PECULIARITY IN THE FORMATION OF THE NITRILE-ESTERS OF DICARBOXY-GLUTACONIC ACID.

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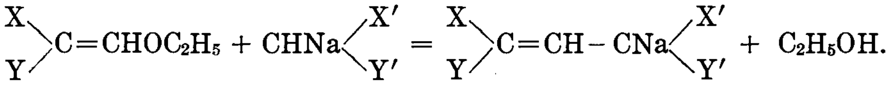
As the introduction to the present paper the previous studies on the synthesis of the nitrile-esters of dicarboxy-glutaconic acid⁽¹⁾ will be outlined. The condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ with the sodiomethylene compound $CHNaX'Y'$ can occur in nine different combinations if each of X, X′, Y, and Y′ represents either $-CN$ or $-COOC_2H_5$; and the products of the nine cases should be different from one another, including all the possible nitrile-esters of dicarboxyglutaconic acid $(HOOC)_2C=CH-CH(COOH)_2$, if the condensation proceeds as follows:



$$ {}^{X}_{Y}\!\!\!>C=CHOC_2H_5 + CHNa<^{X'}_{Y'} = {}^{X}_{Y}\!\!\!>C=CH-CNa<^{X'}_{Y'} + C_2H_5OH. $$

Nevertheless, if the nine condensations are carried out in alcoholic solutions, more than six compounds can not be obtained, for among the nine condensations three pairs yield respectively only one and the same product. In precise expression, the following pair of reactions does not yield two different products which can be expected by the equations:

$$XYC=CHOC_2H_5 + CHNaX'Y' = XYC=CH-CNaX'Y' + C_2H_5OH,$$
$$X'Y'C=CHOC_2H_5 + CHNaXY = X'Y'C=CH-CNaXY + C_2H_5OH.$$

The constitution of the only product has been determined. The sodium atom is always situated at the carbon atom to which the more carbethoxy-groups are attached. The six really obtained compounds are, therefore, as follows:

$(C_2H_5OCO)_2C=CH-CNa(COOC_2H_5)_2$, $C_2H_5OCO(CN)C=CH-CNa(COOC_2H_5)_2$,
$C_2H_5OCO(CN)C=CH-CNa(CN)COOC_2H_5$, $(CN)_2C=CH-CNa(COOC_2H_5)_2$,
$(CN)_2C=CH-CNa(CN)_2$, $(CN)_2C=CH-CNa(CN)COOC_2H_5$.

The following three can not be obtained:

$(C_2H_5OCO)_2C=CH-CNa(CN)COOC_2H_5$, $(C_2H_5OCO)_2C=CH-CNa(CN)_2$,
$C_2H_5OCO(CN)C=CH-CNa(CN)_2$.

Similarly, by the condensation of ethyl ethoxymethylene-cyanoacetate with methyl sodio-cyanoacetate in methyl alcohol and by the condensation

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(1) This Bulletin, **2** (1927), 278; **3** (1928), 219.

of methyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate in ethyl alcohol, the same methyl ethyl sodio-dicyanoglutaconate and from it the same methyl ethyl dicyanoglutaconate semihydrate are obtained.

By and by, the author became aware of the studies on xanthophanic acids by Feist and his co-workers.⁽¹⁾ They describe γ-methyl α-ethyl α, γ-diacetyl-glutaconate and α-methyl γ-ethyl α, γ-diacetyl-glutaconate as different substances. They obtained the former by the condensation of methyl ethoxy-methylene-acetoacetate with ethyl sodio-acetoacetate in ether, and the latter by the condensation of ethyl ethoxy-methylene-acetoacetate with methyl sodio-acetoacetate.

The above two condensations carried out by the present author and giving the same methyl ethyl dicyanoglutaconate are not more different from those by Feist than that cyano-groups took the place of the acetyl-groups and methyl and ethyl alcohols were used as the solvents instead of ether. Thus, to make matters clear, it seemed important to try the synthesis of the nitrile-esters of dicarboxyglutaconic acid in the ethereal medium. For this purpose it is unnecessary to synthesize those compounds with equal attachments at the both ends of the propylene nucleus. The eight condensations shown later were tried; and if the results are collected it can be deduced that four kinds of products are possible in each reaction, and that in the condensation of $XYC=CHOC_2H_5$ with $CHNaX'Y'$, are possible the following four products:

$XYC=CH-CNaX'Y'$, the product of the 1st kind;
$X'Y'C=CH-CNaXY$, the product of the 2nd kind;
$X'Y'C=CH-CNaX'Y'$, the product of the 3rd kind;
$XYC=CH-CNaXY$, the product of the 4th kind.

If $X=X'$ and $Y=Y'$, the four formulae are the same; and in such cases, if the experiment were carried out, only one product would be obtained. The table shows the results of the eight condensations. Individual compounds found in each condensation are placed in the forms of the sodium derivatives under the general formulae showing the kinds. Compounds corresponding to the blank spaces could not be found. Unfortunately, in no reaction all of the possible products could be isolated. Probably, those formed in relatively large quantities or those easy of separation could be isolated. Besides, at the beginning of the experiments on this series of condensations it was beyond expectation that each reaction would give four kinds of products. It was after studying many of the reactions that possibility of four kinds of products was found.

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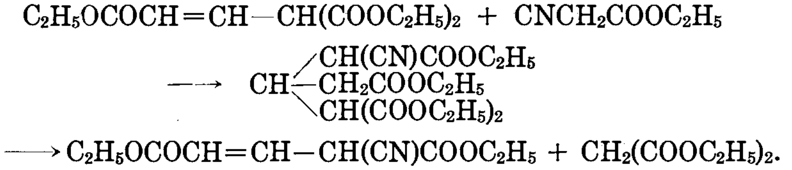
(1) *Ber.*, **59** (1926), 2958.

The mechanism of the reactions can be explained to some extent, if they are compared with the experiments on the synthesis of poly-acetic acids of methane by C. K. Ingold and E. A. Perren.(1) According to them various derivatives of diethyl glutaconate readily react with ethyl sodiocyanoacetate; nevertheless the products of these condensations contain no trace of derivatives of methane triacetic acid, but consist almost wholly of fission products formed from these substances by a decomposition having the character of a retrograde Michael reaction. For instance, triethyl α-carboxyglutaconate gives initially a condensation product, which then undergoes complete fission into diethyl α-cyanoglutaconate and diethyl malonate:



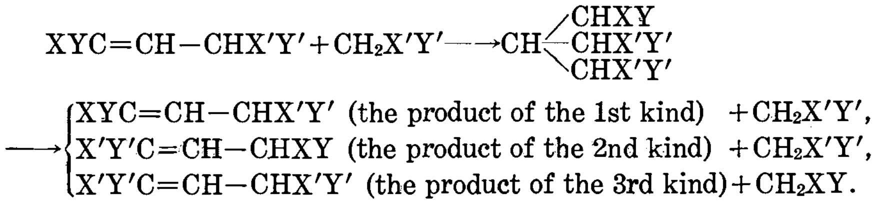
$$C_2H_5OCOCH{=}CH{-}CH(COOC_2H_5)_2 + CNCH_2COOC_2H_5$$
$$\longrightarrow CH\left<\begin{array}{l}CH(CN)COOC_2H_5\\CH_2COOC_2H_5\\CH(COOC_2H_5)_2\end{array}\right.$$
$$\longrightarrow C_2H_5OCOCH{=}CH{-}CH(CN)COOC_2H_5 + CH_2(COOC_2H_5)_2.$$

In the second reaction the group eliminated from the molecule is usually the largest among the substituted acetic acid residues attached to the same carbon atom.

The mechanism of the reaction of the ethoxymethylene compound $XYC{=}CHOC_2H_5$ with the methylene compound $CH_2X'Y'$ which gives four products can be analysed into several processes. Previously(2) the formation of the intermediate addition compound $XYCH{-}CH(OC_2H_5){-}CHX'Y'$ was supposed, but such a hypothesis is not necessary, because the derivatives of methane triacetic acid act not only in place of it, but also in the formation of such products as not to be explained by the former hypothesis. The reaction begins with the formation of the product of the first kind:

$$XYC{=}CHOC_2H_5 + CH_2X'Y'$$
$$\longrightarrow XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} + C_2H_5OH.$$

The product of the first kind partly condenses with the methylene compound $CH_2X'Y'$ present in the reaction medium, and then fission follows:



$$XYC{=}CH{-}CHX'Y' + CH_2X'Y' \longrightarrow CH\left<\begin{array}{l}CHXY\\CHX'Y'\\CHX'Y'\end{array}\right.$$
$$\longrightarrow\left\{\begin{array}{ll}XYC{=}CH{-}CHX'Y' \text{ (the product of the 1st kind)} & +CH_2X'Y',\\X'Y'C{=}CH{-}CHXY \text{ (the product of the 2nd kind)} & +CH_2X'Y',\\X'Y'C{=}CH{-}CHX'Y' \text{ (the product of the 3rd kind)} & +CH_2XY.\end{array}\right.$$

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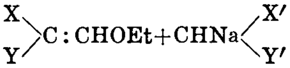
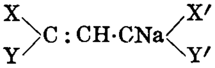
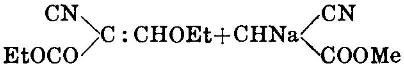
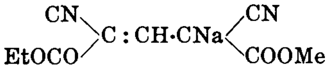
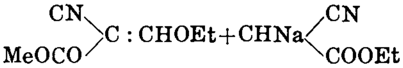
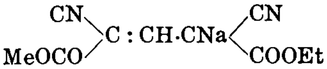
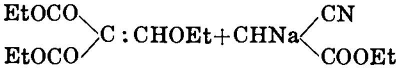
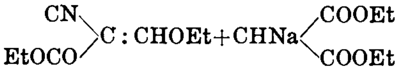
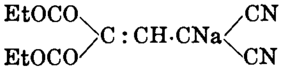
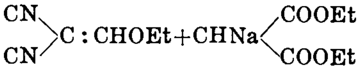
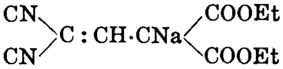
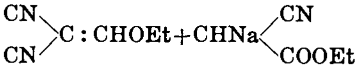
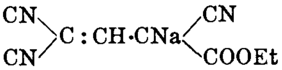
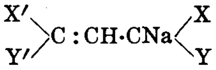
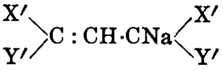
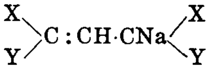
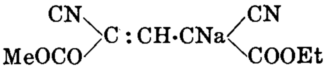
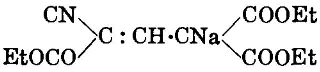
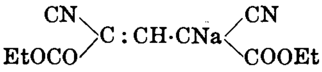
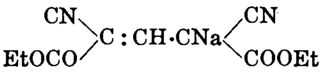
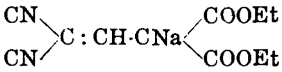
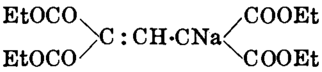
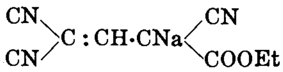
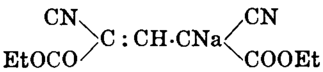
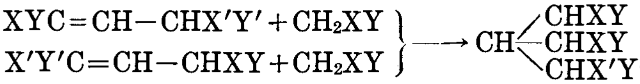
(1) *J. Chem. Soc.*, **119** (1921), 1582.

(2) This Bulletin, **3** (1928), 226.

