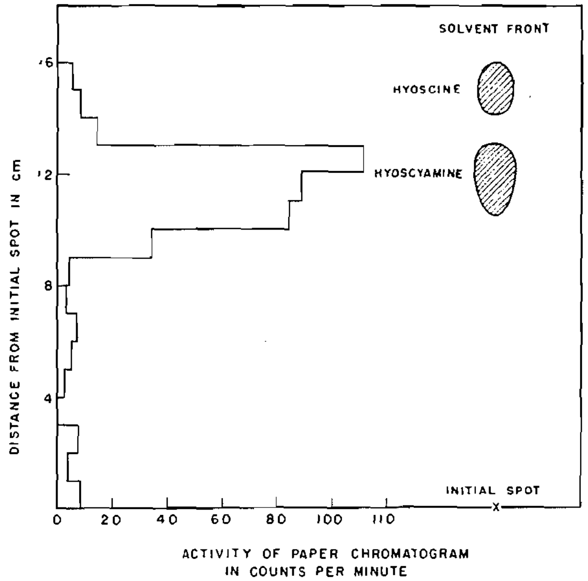


FIG. 2. Paper chromatogram and its activity.

chloroform and applied to the top of the column of prepared celite. The column was then washed with chloroform (350 cc.) which eluted the hyoscyamine as the hydrochloride. Hyoscine was eluted with chloroform saturated with ammonia. The crude alkaloids so obtained were converted to their aurichlorides and crystallized to constant activity. The hyoscine aurichloride had appreciable activity at first, but on repeated crystallization it fell to a negligible value.

Degradation of the Hyoscyamine

1. *Hydrolysis*

The highly active aurichloride was diluted with 2.00 gm. of inactive *l*-hyoscyamine hydrochloride (all subsequent determinations of activity were corrected for this dilution), the mixture refluxed with 20 cc. of 10% sodium hydroxide solution for one half-hour, and the liquor extracted with ether in a continuous extractor for 12 hr. The ether extract was dried over sodium sulphate and the ether distilled off *in vacuo* leaving the residual tropine as a crystalline solid, wt. 1.134 gm., m.p. 45–50°. A small amount was converted to the picrate, m.p. 291–292°. The residual alkaline solution was acidified with hydrochloric acid and again extracted with ether. This second extract, after drying and evaporation *in vacuo*, yielded 1.01 gm. of tropic acid, m.p. 116–117°.

2. *Oxidation of the Tropine*

The active tropine (1.12 gm.) was dissolved in water (23 cc.) containing sulphuric acid (7 cc.). Chromium trioxide (7 gm.) dissolved in a little sulphuric acid of the same dilution was added, and the resulting solution was refluxed in a molten metal bath for three hours. The mixture was then poured onto ice, sodium sulphite was added to reduce the excess chromic acid, and the liquor was then extracted with benzene for 48 hr. The benzene extract was dried and evaporated to dryness *in vacuo* at room temperature; it left a residue of N-methyl succinimide (92.9 mgm.), m.p. 67–68°, not depressed in admixture with an authentic specimen obtained by the method of Menschutkin (15). Found: C, 52.78; H, 6.38%. Calc. for $C_5H_7O_2N$: C, 53.09; H, 6.28%.

3. *Reaction of the N-Methyl Succinimide with Phenyl Magnesium Bromide*

Phenyl magnesium bromide was prepared by stirring a mixture of magnesium (0.72 gm.), dry ether (40 cc.), and bromobenzene (3.5 cc.) until all was dissolved. A solution of the active N-methyl succinimide in benzene (20 cc.) was then added to the reagent and the mixture stirred at room temperature for 24 hr. It was then added to crushed ice containing concentrated sulphuric acid (1 cc.). The ether layer was separated and the aqueous solution was further extracted with ether. The combined ether solution was evaporated and the residue was distilled in steam to remove unreacted bromobenzene and diphenyl. The residual tar in the flask was dissolved in hot alcohol and on cooling, colorless plates of 1-methyl-2,5-diphenylpyrrole (35.6 mgm.) separated, m.p. 196–200°, not depressed by authentic specimen. Found: C, 87.54; H, 6.69; N, 6.17%. Calc. for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00%.

4. *Oxidation of* 1-*Methyl*-2,5-*diphenylpyrrole*

The pyrrole (35 mgm.) was refluxed with potassium permanganate (0.5 gm.) in water (40 cc.) for eight hours. A few drops of ethyl alcohol were added to reduce the excess permanganate, the solution was filtered, acidified with hydrochloric acid, and extracted with ether. The dried ether solution on evaporation left a residue which crystallized from hot water (wt. 6.2 mgm.), m.p. 119–121°, not depressed by mixture with authentic benzoic acid. The mother liquor from the crystallization of the benzoic acid was made almost neutral by the addition of sodium acetate and calcium chloride added to precipitate the oxalic acid as the calcium salt.

The activities of these degradation products of hyoscyamine are shown in Table II.

TABLE II
ACTIVITIES OF HYOSCYAMINE AND ITS DEGRADATION PRODUCTS

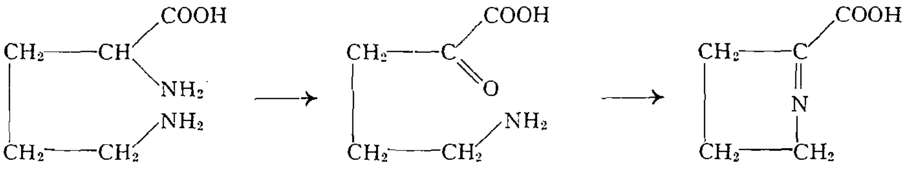
Compound	Specific activity (disintegrations/min./mM.)
Hyoscyamine aurichloride	1.08×10^6
Tropine	0.95×10^6
Tropine picrate	1.06×10^6
Tropic acid	0
N-Methyl succinimide	0.99×10^6
1-Methyl-2,5-diphenylpyrrole	1.00×10^6
Benzoic acid*	0.49×10^6
Calcium oxalate	0

**The benzoic acid has half the specific activity of the hyoscyamine, tropine, etc., because two molecules of benzoic acid are produced on the oxidation of 1-methyl-2,5-diphenylpyrrole.*

DISCUSSION

The degradation of the radioactive tropine shows all the activity to be in the 1 or 5, or both, positions. The symmetry of the molecule renders it impossible to differentiate between these bridge-head carbons by chemical methods. These experiments thus show that ornithine is utilized by the plant for the synthesis of the pyrrolidine ring of tropine. Robinson (18, 19) has suggested that ornithine is the source of putrescine which by oxidation would successively give γ-aminobutyraldehyde and succindialdehyde which is an intermediate in his *in vitro* synthesis of tropinone. Cromwell (1, 2) has isolated putrescine from the leaves of *A. belladonna* and he observed minor increases in the percentage of hyoscyamine following injection of putrescine into the stems of the same plant. However, it has been shown in these laboratories (4) that putrescine-1,4-C^{14}, when fed to *D. stramonium* plants at a stage of growth corresponding to that in the present experiments, did not give rise to radioactive hyoscyamine. Also James (8) has been unable to decarboxylate ornithine to putrescine with extracts or tissue slices from belladonna under a variety of conditions. Putrescine is thus apparently ruled out as an intermediate between ornithine and tropine. Its presence in various plants would seem to represent an alternate pathway of ornithine metabolism.

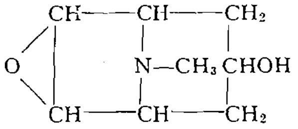
James (6) showed that significant increases in hyoscyamine in *A. belladonna* occurred following the feeding of arginine or ornithine; furthermore he found that aerobic oxidation of ornithine in the presence of a belladonna extract yielded α-keto-δ-aminovaleric acid (VIII). Also an ornithine dehydrogenase has been isolated from *Datura tatula* (8), which was unable to oxidize putrescine and amino acids other than ornithine. Further discussion of the formation of the tropine molecule is merely speculative, although it seems probable that the next intermediate in the reaction sequence is the compound IX which could then react with a three carbon unit to give the tropine skeleton, the carboxyl group being either retained during the condensation and eliminated later, or actually lost during the condensation. Alternatively, the carboxyl group of IX may be utilized to form part of the tropine skeleton by combination with a two carbon fragment such as acetate. This, however, is unlikely since it would result in the oxygen function of the tropine being on carbon 2 instead of 3, if the "head to tail" combination of acetate is assumed. This could be tested by the feeding of carboxyl labelled ornithine, when activity could be expected in position 2 of tropine. A biogenetic scheme involving IX would result in the δ-nitrogen of ornithine being the source of the tropine nitrogen which could be tested by carrying out comparative feeding experiments with δ-N^{15} and α-N^{15} labelled ornithine, when a greater incorporation of N^{15} in the tropine molecule should occur in the former case.



VIII IX

The present experiments also render improbable the suggestions of Mortimer (16, cf. also 20) that the tropane skeleton may be derived from tryptophan.

Since no activity was found in the hyoscine (scopolamine) it would seem that scopine (X) does not arise by the direct hydroxylation of tropine. It is possible that it is produced from a hypothetical hydroxyornithine which could conceivably be obtained from hydroxyproline, analogous to the production of ornithine from proline (23).



X

To complete the picture of tropine biogenesis, or at least the pyrrolidine half of the molecule, ornithine may arise from proline which in turn may come from glutamic acid. This is derived by transamination from α-ketoglutaric acid, an intermediate in the tricarboxylic acid cycle.

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INTENSITY IN THE RAMAN EFFECT

II. STANDARD RAMAN INTENSITIES AND VIBRATIONAL ASSIGNMENTS IN THE CHLOROETHANES[1]

By G. ALLEN[2] AND H. J. BERNSTEIN

ABSTRACT

The standard intensities of the Raman bands of the chloroethanes without rotational isomers (Et; 1,1; 1,1,1; 1,1,1,2; penta, and hexa) have been measured in the liquid phase with a photoelectrically recording Raman spectrometer. Vibrational assignments are proposed which are consistent with the depolarization data, infrared contours, and a vibrational sum rule. The total Raman intensity is a smooth but nonlinear function of the number of chlorine atoms. The sum of the intensities of the bands assigned to hydrogen modes and that for the skeletal modes is also a smooth function of the number of substituents.

Of the existing theories of intensity in the Raman effect only a semiempirical approach of the type developed by Wolkenstein (34) has been used to calculate the intensities of Raman bands for a homologous series of compounds. The Wolkenstein theory is handicapped by rather drastic simplifying assumptions made in developing a model based on bond polarizabilities. For instance it is assumed that the polarizability of a particular bond both in the direction of its length and at right angles to the bond is independent of neighboring atoms. Welsh *et al.* (32) have shown, moreover, that the Wolkenstein theory is inadequate for the calculation of Raman intensities for the gaseous chloromethanes. It is of interest, however, to examine larger molecules and enquire whether there is any evidence for additivity in the Raman intensities of vibrations which can be associated with particular bonds or groups of atoms.

In this investigation the Raman intensities of the chlorosubstituted ethanes in the liquid state have been compared. This, of course, has a marked disadvantage over the study of gaseous compounds because of the effect of molecular interaction (11, 3) on the Raman intensities. Corresponding investigations on the chloromethanes, however, show that the Raman intensities measured in the liquid state are not very different from the results obtained by Welsh *et al.* in their vapor phase investigation (32). A point of interest is whether the chloroethane molecules may be too small to show evidence of additivity because of the strong interaction which must occur between the atoms situated on either carbon atom. However, it will be shown that there is evidence for additivity in this series and one might anticipate that there will be an improvement for larger molecules. The vibrational assignments for the chloroethanes have been correlated with the Bernstein–Pullin sum rule (4).

EXPERIMENTAL

The Raman spectra and depolarization ratios for the chloroethanes were obtained at 27° C. using a White Raman Spectrometer (33) equipped with a

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photoelectrical recording unit. The intensities were recorded and reduced in a manner previously described (3). All the intensities quoted in the following tables are measured relative to the intensity of the 458 cm.$^{-1}$ band of CCl_4, and corrections are applied for convergence error, density, molecular weight, refractive index, etc., to give a series of 'standard intensities of scattering per molecule'. The expression used in obtaining the standard intensities is:

$$S = \frac{I}{I_{458}} \frac{1+\rho_{458}}{1+\rho} \frac{n^2}{n^2_{CCl_4}} \frac{\sigma}{\sigma_{458}} \frac{R_{(n)}}{R_{CCl_4}} \frac{M}{d}\left(\frac{d}{M}\right)_{CCl_4} \times \frac{\Delta\nu}{458}\left(\frac{\nu-458}{\nu-\Delta\nu}\right)^4 \frac{1-e^{-1.44\Delta\nu/T}}{1-e^{-1.44\times 458/T}}$$

$$= \frac{(45|\partial\alpha/\partial Q|^2+7|\partial\gamma/\partial Q|^2)}{(45|\partial\alpha/\partial Q|^2+7|\partial\gamma/\partial Q|^2)_{458\text{cm.}^{-1}}}$$

where I = integrated intensity, ρ = observed depolarization ratio for natural light, n = refractive index of compound, σ = spectral sensitivity of phototube at wave length corresponding to Raman shift, $R_{(n)}$ = reflection loss, M = molecular weight, d = density, $\Delta\nu$ = Raman shift, ν = frequency of exciting line, T = absolute temperature, $\partial\alpha/\partial Q$ = derivative of average polarizability with respect to the normal co-ordinate at the equilibrium position, $\partial\gamma/\partial Q$ = derivative of the anisotropy with respect to the normal co-ordinate at the equilibrium position. All infrared spectra were obtained with a Perkin-Elmer model 12c spectrometer.