	Condensations	
		The First Kind
	 $\mathrm{{}^{X}_{Y}\!>\!C:CHOEt+CHNa\!<^{X'}_{Y'}}$	 $\mathrm{{}^{X}_{Y}\!>\!C:CH\cdot CNa\!<^{X'}_{Y'}}$
1	 $\mathrm{{}^{CN}_{EtOCO}\!>\!C:CHOEt+CHNa\!<^{CN}_{COOMe}}$	 $\mathrm{{}^{CN}_{EtOCO}\!>\!C:CH\cdot CNa\!<^{CN}_{COOMe}}$
2	 $\mathrm{{}^{CN}_{MeOCO}\!>\!C:CHOEt+CHNa\!<^{CN}_{COOEt}}$	 $\mathrm{{}^{CN}_{MeOCO}\!>\!C:CH\cdot CNa\!<^{CN}_{COOEt}}$
3	 $\mathrm{{}^{EtOCO}_{EtOCO}\!>\!C:CHOEt+CHNa\!<^{CN}_{COOEt}}$	
4	 $\mathrm{{}^{CN}_{EtOCO}\!>\!C:CHOEt+CHNa\!<^{COOEt}_{COOEt}}$	 $\mathrm{{}^{CN}_{EtOCO}\!>\!C:CH\cdot CNa\!<^{COOEt}_{COOEt}}$
5	 $\mathrm{{}^{EtOCO}_{EtOCO}\!>\!C:CHOEt+CHNa\!<^{CN}_{CN}}$	 $\mathrm{{}^{EtOCO}_{EtOCO}\!>\!C:CH\cdot CNa\!<^{CN}_{CN}}$
6	 $\mathrm{{}^{CN}_{CN}\!>\!C:CHOEt+CHNa\!<^{COOEt}_{COOEt}}$	 $\mathrm{{}^{CN}_{CN}\!>\!C:CH\cdot CNa\!<^{COOEt}_{COOEt}}$
7	 $\mathrm{{}^{CN}_{EtOCO}\!>\!C:CHOEt+CHNa\!<^{CN}_{CN}}$	
8	 $\mathrm{{}^{CN}_{CN}\!>\!C:CHOEt+CHNa\!<^{CN}_{COOEt}}$	 $\mathrm{{}^{CN}_{CN}\!>\!C:CH\cdot CNa\!<^{CN}_{COOEt}}$

Products		
The Second Kind	The Third Kind	The Fourth Kind
 $\begin{matrix}\mathrm{X'}\\\mathrm{Y'}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}$	 $\begin{matrix}\mathrm{X'}\\\mathrm{Y'}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{X'}\\\mathrm{Y'}\end{matrix}$	 $\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}$
 $\begin{matrix}\mathrm{CN}\\\mathrm{MeOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{CN}\\\mathrm{COOEt}\end{matrix}$		
 $\begin{matrix}\mathrm{CN}\\\mathrm{EtOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$	 $\begin{matrix}\mathrm{CN}\\\mathrm{EtOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{CN}\\\mathrm{COOEt}\end{matrix}$	
	 $\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$	 $\begin{matrix}\mathrm{CN}\\\mathrm{EtOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{CN}\\\mathrm{COOEt}\end{matrix}$
 $\begin{matrix}\mathrm{CN}\\\mathrm{CN}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$		
	 $\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$	
 $\begin{matrix}\mathrm{CN}\\\mathrm{CN}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{CN}\\\mathrm{COOEt}\end{matrix}$		 $\begin{matrix}\mathrm{CN}\\\mathrm{EtOCO}\end{matrix}\!>\mathrm{C:CH\cdot CNa}<\!\begin{matrix}\mathrm{CN}\\\mathrm{COOEt}\end{matrix}$

The fission is possible in three directions. Now, another methylene compound CH_2XY is ready to condense with the product of the first or the second kind, and fission can yield the fourth product besides others:



$$\left.\begin{array}{l} XYC{=}CH{-}CHX'Y' + CH_2XY \\ X'Y'C{=}CH{-}CHXY + CH_2XY \end{array}\right\} \longrightarrow CH\left\langle\begin{array}{l} CHXY \\ CHXY \\ CHX'Y' \end{array}\right.$$

$$\longrightarrow\left\{\begin{array}{ll} XYC{=}CH{-}CHX'Y' & \text{(the product of the 1st kind)} + CH_2XY, \\ X'Y'C{=}CH{-}CHXY & \text{(the product of the 2nd kind)} + CH_2XY, \\ XYC{=}CH{-}CHXY & \text{(the product of the 4th kind)} + CH_2X'Y'. \end{array}\right.$$

If the sodium atom is taken into consideration the relations are somewhat complicated, but fundamentally not altered. The above mentioned are the necessary processes for the formation of the four products; and the real condensations may include many other similar processes of addition and fission; nevertheless, more than the four products can never be expected. It is noteworthy that there are many chances for the more stable product to grow in amount in the cost of the less stable. It is remarkable that tetraethyl dicarboxyglutaconate having the largest groups attached to the central methenyl carbon atom was produced in many of the condensations(1) where it corresponded to any of the possible four kinds of products; and, therefore, it can not be said that the largest group is eliminated in the form of a methylene compound from the molecule of the intermediate methane triacetic acid derivative.

In the condensation in alcohol one product is prevalent. The reaction is of the homogeneous system, the materials and the products existing both in the dissolved state; and this facilitates the establishment of equilibrium, allowing the product the most table in the condition of that time to prevail. On the other hand, in the reaction in ether only one of the materials, the ethoxy-methylene compound, and none of the products, go into solution, and it is probable that various substances exist in various proportions in various places, and this permits many of the possible products to survive.

The fact that two isomeric compounds which differ from each other only in the position of the double union, and consequently of the sodium atom, the best example being diethyl *α*-sodio-*γ*, *γ*-dicyano-propylene-*α*, *α*-dicarboxylate and diethyl *α*-sodio-*α*, *α*-dicyano-propylene-*γ*, *γ*-dicarboxylate, are distinctly different is incompatible with the normal theory of J. F. Thorpe, which was already rejected by the present author and others.(2)

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(1) The synthesis of the esters of acetyl-propylene-carboxylic acids is included, the results of which will be published later.

(2) This Bulletin, **3** (1928), 205; R. Malachowski u. M. Maslowski, *Ber.*, **61** (1928), 2521; R. Malachowski, *Ber.*, **62** B (1929), 1323.

Further the present investigation has thrown light on some obscure points in the previous experiments. The fact that two isomeric derivatives of dicarboxyglutaconic acid which differ from each other only in the positions of the double union and the sodium atom always proved to be identical is nothing but that one of the two possible isomerides was more stable and formed exclusively, the present investigation indicating that sometimes the less stable form can be obtained by the condensation in ether.

Experimental Part.

It seems convenient to begin with describing some of the products, especially concerning the methods of separation and identification, for the same substances may appear in more than one reactions. The following are all the known substances, and new compounds will be described in the places where they are met for the first time.

Tetraethyl α, γ-dicarboxyglutaconate, $(C_2H_5OCO)_2C=CH-CH(COOC_2H_5)_2$. Its sodium derivative is sparingly soluble in cold water and imparts opacity to water probably owing to its partial hydrolysis. It can be recrystallised from alcohol. The free ester formed by the action of dilute hydrochloric or sulphuric acid on the sodium compound is a colourless oil, and is identified by elementary analysis. It requires C=54.51; H=6.72%.

Triethyl γ-cyano-α-carboxyglutaconate, $C_2H_5OCO(CN)C=CH-CH(COOC_2H_5)_2$. The sodium derivative is easily soluble in water, and its alcoholic solution gives violet colouration with ferric chloride. The free cyano-ester is an oil, requiring N=4.94%. It is easily transformed into diethyl α, α'-dioxypyridine-β, β'-dicarboxylate $C_{11}H_{13}O_6N$ requiring N=5.49% and melting at 199°.

The esters of α, γ-dicyanoglutaconic acid, $ROCO(CN)C=CH-CH(CN)COOR$. Their sodium derivatives are all fine needle crystals, easily soluble in hot water. The corresponding free cyano-esters can not be obtained, but instead of them their semihydrates are always formed. Dimethyl, diethyl, and one of the methyl ethyl compounds have been obtained. The semihydrates are all yellow crystalline substances and can be identified by analysis and melting points.

Dimethyl compound:	$(C_9H_8O_4N_2)_2 \cdot H_2O$,	[225°]	N=12.90%;
Methyl ethyl compound:	$(C_{10}H_{10}O_4N_2)_2 \cdot H_2O$,	[197°]	N=12.12%;
Diethyl compound:	$(C_{11}H_{12}O_4N_2)_2 \cdot H_2O$,	[183°]	N=11.43%.

Further the diethyl compound gives a picrate of formula $C_{11}H_{16}O_6N_2 \cdot C_6H_2(NO_2)_3OH$ melting at 196-197°.

Diethyl γ, γ-dicyano-propylene-α, α-dicarboxylate, $(CN)_2C=CH-CH(COOC_2H_5)_2$. The sodium derivatite is easily soluble in water. On acidifying its aqueous solution an oily substance is precipitated. This is the free cyanoester, but after a short time it changes into colourless crystals of diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate $(NH_2CO)_2C=CH-CH(COOC_2H_5)_2$ which melts at 139-140°, changing opaque on prolonged heating. The free cyano-ester dissolved in alcohol changes into diethyl γ-cyano-γ-carbamyl-propylene-α, α-dicarboxylate $NH_2CO(CN)C=CH-CH(COOC_2H_5)_2$ melting at 212°.

Ethyl α, γ, γ-tricyano-propylene-α-carboxylate, $(CN)_2C=CH-CH(CN)COOC_2H_5$. The free cyano-ester can not be obtained, but the semihydrate $(C_9H_7O_2N_3)_2 \cdot H_2O$ melting at 190° and requiring $N=21.21\%$.

α, α, γ, γ-Tetracyano-propylene, $(CN)_2C=CH-CH(CN)_2$. This compound can be isolated only in its sodium derivative, which crystallises in needles from the aqueous solution. The aqueous solution produces no precipitation on acidifying, and if the aqueous solution acidified with hydrochloric acid is evaporated up in vacuum in the desiccator furnished with sulphuric acid and soda-lime, the crystals of the original sodium compound can be recovered. On adding a silver nitrate solution to the aqueous solution of the sodium compound a white precipitate is produced which is insoluble in dilute nitric acid.

Experimental Procedure. The first course of the reactions is to prepare the sodium derivatives of the methylene compounds. The sodium derivative of diethyl malonate was prepared by adding an excess (ten percent more than the theoretical quantity) of this ester to finely granulated metallic sodium covered with a large amount of pure ether. When the evolution of hydrogen is over and sodium disappears, the reaction is completed, and a paste of diethyl sodio-malonate is obtained.

Methyl sodio-cyanoacetate is prepared similarly, except that a small quantity of methyl alcohol is added to accelerate the reaction, and after the reaction is completed the solid is collected, dried in vacuum over sulphuric acid, weighed, and mixed with pure ether.

Ethyl sodio-cyanoacetate is prepared by adding the free ester to an alcoholic solution of sodium ethylate, the white crystals being collected, washed with pure ether, and well dried in vacuum. Sodio-malonitrile is prepared similarly.

In every case the sodio-methylene compound is mixed with pure ether and the calculated amount of the ethoxymethylene compound is added gradually under constant stirring. The reaction mass is from pale yellow to dark red. After standing for a length of time, the solid is separated from ether by filtration or by dissolution in water. Then the solid or the aqueous solution is subjected to the process of separation and identification.