Purification of Materials

Hexachloroethane was purified by a series of crystallizations from alcohol–water mixtures. The white solid sublimes at 188° C.

Pentachloroethane was obtained by the fractional distillation of a commercial sample through a Fenske-type column (n^{25}_D = 1.503).

Pentachloroethane-*d* was made by Dr. L. C. Leitch from $CDCl = CCl_2$.

uns-Tetrachloroethane and uns-tetrachloroethane-d_2 were also obtained from Dr. Leitch (n^{25}_D = 1.480).

Methyl chloroform: A reagent-grade Eastman Kodak sample was fractionally distilled through a Fenske-type column (n^{25}_D = 1.438).

1,1-Dichloroethane was prepared in a similar manner to methyl chloroform (n^{25}_D = 1.415).

Ethyl chloride was also an Eastman Kodak sample. Some difficulty was experienced in purifying the compound, but it was finally accomplished by distillation under vacuum.

RESULTS

In the following sections each compound is dealt with separately. Only relative intensities are given for C_2Cl_6 because it is a solid at room temperature, but the assignment for this molecule is needed for the sum-rule application (4). For the remaining chloroethanes we have reported Raman intensities in terms of scattering coefficients per unit volume $\bar{S} = (I/I_{458}) \cdot (\sigma/\sigma_{458})$ and also in terms of S. The observed depolarization ratios, together with the true ratios obtained from the linear relationship previously described (3, 26), are presented. Where necessary we have obtained infrared data for use in making assignments.

Hexachloroethane

The Raman spectrum of C_2Cl_6 has been reported previously for solutions in organic solvents (13) and for the solid (21), from which it has been concluded that the molecule belongs to the point group D_{3d}. Electron diffraction data have confirmed this (22). All six Raman-active fundamentals have been observed (13, 21) but only two of the five allowed infrared fundamentals have been reported. In the present work we have reinvestigated both the infrared and Raman spectra of C_2Cl_6 in carbon tetrachloride and cyclopentane solutions. A third fundamental has been found in the infrared spectrum and we have obtained sufficient combination tones to allow a reasonable estimate of the frequency of the two missing infrared bands to be made. The results are given in Tables I and II.

TABLE I

WAVE NUMBERS OF FUNDAMENTALS OF C_2Cl_6

Wave number	Type	ρ_{true}	Intensity	Remarks
978	a_{1g} R.	0.40	8	*a, b*
432		0.10	100	*a, b*
163				Not observed
678	a_{2u} I.R.			*c, d, e*
376				*d, e*
778	e_u I.R.			*c*
[280]				
[115]				
860	e_g R.	0.86	49	*a, b*
341		0.86	70	*a, b*
224		0.86	68	*b*

The wave numbers enclosed in brackets are estimated from combination tones.
[a] *Raman spectrum, observed in CCl_4 solution.*
[b] *Raman spectrum, observed in cyclopentane solution.*
[c] *I.R., saturated solution in cyclopentane, NaCl optics, 0.6 mm. cell.*
[d] *I.R., saturated solution in CCl_4, CsBr optics, 1.5 mm. cell.*
[e] *I.R., saturated solution in cyclopentane, CsBr optics, 1.5 mm. cell.*

The Raman spectrum agrees with previous investigations (13, 21) although the band at 163 cm.$^{-1}$ was not observed because of the presence of a grating ghost at 166 cm.$^{-1}$. It is interesting to note that ν_{CC} at 978 cm.$^{-1}$ for this molecule is only 15 cm.$^{-1}$ less than ν_{CC} in ethane (15).

With CsBr optics it was possible to observe the a_{2u}-type band at 376 cm.$^{-1}$ and establish that the two unobserved infrared bands lie below 300 cm.$^{-1}$. In assigning the infrared bands we have been guided by a calculation reported by Simanouchi (28), viz:

$$a_{2u}\ 696,\ 368\ \text{cm.}^{-1};\quad e_u\ 743,\ 271,\ 130\ \text{cm.}^{-1}.$$

Further evidence for the assignment of the bands observed at 678 and 778 cm.$^{-1}$

TABLE II

WEAKER INFRARED BANDS OF C_2Cl_6

Wave number	Interpretation	Symmetry type	Remarks
1750	978 + 778 = 1756	E_u	*f, g*
1634	860 + 778 = 1638	$A_{1u} + E_u$	*f, g*
1514	860 + 678 = 1538	E_u	*g*
1416	?		*f*
1357	978 + 376 = 1354	A_{2u}	*f*
1260 v.v.w.	?		*c, f*
1212	432 + 778 = 1210	E_u	*c*
1140	710 + 432 = 1142	E_u	*c, f*
1123	342 + 778 = 1120	$A_{1u} + E_u$	*c*
1090	978 + [115]	E_u	*c*
1051	710 + 342 = 1052	$A_{1u} + E_u$	*c*
1023	678 + 342 = 1020	E_u	*c, f*
1006	778 + 224 = 1002	$A_{1u} + E_u$	*c, f*
977	860 + [115]	$A_{1u} + E_u$	*f*
847	163 + 678 = 841	A_{2u}	*c*
809 m.	376 + 432 = 808	A_{2u}	*c*
710 m.	342 + 376 = 718 432 + [280]	E_u E_u	*c*
693	978 − [280]	E_u	*c, d, e*
615	342 + [280] 778 − 163 = 615	$A_{1u} + E_u$ E_u	*d, e*
575	858 − [280]	$A_{1u} + E_u$	*d, e*
542	376 + 163 = 539	A_{2u}	*d*
527	?		*d*
482	860 − 376 = 484	E_u	*e*
443	163 + [280]	E_u	*e*
344	778 − 432 = 346	E_u	*d, e*

The wave numbers enclosed in brackets are estimated from combination tones. See Table I for footnotes a, b, c, d, and e.

[f] *I.R., saturated solution in* CCl_4*, NaCl optics, 0.1 and 0.6 mm. cell.*

[g] *I.R., saturated solution in* C_2Cl_4*, NaCl optics, 0.6 mm. cell.*

In all tables s = *strong,* m = *medium,* w = *weak,* b = *broad,* v = *very,* sh = *shoulder.*

was obtained from an inspection of band widths in dilute solution. For example, we find that the a_1-type band at 667 cm.$^{-1}$ of $CHCl_3$ in inert solvents is narrower than the e-type band at 760 cm.$^{-1}$. Similarly in CH_3CCl_3 the a_1-type band at 526 cm.$^{-1}$ is narrower than the e-type band at 720 cm.$^{-1}$. In C_2Cl_6 we find the half-band widths to be 14 cm.$^{-1}$ for the 678 cm.$^{-1}$ band and 20 cm.$^{-1}$ for the 778 cm.$^{-1}$ band, consistent with the assignment.

In attempting to estimate the low lying infrared-active fundamentals from the observed combination tones the values of 115 and 280 cm.$^{-1}$ are indicated. These are not inconsistent with the values recently calculated by Cleveland (7) at 138 ± 20 cm.$^{-1}$ and 270 ± 20 cm.$^{-1}$. Furthermore, a weak depolarized Raman band in the spectrum of liquid C_2Cl_6 at 274 cm.$^{-1}$ has been found by Daasch (9). It is difficult to account for this band in terms of combination or difference tones of the proposed fundamentals, but if the band is attributed to an e_u-type mode appearing in the Raman effect because of a breakdown of selection rules, the explanation is consistent with the present assignment.

The wave number of the torsional mode (a_{1u} which is inactive in both infrared and Raman) is estimated to be at ~50 cm.$^{-1}$ since in $CHCl_2 . CCl_3$ it is observed at 82 cm.$^{-1}$ and in $CH_2Cl . CCl_3$ it is observed at 117 cm.$^{-1}$.

Pentachloroethane and Pentachloroethane-d

Pentachloroethane belongs to the point group C_s and has 11 a'-type fundamentals which are polarized and 7 a''-type fundamentals which are depolarized. The a'-type fundamentals can be characterized approximately as one ν_{CH}, one δ_{CH}, one ν_{CC}, three ν_{CCl}, and five skeletal deformation vibrations. The a''-type fundamentals comprise one ν_{CH}, two ν_{CCl}, three skeletal deformations, and the torsional mode. When the present investigation was begun there was not a complete vibrational assignment for pentachloroethane but concurrently Nielsen and Liang (23) have published a complete assignment which proved to be identical with our results.

The Raman and infrared spectra of C_2HCl_5 are presented in Table III, the upper field lists the fundamentals and the lower field contains only combination tones. The corresponding data for C_2DCl_5 are collected in Table IV.

TABLE III

C_2HCl_5

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
2985	ν_{CH}	0.49	0.35	0.370	5.09	~2985	s.		a'
1252	δ_{CH}	0.82	0.68	0.042	0.141	1253	m.	~0.0	a'
1208	δ_{CH}	0.94	0.80	0.076	0.226	1208	m.	0.023	a''
1022	ν_{CC}	0.50	0.36	0.066	0.208	1022	m.	0.027	a'
836	ν_{CCl}	1.00	0.86	0.766	1.500	N.o.			a''
820	ν_{CCl}	~0.65	~0.50			820	s.	0.185	a'
774	ν_{CCl}	0.90	0.76	~0.029	0.050	770	s.	0.435	a''
725	ν_{CCl}	0.28	0.15	0.072	0.174	724	s.	0.133	a'
582	ν_{CCl}	0.33	0.20	0.292	0.519	582[c]	s.		a'
405	Skeletal deformations	0.30	0.17	0.876	0.979	404[c]	s.		a'
328		0.96	0.82	0.560	0.306	326[c]	s.		$a' + a''$
278		0.90	0.76	0.091	0.040	N.i.			a'
238		1.00	0.86	0.456	0.143	N.i.			a''
225		1.00	0.86			N.i.			a'
175		0.98	0.85	0.185	0.038	N.i.			a'
165		1.00	0.86	0.060	0.011	N.i.			a''
82	Torsion	~1.00	~0.86	0.15	0.01	N.i.			a''
1670	2 × 836					1051	v.w.	724 + 326	
1638	2 × 820					995	v.w.	770 + 225	
1540	725 + 820					910	w.	582 + 326	
1442	2 × 725					861	w.	582 + 278	
1409	820 + 582					647[c]	m.	2 × 326	
						490[c]	w.	326 + 165	
						443[c]	w.	2 × 225	
						369[c]	w.	770 − 404	

[a] *Raman, pure liquid, reflection loss* $R_{(n)} = 1.09$.
[b] *I.R., pure liquid, NaCl optics, 0.025 mm. cell.*
[c] *I.R., cyclopentane solution, CsBr optics, 1.5 mm. cell.*
[d] *I.R., intensity of 5% solution in* CS_2*, NaCl optics, 0.025 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

In both compounds only 17 out of a total of 18 fundamentals are observed. To account for the missing fundamental, Nielsen *et al.* (23) have chosen the

TABLE IV

C_2DCl_5

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
2230	ν_{CD}	0.49	0.35	0.244	2.15	2230	s.		a'
1053	ν_{CC}	0.50	0.36	0.096	0.315	1052	w.	~0.0	a'
948	δ_{CD}	0.90	0.76	0.065	0.147	947	s.	0.082	a'
927	δ_{CD}	1.00	0.86	0.165	0.350	926	s.	0.055	a''
808	ν_{CCl}	1.00	0.86	0.262	0.467	808	s.	0.139	a''
781	ν_{CCl}	0.74	0.60	0.198	0.389	780	s.	0.219	a'
756	ν_{CCl}	1.00	0.86	0.077	0.124	756	s.	0.328	a''
708	ν_{CCl}	0.26	0.13	0.118	0.283	707	s.	0.063	a'
569	ν_{CCl}	0.35	0.22	0.311	0.526	569[c]	s.		a'
406	Skeletal deformations	0.32	0.19	0.841	0.926	404[c]	s.		a'
328		1.00	0.86	0.545	0.293	327[c]	s.		$a' + a''$
279		0.88	0.74	0.086	0.038	N.i.			a'
238		1.00	0.86	0.452	0.143	N.i.			a''
226		1.00	0.86			N.i.			a'
175		1.00	0.86	0.193	0.039	N.i.			a'
165		1.00	0.86	0.060	0.011	N.i.			a''
82	Torsion	~1.00	~0.86	~0.15	~0.01	N.i.			a''
724	328 + 406					1075	v.w.	327 + 756	
						1032	v.w.	226 + 808	
						1020	v.w.	238 + 780	
						888	w.b.	175 + 707 82 + 808	
						862	w.b.	82 + 780	
						722	v.w.	404 + 327	
						680[c]	m.	278 + 404	
						479[c]	v.w.	707 − 226 404 + 82	
						452[c]	w.	780 − 327 175 + 279	
						428[c]	w.	707 − 279	
						382[c]	w.	780 − 404 165 + 226	

[a] *Raman, pure liquid, reflection loss $R_{(n)} = 1.09$.*
[b] *I.R., pure liquid, NaCl optics, 0.025 mm. cell.*
[c] *I.R., cyclopentane solution, CsBr optics, 1.5 mm. cell.*
[d] *I.R., intensity of 5% solution in CS_2, NaCl optics, 0.025 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

band at 328 cm.$^{-1}$ to be double because of its high depolarization ratio of ~0.80. Quite independently we have chosen this band to be double because on comparing the spectra of the light and heavy compounds the contour of this band changes whereas the contours of the bands at 225, 238, 278, and 405 cm.$^{-1}$ are unchanged. The half-band width of the 328 cm.$^{-1}$ band is in fact ~10% greater in C_2DCl_5 and its peak height is ~10% less than in C_2HCl_5.

A comparison of the spectra of C_2HCl_5 and C_2DCl_5 shows that there is no difficulty in matching the corresponding vibrational modes except for ν_{CC}. Although ν_{CC} in the *d*-compound is at higher wave numbers than in the light compound, by elimination there remains little choice for its assignment. The other noteworthy feature is that the Raman band at 836 cm.$^{-1}$ is not observed in the infrared spectrum of C_2HCl_5; in the *d*-compound the corresponding band at 808 cm.$^{-1}$ is strong in both the infrared and Raman spectra.

The assignments given above are acceptable from the point of view of the Teller–Redlich product rule (14) for isotopic substitution. The observed product ratio is 2.59, whereas the theoretical ratio is calculated to be 2.64. Using the Bernstein–Pullin sum rule (4) for isotopic substitution the calculated difference between the sums of the wave numbers of the fundamentals ($\Sigma\nu_{C_2HCl_5} - \Sigma\nu_{C_2DCl_5}$) should be ~1300 cm.$^{-1}$; the observed difference is 1417 cm.$^{-1}$.

Tetrachloroethane and Tetrachloroethane-d_2

Tetrachloroethane also belongs to the point group C_s. The a'-type fundamentals can be characterized approximately as one ν_{CH}, two δ_{CH_2}, one ν_{CC}, three ν_{CCl}, and four skeletal deformation vibrations; the a''-type comprise one ν_{CH}, two δ_{CH_2}, one ν_{CCl}, two skeletal deformations, and the torsional mode.

TABLE V

$CH_2Cl \cdot CCl_3$

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
3016	ν_{CH}	1.00	0.86	0.249	2.06	~3000	s.		a''
2961	ν_{CH}	0.27	0.14	0.384	4.85	~2960	s.		a'
1420	δ_{CH_2}	0.96	0.81	0.87	0.254	1415	s.	~0.00	a''
1280	δ_{CH_2}	0.75	0.61	0.032	0.092	1280	s.	0.033	a'
1200	δ_{CH_2}	0.84	0.70	0.047	0.118	1200	s.	0.037	a'
1056	ν_{CC}	0.58	0.44	0.045	0.113	1055	s.	0.036	a'
958	δ_{CH_2}	1.00	0.86	0.024	0.042	958	s.	0.153	a''
812	ν_{CCl}	0.73	0.59	0.516	0.855	810	s.	0.106	a'
746	ν_{CCl}	0.40	0.27	0.050	0.093	~ 750	s.	0.315	a'
720	ν_{CCl}	1.00	0.86	0.195	0.241	~ 730	s.	0.253	a''
549	ν_{CCl}	0.27	0.14	0.468	0.646	550[c]	s.		a'
380	Skeletal deformations	0.34	0.21	0.533	0.423	380[c]	s.		a'
334		0.98	0.85	0.163	0.072	335[c]	s.		a'
306		1.00	0.86	0.216	0.084	305[c]	s.		a''
240		0.92	0.78	0.383	0.106	N.i.			$a' + a''$
157		0.85	0.71	0.10	0.014	N.i.			a'
117	Torsion	1.00	0.86	0.20	0.016	N.i.			a''
760	2 × 380					895	w.	157 + 746	
489	157 + 334					672[c]	m.	1415 − 746 2 × 335	
						596	w.	720 − 117 2 × 305	
						508	w.	810 − 305 746 − 240	
						471	m.	2 × 240 1280 − 810	
						436	m.	746 − 305 810 − 380	

[a] *Raman, pure liquid, reflection loss $R_{(n)}$ = 1.02.*
[b] *I.R., pure liquid, NaCl optics, 0.02 mm. cell, cf. Bernstein (1).*
[c] *I.R., pure liquid, CsBr optics, 2.0 mm. cell.*
[d] *I.R., intensity of 5% solution in cyclopentane, NaCl optics, 0.025 mm. cell.*
N.i. = not investigated.

Bernstein (1) made a tentative assignment of $CH_2Cl\,.\,CCl_3$ and $CD_2Cl\,.\,CCl_3$ on the basis of the infrared spectra of the two molecules together with the Raman spectrum of $CH_2Cl\,.\,CCl_3$ reported by Mizushima *et al.* (20). We have reinvestigated both compounds and our results are presented in Tables V and VI. An identical assignment for $CH_2Cl\,.\,CCl_3$ has since been published by Nielsen *et al.* (23).

In assigning the fundamentals for $CD_2Cl\,.\,CCl_3$ several points of interest arise. A comparison of the depolarization ratios and intensities suggests that

TABLE VI

$CD_2Cl\,.\,CCl_3$

Raman[a]						Infrared[b]			
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Optical density[d]	Assignment
2266	ν_{CD}	1.00	0.86	0.173	0.933	~2260	s.		a''
2218	ν_{CD}	0.29	0.16	0.163	1.31	~2210	s.		Fermi doublet $a' + 2 \times 1105$ $a' = 2190$
2154		0.35	0.22	0.146	1.08	~2150	m.		
1105	δ_{CD_2}	0.70	0.56	0.021	0.051	1104	m.	0.026	a''
1036	ν_{CC}	0.65	0.51	0.086	0.201	1033	m.	0.013	a'
960	δ_{CD_2}	1.00	0.86	0.061	0.109	958	s.	0.064	a'
935	δ_{CD_2}	1.00	0.86	0.055	0.096	933	s.	0.199	a'
787	ν_{CCl}	0.80	0.66	0.295	0.453	786	s.	0.318	a'
728	ν_{CCl} or δ_{CD_2}	0.50	0.36	0.118	0.198	727	s.	0.166	a''
685	δ_{CD_2} or ν_{CCl}	0.40	0.27	0.033	0.056	684	s.		a'
660	ν_{CCl}	1.00	0.86	0.138	0.153	660[c]	s.		a''
529	ν_{CCl}	0.29	0.16	0.451	0.590	530[c]	s.		a'
379	Skeletal deformations	0.33	0.20	0.491	0.393	380[c]	s.		a'
305[e]		1.00	0.86	0.363	0.143	305	s.		$a'' + a'$
240		0.90	0.77	0.356	0.100	N.i.			$a' + a''$
158		0.85	0.71	~0.10	~0.014	N.i.			a'
117	Torsion	~1.00	~0.86	~0.20	~0.016	N.i.			a''
1433	2 × 728					1280	w.		1033 + 240
1238	935 + 305 728 + 529					1240	w.		933 + 305 727 + 530
752	2 × 379					1185	w.		660 + 530
						1070	w.		958 + 117 684 + 380
						1010	w.		2 × 530
						942	w.		786 + 158
						875	w.		727 + 158
						861	m.		1104 − 240
						832	w.		530 + 305
						753	w.		2 × 380
						715	w.		958 − 240
						606[c]	w.		2 × 305
						483[c]	w.		2 × 240 786 − 305
						425[c]	m.		305 + 117 727 − 305

[a] *Raman, pure liquid, reflection loss,* $R_{(n)} = 1.02$.
[b] *I.R., pure liquid, NaCl optics, 0.025 mm. cell.*
[c] *I.R., cyclopentane solution, CsBr optics, 2.0 mm. cell.*
[d] *I.R., intensity of 5% solution in* CS_2*, NaCl optics, 0.025 mm. cell.*
[e] *305 cm.*$^{-1}$ *is taken as a doublet, see text.*
N.i. = not investigated.

the band at 728 cm.$^{-1}$ is a deuterium deformation mode rather than a C—Cl stretching mode. In the low lying region we find that the bands at 117, 157, and 380 cm.$^{-1}$ appear in both spectra at the same positions and with approximately the same intensities. The band at 240 cm.$^{-1}$ in $CD_2Cl\,.\,CCl_3$ increases in band width by about 40% with no change in the integrated intensity. With narrow slits (1.5 cm.$^{-1}$) it is possible to see a shoulder on the lower wave number side of this band indicating that the band at 240 cm.$^{-1}$ in $CH_2Cl\,.\,CCl_3$ is indeed double. Further, the band at 334 cm.$^{-1}$ in $CH_2Cl\,.\,CCl_3$ is absent in the spectra of $CD_2Cl\,.\,CCl_3$, and the band at 305 cm.$^{-1}$ in the *d*-compound increases in intensity. In fact, the sum of the Raman intensities of the 305 and 334 cm.$^{-1}$ bands in the light compound is approximately equal to the intensity of the 305 cm.$^{-1}$ band in the *d*-compound. It would seem therefore that the band at 334 cm.$^{-1}$ has shifted to 305 cm.$^{-1}$ on deuteration and this band is therefore associated with a skeletal deformation mode involving the CH_2Cl group.

The assignments given in Tables V and VI give a value of 6.8 for the isotopic product rule ratio; the value calculated from theory is 7.04. The Bernstein–Pullin sum rule for isotopic substitution predicts a difference of 2600 cm.$^{-1}$ between the two sums, $\Sigma\nu_{C_2H_2Cl_4}$ and $\Sigma\nu_{C_2D_2Cl_4}$; the observed difference is 2830 cm.$^{-1}$.

Methyl Chloroform

We have reinvestigated the Raman spectrum of methyl chloroform and conclude that the most recent assignment is acceptable (29). Our results are given in Table VII.

TABLE VII

CH_3CCl_3

		Raman[a]				
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Assignment
2942	ν_{CH_3}	0.21	0.08	0.393	4.766	a_1
1378	δ_{CH_3}	0.50	0.37	0.007	0.025	a_1
1068	ν_{CC}	0.84	0.70	0.069	0.139	a_1
522	ν_{CCl_3}	0.20	0.07	0.645	0.813	a_1
342	s. d	0.69	0.55	0.565	0.281	a_1
200 ± 20[b]	Torsion					a_2
3004	ν_{CH_3}	1.01	0.86	0.485	3.655	e_1
1444	δ_{CH_3}	1.02	0.86	0.074	0.199	$e_1 + 2 \times 713$
1420		0.88	0.74	0.066	0.184	
1082	δ_{CH_3}	1.02	0.86	0.059	0.109	e_1
713	ν_{CCl_3}	1.02	0.86	0.513	0.570	e_1
301	s. d	N.o.				e_1
240		1.00	0.86	0.523	0.129	e_1

[a] *Raman, pure liquid. Reflection loss, $R_{(n)}$ = 1.06.*
[b] *Estimated from thermodynamic data, Ref. 10.*
N.o. = not observed.
S. d = skeletal deformation.

The Raman band at 1069 cm.$^{-1}$ is assigned as ν_{CC} and seems to be in agreement with the general trend in the series $C_2H_5Cl - C_2HCl_5$. This accounts satisfactorily for all the a_1 fundamentals. Only one e-type fundamental is uncertain and we have taken Nielsen's assignment (29) in this case. Although this band at 301 cm.$^{-1}$ was not observed in the present investigation it has been observed by Nielsen *et al.* (29), Kohlrausch (17), and Wagner (31). Recently Pitzer and Hollenberg (25) have obtained the far infrared spectrum of CH_3CCl_3 and have not observed any absorption around 300 cm.$^{-1}$. From their data they conclude that this e-type fundamental should be at 351 cm.$^{-1}$ and the torsion mode has a frequency of ∼200 cm.$^{-1}$. The calculated value of the potential barrier hindering internal rotation is ∼3000 cal./mole from these data. If 301 cm.$^{-1}$ is taken as the frequency of the fundamental the calculated potential barrier is 2000 cal./mole and the torsion frequency is estimated at 170 cm.$^{-1}$. The assignment given by El-Sabban *et al.* (10) gives 2800 cal./mole and 205 cm.$^{-1}$ respectively. All assignments give a value for the potential barrier some 1000 cal./mole lower than has been obtained for ethyl chloride (12). It might be expected from steric and additivity considerations that the barrier in methyl chloroform should be higher than in ethyl chloride but this simple model ignores the possibility of a redistribution of electronic charge in the two molecules. It is quite conceivable that electrostatic forces resulting from such a change could reduce the height of the barrier. In view of this uncertainty we feel that one cannot discriminate between the assignments by considering the values derived for the potential barrier hindering free rotation.