(1) *Condensation of ethyl ethoxymethylene-cyanoacetate with methyl sodio-cyanoacetate.* The semihydrate of the free cyano-ester obtained from the crude condensation product melted at 193°. Then the crude sodium compound was recrystallised four times from water, and the purified substance was transformed into the semihydrate, the latter being recrystallised once from absolute alcohol. It melted at 190°. Anal. Found: N=12.06, 12.23%. Nevertheless, this specimen is not identical with the already known methyl ethyl dicyanoglutaconate semihydrate, because there is a remarkable difference not only in the melting points, but also in the solubilities in absolute alcohol, the already known compound being insoluble in boiling alcohol while the new tolerably soluble in hot alcohol.

The author believes that the crude product was a mixture of the two isomeric methyl ethyl sodio-dicyanoglutaconates, and the specimen melting at 193° was the corresponding mixture of the semihydrates. The substance obtained by recrystallisation of the crude sodium compound was one of the isomerides, and that different from the already known.

(2) *Condensation of methyl ethoxymethylene-cyanoacetate with ethyl sodio-cyanoacetate.* The specimen of the semihydrate obtained from either the crude or the recrystallised sodium compound melted at 196°. It can be said that the product was pure and unique; and, therefore, it is very natural to consider it the product of the first kind, that is γ-methyl α-ethyl α-sodio-α, γ-dicyanoglutaconate.

The sodium compound obtained in condensation 1 and giving the semihydrate melting at 190° is the α-methyl γ-ethyl compound. The only product of the condensations in alcohol is the γ-methyl α-ethyl compound, for it gives the semihydrate with the higher melting point.

(3) *Condensation of diethyl ethoxymethylene-malonate with ethyl sodio-cyanoacetate.* The yellow pasty mass obtained by the reaction was dissolved in water. After a short time a crystalline substance separated from the solution. This was identified with diethyl α-sodio-dicyanoglutaconate by its transformation into diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.52%.

On acidifying the aqueous solution filtered from the above crystalline substance two kinds of substances separated, one being crystalline and the other oily. The former was identified with diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.50%. Melting point: 183°. The latter was collected by dissolving it in ether and evaporating the ethereal solution. On standing for three weeks the oil was partly changed into crystals. The part which remained oily was purified by dissolving it in ether, extracting with a ten percent solution of sodium carbonate, acidifying the soda solution, extracting the oil with ether, and evaporating the dried ethereal solution. This was found to be nearly pure triethyl cyano-carboxy-glutaconate. Anal. Found: N=4.82%. Its alcoholic solution gave dark brown colouration with ferric chloride, which showed that the compound was triethyl γ-cyano-α-carboxy-glutaconate.(1) The crystalline part contained 5.71% of nitrogen and melted at 190–195°. It was probably diethyl α, α'-dioxy-pyridine-β, β'-dicarboxylate formed by the transformation of the triethyl cyano-carboxy-glutaconate.

(4) *Condensation of ethyl ethoxymethylene-cyanoacetate with diethyl sodio-malonate.* The crude mass obtained by the reaction was dissolved in water, and the aqueous solution was acidified with dilute hydrochloric acid. The whole was shaken with ether, and the ethereal and the aqueous solutions were treated separately.

The aqueous solution gave a small amount of a yellow crystalline substance. This was identified with diethyl dicyanoglutaconate semihydrate. Anal. Found: N=11.61%. Melting point: 183°.

The ethereal solution was shaken with a ten percent solution of sodium carbonate. The soda solution gave an enormous quantity of sparingly soluble solid, which contained 5.81% of nitrogen and seemed to consist mainly of diethyl α,α'-dioxy-pyridine-β,β'-dicarboxylate. The solid was digested with cold hydrochloric acid, washed, and dried. This was found to be the above pyridine derivative. Anal. Found: N=5.62%. Melting point: 199°.

The presence of alcohol in the mother liquor could be detected by its odour, indicating that the above pyridine derivative was formed from triethyl cyanocarboxyglutaconate according to the following equation:

$$C_{13}H_{17}O_6N + H_2O = C_{11}H_{13}O_6N + C_2H_5OH.$$

This triethyl cyanocarboxyglutaconate can be assumed to be the γ-cyano-α-carboxy-compound, that is the product of the first kind and more stable than the α-cyano-γ-carboxy-compound.

The mother liquor was acidified. The oily drops were collected, and transformed into a yellow crystalline sodium compound by shaking with a soda solution. This was identified with tetraethyl α-sodio-dicarboxy-glutaconate by the analysis of the free ester obtained from it. Anal. Found: C=54.60; H=6.74%.

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(1) Cf. this Bulletin, **3** (1928), 221.

(5) *Condensation of diethyl ethoxymethylene-malonate with sodio-malonitrile.* The condensation mass was dissolved in water. Crystals separated from the aqueous solution. These crystals and the mother liquor were treated separately.

The crystalline sodium compound was recrystallised from alcohol. Its alcoholic solution gave reddish violet colouration with ferric chloride. On acidifying its aqueous solution it was transformed into a colourless crystalline substance, which was identified with diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate by its melting point. Further the sodium compound could be transformed into diethyl γ-cyano-γ-carbamyl-propylene-α, α-dicarboxylate. Hence, it is diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate.

The aqueous mother liquor filtered from the above crystalline sodium compound was acidified, and shaken with ether. The two liquid layers were treated separately.

On evaporating the ethereal solution a small amount of oil was obtained, which was then transformed into a crystalline sodium compound by shaking with a soda solution. This was probably tetraethyl α-sodio-dicarboxy-glutaconate, but the substance was not sufficient in purity and quantity for analysis.

It was expected that the aqueous solution might contain sodio-tetracyano-propylene. It was evaporated to a brown mass in vacuum over sulphuric acid and soda-lime. The brown mass was digested with alcohol, and the alcoholic solution was evaporated in vacuum to a crystalline mass. This was recrystallised twice from a small amount of water, animal charcoal being used to decolourize the solution. In this way nearly colourless needle crystals of a sodium compound were obtained. This substance resembles the sodium derivative of tetracyanopropylene as regards the properties, so that it was considered to be the expected substance until it was analysed. Anal. Found: $N=10.6\%$. The nitrogen content is equal to that of diethyl α-sodio-γ, γ-dicyanopropylene-α, α-dicarboxylate ($N=10.9\%$), but the properties unequal, the new sodium compound being apparently unchangeable by acidifying its aqueous solution, just as same as sodio-tetracyano-propylene. The compound in question, therefore, can be nothing but diethyl α-sodio-α, α-dicyano-propylene-γ, γ-dicarboxylate $(C_2H_5OCO)_2C=CH-CNa(CN)_2$, the product of the first kind of this condensation.

(6) *Condensation of ethoxymethylene-malonitrile with diethyl sodio-malonate.* The condensation mass was dissolved in water and the solution was acidified. Most of oil which separated out changed into colourless crystals after a short time, but among them some brown oil drops remained. The crystalline part was collected, washed with water, and then with ether,

the oily part being collected in the wash ether. The crystalline substance, the ethereal solution, and the aqueous mother liquor were treated separately.

The crystalline substance was identified with diethyl γ, γ-dicarbamyl-propylene-α, α-dicarboxylate. Hence, the original sodium compound is diethyl α-sodio-γ, γ-dicyano-propylene-α, α-dicarboxylate.

The ethereal solution gave an oil on evaporation. It was then transformed into a yellow crystalline sodium compound by shaking with a soda solution. This was identified with tetraethyl α-sodio-dicarboxyglutaconate by the analysis of the free ester obtained from it. Anal. Found: C=54.38; H=6.75%.

The aqueous mother liquor was expected to contain diethyl α-sodio-α, α-dicyanopropylene-γ, γ-dicarboxylate or more possibly sodio-tetracyanopropylene. But only a crystalline substance containing about 16% of nitrogen was isolated. It was probably a decomposition compound of either of them.

(7) *Condensation of ethyl ethoxymethylene-cyanoacetate with sodio-malonitrile.* The condensation seemed not to take place at the ordinary temperature, for on mixing these substances in pure ether no apparent change was observed. The mixture was heated for some time, and after evaporating most of ether it was kept at the room temperature for some ten days. Then the solid was dissolved in water and the aqueous solution was acidified, when dark brown oil separated out, which was extracted with ether.(1) From the ethereal solution, on drying with calcium chloride, yellow crystals separated. Anal. Found: N=18.95%. It seemed to be a mixture of ethyl tricyanopropylene-carboxylate semihydrate and diethyl dicyanoglutaconate semihydrate. Then it was recrystallised from alcohol. Anal. Found: N=17.41%. After recrystallisation the nitrogen content decreased, indicating that a mixture was being handled. It was easily found that the mixture contained diethyl dicyanoglutaconate semihydrate, for the alcoholic mother liquor of the above recrystallisation gave the characteristic picrate. The authentic specimen of ethyl α, γ, γ-tricyano-propylene-α-carboxylate semihydrate gives no product with picric acid. Another component of the mixture is believed to have been ethyl α, γ, γ-tricyanopropylene-α-carboxylate semihydrate, its mother substance being ethyl α-sodio-α, γ, γ-tricyanopropylene-α-carboxylate, the product of the second kind of this condensation. If it were the product of the first kind,

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(1) None of the nitrile-esters of dicarboxyglutaconic acid which give semihydrates has ever separated in the form of oil, the present case being the only exception; but it can be considered that the separation of oil was due to the presence of malonitrile which would be formed from the sodio-malonitrile.

ethyl α-sodio-α, α, γ-tricyano-propylene-γ-carboxylate, it would be stable to acid, for the two known α-dicyano compounds are so.

(8) *Condensation of ethoxymethylene-malonitrile with ethyl sodio-cyano-acetate.* The crude product was purely white. On acidifying its aqueous solution a yellow crystalline substance was obtained, which was found to be nearly pure ethyl α, γ, γ-tricyanopropylene-α-carboxylate semihydrate. Anal. Found: N=20.72, 20.75%. The only product is, therefore, ethyl α-sodio-α, γ, γ-tricyano-propylene-α-carboxylate, the product of the first kind.

Summary.

From the results of eight reactions it was deduced that the four compounds,

$XYC=CH-CNaX'Y'$,
$X'Y'C=CH-CNaXY$,
$X'Y'C=CH-CNaX'Y'$,
$XYC=CH-CNaXY$,

can be produced in the condensation of the ethoxymethylene compound $XYC=CHOC_2H_5$ with the sodio-methylene compound $CHNaX'Y'$, where each of X, X', Y, and Y' represents either $-CN$ or $-COOC_2H_5$.

The author expresses his hearty thanks to Prof. Matsubara for his kind inspection of this paper.

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RÖNTGEN ANALYSIS OF COPPER AMALGAMS.

By **Nobuyuki KATOH.**

Received November 18, 1929. Published January 28, 1930.

In the author's previous paper⁽¹⁾ the following results were published:

(1) The solid phase existing in high mercury amalgams has γ stracture⁽²⁾ and the lattice dimention is $a=9.401\text{Å}$.

(2) The solid phase prepared by squeezing high mercury amalgams under high pressures has the dimention just described.

(3) The upper copper limit of the homogenity range of the γ phase lies somewhere between 27.1-29.9 weight per cent of copper.

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(1) N. Katoh, *Z. physik Chem.*, [B] **6** (1920), 27.

(2) See Westgren and Phragmen, *Phil. Mag.*, [6] **50** (1925), 311.

(4) High copper amalgams consist in copper and the γ phase at ordinary temperature.