1,1-Dichloroethane

1,1-Dichloroethane belongs to the point group C_s and the a'-type vibrations comprise three ν_{CH}, four δ_{CH}, one ν_{CC}, one ν_{CCl}, and two skeletal deformations. The a''-type vibrations include one ν_{CH}, three δ_{CH}, one ν_{CCl}, one skeletal deformation, and the torsional mode. The Raman spectrum of 1,1-dichloroethane has been investigated several times (24, 6, 18) but no depolarization data have been reported. Thompson and Torkington (30) have reported the infrared spectrum from 3000 to 600 cm.$^{-1}$ and have made a tentative assignment based on a correlation of Raman and infrared data. The results of our investigations are given in Table VIII.

The assignment of ν_{CH} at 2989 cm.$^{-1}$ is made by analogy with $CHCl_2.CCl_3$. This a''-type band appears slightly polarized because it is overlapped by the polarized band at 3007 cm.$^{-1}$. The δ_{CH} modes are assigned to bands at 1224 cm.$^{-1}$ and 1276 cm.$^{-1}$, again by analogy with $CHCl_2 . CCl_3$, and the δ_{CH_3} modes are chosen to be 980, 1056, 1380, and two at 1440 cm.$^{-1}$. Support for the assignment of the 1440 and 1380 cm.$^{-1}$ bands is obtained from the fact that in CH_3CCl_3 there is a doubly degenerate fundamental at 1430 cm.$^{-1}$ and an a_1-type band at 1380 cm.$^{-1}$; furthermore, the 1440 cm.$^{-1}$ band in $CHCl_2CCl_3$ is broad and has more than twice the intensity of other δ_{CH_3} bands.

ν_{CC} can be assigned either to 980 cm.$^{-1}$ or to 1088 cm.$^{-1}$ since they are both polarized; we have chosen the 1088 cm.$^{-1}$ band in keeping with the assignment of the other chloroethanes where ν_{CC} is in the 1050 cm.$^{-1}$ region. There are two ν_{CCl} modes, one polarized and the other depolarized, which are assigned to the strong bands at 643 and 690 cm.$^{-1}$ respectively. The three

TABLE VIII

CH_3CHCl_2

Raman[a]						Infrared[c]		
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Assignment
3007	ν_{CH_3}	0.5	0.4	0.737	5.67	3005[b]	m.	a'
2989	ν_{CH}	0.8	0.7			2985[b]	s.	a''
2934	ν_{CH_3}	0.23	0.10	0.481	5.01	2932[b]	s.	a'
2864	ν_{CH_3}	0.25	0.12	0.045	0.442	2868[b]	m.	a'
1440	δ_{CH_3}	0.93	0.78	0.123	0.298	1442	m.	$a'' + a'$
1380	δ_{CH_3}	0.65	0.52	0.017	0.044	1380	m.	a'
1276	δ_{CH}	0.70	0.56	0.051	0.121	1278	m.	a'
1224	δ_{CH}	1.00	0.86	0.020	0.038	1226	s.	a''
1088	ν_{CC}	0.70	0.56	0.029	0.057	1087		a'
1056	δ_{CH_3}	1.00	0.86	0.032	0.051	1056		a''
980	δ_{CH_3}	0.92	0.78	0.058	0.087	979		a'
690	ν_{CCl}	1.00	0.86	0.266	0.251	N.i.		a''
643	ν_{CCl}	0.29	0.16	0.459	0.616	N.i.		a'
405	Skeletal deformations	0.30	0.17	0.162	0.112	N.i.		a'
316		0.95	0.81	0.104	0.035	N.i.		a''
274		0.78	0.64	0.280	0.084	N.i.		a'
N.o.	Torsion							a''
						1325	w.	643 + 690
						1351	w.	979 + 274

[a] *Raman spectrum, pure liquid, reflection loss,* $R_{(n)} = 1.13$.
[b] *I.R., pure liquid, LiF optics, 0.12 mm. cell.*
[c] *I.R., pure liquid, NaCl optics, 0.12 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

intense Raman bands in the 300 cm.$^{-1}$ region are assigned to skeletal deformation modes according to their depolarization ratios.

After this work had been completed we became aware of the Progress Report for the U.S. Atomic Energy Commission (June 1953) submitted by J. R. Nielsen which included the Raman and infrared spectra of 1,1-dichloroethane. The assignment reported therein by Nielsen, Lang, and Daasch is identical with our independent assignment.

Ethyl Chloride

This molecule also belongs to the point group C_s and in this case the a'-type vibrations comprise three ν_{CH}, five δ_{CH}, one ν_{CC}, one ν_{CCl}, and a skeletal deformation mode. The a''-type vibrations are made up of two ν_{CH}, four δ_{CH}, and the torsional mode. The Raman spectrum of liquid C_2H_5Cl has been reported (16) but only one infrared investigation (8) could be found; this was a study of C_2H_5Cl vapor using rock salt optics. Linnett (19) and Gordon and Giaugue (12) have both made tentative assignments for the molecule for the purposes of calculating thermodynamic functions and consequently little attention was directed to the assignment of bands in the 1000–1500 cm.$^{-1}$ region. We have obtained the infrared spectrum of the solid and the liquid (cf. Fig. 1) in the regions 700 cm.$^{-1}$ to 1500 cm.$^{-1}$ and 2800–3500 cm.$^{-1}$. All

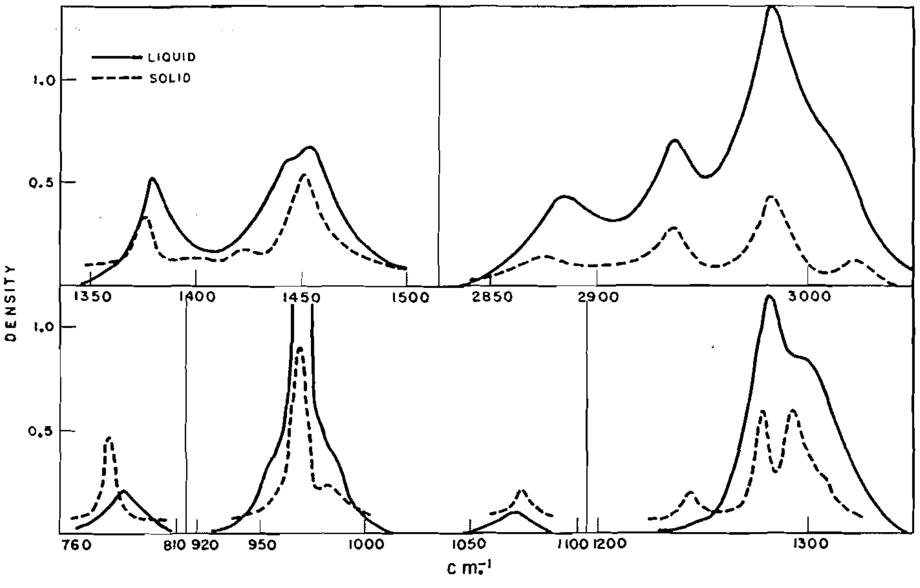

FIG. 1. Infrared spectrum of ethyl chloride.

TABLE IX

CH_3CH_2Cl

Observed spectra (in cm.$^{-1}$)

Raman[a] liquid	Raman[b] liquid	I.R.[c] vapor	I.R.[d] vapor	I.R.[e] liquid	I.R.[f] solid	Assignment
	3020 (8, *d*)			∼3015 (m)	3023 (m)	a''
2978 (0)	2983			2981 (s)	2983 (s)	a''
2966 (8, *p*)	2966 (12, *p*)					a'
2932 (8, *p*)	2933 (12, *p*)	2940		2936 (s)		a'
2877 (4, *p*)	2880 (5, *p*)			2883 (m)	2875 (m)	a'
1447 (4, *p*)	1452 (2½, *p*)	1455	1454	1454 (s)	1452 (s)	$a' + a''$
				∼1440 (m)	∼1420 (w)	a''
		1400	1395			
1385 (3*b*, *d*)	∼1380 (½*b*, *d*)		1375	1380 (m)	1380 (m)	a'
				1305 (w)	∼1310 (w)	2 × 658
			1297		1295 (s)	
1281 (0, *b*)	∼1280 (½*b*, *p*)	1285	1278	1282 (s)	1279 (s)	a'
1238 (0)	1244 (½, *p*)			1245 (w)	1242 (w)	a'
1071 (3, *p*)	1072 (1, *p*)			1071 (m)	1073 (w)	a'
		985	980	985 (w)	985 (w)	a''
968 (3, *p*)	970 (1½*b*, *p*)	970	968	968 (s)	968 (s)	a'
				947 (w)	947 (w)	
N.o.	N.o.	790	783	783 (s)	780 (s)	a''
656 (10, *p*)	658 (10, *p*)	660	N.i.	N.i.	N.i.	a'
439 (½)						
335 (5, *p*)	335 (2, *p*)	N.i.	N.i.	N.i.	N.i.	a'

[a] *Ref. 16.*
[b] *Present investigation.*
[c] *Ref. 8.*
[d] *Present investigation, 400 mm. pressure, NaCl optics, 10 cm. path.*
[e] *Present investigation, −25° C., NaCl and LiF optics, 0.025 mm. cell.*
[f] *Present investigation, −180° C., NaCl and LiF optics, thin deposit.*

the experimental data are collected in Table IX, and the Raman intensities are presented in Table X.

TABLE X

CH_3CH_2Cl

Raman[a]						Infrared[b]		
Wave number	Approximate character	$\rho_{obs.}$	ρ_{true}	$\bar{S}$	S	Wave number	Intensity	Assignment
~3020	ν_{CH_2}	1.00	0.86	0.475	2.68	~3015	m.	a''
2983	ν_{CH_3}	1.00	0.86			2981	s.	a''
2966	ν_{CH_2}	0.42	0.29	0.696	5.46	N.o.		a'
2933	ν_{CH_3}	0.29	0.16	0.694	5.87	2936	s.	a'
2880	ν_{CH_3}	0.28	0.15	0.337	2.79	2883	m.	a'
1452	δ_{CH_3}	0.94	0.80	0.137	0.292	1454	s.	$a' + a''$
N.o.	δ_{CH_2}					~1440	m (sh)	a''
~1380	δ_{CH_3}	1.0	0.86	0.012	0.023	1380	m.	a'
~1280	δ_{CH_2}	0.5	0.4	0.024	0.047	1282	s.	a'
1244	δ_{CH_2}	0.4	0.3	0.030	0.072	1245	w.	a'
1072	ν_{CC}	0.45	0.32	0.066	0.127	1071	w.	a'
N.o.	δ_{CH_3}					985	w.	a''
970	δ_{CH_2}	0.88	0.74	0.072	0.095	968	v.s.	a'
N.o.	δ_{CH_3}					783	s.	a''
658	ν_{CCl}	0.39	0.26	0.571	0.627	N.i.		a'
335	s.d.	0.56	0.42	0.124	0.049	N.i.		a'
N.o.	Torsion							a''

[a] *Raman, pure liquid, reflection loss, $R_{(n)} = 1.20$.*
[b] *I.R., liquid at −25° C., NaCl and LiF optics, 0.025 mm. cell.*
N.o. = not observed.
N.i. = not investigated.

Only four ν_{CH} bands have been observed hitherto. We observed the fifth at 3023 cm.$^{-1}$ in the Raman spectrum of the liquid and at ~3020 cm.$^{-1}$ in the infrared spectrum of the solid corresponding to the shoulder at ~3015 cm.$^{-1}$ in the infrared spectrum of the liquid. The five ν_{CH} modes are assigned according to their depolarization ratios. The ν_{CCl} and δ_{CCl} modes are undoubtedly the low lying bands at 658 and 335 cm.$^{-1}$ respectively. ν_{CC} is assigned to the polarized band at 1072 cm.$^{-1}$. There are nine hydrogen deformation modes to be assigned, five of species a' and four of species a''. Three of the bands should lie in the 1450 cm.$^{-1}$ region, two associated with the methyl group of type a' and a'', and one a''-type fundamental from the methylene group. These are assigned to the 1450 and 1420 cm.$^{-1}$ bands respectively. The 1380 cm.$^{-1}$ band is probably an a'-type methyl group fundamental by analogy with CH_3CCl_3 and CH_3CHCl_2. The five remaining deformation vibrations observed at 1282, 1242, 985, 970, and 780 cm.$^{-1}$ are assigned in Table IX.

It is of interest to note that the liquid band at 1282 cm.$^{-1}$ appears as a doublet in the infrared spectrum of the solid. A similar splitting has been reported recently by Brown and Sheppard (5) for solid ethyl bromide.