The samples used in the present investigation were prepared at the Minerallogical Institute in Oslo.(1)

For the powder photograms the Cr-K-radiation were used from a tube of the Siegbahn type, which was run with about 45 kilo-volts and 7.5ma. All cameras were designed by Dr. Phragmen.(2) The powder photograms were taken with three cameras of the focussing type, covering whole diffraction range. The cameras were calibrated with sodium chloride. The exposure time varied 5 to 9 hours. All the dimention values based on the length 5.6280Å for the edge of the elementary cube of the sodium chloride.

The photograms were rather weak by want of the practice of handling cameras. The result of the measurement and calculation was shown in the Table 1 and confirmed the former view.

In the case of a good photogram on which every line can be measured accurately, the determination of the lattice dimention may be carried out by means of the most deviated interferences.(3) The figures from each interference agree very well and it needs not farther calculation. But it is reasonable to take all the interferences when the photogram was weak.

The author used three photograms taken by the different cameras for determination of the γ phase. Taking $\mathrm{tg}^2\vartheta$ as the weight of the each observation of the interference lines, the constant χ in the equation $\sin^2\vartheta = \chi\ (h^2+k^2+l^2)$ calculated for each photogram by the following formura.(4)

$$\chi=\frac{\Sigma\chi\,\mathrm{tg}^2\vartheta}{\Sigma\,\mathrm{tg}^2\vartheta}, \qquad \Delta\chi=\pm\sqrt{\frac{\Sigma[(\chi-\chi_0)\,\mathrm{tg}\,\vartheta]^2}{(n-1)\Sigma\,\mathrm{tg}^2\vartheta}}$$

For the photogram taken by camera 5, $\chi=0.01481\pm0.00001$

,, ,, ,, ,, ,, 6, $\chi=0.01475\pm0.00003$

,, ,, ,, ,, ,, 8, $\chi=0.01478\pm0.00001$

Then the most probable value of the constant was found by taking the weighted mean of the three figures as follows.

$$\chi=0.01479 \qquad (\text{for Cr}-\text{K}_\alpha)$$

and the dimention of the γ phase is

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(1) N. Katoh, loc. cit.

(2) Westgren and Phragmen, loc. cit.

(3) G. Hägg, Dissertation, 5, 1929 (Uppsala).

(4) E. Broch, *Z. physik. Chem.*, **127** (1927), 452.

a=9.399 Å

a=9.401Å (by Debye cameras)⁽¹⁾

Tammann⁽²⁾ observed the existence of the α phase by the thermal analysis but the present author could not find it in the specimens tempered at 100°C. for 48 hours. The powder photograms of a 70.5% Cu amalgam quenched at 380°C, and pure copper tempered at 100°C. taken with the same camera were compared. All the copper lines agree very well, so that the existence of α phase at this temperature is doubtful one but it needs farther investigation to settle this question.

Table 1.

Cr. Radiation. Cu—Hg (24.1% cu).

Intensity	Radiation	*h k l*	$\mathrm{Sin}^2\frac{\theta}{2}\cdot 10^4$	$((h^2+k^2+l^2)\chi 10^5$
w	β	310	1231	10.1231
s	α	310	1482	10.1482
w	β	321	1722	14.1230
v w	α	322	1777	12.1481
s	α	321	2072	14.1480
m	β	330,411	2246	18.1248
s	α	330,411	2660	18.1478
v·w	β	332	2730	22.1241
v w	α	332	3238	22.1472
w	α	442,600	5336	36.1482
w	β	622	5402	44.1228
m	α	532,611	5616	38.1478
m	α+β	631	5669	46.1233*
v w	β	444	5870	48.1223
v w	β	543,550,710	6099	50.1220
v·w	α	541	6187	42.1473
m	α	622	6504	44.1478
m	α	631	6787	46.1475
s	α	444	7081	48.1475
m	α	543,550,710	7361	50.1472
w	α		7762	*
s	α_1	552,633,721	7981	54.1478
w	α_2	552,633,721	8010	54.1483
v w	β	811,741,554	8123	66.1231
w	α	642	8326	56.1483
w	α_1	651,732	9126	62.1471
w	α_2	651,732	9160	62.1478

* Extra lines.

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(1) W. Katoh, loc. cit.

(2) G. Tammann and Th. Stassfurth, *Z. anorg. Chem.*, **143** (1925), 357.

$\mathrm{Cr\ K}_{\alpha_1}=2.2848\,\text{Å}$ $\quad$ $\mathrm{Sin}^2\vartheta=0.01479\,(h^2+k^2+l^2)$ $\quad$ for CrK_α

$\mathrm{Cr\ K}_{\alpha_2}=2.2890\,\text{Å}$ $\quad$ $a=9.399\,\text{Å}$

$\mathrm{Cr\ K}_\beta=2.0805\,\text{Å}$

$\mathrm{Cr\ K}_\alpha=2.2862\,\text{Å}$

Finally, the author desire to thank Professor A. Westgren, Ph.D., whok indly allowed him to carry out this work at the Röntgen Laboratory in the Stockholm Högskola.

October 25, 1929.

University of Stockholm,
Sweden.

ÜBER DIE OXYDATION KATHODISCH REDUZIERTER CHROMSÄURELÖSUNGEN AN PLATINANODEN.

Von Shiro TAKEGAMI.

Eigegangen am 22. November 1929. Ausgegeben am 28. Januar 1930.

Wie Roudnick⁽¹⁾ in Bestätigung früherer Angaben von Erich Müller und F. Soller⁽²⁾ mitteilt, ist bei der Elektrolyse wässriger Lösungen von Chromsäure die anodische Oxydation des kathodisch gebildeten dreiwertigen Chroms zu Chromsäure an Bleianoden gegenüber an Platinanoden stark begünstigt. An Platinanoden ist sowohl bei Stscherbakow und Essin⁽³⁾ sowie bei Roudnick die Oxydation in Prozenten der Stromarbeit eine auffallend schwankende. So finden erstere z.B. in ihrem Versuch 1 in zeitlich aufeinanderfolgenden Werten 10.0%, 2.8% und 7%, Roudnick in seinem Versuch 2 4.6%, 3.3%, 0.0%, 0.0%, 4.9%. Bei letzterem bleibt also, wie man sieht, unter Umständen die Oxydation völlig aus. Diese Erscheinung führt der Autor darauf zurück, dass ähnlich wie an der Kathode auch an der Anode ein Diaphragma gebildet wird, welches das Cr(3) hindert, auf die Anode zu treffen. Er konnte in der Tat feststellen, dass letztere nach ihrem Gebrauche einen grüngelben Schimmer aufwies, der durch Behandlung mit verdünnter Salzsäure oder Natronlauge unverändert blieb, durch heisse Natronlauge aber unter Gelbfärbung dieser verschwand.

,,Besondere Versuche zeigten, dass ein solches Diaphragma auf der Platinanode bei der Elektrolyse reiner Chromsäure nicht entsteht, sondern

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(1) *Z. Elektrochem.*, **35** (1929), 249.
(2) Ebenda, **11** (1905), 863.
(3) Ebenda, **33** (1928), 245.

nur, wenn sie Cr(3) enthält, woraus zu schliessen ist, dass es sicher hier—wie an der Kathode—um die Bildung eines chromsauren Chromoxydes handeln muss, deren Mechanismus allerdings hier weniger durchsichtig ist."

Roudnick hat sich bemüht, unter mannigfacher Variation der Versuchsbedingungen dieses Diaphragma zu vervollkommnen, um eine Elektrode herzustellen, die die anodische Oxydation völlig und sicher auf die Dauer zu unterbinden vermöchte, was ihm aber nicht gelang.

Meine eigenen Versuche bewegten sich in derselben Richtung. Nur glaubte ich, durch Wahl anderer Versuchsbedingungen eher zum Ziele zu kommen. Ist nämlich, wie Roudnick angibt, die Gegenwart von Cr(3) Bedingung für die Bildung des Diaphragmas, so ist es möglich, dass eine bestimmte Mindestkonzentration davon benötigt wird. Arbeitet man nun mit einer kathodischen Stromdichte, wie Roudnick, bei der metallisches Chrom abgeschieden wird, so ist die kathodische Reduktion wesentlich geringer als wenn man diese Stromdichte so wählt, dass sich kein Chrom abscheidet. Sie teilt sich zudem im ersten Falle noch in die Reduktion zu Cr(3) und zu Cr met., während im letzten Falle nur Cr(3) gebildet wird. Mit anderen Worten: Man kommt bei der Wahl kleiner Stromdichten ohne Chromabscheidung zu höheren Cr(3)-Konzentrationen. Es war mithin möglich, dass Roudnick, der dies nicht tat, keine für die Diaphragmenbildung hinreichende Cr(3)-Konzentrationen in seiner Lösung hatte. Bei meinen Versuche wurde also in erster Linie Wert darauf gelegt, die kathodische Stromdichte unterhalb der Grösse zu halten, bei der sich metallisches Chrom abscheidet. Im übrigen wurden sie in ähnlicher Weise wie die von Roudnick ausgeführt.

Der elektrolytische Trog bestand aus einem Glasbecher von 8 cm. Höhe und 5 cm. Durchmesser, der mit einem Gummistopfen verschlossen war. Dieser hatte eine Anzahl Bohrungen zur Durchführung der Elektroden und zur Ableitung der während der Elektrolyse entwickelten Gase. Diese wurden in der üblichen Weise in einem Gasfangrohr gesammelt und mit den aus einem dahinter geschalteten Knallgascoulometer in der gleichen Zeit entwickelten verglichen. Der Sauerstoff dieser Gase wurde durch Absorption in einer Kupferpipette bestimmt. Durch eine Bohrung des Stopfens war noch ein längeres Glasrohr bis auf den Boden des Bechers geführt, das für gewöhnlich aussen durch einen Stopfen verschlossen war, das aber im Bedarfsfalle dazu diente, nach Entfernung des Stopfens, den Elektrolyten so weit anzusaugen, dass die Anode aus der Lösung herausragte und mit dem Auge betrachtet werden konnte (um zu sehen, ob sich ein Überzug gebildet hatte).

Der Trog stand in einem Thermostaten, vermittels dessen die Temperatur auf 30°C. gehalten wurde. Die beiden Elektroden, die sich planparallel gegenüberstanden, bestanden aus Platin. Verwendet wurden stets 100 c.c. 25%iger Chromsäurelösung. Damit an der Kathode überhaupt eine Reduktion stattfindet, ist es nötig, dass HSO_4-Ionen gegenwärtig sind. Bei den ersten Versuchen, bei denen 0.04 bis 0.05 gr. Na_2SO_4 auf 100 c.c. Lösung gelöst wurden, zeigte sich nur zu allem Anfang eine geringe Reduktion, die bald auf Null absank. Deshalb wurden die weiteren Versuche mit 0.2 gr., ev. mehr, Na_2SO_4 pro 100 c.c. angestellt.

Versuch 1.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.2 gr. Na_2SO_4.
Stromstärke: 0.368 Amp.
Stromdichten: $D_A=0.05$ Amp/qcm; $D_K=0.0124$ Amp/qcm.(1)
Temperatur: 30°C.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduction
	H_2	O_2	H_2	O_2		
8 – 23	44.6	22.3	1.5	20.3	8.96	96.63
30 – 50	59.6	29.8	1.8	28.2	5.36	96 98
59 – 79	59.8	29.9	2.1	29.2	2.34	96.48
87–107	60.4	30.2	6.0	30.4	0.0	90.06
115–135	59.2	29.6	7.9	29.6	0.0	86.65
145–165	58.6	29.3	28.2	30.3	0.0	51.87

Nach jeder beendeten Gasanalyse wurde die Anode besehen; es konnte keinerlei Belag auf derselben entdeckt werden.