The infrared and Raman spectrum of liquid ethyl chloride together with an assignment of the fundamental modes has also been reported by Nielsen, Liang, and Daasch in the Progress Report of the U.S.A.E.C. (cf. section on CH_3CHCl_2). Our assignment for the C—H modes differs from that reported by Nielsen, Liang, and Daasch. In the ν_{CH} region these authors have assigned the infrared band at 3010 cm.$^{-1}$ and the Raman band at 2980 cm.$^{-1}$ to the same vibrational mode since they do not observe the Raman band at 3020 cm.$^{-1}$. Similarly the infrared band at 2985 cm.$^{-1}$ is identified with the Raman band at 2965 cm.$^{-1}$. The assignment given in Table IX is preferred because the discrepancies in the positions of corresponding bands in the Raman and infrared spectra have been removed. The weak band at 2880 cm.$^{-1}$ can now be explained as the overtone of 1452 cm.$^{-1}$. Consistent with the assignment of 1,1-dichloroethane and uns-tetrachloroethane we assign two a'' and one a' type in the 1450 cm.$^{-1}$ region. This requires that the band at 1242 cm.$^{-1}$ is of type a'. Nielsen, Liang, and Daasch assign two a' and one a'' type modes in the 1450 cm.$^{-1}$ region and consider 1242 cm.$^{-1}$ to be of type a''.

Raman Intensities

In the expression used for obtaining standard intensities we have not attempted to account for the reduced masses corresponding to the various vibrational modes. In Table XI intensity contributions from the hydrogen stretching and bending modes, from the chlorine stretching and bending modes, and from the C—C stretching mode have been summed for each molecule studied in this investigation. The total Raman intensity ΣS (where S is defined as on p. 1125) is also given in the table. The values of ΣS are plotted against the number of Cl atoms per molecule in Fig. 2. It will be noticed that within the limits of experimental error (±10%) all the points lie on smooth curves.

TABLE XI

RAMAN INTENSITIES FOR CHLOROETHANES AT 27° C.

ΣS

	$\Sigma S_{\delta_{CCl}}$	$\Sigma S_{\nu_{CCl}}$	$S_{\nu_{CC}}$	$\Sigma S_{\delta_{CH}}$	$\Sigma S_{\nu_{CH}}$	$\Sigma S_{\text{total skeletal}}$	$\Sigma S_{\text{total CH}}$	$\Sigma S_{\text{total intensity}}$
C_2H_5Cl	0.04_9	0.62_8	0.12_7	0.52_8	16.80	0.80	17.33	18.13
CH_3CHCl_2	0.23_1	0.86_7	0.05_7	0.64_0	11.12_5	1.15	11.76	12.92
CH_3CCl_3	0.41_0	1.38_3	0.13_9	0.51_8	8.42_4	1.93	8.94	10.87
CH_2ClCCl_3	0.71_6	1.83_4	0.11_3	0.50_6	6.91_2	2.66	7.41	10.08
$CHCl_2CCl_3$	1.52_6	2.24_8	0.20_8	0.36_6	5.08_9	3.99	5.45	9.44

There is some evidence in these results for additive contributions from particular groups in the chloroethane series. For instance, the intensity contribution from ν_{CCl} modes in CH_3CCl_3 is 1.38 units and in CH_3CH_2Cl is 0.63, from which we estimate the intensity contribution from ν_{CCl} modes in CCl_3CH_2Cl to be 2.01 units. The observed value is 1.83 units. For CCl_3CHCl_2 the computed value is 2.25 units coincident with the observed value. The same order of agreement is found for ν_{CH} modes. There is no evidence for additivity among deformation modes.

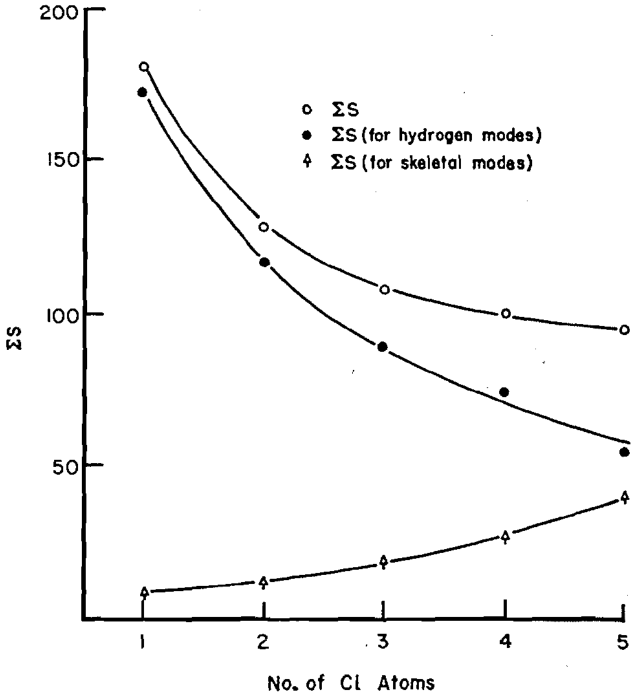

FIG. 2. Standard Raman intensities in chloroethanes.

TABLE XII

RAMAN INTENSITIES FOR LIQUID CHLOROMETHANES AT 27° C.

CCl_4[a]			$CHCl_3$[b]			$C_2H_2Cl_2$[c]		
Wave number	$\rho_{obs.}$	S	Wave number	$\rho_{obs.}$	S	Wave number	$\rho_{obs.}$	S
218	1.01	0.148	261	1.00	0.173	283	0.65	0.119
314	1.01	0.309	365	0.33	0.303	700	0.31	0.718
458	0.21	1.000	669	0.23	0.661	736	1.01	0.156
762 790	1.01	0.791	761	0.99	0.411	898	N.o.	N.o.
			1215	0.96	0.200	1148	1.00	0.051
			3019	0.42	3.010	1255	0.30	0.082
						1420	0.94	0.200
						2984	0.26	3.615
						3048	1.00	0.880

[a] *Reflection loss,* $R_{(n)} = 1.00$.
[b] *Reflection loss,* $R_{(n)} = 1.06$.
[c] *Reflection loss,* $R_{(n)} = 1.10$.
N.o. = not observed.

TABLE XIII

RAMAN INTENSITIES FOR CHLOROMETHANES

		$\Sigma S_{\delta_{\mathrm{CCl}}}$	$\Sigma S_{\nu_{\mathrm{CCl}}}$	$\Sigma S_{\delta_{\mathrm{CH}}}$	$\Sigma S_{\nu_{\mathrm{CH}}}$	$\Sigma S_{\text{total intensity}}$
CCl_4	Vapor	0.428	2.04			2.47
	Liquid	0.457	1.79			2.25
$CHCl_3$	Vapor	0.647	1.379	0.238	2.86	5.13
	Liquid	0.476	1.07	0.200	3.01	4.76
CH_2Cl_2	Vapor	0.108	0.900	0.168	3.28	4.46
	Liquid	0.119	0.874	0.333	4.50	5.83
CH_3Cl	Vapor		0.834	0.39	7.40	8.62
CH_4	Vapor			1.09	34.40	35.5

The only other data for Raman intensities in a homologous series are those reported by Welsh *et al.* (32) for the gaseous chloromethanes. In Table XIII we present their data reduced to our standard intensity scale*, along with our results for three liquid chloromethanes (cf. Table XII). These data are plotted in Fig. 3. The general features of the curve are the same as for the chloroethanes; in both cases intensity contributions from C—H modes are much

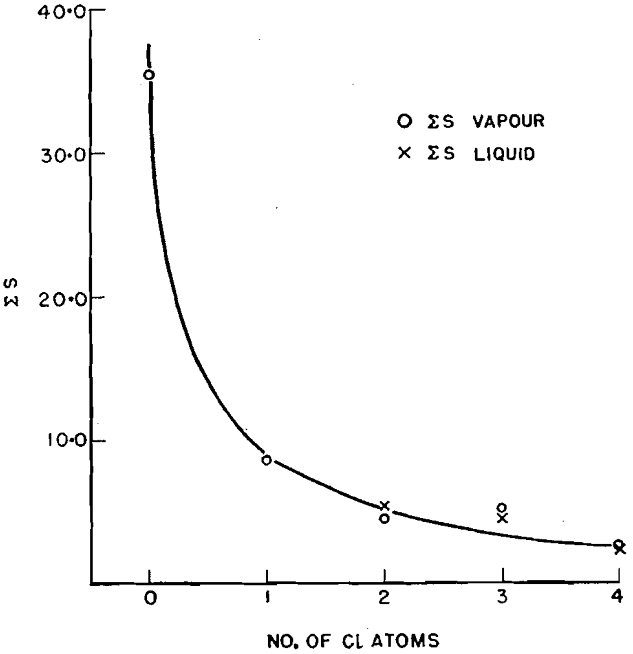

FIG. 3. Standard Raman intensities in the chloromethanes.

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*The reduced integrated intensities (i_λ) reported by Welsh and Crawford include $(Q_0)^2 = \lambda/8\pi^2 c\nu_\lambda$ (cf. p. 580, Ref. 32). They are reduced to our scale by the following transformation

$$S = \left(\frac{i_\lambda \times \nu_\lambda}{1+\rho_{\mathrm{true}}}\right)_{\nu_\lambda} \Big/ \left(\frac{i_\lambda \times \nu_\lambda}{1+\rho_{\mathrm{true}}}\right)_{458}$$

where subscript ν_λ refers to the Raman line under consideration and where subscript 458 refers to the line at 458 cm.$^{-1}$ in CCl_4.

larger than the contributions from C—Cl modes. It is difficult to tell whether the inflection in the chloromethane curve for intensities in the vapor phase is real (13), since it does not occur in the liquid phase results.

Application of the $\Sigma\nu$ Rule to the Chloroethanes

The constitutive properties of the substituted ethanes are given in terms of five parameters (2). For the compounds studied in this investigation the $\Sigma\nu$ for all modes can be expressed in the following manner:

$$\begin{aligned}
&C_2Cl_6 &&: \Sigma\nu = P\\
&C_2HCl_5 &&: \Sigma\nu = P + \alpha\\
&C_2H_2Cl_4 &&: \Sigma\nu = P + \alpha + \beta\\
&C_2H_3Cl_3 &&: \Sigma\nu = P + 3\beta\\
&C_2H_4Cl_2 &&: \Sigma\nu = P - 2\alpha + 3\beta + \gamma + 2\delta\\
&C_2H_5Cl &&: \Sigma\nu = P - 5\alpha + 4\beta + 2\gamma + 4\delta\\
&C_2H_6 &&: \Sigma\nu = P - 9\alpha + 6\beta + 3\gamma + 6\delta\,.
\end{aligned}$$

The nomenclature of Ref. 2, which includes rotational isomers, has been used here. Since there are no rotational isomers in the above molecules, the parameters are reduced to four, viz., P, α, β, $(\gamma + 2\delta)$.

Since the assignments for C_2H_6, $C_2H_4Cl_2$, $C_2H_2Cl_4$, and C_2HCl_5 are less ambiguous than those for the other molecules the $\Sigma\nu$ for these molecules have been used to evaluate the parameters. A further requirement of the model from which the sum rule was derived (2) is that the second difference of $\Sigma\nu$ for the parabolae containing the points C_2H_6, C_2H_5Cl, $C_2H_4Cl_2$, $C_2H_3Cl_3$, and $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 is the same as that for the chloromethanes. The value of this second difference $(\alpha - \beta)$ is taken as 450 cm.$^{-1}$ based on the least squares fitting of $\Sigma\nu$ for the chloromethanes (4). We have four data from which to evaluate three unknowns and have accomplished this by the method of averages in which the sum of the residues is made zero (27). This yields

$$P = 7927, \qquad \alpha = 4493, \qquad \beta = 4043, \qquad (\gamma + 2\delta) = 13255.$$

With these values of the parameters the $\Sigma\nu$ for C_2Cl_6, $C_3H_3Cl_3$, and C_2H_5Cl have been calculated and compared with the observed sums in Table XIV.

TABLE XIV

SUM RULE FOR CHLOROETHANES

Molecule	$\Sigma\nu$obs.[a], cm.$^{-1}$	$\Sigma\nu$calc., cm.$^{-1}$	Obs. − calc., cm.$^{-1}$
C_2Cl_6	7873	7927	−54
C_2HCl_5	12428	12420	+ 8
uns-$C_2H_2Cl_4$	16492	16463	+29
1,1,1-$C_2H_3Cl_3$	19992[b]	20056	−64
	20092[c]		+36
1,1-$C_2H_4Cl_2$	24231	24325	−94
C_2H_5Cl	28084	28144	−60
C_2H_6	31550	31513	+37

[a] *For purposes of the computation the following values for the torsional modes have been used: C_2Cl_6 = 50 cm.$^{-1}$, $C_2H_3Cl_3$ = 200 cm.$^{-1}$, $C_2H_4Cl_2$ = 225 cm.$^{-1}$, C_2H_5Cl = 250 cm.$^{-1}$.*

[b] *Ref. (29).*

[c] *Ref. (25).*

The application of the sum rule to C_2H_5Cl indicates a satisfactory assignment whereas the value of $\Sigma\nu$ obtained from the assignment of Nielsen *et al.* would be 27950. The calculated and observed sums for C_2Cl_6 are in satisfactory agreement and the calculated sum for $C_2H_3Cl_3$ is not inconsistent with either the Nielsen (29) or the Pitzer (25) assignments.

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SOME ASPECTS OF THE TOLUENE PYROLYSIS[1]

By Arthur T. Blades[2] and E. W. R. Steacie

The extensive use of the toluene carrier gas technique by Szwarc (7, 8) and co-workers has attracted wide interest (1, 2, 4, 6) in the mechanism of the pyrolysis of toluene in the past few years. The present note is concerned with the reactions of hydrogen atoms with toluene-d_3 and of benzyl radicals with *p*-fluorotoluene.

REACTION OF HYDROGEN ATOMS WITH TOLUENE

According to Szwarc, radicals in general react with toluene in the following manner:

$$R^\cdot + C_6H_5CH_3 \rightarrow RH + C_6H_5CH_2^\cdot \qquad [1]$$

$$2C_6H_5CH_2^\cdot \rightarrow C_{14}H_{14}. \qquad [2]$$

He found it necessary, however, to propose an additional mechanism for the reaction of hydrogen atoms with toluene since methane as well as hydrogen is a product of the pyrolysis of toluene. Two radically different mechanisms might be proposed for the production of methane in this instance.

I

$$C_6H_5CH_3 \rightarrow C_6H_5CH_2^\cdot + H^\cdot \qquad [3]$$

$$H^\cdot + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2^\cdot \qquad [4]$$

$$H^\cdot + 2C_6H_5CH_3 \rightarrow CH_4 + C_6H_6 + C_6H_5CH_2^\cdot \qquad [5]$$

or

II

$$C_6H_5CH_3 \rightarrow C_6H_5^\cdot + CH_3^\cdot \qquad [6]$$

$$CH_3^\cdot + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2^\cdot \qquad [7]$$

Since the ratio of H_2 to CH_4 in the products is independent of temperature, it follows that either $E_3 = E_6$ or $E_4 = E_5$. Szwarc reasoned that the activation energy for the over-all decomposition (77.5 kcal./mole) was too low for E_6 and hence assumed that mechanism I was responsible for the methane production. Recent studies on the kinetics of the pyrolysis (2) and on the photobromination (1) of toluene suggest that this activation energy may not be reliable and hence that mechanism II cannot be ruled out by this argument.

Szwarc (5) has produced hydrogen atoms by the pyrolysis of *n*-propyl benzene in the presence of toluene and found both hydrogen and methane in the products in roughly the same proportion as in the toluene pyrolysis.

$$C_6H_5C_3H_7 \rightarrow C_6H_5CH_2^\cdot + C_2H_5^\cdot$$

$$C_2H_5^\cdot \rightarrow H^\cdot + C_2H_4$$

$$H^\cdot + C_6H_5CH_3 \rightarrow H_2 + C_6H_5CH_2^\cdot$$

$$H^\cdot + 2C_6H_5CH_3 \rightarrow CH_4 + C_6H_6 + C_6H_5CH_2^\cdot$$

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[1] *Issued as N.R.C. No. 3412.*

[2] *National Research Council of Canada Postdoctorate Fellow 1952–1954.*

It is conceivable, however, that propyl benzene, like propane, might decompose by a molecular mechanism into methane and the corresponding olefin.

$$C_3H_8 \rightarrow CH_4 + C_2H_4$$
$$C_6H_5C_3H_7 \rightarrow CH_4 + C_6H_5CHCH_2$$

By carrying out the pyrolysis of *n*-propyl benzene in an excess of toluene-d_3, it was hoped that further light might be thrown on the mechanism of the decomposition of propyl benzene and on the reaction of hydrogen atoms with toluene.

The "toluene-d_3" was prepared in these laboratories by Dr. L. C. Leitch and was found to contain 66% d_3, 29% d_2, and 5% d_1 toluene. The propyl benzene was pyrolyzed at 995° K., at a total pressure of 1.7 cm. Hg, a contact time of 0.45 sec., and a toluene to propyl benzene ratio of 40 to 1, in an apparatus similar to that described previously (2). Under these conditions the propyl benzene was about 30% decomposed, the products being hydrogen, methane, ethane, ethylene, benzene, and bibenzyl. Mass spectra of the various fractions indicated:

$$H_2 : HD : D_2 = 1 : 1 : \sim 0$$
$$CD_4 : CD_3H : CD_2H_2 = 1 : 1.5 : \sim 1.$$

The benzene was mostly C_6H_6 but small percentages of C_6H_5D may also have been present.

The production of deuterated methanes in this pyrolysis rules out the intramolecular production of methane in the propyl benzene pyrolysis and confirms Szwarc's belief that hydrogen atoms produce methane when reacting with toluene. The fact that he also found roughly the same H_2 to CH_4 ratio in the decompositions of both toluene and *n*-propyl benzene is strong evidence that mechanism II is unimportant in the toluene pyrolysis.

Szwarc has suggested two mechanisms for the production of methane when hydrogen atoms react with toluene. With deuterated toluene these are:

$$\begin{array}{lll} \text{III} & H^{\cdot} + C_6H_5CD_3 & \rightarrow C_6H_5^{\cdot} + CD_3H \\ & C_6H_5^{\cdot} + C_6H_5CD_3 & \rightarrow C_6H_5D + C_6H_5CD_2^{\cdot} \\ \text{IV} & H^{\cdot} + C_6H_5CD_3 & \rightarrow CD_3^{\cdot} + C_6H_6 \\ & CD_3^{\cdot} + C_6H_5CD_3 & \rightarrow CD_4 + C_6H_5CD_2^{\cdot}. \end{array}$$

Thus with the deuterated toluene used here, mechanism III would give CD_3H, CD_2H_2 etc., C_6H_5D, and C_6H_6 while mechanism IV would give CD_4, CD_3H etc., and C_6H_6. The production of CD_4, CD_3H etc., and C_6H_6 in the present experiments is then good evidence for mechanism IV but III may contribute to a minor degree.

The ratio of H_2 to HD is surprising in view of the fact that the side chain of the toluene was 87% deuterated. This leads to the suspicion that hydrogen atoms may be abstracting from the ring as well as from the side chain. Trotman-Dickenson and Steacie (9) give data for the relative rates of abstraction from benzene and toluene by methyl radicals at 450° K. On extrapolation to 1000° K. these data suggest that about 10% of radicals will abstract from the ring in normal toluene, and with toluene deuterated on the side chain this percentage would certainly be higher.

REACTION OF BENZYL RADICALS WITH *p*-FLUOROTOLUENE

The relative unreactivity of the benzyl radical is the basis of the so-called "toluene carrier gas technique" for studying free radical decomposition reactions. In a high mole ratio of toluene to decomposing compound, a radical will tend to react preferentially with toluene to give RH and a benzyl radical (reaction [1]) thereby converting a reactive radical into a molecule and an inert radical. Under the correct conditions of concentration and temperature, these benzyl radicals will dimerize to bibenzyl. Since the technique has been used at temperatures where bibenzyl would be expected to decompose rapidly however, it would be possible for abstraction reactions of benzyl to compete with the dimerization process. To test this, some studies on the relative rates of the reactions

$$C_6H_5CH_2^{\cdot} + p\text{-}C_6H_4FCH_3 \rightarrow C_6H_5CH_3 + C_6H_4FCH_2^{\cdot} \quad [8]$$

and

$$2C_6H_5CH_2^{\cdot} \rightarrow C_{14}H_{14} \quad [9]$$

have been attempted by pyrolyzing bibenzyl in the presence of an excess of *p*-fluorotoluene.

The apparatus for the pyrolysis of bibenzyl was similar to that referred to above. The bibenzyl was introduced by passage of the *p*-fluorotoluene over it at 110° C. The major products were mixtures of fluorinated bibenzyls which were pumped free of *p*-fluorotoluene at 0° C. Quantities of hydrogen (80%) and methane (20%) were produced varying from 1 to 5% of the bibenzyl passed through the reactor.

Analysis of the bibenzyl fraction was attempted from its infrared absorption spectrum in CS_2 solution. Unfortunately, different absorption bands gave radically different analyses and the conclusion was reached that monofluorobibenzyl was also a product along with the di-*p*-fluorobibenzyl. Analyses were thereby limited to combustion of the mixture and this is unsatisfactory for kinetic data. A typical run at 994° K., contact time of 0.253 sec., pressure of 1.35 cm. Hg, and mole ratio of *p*-fluorotoluene to bibenzyl of 50 to 1 yielded the information that the equivalent of 35% of the bibenzyl was converted to di-*p*-fluorobibenzyl.

The following reaction scheme is consistent with the observations if the small amounts of H_2 and CH_4 are neglected.

$$(C_6H_5CH_2)_2 \rightleftharpoons 2C_6H_5CH_2 \quad [10]$$

$$C_6H_5CH_2 + C_6H_4FCH_3 \rightarrow C_6H_4FCH_2 + C_6H_5CH_3 \quad [11]$$

$$2C_6H_4FCH_2 \rightleftharpoons (C_6H_4FCH_2)_2 \quad [12]$$

$$C_6H_5CH_2 + C_6H_4FCH_2 \rightleftharpoons C_6H_4FCH_2CH_2C_6H_5 \quad [13]$$

The production of fluorinated bibenzyls confirms the belief that reaction [11] will compete favorably with the reverse of reaction [10] in the neighborhood of 1000° K. under conditions commonly used in the toluene carrier gas technique.

GENERAL CONCLUSIONS

It has been demonstrated that methane is a product of the reaction of hydrogen atoms with toluene thereby confirming the Szwarc mechanism for the decompositions of toluene and *n*-propyl benzene. The evidence is consistent with the following mechanism:

$$H^\cdot + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3^\cdot$$
$$CH_3^\cdot + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2^\cdot.$$

Szwarc used the activation energy for the decomposition of toluene to decide on the mechanism; confirmation of the mechanism does not, however, prove the correctness of this activation energy nor does it cast doubt on the higher value obtained by the photobromination of toluene (1, 3). It is worthy of note, however, that this latter is a maximum value and that the true value is less by the activation energy of the reaction

$$C_6H_5CH_2^\cdot + Br_2 \rightarrow C_6H_5CH_2Br + Br^\cdot$$

and there is no a priori reason for supposing that this is zero.

Evidence has also been presented suggesting that radicals may abstract hydrogen atoms from the ring as well as the side chain in toluene but there is no indication as to how serious a complication this might be in the toluene carrier gas technique. Presumably the resulting tolyl radicals would disappear rapidly by reaction with toluene.

$$C_6H_4CH_3^\cdot + C_6H_5CH_3 \rightarrow C_6H_5CH_3 + C_6H_5CH_2^\cdot$$

Under the conditions of the toluene carrier gas technique in the neighborhood of 1000° K., abstraction by benzyl radicals has been shown to compete with combination. This implies that, when this technique is used in this temperature region, complications must be anticipated from reactions of the type

$$C_6H_5CH_2^\cdot + RH \rightarrow C_6H_5CH_3 + R^\cdot$$

where RH is the decomposing molecule, especially when the R—H bond is weak.

Horrex and Miles (4) have studied the pyrolysis of bibenzyl and arrived at the rate expression

$$k = 2 \times 10^9\, e^{-48{,}000/RT}\ \text{sec.}^{-1}$$

for the decomposition into two benzyl radicals. Under the experimental conditions used in the above experiment this would predict only about 2% decomposition of the bibenzyl. Since a minimum of 35% was decomposed, it is suggested that the above rate expression is in error owing to the neglect of the recombination step in their mechanism.

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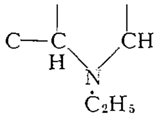
LYCOCTONINE: THE ENVIRONMENT OF THE NITROGEN[1]

By O. E. Edwards and Léo Marion

In an earlier paper (2) the question of the presence of N-alkyl groups in the aconite and delphinium alkaloids was reviewed. Since then the occurrence of an N(β-hydroxyethyl) group in atisine has been indicated since it has been proved to be present in tetrahydroatisine (3), and very recently the presence of an N-ethyl group in delsine (almost certainly identical with lycoctonine) has been decisively demonstrated by Abubakirov and Yunusov (1). Still more recently the presence of an N-ethyl group in aconitine has been confirmed (4). We wish to record our proof of the presence of an N-ethyl group in lycoctonine by a route different from that used by the Russian workers.

Hydroxylycoctonine has been oxidized by permanganate in acetone. The course of oxidation parallels that of lycoctonine itself, the main products being hydroxylycoctonam, des(oxymethylene)-hydroxylycoctonam, and hydroxylycoctonamic acid. The formation of these products in good yield provided confirmation of the earlier conclusion (2) that the carbinolamine hydroxyl in hydroxylycoctonine was on a carbon holding no hydrogen.