Aus diesem Versuch geht hervor, dass bei der hier stattfindenden starken Reduktion nur zu Beginn eine Oxydation beobachtet wird, die mit der Zeit auf Null zurückgeht. Dies konnte im Sinne obiger Vermutung auf die mit der Zeit steigende Cr(3)-Konzentration zurückgeführt werden. Ist, wie Roudnick annimmt, die Störung der Oxydation durch ein anodisches Diaphragma bedingt, so ist dieses in meinem Falle in keiner Weise zu erkennen. Der allmähliche Rückgang der Oxydation scheint darauf hinzudeuten, dass die Ausbildung desselben Zeit erfordert.

Wie der folgende Versuch zeigt, ist aber die *allmähliche* Ausbildung nur dann wahrnehmbar, wenn die Cr(3)-Konzentration noch nicht bis zu einer gewissen Höhe angewachsen ist. Bei diesem Versuche wurden nämlich zwei gleiche Anoden (a) und (b) in den elektrolytischen Trog eingebaut und zunächst mit (a) gearbeitet, bis die Oxydation auf 0% abgesunken war. Dann wurde schnell (a) aus und dafür (b) eingeschaltet und unmittelbar weiter elektrolysiert. Dabei war an der Elektrode die Oxyda-

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(1) Bei Berechnung der Stromdichte wurde nur *eine* Seite der Elektrode als vom Strom belastet angesehen.

tion sofort Null. Führt man also das Ausbleiben der letzteren auf ein Diaphragma zurück, so muss man annehmen, dass dieses bei Anwesenheit hinreichender Mengen Cr(3) sich sofort bildet.

Versuch 2.

Versuchsbedingungen des Vers. 1							
Anode	Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
		H_2	O_2	H_2	O_2		
a	5– 25	53.2	26.6	2.3	24.1	9.40	95.68
	30– 50	53.2	26.6	0.9	26.5	0.37	98.31
	55– 72	45.0	22.5	0.8	22.8	0.0	98.22
b	0– 20	58.6	29.3	0.8	29.4	0.0	98.64
	24– 44	58.6	29.3	0.7	29.7	0.0	98.82
	49– 69	58.2	29.1	0.6	29.2	0.0	98.97
	73– 93	57.4	28.7	0.6	28.6	0.0	98.96
	98–118	58.6	29.3	0.5	29.3	0.0	99.15

Auch bei diesem Vers. 2 konnte keine Veränderung der Anode wahrgenommen werden. Jedenfalls erkennt man aber, dass bei hoher kathodischer Reduktion und damit verbundener hoher Cr(3)-Konzentration in der Tat die anodische Oxydation verschwindet.

Der folgende Versuch 3 wurde längere Zeit fortgesetzt, um zu sehen, wie sich die Verhältnisse bei andauernder Anreicherung des Cr(3) gestalten.

Versuch 3.

Versuchsbedingungen wie bei Vers. 1						
Min. nach Beginn	Coulometer		Zellengas		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
8– 28	53.8	26.9	1.7	24.8	7.81	96.84
33 – 53	53.8	26.9	1.1	27.1	0.0	97.96
56– 76	53.6	26.8	0.6	27.0	0.0	98.88
79– 99	53.6	26.8	2.8	27.2	0.0	94.78
102–122	53.8	26.9	7.5	27.2	0.0	86.06
124–144	53.6	26.8	9.0	27.0	0.0	83.21
146–166	54.0	27.0	29.2	27.0	0.0	45.93
170–190	53.4	26.7	53.0	26.4	1.44	0.75
194–214	53.6	26.8	53.0	26.0	2.98	1.12
218–238	53.2	26.6	53.2	25.4	4.72	0.0
242–262	53.2	26.6	52.8	25.6	3.76	0.75
266–286	53.0	26.5	52.4	26.0	1.89	1.13
290–310	53.2	26.6	52.5	25.5	4.13	1.32
315–335	53.4	26.7	52.2	26.3	1.20	2.25

In diesem Versuche tritt uns die merkwürdige Erscheinung entgegen, dass die *Reduktion* nach einer länger andauernden Elektrolyse auf ganz kleine Werte herabgeht. Es liegt dies nicht an einer Verarmung an Chromsäure, denn die Analyse ergab einen Gehalt von 12.5 Cr(6) d. i. 24 gr. CrO_3 gegen 25 gr. zu Beginn und 0.5 gr. Cr(3). Es zeigt sich das auch darin, dass nach Unterbrechung der Elektrolyse und nach Fortsetzung derselben nach einer gewissen Pause die Reduktion wieder ihre anfänglich hohen Werte annimmt, um wieder innerhalb längerer Zeit nahezu zu verschwinden, wie aus Vers. 4 hervorgeht.

Versuch 4.

Fortsetzung der Elektrolyse von Vers. 3.						
Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
10– 30	52.8	26.4	1.2	24.5	7.2	97.73
33– 53	52.6	26.3	1.0	24.8	5.7	98.10
55– 75	53.0	26.5	1.4	26.4	0.38	97.36
79– 99	53.6	26.8	8.1	26.9	0.0	84.89
101–121	52.8	26.4	18.3	26.4	0.0	65.34
123–143	53.0	26.8	41.4	26.4	0.38	21.89
147–167	53.2	26.6	51.8	25.2	5.26	2.63
169–189	53.2	26.6	52.1	25.9	2.63	2.07
191–211	52.8	26.4	51.8	25.8	2.27	1.89
Elektrolyse 16 Stunden unterbrochen und wieder eingeschaltet						
10– 30	54.6	27.3	1.8	24.2	11.36	96.70
33– 53	54.2	27.1	1.0	24.8	8.49	98.10
56– 76	53.6	26.8	0.8	25.0	6.72	98.51
79– 99	53.0	26.5	0.6	24.8	6.54	98.87
102–122	53.6	26.8	0.5	24.8	7.46	99.07
125–145	52.8	26.4	0.8	25.2	4.54	98.49
147–167	51.8	25.9	17.5	24.6	5.02	66.21
170–190	52.6	26.3	45.6	25.4	3.42	13.31
192–212	52.0	26.0	50.3	23.9	8.08	3.27
217–237	52.4	26.2	51.3	24.7	5.72	2.10

Selbst nach dieser langen Dauer konnte von einer Verarmung an Chromsäure nicht die Rede sein, da noch 11.5 gr. Cr(6) d. i. 22.1 gr. CrO_3 vorhanden waren neben 1.5 gr. Cr(3).

Die Kathode erholt sich also gewissermassen immer wieder nach einer Ruhepause, um bei der andauernden Elektrolyse mit der Zeit reduktionsunfähig zu werden. Man kann das vielleicht so erklären, dass bei Gegenwart von Cr(3) im Elektrolyten das Diaphragma auf der Kathode, welches nach E. Müller aus chromsaurem Chromoxyd besteht, sich mit der Zeit so verdickt, dass das HSO_4'-Ion nun nicht mehr bei Potentialen unterhalb der Wasserstoffentwicklung hindurchgezogen und dadurch seine die Reduktion hervorrufende Wirkung vernichtet wird.(1) Wird der Strom unterbrochen, dann wird dieser Überzug gelöst und bedarf nun wieder einer gewissen Zeit, um sich zur hinreichenden Dicke auszubilden. Die Länge dieser Zeit hängt vermutlich von äusseren Umständen ab und dürfte grösser sein, wenn gerührt wird, was allerdings erst untersucht werden müsste, weil ja an sich von dem Zeitpunkte an, wo die Reduktion verschwindet, durch die nun heftigere Wasserstoffentwicklung eine verstärkte Rührung gegeben ist.

Was nun die Oxydation anbetrifft, so fällt es auf, dass dieselbe von dem Moment, wo die Reduktion verschwindet, bei Vers. 3 wieder in Erscheinung tritt. Später bei der Fortsetzung der Elektrolyse in Vers. 4 wird sie nur noch einmal Null und ist im übrigen recht unregelmässig. Da bei Vers. 3 nach der 166 Minute die Reduktion nahezu Null ist, so ist für die folgenden Stadien auch die Cr(3)-Konzentration nahezu konstant. Wenn trotzdem die Oxydationswerte schwanken, so gewinnt man den Eindruck, dass die Cr(3)-Konzentration für die anodischen Verhältnisse nicht allein massgebend ist. Um zu sehen, ob vielleicht die Konzentration des Na_2SO_4 einen Einfluss hat, wurden noch 2 Versuche, 5 und 6, mit Erhöhung derselben angestellt.

Versuch 5.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.5 gr. Na_2SO_4
Stromstärke, Stromdichten und Temperatur wie bei Vers. 1.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
6—26	58.8	29.4	2.5	25.3	13.95	95.75
34—54	58.4	29.2	1.3	28.5	2.40	97.79
64—84	57.2	28.6	1.0	27.0	5.59	98.25
95—115	57.8	28.9	1.4	26.0	10.04	97.58
125—145	58.8	29.4	1.8	27.3	7.14	96.94
154—174	58.4	29.2	2.4	27.3	6.51	95.89

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(1) E. Müller und O. Essin, *Z. Elektrochem.*, **35**, Heft 12.

Versuch 6.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 1.0 gr. Na_2SO_4
Stromstärke, Stromdichten und Temperatur wie bei vorigem Vers.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
5– 25	59.4	29.7	2.2	25.9	12.99	96.30
33– 53	57.8	28.9	1.6	27.2	5.88	97.23
62– 82	59.4	29.7	1.0	28.8	3.03	98.31
90–110	59.0	29.5	1.0	29.0	1.69	98.31
118–138	59.4	29.4	1.1	28.9	1.70	98.15

Wenn man auch aus Vers. 5 den Eindruck gewinnt, dass die Erhöhung der Na_2SO_4-Konzentration von 0.2 auf 0.5 gr./100 c.c. gegenüber Vers. 3 die Oxydation erhöht, so wird er doch durch Vers. 6, wo 1 gr. Na_2SO_4 verwendet wurde, wieder verwischt, indem hier die Oxydation nicht noch weiter steigt, sondern wieder absinkt, und sie zudem wieder grosse Schwankungen zeigt.

Schliesslich wurden noch 2 Versuche, 7 und 8, mit kleinerer anodischer Stromdichte angestellt, bei denen auch der Gehalt an Na_2SO_4 verschieden war.

Versuch 7.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.2 gr. Na_2SO_4
Stromstärke: 0.067 Amp.
Stromdichten: $D_A=0.01$ Amp/qcm; $D_K=0.00226$ Amp/qcm.
Tem.: 30° C.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
10– 80	44.6	22.3	2.6	18.6	16.60	94.17
84–154	44.0	22.0	6.8	21.0	4.55	98.18
157–227	43.6	21.5	0.4	21.4	0.48	99.07
mit neuer Anode fortgesetzt						
13– 83	43.0	21.5	0.8	20.8	3.26	98.14
86–156	43.0	21.5	0.4	21.1	1.89	99.07

Versuch 8.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 1.0 gr. Na_2SO_4
sonst wie bei vorigem Versuch.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
17– 77	38.4	19.2	2.1	15.6	18.75	94.53
80–150	43.8	21.9	1.0	20.5	6.39	97.13
154–224	43.8	21.9	0.8	21.0	4.29	98.18
229–299	43.6	21.8	0.6	21.0	3.67	98.62
231–318	53.8	26.9	0.5	26.7	0.74	99.07

Bei der geringeren anodischen Stromdichte kommt ebenfalls die Oxydation mit der Zeit auf Null, nur dauert es längere Zeit. Ob sie sich nun hier für längere Zeit auf Null hält oder wie bei Vers. 3/4 später wieder ansteigt, wurde wegen der infolge der geringen Stromstärke benötigten ausserordentlich langen Zeit nicht untersucht.