As was expected on the basis of the assumed carbinolamine lactam structure for hydroxylycoctonam, this compound was hydrolyzed by hot dilute acid to give ethylamine. This was characterized as its picrate. Thus the environment of the nitrogen in lycoctonine has been proved beyond doubt to be as shown in the following partial formula:



The demonstration of the presence of an N-ethyl group in lycoctonine (delsine) coupled with the good evidence for its presence in aconitine makes it appear likely that this unusual alkyl substituent is of widespread occurrence in the aconite and delphinium alkaloids. Although Abubakirov and Yunusov showed (1) that some formaldehyde can arise from the alkaloids after removal of the N-alkyl, the formation of acetaldehyde or formaldehyde in the course of the permanganate oxidation seems to be the most reliable guide to the nature of the N-alkyl, short of more elaborate proof as above.

Hydroxylycoctonam was only very slowly attacked by periodic acid despite the presence of the vicinal glycol. In addition, methyl hydroxylycoctonamate was only slowly hydrolyzed by alkali at room temperature, in contrast to the behavior of methyl lycoctonamate (2).

Abubakirov and Yunusov suggest that the name lycoctonine be abandoned in favor of delsine. We consider the former so well established in the literature (since 1866) that to change the name merely to indicate that it occurs mainly

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in delphinium species seems unwise. Hence we intend to continue using the designation lycoctonine.

Hydroxylycoctonine: Permanganate Oxidation A

Powdered potassium permanganate (627 mgm.) was added in small portions over a period of six hours to a solution of 163 mgm. of hydroxylycoctonine in 15 cc. of acetone containing 0.2 cc. of acetic acid. An excess persisted after this amount had been added. The suspension was filtered and the manganese dioxide washed well with acetone. The acetone was boiled off, and the residue taken up in water which had previously been used to wash the manganese dioxide. The products were separated into 122 mgm. of neutral, 10 mgm. of acidic, and 4 mgm. of basic material.

The neutral product was dissolved in 10% chloroform in benzene and adsorbed on 3.5 gm. of alumina, activity 3. A 50% benzene–chloroform mixture (180 cc.) eluted 49 mgm. which crystallized readily from ether. Chloroform (90 cc.) eluted 38 mgm. which also crystallized from ether.

Des(oxymethylene)-hydroxylycoctonam

The readily eluted neutral compound, after four recrystallizations from acetone and acetone–ether, gave 25 mgm. of prisms, which softened at 206° and melted by 217°, $[\alpha]_D$ 24 ± 3° (c = 0.9 in ethanol). Found: C, 61.28; H, 7.66. Calc. for $C_{24}H_{37}O_8N$: C, 61.65; H, 7.98. Infrared absorption peaks: 3490, 3410 (hydroxyls), 1635 cm.$^{-1}$ (lactam).

Hydroxylycoctonam

The more strongly adsorbed neutral compound melted at 194–200° after one recrystallization from acetone–ether (21 mgm.). This was combined with the corresponding product from oxidation *B*. The melting point proved erratic, probably owing to solvation. After recrystallization, purification by chromatography on alumina, and further recrystallization from acetone–ether, the compound was obtained as rhombic plates, m.p. 190–208°. $[\alpha]_D^{27}38 \pm 2°$ (c = 1.76 in ethanol). Found: C, 60.86, 60.99; H, 8.02, 8.10. Calc. for $C_{25}H_{39}O_9N$: C, 60.34; H, 7.90. Infrared absorption peaks: 3460, 3390 (hydroxyls), 1631 cm.$^{-1}$ (lactam). Hydroxylycoctonam was recovered in over 75% yield after 46 hr. in 0.05 *N* periodic acid solution buffered to pH 5.

Hydroxylycoctonine: Permanganate Oxidation B

Powdered potassium permanganate was added to a solution of 1.19 gm. of hydroxylycoctonine in 20 cc. of acetone containing 1 cc. of acetic acid. The reaction slowed markedly after 0.8 gm. of permanganate had been added. After 0.5 cc. of water had been added, a further 0.14 gm. of permanganate was readily consumed. (Total reaction time, three hours.) The product was worked up as in *A* to give 774 mgm. of neutral and 250 mgm. of acidic material. The neutral material was separated by careful chromatography on alumina into 120 mgm. of amorphous, more readily eluted product, 450 mgm. of hydroxylycoctonam, and a small quantity of amorphous strongly adsorbed product. No des(oxymethylene)-hydroxylycoctonam was found.

Methyl Hydroxylycoctonamate

The acidic material obtained from the permanganate oxidation of hydroxylycoctonine (as in procedure *B*) was converted to methyl esters using diazomethane in methanol–ether. The 460 mgm. of ester was adsorbed from benzene on 14 gm. of neutral alumina, activity 3. Benzene (75 cc.) and 25% chloroform in benzene (50 cc.) eluted 38 mgm. Pure chloroform (175 cc.) and 1% methanol in chloroform (75 cc.) eluted 313 mgm. which crystallized readily from methanol–ether. After one recrystallization from methanol–ether the 227 mgm. of glistening prisms melted at 252–256°. Further recrystallization did not change the melting point. $[\alpha]_D^{27}$ 25 ± 1° ($c = 1.67$ in ethanol). Found: C, 59.37; H, 7.30; OCH_3, 30.15. Calc. for $C_{26}H_{39}O_{10}N$: C, 59.41, H, 7.48; 5 OCH_3, 29.52. Infrared absorption peaks: 3510, 3450 (hydroxyls), 1745 (ester), 1668 cm.$^{-1}$ (lactam).

The methyl ester was approximately 5% hydrolyzed in four hours at room temperature by 1 *N* potassium hydroxide in 50% aqueous methanol. After 20 hr. in 1.5 *N* alkali in 50% aqueous methanol the ester was 80% hydrolyzed. The 20% of unchanged ester crystallized readily from ether, m.p. 252–255°. Attempts to induce crystallization of the acid failed.

Ethylamine from Hydroxylycoctonam

A solution of 70 mgm. of hydroxylycoctonam in 4 cc. of freshly prepared 1 *N* sulphuric acid was heated in a sealed tube at 100° for 12 hr. and at 160° for 10 hr. At the higher temperature a tar was formed. The tube was cooled and the contents filtered into a flask with an attached Vigreux column. The tube and funnel were washed with dilute sodium hydroxide. The washings were combined with the main solution and the whole distilled until less than 1 cc. remained. Three pellets of sodium hydroxide were added to the distillate, and this was redistilled. Freshly crystallized picric acid (65 mgm.) was added to the distillate, and the resulting solution taken to dryness under reduced pressure. The excess picric acid was extracted with ether leaving 19 mgm. of crystalline picrate, m.p. 167–169°. After one recrystallization from methanol–ether it melted at 169–170°. This did not depress the melting point of authentic ethylamine picrate (m.p. 169–170°), and the infrared spectra of the two compounds were identical. Found: C, 34.99; H, 3.65. Calc. for $C_8H_{10}N_4O_7$: C, 35.04; H, 3.68.

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A NEW CONCEPT ON THE MECHANISM OF AUTOXIDATION OF METHYL OLEATE, LINOLEATE, AND LINOLENATE[1]

By N. A. Khan[2]

In Farmer's modified theory describing "universal initiation" (4) and in Hilditch's theory (10) of transitory formation of cyclic peroxide, which both advocate an oxidative attack on olefines by addition at the double bond, there are two major defects: (*a*) neither makes any provision for the energy ($\leqslant$ 64 kcal.) needed for opening up one bond (20) of the double bond $(-\dot{C}-\dot{C}-)$, (*b*) Farmer's postulation leads to the formation of an unstable diradical system (21) and Hilditch's to a cyclic four-membered ring under a considerable amount of strain (7). In this paper, a suitable theory which eliminates both these defects in Farmer's and Hilditch's theories will be proposed and explained.

The recent research in the field of autoxidation supports Farmer's theory. The agreement has arisen, perhaps, because of an inadequate appreciation of the reaction sequence in autoxidation. The reaction patterns in each of the four periods (12) involved in autoxidation are different. These periods ((*A*) induction period, (*B*) peroxidation period, (*C*) period of main autoxidation, and (*D*) period of decline in autoxidation) are represented in Fig. 1. The initiation processes of autoxidation occur during the induction (*A*) and peroxidation (*B*) periods. Robertson and Waters (17) have described the

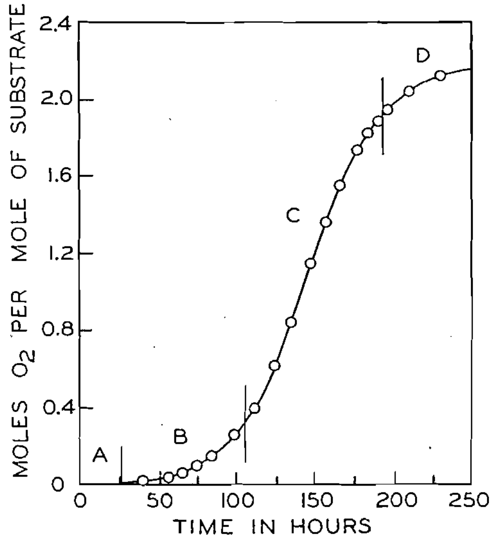

FIG. 1. Course of oxidation of methyl oleate at 75° C.

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advantages of the studies on the entire reaction sequence by autoxidizing tetralin. Our objective is to study the mechanism of initial reaction that leads to the quantitative formation of hydroperoxides. Temperature is maintained below 0° in autoxidizing the fatty acid esters to about five per cent peroxide contents. It is our experimental observation that the hydroperoxides from these substances do not decompose under such conditions. The quantitative recovery of the oxygenated materials representative of the initiation processes in autoxidation is also taken into consideration.

Hydroperoxidation, like many organic reactions (11), has to pass over the energy barrier and is appreciably slow at the start, giving rise to the induction period. Once started, it proceeds very smoothly, the rate increasing with the concentration of peroxides (the slope of the curve *B*, Fig. 1). However, it may be carried on indefinitely at a suitable temperature below 0° for the different substances used.

In our preliminary experiments, monomeric monohydroperoxides were obtained from methyl linoleate (13, 14) and linolenate (14) autoxidized below 0° without any agitation. Such results are found reproducible if the temperature of oxidation is maintained at −10° and the temperatures during the isolation procedures below 10° C. Methyl oleate is also found to form monomeric monohydroperoxide quantitatively at 0° in a period of several years. The physical and chemical analyses (Table I) of the products obtained on the reduction of the peroxides by stannous chloride indicate the pure monomeric character of each hydroperoxide.

TABLE I
PROPERTIES OF THE REDUCED HYDROPEROXIDES

			Infrared absorption		
	H_2/mole	OH/mole	*Cis, trans*-conjugated 10.55 μ	*Trans, trans*-conjugated 10.12 μ	Isolated *trans* nonconjugated 10.36 μ
1. Reduced methyl oleate hydroperoxide[a]	1.0	1.0	—	—	Strong[b]
2. Reduced methyl linoleate hydroperoxide[a]	2.0	1.0	Very strong[c]	—	—
3. Reduced methyl linolenate hydroperoxide[a]	2.89	1.0	Very strong[c]	—	—

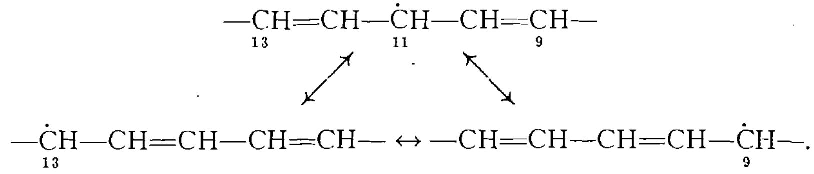
[a] *Peroxide value of the unreduced peroxides ranged between 6030 and 6125 m.e./kgm.*
[b] *About 62% isolated trans compared to methyl elaidate.*
[c] *About 100% cis, trans-conjugated compared to pure cis, trans-conjugated linoleate (Jackson et al. J. Am. Oil Chemists' Soc. 29: 229. 1952).*

Further support for formation at the initial stages of autoxidation of a single hydroperoxide by each of the above-mentioned substances has been obtained from our microdistillation data. Each of the substances was oxidized (methyl oleate at 25–30°, linoleate and linolenate at −10°) to 5% and 10% peroxide content. The peroxides were concentrated by countercurrent extraction between two immiscible phases: 89% alcohol and petroleum ether (b.p. 30–60° C.). The peroxide concentrates were reduced by stannous chloride, and the reduced products distilled by means of a special apparatus (16) and found in all cases to consist of 98–100% monomers [such may not, of course, be the case for many competing reactions of initiation, propagation, and termination involved in free radical mechanisms proposed by Farmer (2, 4, 18*a*)].

The hydroperoxides isolated from autoxidized linoleate consist of two positional (9- and 13-) conjugated isomers (13, 15) and those from oxidized linolenate, four positional (9-, 12-, 13-, and 16-) conjugated isomers (14). Methyl oleate hydroperoxide is found to contain two positional isomers (9-hydroperoxide-10-octadecenoate and 10-hydroperoxido-8-octadecenoate) on the basis of scission products. The methyl oleate hydroperoxide was split by permanganate in acetone and the scission products were separated into two fractions consisting essentially of mono- and di-carboxylic acids by the methods of Swift *et al.* (19). The di-carboxylic acid fraction was further separated into two additional fractions (one, m.p. 139.0–141.0° C., n.e. 89.3–89.7, and two, m.p. 97.5–98.6° C., n.e., 94.0–95.0). The latter product on recrystallization melted at 104.0–105.0° C. The original mixture may be considered to be suberic acid (m.p. 141.0° C., n.e. 87.0) and azelaic acid (m.p. 106.0° C., n.e. 94.0) accounting for the two isomers of methyl oleate hydroperoxide. The formation of these two isomers has been observed by Swern *et al.* (18*b*) during the autoxidation of methyl oleate.

It seems that the formation of these isomers is possibly associated with a three-carbon system (one double bond and its alpha-methylenic group) and a compulsory shift of the double bond. This can not happen with the mechanism involving free radicals followed by chain reactions. Consequently, these isomers are not the same as those predicted on Farmer's theory (2, 4, 5).

The hydroperoxides from photo-chlorophyll oxidation of methyl *cis,cis*-linoleate contain the nonconjugated isomer probably positional at carbon-11 with an isolated *trans* double bond (absorbing in the infrared region of 10.36 μ) in addition to the isomers (probably positional at carbons 9 and 13, shown below) having *cis*, *trans*- and *trans*, *trans*- conjugated double bonds (absorbing at 10.15 and 10.55 μ). This means that activated chlorophyll maintains a high energy level to pull off an alpha-methylenic hydrogen and to form a free radical at carbon-11 causing resonance:



$$\underset{13}{\mathrm{-CH}}\mathrm{=CH-}\underset{11}{\mathrm{\dot{C}H}}\mathrm{-CH=}\underset{9}{\mathrm{CH}}\mathrm{-}$$

$$\mathrm{-}\underset{13}{\mathrm{\dot{C}H}}\mathrm{-CH=CH-CH=CH-} \leftrightarrow \mathrm{-CH=CH-CH=CH-}\underset{9}{\mathrm{\dot{C}H}}\mathrm{-.}$$

These processes give rise to three isomers: 9- and 13- conjugated and 11-nonconjugated hydroperoxides. These are, indeed, the positional isomers of hydroperoxides obtained on photo-chlorophyll oxidation of *cis,cis*-linoleate. However, autoxidation of methyl linoleate does not form a nonconjugated hydroperoxide at carbon-11 with an isolated *trans* double bond, but it forms the completely conjugated products. Such selective isomerization and freedom from 11-hydroperoxide indicate that the alpha-methylenic group at carbon-11 may not possibly be attacked by oxygen to form a free radical. By analogy, this may be applied to other olefinic substances used. Moreover, the failure of Robertson and Waters (17) to detect, by the pyridine reaction, the formation of free radicals during the autoxidation of tetralin may indicate a mechanism of the initiation processes involving no free radicals.

Polymer formation is not characteristic of hydroperoxidation. Only monomeric products (12, 13, 14) are formed by autoxidation of the olefinic substances at the initial stages. This may explain why Farmer and his group (6) found it difficult to isolate characteristic dimeric products from even drastically autoxidized olefines. Polymerization is usually a criterion of the double-bond attack (3) and can, therefore, be used as evidence of the production of free radicals or fragments impregnated with energy. Thus, the initiation processes probably do not involve polymerization. Consequently, the formation of free radicals and the direct double-bond attack may not occur in these processes.

From consideration of all these findings, the following mechanistic concept of the initial stages of autoxidation (Fig. 2) on the basis of modern electronic

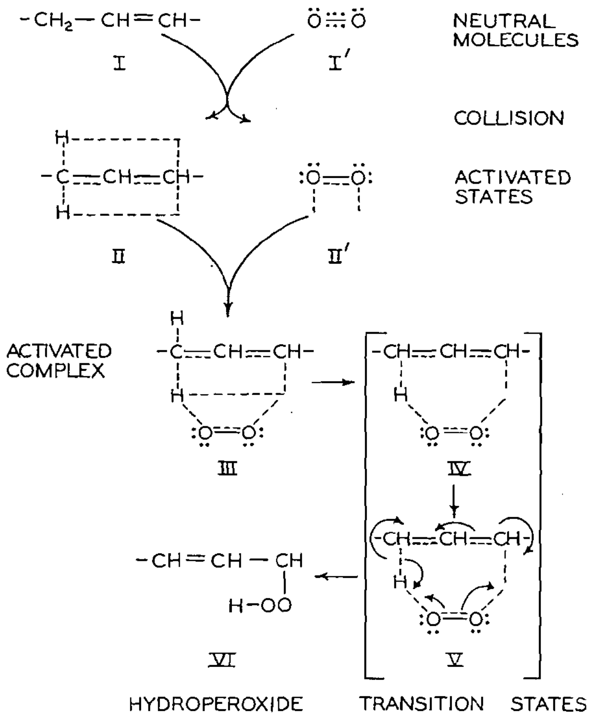


FIG. 2. Mechanism of the initiation processes in autoxidation reactions.

theory is introduced: Only a three-carbon system (Fig. 2, I) consisting of a double bond and an alpha-methylenic group is represented because of its being mainly involved in autoxidation reactions in all cases with differences in reactivity (9). After usual collisions, both the oxygen molecule (I′) and the olefine portion (I) attain certain activated states (II and II′) because of resonance due to hyperconjugation (1*b*) in the three-carbon system (I) and also unpaired electrons in the oxygen molecule (I′). Such an activation leads to complex formation (8) (III). The next step is the formation of transition states which are strain-free (7), electronically and energetically sound (11) six-membered rings (IV and V). It is possible by proper rearrangement of electrons (V) to obtain a hydroperoxide (VI) with a compulsory shift of the double bond. The amount of energy available in the transition state (V) may well decide the extent of *cis*, *trans*-isomerization in this hydroperoxide.

This cyclic mechanism involving the six-membered ring is not new. It has been successfully applied to other organic reactions (1*a*). Such a mechanism seems to be quite appropriate in elucidating the initiation processes of autoxidation reactions. Of course, the activity of the π electrons in the transition states (IV–V, Fig. 2) may vary under different circumstances, increasing or decreasing the half-life of these transitory cyclic peroxides. This may explain the formation of six-membered cyclic peroxides during the autoxidation of conjugated dienes (4) and polycyclic hydrocarbons: rubrene, α-terpene, etc. (4, 21).

The mechanism outlined plays a role in the formation of peroxides during the initial stages. These include the induction period (stepwise initiation and crossing of the energy barrier (II–V, Fig. 2)). The initial stages pass into the main autoxidation reaction when a critical concentration of peroxide is attained. Following this, decomposition of peroxides sets in to start off the more rapid rate of autoxidation by means of free radicals, chain reactions, and polymerizations. Farmer's theory may be effective in this period of main autoxidation, where energy problems are solved. Of course, many complex processes may also occur. The suggested mechanism at the initial stages of autoxidation possibly plays a minor role in this main autoxidation reaction. It thus supplements Farmer's theory for the elucidation of autoxidation reactions.

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DIRECT CURRENT POWER SUPPLY FOR AH-6 MERCURY ARCS*

By S. G. Whiteway and C. R. Masson

In the photochemical determination of absolute radical reaction rates by the rotating sector method (1), it is sometimes necessary to use an ultraviolet source of high intensity. The source must be capable of producing a beam small enough to be cleanly chopped. In addition, it should operate on direct current, so that the only time intermittency is that produced by the sector.

The General Electric AH-6 mercury arc, designed to operate on alternating current, combines the desired features of small source size and high intensity (1000 w. output). This note describes a direct current supply and controls which enable us to operate the AH-6 on direct current (Fig. 1).

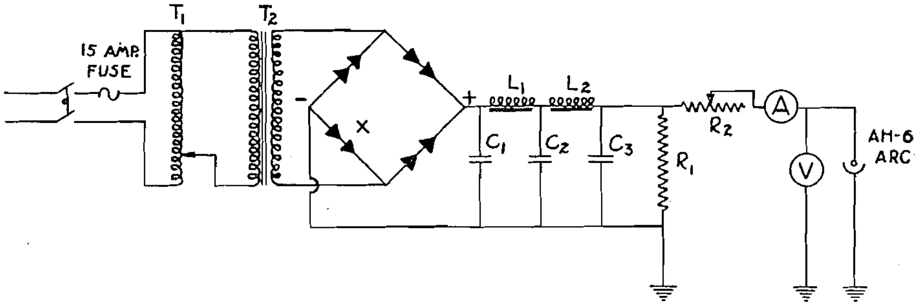

Fig. 1. Wiring diagram of power supply.
T_1—10 amp. Variac
T_2—59 G37 General Electric transformer
L_1, L_2—7 h., 1.5 amp. d-c.
C_1, C_2, C_3—8 μf., 1500 DCWV.
X—Selenium rectifiers, Federal Telephone and Radio Corp. 131H24AX1.
R_1—50000 Ω, 150 w.
R_2—500 Ω, 100 w. rheostat.

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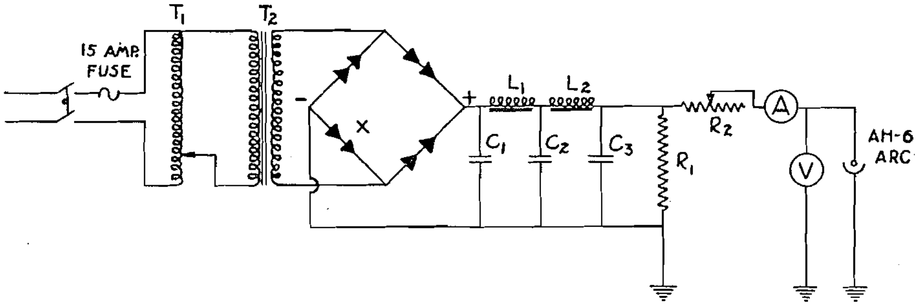

Fig. 1. Wiring diagram of power supply.
T_1—10 amp. Variac
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L_1, L_2—7 h., 1.5 amp. d-c.
C_1, C_2, C_3—8 μf., 1500 DCWV.
X—Selenium rectifiers, Federal Telephone and Radio Corp. 131H24AX1.
R_1—50000 Ω, 150 w.
R_2—500 Ω, 100 w. rheostat.

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*Issued as N.R.C. 3406.

The 110 v. alternating mains current, controlled by a 10 amp. Variac, is transformed by a General Electric 1200 v. ballast transformer. Rectification is accomplished by eight selenium rectifiers in a bridge circuit, with two stacks in series in each arm of the bridge. The direct current is filtered by three condensers, two choke coils, and a bleeder resistance. The lamp circuit contains a current limiting rheostat and ammeter in series, and an electrostatic voltmeter in parallel with the lamp.

The lamp is mounted in a quartz envelope, through which precooled distilled water is circulated. The envelope in turn is surrounded by a water-cooled brass jacket containing a 3 cm. by 0.5 cm. slit. The distilled water supply, brass jacket, negative electrode of the lamp, and power supply chassis are all grounded.

In operation, with R_2 full in, the Variac is turned up to give a static voltage of about 750 v. across the lamp. The arc is then struck by holding a Tesla coil to the brass jacket, after which the Variac is turned up to deliver full mains voltage and R_2 adjusted to give about 1.5 amp. through the lamp. A new lamp will heat up after about thirty seconds. As the intensity suddenly increases, R_2 must be rapidly taken out of the circuit and the Variac set so as to deliver about 100 v. Under these conditions the voltage drop across the lamp is 600 v., the current 1.0 to 1.2 amp.

The light intensity has been measured only with respect to the photolysis of di-*n*-propyl ketone. In this case it is great enough to fulfill the requirements of the rotating sector method. Individual lamps vary markedly in their aging characteristics, although in general the intensity decreases somewhat with operating time, as measured by the rates of production of carbon monoxide and ethylene (2). Although not visible to the eye, a film becomes deposited on the lamp and quartz envelope after several hours. This is thought to be iron oxide which probably originates from a ferrous component in the assembly used for mounting the lamp. Wiping the lamp with lens tissue moistened with dilute acetic acid removes the deposit and raises the output intensity.

With some lamps the current required for the initial heating increased with operating time. With the present power supply, this effectively determined the useful lifetime of this type of lamp (10 hr. was the maximum) since 1.6 amp. is about the largest current that can be drawn. On the other hand, the lamp now in use has run for a total of 16 hr., with about thirty starts and stops, and shows no sign of deterioration.

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