Bei allen bisher angeführten Versuchen war an der Kathode kein Chrom abgeschieden worden. Es wurde deshalb noch einer angestellt, bei dem dieses der Fall war.—Vers. 9.

Versuch 9.

Elektrolyt: 100 c.c. Lösung mit 25 gr. CrO_3 und 0.2 gr. Na_2SO_4.
Stromstärke: 0.336 Amp.
Stromdichten: $D_A = 0.05$ Amp/qcm; $D_K = 0.20$ Amp/qcm.
Temp.: 30° C.

Min. nach Beginn	Coulometer		Zelle		% Oxydation	% Reduktion
	H_2	O_2	H_2	O_2		
7– 27	53.8	26.9	32.0	25.8	3.99	40.52
29– 49	52.8	26.4	34.2	26.4	0.0	35.23
52– 72	52.8	26.4	35.4	26.0	1.51	32.96
75– 95	53.2	26.6	36.4	25.9	2.63	31.58
97–117	52.4	26.2	36.4	25.2	3.82	20.53
120–140	52.6	26.3	37.6	25.1	4.56	28.14
143–163	52.6	26.3	37.8	25.1	4.56	28.49
166–186	53.0	26.5	37.9	25.5	3.77	29.49
188–208	52.6	26.3	38.1	25.5	3.04	29.46
211–231	52.6	26.3	38.4	25.5	4.94	27.00

In Vers. 9 haben wir ähnliche Verhältnisse wie Roudnick. Die Stromausbeute an metallischem Chrom betrug 18.5%, die durchschnittliche Reduktion 30.6%, sodass nur 12.1% auf die Bildung von Cr(3) entfallen. Wenn auch die Oxydation hier im Durchschnitt grösser ist als in Vers. 1, so kann man dies doch nicht ohne weiteres im Sinne der eingangs geäusserten Vermutung deuten, dass nämlich die höhere Cr(3)-Konzentration bei letzterem Versuche daran Schuld ist, weil gerade in den Anfangsstadien des Vers. 9 die Oxydation ganz erheblich kleiner ist als in Vers. 1, während doch die Cr(3)-Konzentration entsprechend den Reduktionsprozenten (auf Cr(3) berechnet) dort 12%, hier 96%, bei Vers. 9 wesentlich kleiner sein muss. Vielmehr muss man im Hinblick auf die ausserordentlichen Schwankungen in den Oxydationswerten eingestehen, dass die Erscheinungen an der Anode von noch unerkannten Faktoren bestimmt werden.

Trotzdem ich bei keinem meiner Versuche irgend eine Änderung der Anode erkennen konnte, neige ich doch auch zu der Ansicht, die Roudnick ausgesprochen hat, dass eine Filmbildung auf der Anode eine Rolle spielt. Schwer ist sonst die bei fast allen meinen Versuchen zu beobachtende Abnahme der Oxydation in den ersten Stadien der Elektrolyse, die besonders deutlich bei den geringen anodischen Stromdichten der Vers. 7 und 8 in Erscheinung tritt, zu deuten. Denn da es sich um eine Oxydation des Cr(3) handelt, so sollte man normalerweise eine Steigerung derselben mit der Zeit erwarten, da mit dieser auch die Cr(3)-Konzentration wächst. Ein Zusammenhang zwischen dieser und den Oxydationswerten ist aber nirgends zu erkennen. Möglicherweise sind die schwankenden Daten der letzteren darauf zurückzuführen, dass der Film durch die Sauerstoffentwicklung verletzt wird und dass deren Wirkung von unkontrollierbaren Umständen abhängt.

Wenn es mir nicht gelungen ist, wie Roudnick eine mit einem sichtbaren Überzug versehene Anode zu erhalten, mag das vielleicht dem Umstande zuzuschreiben sein, dass ich bei einer um 10° tieferen Temperatur gearbeitet habe. Möglicherweise bringt das Studium des Einflusses der Temperatur auf die anodischen Erscheinungen uns der Lösung der interessanten Fragen näher.

Herrn Prof. Dr. Erich Müller danke ich für die Anregung zu dieser Untersuchung und für seine Unterstützung.

Juli 1929.

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ON THE THERMAL DECOMPOSITION OF ALIPHATIC ETHERS.

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The ether has hitherto been considered to be stable to chemical reagents and to heat.(1) But the nature of the ether has not yet been made clear, as the chemistry of ether has advanced little. Recently S. Komatsu and his co-workers are exploiting the field of the chemistry.(2) The writer made some experiments on the thermal decomposition of aliphatic alcohols,(3) concluding that the alcohols are decomposed into corresponding olefines through the stages of the corresponding ethers: $R.CH_2OH \rightarrow (R.CH_2)_2O + H_2O \rightarrow R':CH_2+H_2O$. For introducing the conclusion, the writer proved that the corresponding ethers were formed and that the thermal effects of ether-formation were always larger than those of other possible cases.

It will however be proper to discuss the problem with the result of the thermal decomposition of the corresponding ethers under the same conditions. On one side for above purpose and on the other for obtaining some data for making clear the nature of the ether, especially for getting some idea on the affinity of alkyl groups to oxygen, the writer made the present experiments as works on the field are found scarcely in the chemical literature.

In 1835, J. Liebig(4) observed that ethyl ether was decomposed into aldehyde, a burnable gas and water when its vapour was passed through a heated glass tube filled with glass pieces and the formation of acetylene in the reaction was also observed.(5) W. Tischtschenko(6) reported that the ether was mainly decomposed into aldehyde and paraffines when heated at high temperature, unsaturated hydrocarbons, carbon monoxide and hydrogen being also produced. On passing ethyl ether through a tube filled with pumice or a mixture of pumice and zinc dust at about 500°, Nef(7) observed the formation of ethylene, carbon monoxide, hydrogen,

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(1) V. Meyer und P. Jacobson, "Lehrbuch der organischen Chemie," I-1, 289, (Leipzig: Veit & Comp.), 1907; J. B. Sendrens, *Compt. rend.*, **146** (1908) 1211; J. Houben, "Die Methoden der organischen Chemie," III, 136 (H. Meerwein), (Leipzig: Georg Thieme.), 1923.

(2) Private communication.

(3) This Bulletin, **4** (1929), 177.

(4) *Ann.*, **14** (1835), 134.

(5) M. Berthelot, *Ann.*, **116** (1860), 117.

(6) *Chem. Zentr.*, (1900) I, 586

(7) *Ann.*, **318** (1901), 198:

methane and ethene with a small amount of acet- and croton-aldehydes Under high temperature and pressure, ethyl ether was decomposed into ethylene and water in the presence of iron and alumina⁽¹⁾; the same decomposition occurred at 200-300° in contact with alumina.⁽²⁾ When ethyl ether was passed through a heated platinum tube, the principal change was the formation of ethane and acetaldehyde accompanied by ethylene and water⁽³⁾. But ethyl ether in gaseous state, when heated at about 500° in a silica bulb without catalyst, did not decompose according to the formula, $C_2H_5{\cdot}O{\cdot}C_2H_5=2C_2H_4+H_2O$, but carbon monoxide separated from the molecule, the net result being thus: $CO+2CH_4+0.5C_2H_4$.⁽⁴⁾ Ethyl ether gave ethyl alcohol when heated with alumina under ordinary pressure⁽⁵⁾ or when treated with silicon tetrachloride⁽⁶⁾ or with disilicon hexachloride.⁽⁷⁾

Propyl ether behaved similar to ethyl ether when heated.⁽⁸⁾ The thermal decompositions of dimethyl and di-isopropyl ether and some mixed ethers were studied to some extent.⁽⁹⁾

As the experimental materials, ethyl, *n*-propyl, *n*-butyl, *n*-amyl and ethyl-*n*-butyl ethers and *n*-amyl alcohol are used for making comparative studies.

The experiment was conducted under the same conditions, using the same apparatus and catalyst as in the case of the alcohol. Small grains of Japanese acid clay are filled into a hard glass tube and dried and activated at 350–400°. When the temperature of the catalyst attained a desired one, the sample is gradually dropped into one end of the tube at a definite rate. It is there evaporated and acted with the clay. The produced liquid and gas are collected into proper receivers and analysed. The gas is analysed by ordinary absorption method combining a combustion one for hydrogen and paraffines. As to the liquid product, water, alcohols, ethers and sometimes aldehydes are estimated by fractional distillation, by combining the action of toluene, sodamide and others. Alcohols are proved by the formation of their phenylurethanes or benzoylesters.

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(1) W. Ipatieff, *Ber.*, **37** (1904), 2994; *Chem. Zentr.*, (1904), II, 1020.

(2) J. B. Sendrens, *Compt. rend.*, **146** (1908), 1211; *Bull. soc. chim.*, [4] **3** (1908), 823; C. J. Engelder, *J. Phys. Chem.*, **21** (1917), 698.

(3) E. Peytral, *Bull soc. chim.* [4] **35** (1924), 964.

(4) C. N. Hinshelwood, *Proc. Roy. Soc.* (London), [A] **114** (1927), 84.

(5) W. Ipatieff, loc. cit.

(6) F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, (1927), 2734.

(7) F. S. Kipping and R. A. Thompson, *J. Chem. Soc.*, (1928), 1989.

(8) W. Tischtschenko, loc. cit.

(9) C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc.* (London), [A] **115** (1927), 215; J. V. S. Glass and C. Norman *J. Chem. Soc.*, (1929), 1815; J. V. S. Glass and C. N. Hinshelwood, ibid., (1929), 1804.

When aliphatic ethers are passed over heated Japanese acid clay, they are decomposed into corresponding olefines, alcohols and water, small amounts of aldehydes, gaseous compounds, sometimes of esters and a kind of petroleum hydrocarbons (at high temperature) being also produced. A very small amount of free carbon is precipitated on the catalyst, the higher the temperature, the more the amount of carbon.

The mechanism of the thermal decomposition of aliphatic ethers in the presence of Japanese acid clay is assumed to be as follows:

$$R\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot R = 2R\cdot CH:CH_2 + H_2O.$$

Figures on the succeeding pages show the mutual quantitative relations between the decomposition products at different temperatures from ethyl, propyl, butyl, amyl and ethyl-butyl ethers and amyl alcohol. That the ratios of olefines and water produced are almost constant (2:1) at above ca. 300° and that the yields of olefines from ethers are always larger than those from corresponding alcohols will explain the above reaction mechanism, i.e., two alkyl groups are split off from oxygen at the same time at the temperatures.

In the case of ethyl-butyl ether, the decomposition product is a mixture of ethylene, butylene, ethyl and butyl alcohols and water, where the amounts of butylene and ethyl alcohol being larger than those of ethylene and butyl alcohol. The affinity between butyl proup and oxygen is therefore weaker than that between ethyl group and oxygen: $C_2H_5 > C_4H_9$.

On the formation of alcohols at low temperature, the writer wishes to assume the following reaction:

$$R\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot R = R\cdot CH:CH_2 + R\cdot CH_2\cdot CH_2\cdot OH.$$

As mentioned before, the ether has hitherto been thought as a stable compound; this conception will be correct in a certain limit, but it will not be proper to assume it very stable. Not only by the action of acids, but also even by alkalies, it is decomposed, especially at elevated temperatures.

On the hydrolysis of the ether by acids, some works⁽¹⁾ have been recorded, the decomposition product being different according to the temperature, at which the ether is treated:

$$R\cdot O\cdot R' + HX \begin{array}{l} \nearrow RX\ \ + R'OH, \\ \longrightarrow ROH + R'X, \\ \searrow RX\ \ + R'X. \end{array}$$

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(1) R. D. Silva, *Ann. chim. phys.*, [5] **7** (1876), 429; W. Lippert, *Ann.*, **276** (1893), 148; A. Michael. *J. prakt. Chem.*, [2] **64** (1901), 106, etc.

As the name indicates, the Japanese acid clay reacts acidic. The liquid products in the reactions are always acidic. When ethyl, propyl or butyl ether is heated in a sealed tube at 200–250° with water in the presence of the clay, corresponding alcohols are produced, the amount being however small. H. Inoue⁽¹⁾ observed the hydrolysis of acetic ester by passing it over Japanese acid clay at about 200°. And W. Ipatieff⁽²⁾ reported the formation of ethyl alcohol by the thermal decomposition of ethyl ether under the influence of alumina. A. Skrabal and H. Airoldi⁽³⁾ measured the saponification constant of ethyl ether under the influence of benzene sulphonic acid and S. K. Kulkarni Jatkar and H. E. Watson⁽⁴⁾ calculated the equilibrium constant of the reaction, $C_2H_5{\cdot}O{\cdot}C_2H_5+H_2O \rightleftarrows 2C_2H_5OH$.

From these facts, there is a possibility to suppose that the alcohol is produced by the hydrolysis of the ether due to the special characteristics of the clay:

$$R{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}R + H_2O = 2R{\cdot}CH_2OH.$$

And it will of course be natural to suppose a very small amount of alcohol present in the liquid product is formed by the hydrolysis, but the saponification constant of Skrabal and Airoldi is only 9×10^{-5} at 98° and the equilibrium constant of Jatkar and Watson is 7.3 at 227°. Would the hydrolysis be permitted, the degree will be very small, while the amount of the alcohol determined is not small; the writer wishes therefore to propose the above reaction mechanism:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}R = R{\cdot}CH{:}CH_2 + R{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

As will be seen from the tables and diagrams the clay represents a special characteristics to the ether, the lower the temperature, the less the decomposition to the olefines, but larger the production of alcohols. At above ca. 300°, almost complete decomposition takes place rapidly i.e., at high temperature, almost all of the ether is decomposed into olefine and water.

As in the case of the alcohol, the amounts of the produced olefines increase with the rise in the reaction temperature, which is shown in Fig. 1. At above ca. 300°, the decomposition is extremely promoted. There is almost no difference between the amounts of the produced olefines according to the difference of the ether. In the case of ethyl ether, the rate of the formation of ethylene is slightly less than the cases of other ethers.

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(1) Private communication; cf. this Bulletin, **1** (1926), 157.

(2) Loc. cit.

(3) *Monatsh. f. Chem.*, **45** (1924), 13.

(4) *J. Indian Inst. Sci.* [A] **9** (1926), 99; *Chem. Abstr.*, **21** (1927), 386.

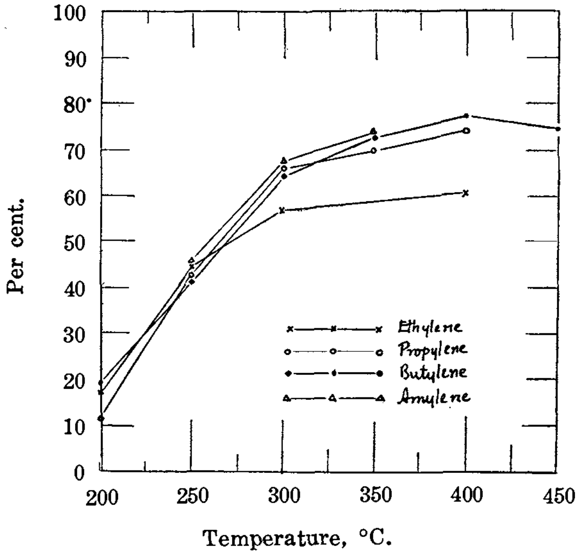

Fig. 1.

The double bond of the olefine produced belongs generally to the carbon atom linked with oxygen:

$$R\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot R \rightarrow R\cdot CH:CH_2.$$

But in the case of butyl ether, butylene is a mixture of α-and β-isomers, the latter being predominated. And amylene produced from amyl alcohol and ether is also a mixture of α-compound ($CH_3\cdot CH_2\cdot CH_2\cdot CH:CH_2$) and β-one ($CH_3\cdot CH_2\cdot CH:CH\cdot CH_3$); these will be produced by the migration of double bond by the further action of the heated clay for producing more stable isomers.

At low temperatures (mainly at 200–250°), corresponding alcohols are produced, the amount of which decreasing rapidly with the rise of temperature. Ester is produced in the case of ethyl ether, but not distinct in the cases of other ethers. Aldehyde is produced in small amounts at every cases. The amounts of carbon monoxide, hydrogen and aldehyde isolated are not large, the formation of aldehyde in the reaction will not therefore be large.

Ethyl Ether. Pure ethyl ether is used after distilling over metallic sodium, boiling point of which being 35°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 1, 2, 3 and 4, and the mutual relations of the main products are shown in Figs. 2 and 3.

Table 1.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %	Liquid yield %
				Liquid, gr.	Gas, L.		
33	73.4	200	0.35	40	11.65	16.4	54.5
34	58.3	200	0.34	28	9.87	18.6	48.0
35	87.1	250	0.34	21	39.09	50.5	24.1
36	104.4	250	0.34	29	36.22	38.4	27.8
37	126.0	250	0.33	32	58.73	53.2	25.4
38	117.4	300	0.33	25	61.49	58.8	21.3
39	118.8	300	0.32	27	63.86	55.1	22.7
40	86.4	400	0.34	19	47.57	59.0	22.0
41	104.8	400	0.35	22	56.16	62.6	21.0

Table 2.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
33	200	82.5	6.4	0.4	6.8	1.4	2.5
34	200	88.0	2.1	0.2	5.4	2.1	2.2
35	250	89.9	3.1	0.2	4.7	1.0	1.1
36	250	88.4	3.6	0.4	3.4	1.0	3.2
37	250	91.2	3.1	0.2	2.8	1.0	1.7
38	300	89.7	5.1	0.2	2.2	1.0	1.8
39	300	81.9	3.0	0.2	7.3	3.2	4.4
40	400	85.6	1.8	0.4	4.0	3.2	5.0
41	400	93.4	2.4	0.4	1.2	1.4	1.2

Table 3.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde	Ester
33	200	61.8	19.8	14.8	0.52	+
34	200	57.5	23.2	14.3	0.43	+
35	250	6.2	25.7	68.1	0.05	+
36	250	21.7	26.2	44.8	0.66	+
37	250	10.0	20.0	65.6	0.19	+
38	300	2.4	1.2	94.0	0.02	+
39	300	trace	4.1	92.6	0.02	+
40	400	0	0.5	97.4	0.02	−
41	400	0	0.3	95.5	0.01	−

Table 4.

Yields of the Main Substance, mol per cent.

No.	Reaction temp.	Ethylene	Ether	Alcohol	Water
33	200	43.4	33.3	17.2	33.3
34	200	49.6	28.0	17.8	28.0
35	250	133.6	1.7	10.2	67.2
36	250	101.5	7.7	12.1	51.1
37	250	140.6	2.4	8.2	68.8
38	300	155.3	0.6	0.4	82.7
39	300	145.4	trace	1.3	89.2
40	400	156.1	0	0.9	88.3
41	400	165.5	0	0.5	82.7

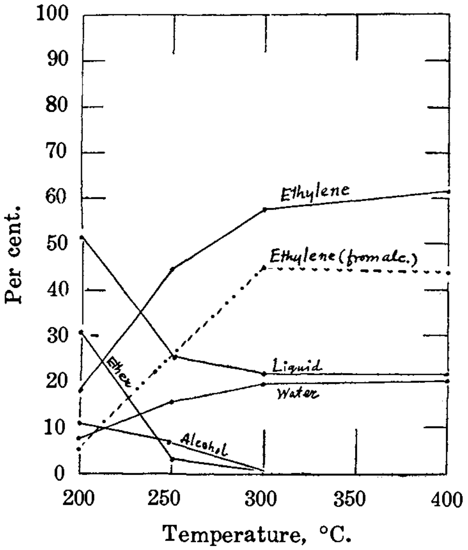

Fig. 2.

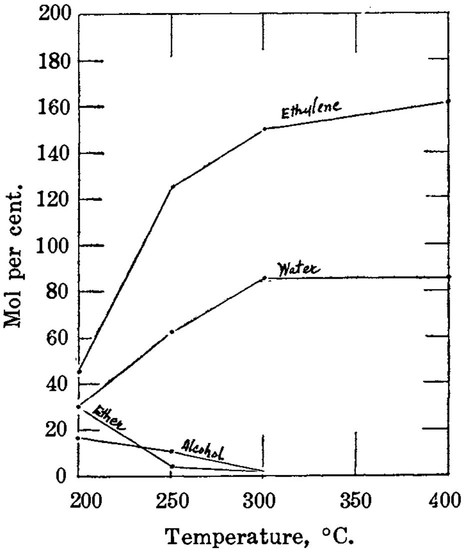

Fig. 3.

n-Propyl Ether. One part of the ether is prepared from n-propyl alcohol by the method of Kraft(1) and the other is Eastman's product. They are carefully purified by distilling over metallic sodium, boiling point of which being 90–91°. The experimental conditions, decomposition products and the analytical results of the products are tabulated in Tables 5, 6, 7, and 8, and the mutual relations of the main compounds are shown in Figs. 4 and 5.

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(1) *Ber.*, **26** (1893), 2829.

Table 5.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temerature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Propylene yield, %	Liquid, yield, %
				Liquid, gr.	Gas, L.		
42	46.0	200	0.31	33.0	2.52	9.2	71.7
43	46.0	200	0.31	30.5	4.38	13.9	66.3
44	46.0	250	0.31	20.0	10.81	41.5	43.5
45	46.0	250	0.31	20.0	10.99	43.2	43.5
46	46.0	300	0.31	8.5	16.49	65.2	18.5
47	46.0	300	0.31	8.7	17.52	68.5	18.9
48	46.0	350	0.31	8.0	17.98	67.2	17.4
49	46.0	350	0.31	8.4	18.17	70.8	18.3
50	46.0	400	0.31	8.0	18.63	73.3	17.4
51	46.0	400	0.31	8.5	19.47	75.2	18.5

Table 6.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
42	200	89.2	1.0	1.2	3.0	2.7	1.0
43	200	77.4	0.5	0.2	2.5	1.1	0.6
44	250	94.0	0.6	0.2	2.4	1.3	0.5
45	250	96.2	1.0	0.2	1.4	0.9	0.3
46	300	96.8	0.6	0.4	0.8	1.3	0.1
47	300	95.8	1.0	0.2	1.0	1.2	0.4
48	350	94.2	0.6	0	1.2	1.8	0.5
49	350	95.4	0.6	0.2	1.4	1.1	0.5
50	400	96.4	0.4	0.2	1.2	1.2	0.4
51	400	94.6	0.8	0.3	1.2	2.0	0.7

Table 7.

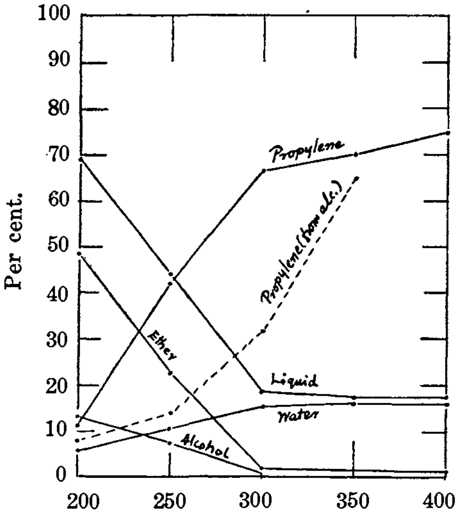
Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde
42	200	74.9	17.6	3.0	0.12
43	200	63.9	18.7	13.1	0.08
44	250	52.0	16.5	25.5	0.24
45	250	52.5	17.0	24.5	0.19
46	300	8.2	2.4	83.5	0.09
47	300	8.1	2.3	86.2	0.09
48	350	3.8	0.3	93.8	0.02
49	350	2.4	0.2	95.2	0.01
50	400	7.5	trace	90.0	0.02
51	400	3.5	trace	94.1	0.01

Table 8.

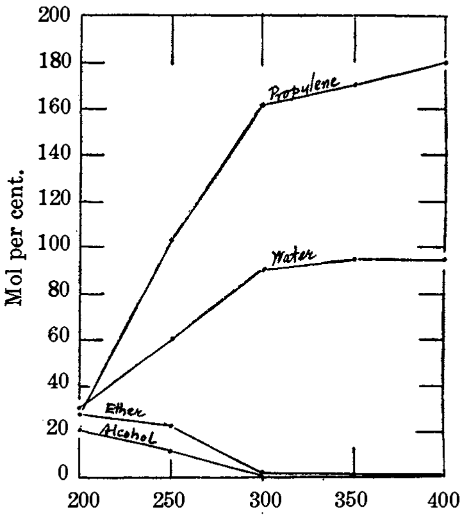
Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Propylene	Ether	Alcohol	Water
42	200	22.2	53.8	21.6	12.4
43	200	33.5	42.4	21.1	49.3
44	250	100.8	22.7	12.2	62.9
45	250	104.8	22.9	12.7	60.4
46	300	158.1	1.6	0.7	87.6
47	300	166.3	1.6	0.7	92.7
48	350	167.9	0.7	0.1	92.7
49	350	171.9	0.4	0.1	98.7
50	400	178.1	1.3	trace	88.9
51	400	182.5	0.7	trace	98.7



Temperature, °C.

Fig. 4.



Temperature, °C.

Fig. 5.

***n*-Butyl Ether.** Pure ether of Eastman Kodak Co. is used after distilling over metallic sodium, boiling point of which being 140–141°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 9, 10, 11 and 12, and the mutual relations of the main compounds are diagramed in Figs. 6 and 7.

Table 9.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Butylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
52	46.0	200	0.31	34.0	3.51	15.3	73.9
53	46.0	200	0.31	30.0	4.95	23.6	65.2
54	42.5	250	0.35	22.0	6.31	33.3	51.8
55	46.0	250	0.31	21.0	9.50	49.5	45.7
56	50.0	300	0.31	13.0	13.01	61.6	26.0
57	46.0	300	0.31	9.0	13.04	67.4	19.6
58	44.4	350	0.32	8.0	14.16	78.8	18.0
59	46.0	350	0.31	8.0	13.93	71.2	18.5
60	47.0	400	0.34	8.0	19.79	83.2	17.0
61	46.0	400	0.31	8.0	14.20	72 3	17.4
62	46.0	450	0.31	6.5	14.66	74.7	14.1
63	46.0	450	0.31	6.5	14.93	74.8	14.1

Table 10.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
52	200	80.0	1.2	1.0	2.8	2.7	8.2
53	200	87.8	1.6	1.2	2.4	1.5	4.1
54	250	89.7	0.4	0.8	2.0	3.0	4.1
55	250	95.6	1.8	0.5	0.2	0.8	1.1
56	300	94.5	0	0.4	3.1	0.7	1.3
57	300	95.0	1.4	0.2	1.0	1.0	1.4
58	350	93.7	3.1	0.2	1.0	0.5	1.5
59	350	94.0	0.8	0.4	1.6	0.8	2.4
60	400	78.9	2.8	0.6	2.8	2.6	8.6
61	400	93.6	0.4	0.6	1.8	1.0	2.2
62	450	93.6	0.8	0.6	1.2	1.3	2.6
63	450	92.0	0.6	0.8	1.4	1.5	3.7

Table 11.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde
52	200	73.2	15.3	5.9	0.05
53	200	70.0	11.3	8.0	0.06
54	250	47.7	6.4	15.5	0.05
55	250	69.5	13.3	17.1	0.06
56	300	33.8	9.2	52.3	0.04
57	300	35.6	4.4	60.0	0.06
58	350	22.6	1.1	76.0	0.06
59	350	31.8	2.4	65.9	0.05
60	400	12.5	1.3	86.3	0.04
61	400	28.5	1.3	70.0	0.04
62	450	23.1	3.1	72.3	0.05
63	450	18.5	3.1	76.9	0.05

Table 12.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Butylene	Ether	Alcohol	Water
52	200	36.8	54.1	19.8	31.4
53	200	53.8	45.6	13.0	37.6
54	250	76.7	24.5	5.8	58.0
55	250	121.7	31.7	10.8	56.3
56	300	143.2	8.9	4.2	98.2
57	300	155.7	7.1	1.4	84.9
58	350	173.0	4.1	0.3	97.6
59	350	164.2	5.9	0.9	88.0
60	400	191.1	2.2	0.3	95.3
61	400	167.0	5.1	0.3	88.0
62	450	172.6	3.4	0.9	73.9
63	450	172.6	2.6	0.9	78.7

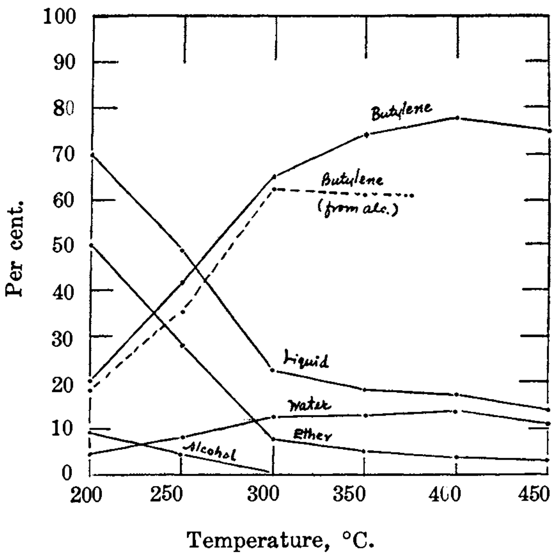


Fig. 6.

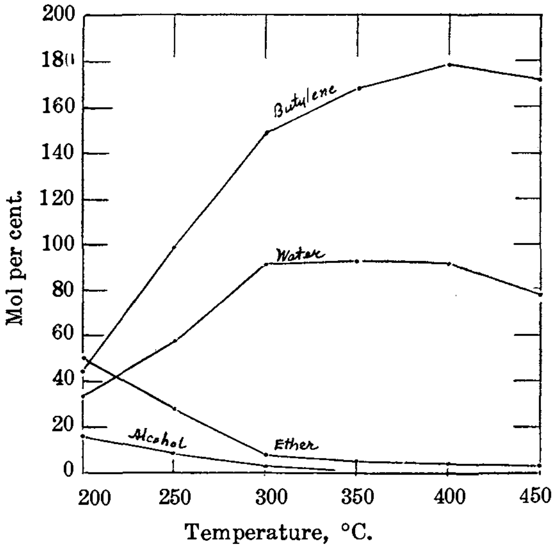


Fig. 7.

n-**Amyl Ether.** Pure ether of Eastman Kodak Co. is purified by distilling over metallic sodium, boiling point of which being 90–91°. The experimental conditions, decomposition products and the analytical results of the products are tabulated in Tables 13, 14, 15 and 16, and the mutual relations of the main products are shown in Figs. 8 and 9.

Table 13.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Amylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
64	45	250	0.3	41.0	0.3	45.3	91.1
65	45	300	0.3	42.0	0.4	67.1	93.3
66	45	350	0.3	42.0	0.4	74.8	93.3

Table 14.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
64	250	0	0.4	1.0	19.6	0	0
65	300	0	0.4	0	19.4	0	0
66	350	0	0	0	20.0	0	0

Table 15.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water	Aldehyde
64	250	49.7	35.4	8.1	6.8	+
65	300	71.9	17.1	2.7	8.8	+
66	350	80.1	8.1	0.8	11.0	+

Table 16.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water
64	250	102.2	32.2	13.3	54.7
65	300	162.4	15.9	4.5	68.4
66	350	180.8	7.6	1.4	89.8

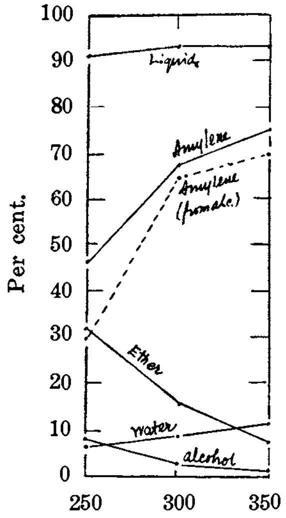


Fig. 8.

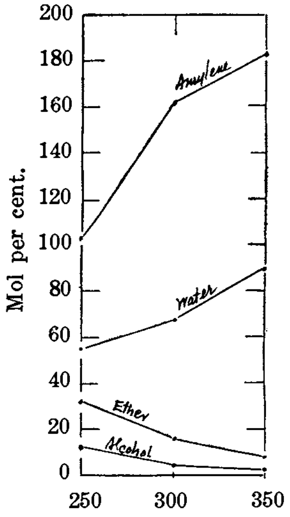


Fig. 9.

Ethyl-*n*-Butyl Ether. Pure product of Eastman Kodak Co. is repeatedly distilled over metallic sodium, boiling point of which being 91-91.5°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 17, 18, 19 and 20, and the mutual relations of the main products are shown in Figs. 10 and 11. The ether is also prepared from *n*-butyl alcohol and ethyl iodide using sodamide as a condensing agent, which is a good method for the preparation of the ether or of similar compounds.

Table 17.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %	Butylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.			
67	50	200	0.28	45	1.69	1.4	8.6	90.0
68	50	250	0.28	27	6.83	7.9	36.5	54.0
69	70	350	0.29	15	22.75	20.1	44.5	21.4

Table 18.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
67	200	75.4	0.4	1.0	5.0	4.2	6.2
68	250	90.2	3.0	0.4	2.2	2.0	1.2
69	350	90.2	3.2	0.6	1.4	2.4	2.2

Table 19.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Ethyl Alcohol	Butyl Alcohol	Water	Aldehyde	Low boiling fraction	High boiling fraction
67	200	46.6	7.7	1.7	6.0	+	26.9	11.1
68	250	24.2	9.6	1.1	19.3	+	36.0	9.8
69	350	9.1	1.1	trace	74.7	+	0.5	14.7

Table 20.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Ethylene	Butylene	Ether	Ethvl alcohol	Butyl alcohol	Water
67	200	5.0	15.6	41.9	15.5	2.1	30.6
68	250	28.6	66.5	13.1	11.5	0.8	59.0
69	350	73.3	80.4	2.0	4.4	trace	95.8

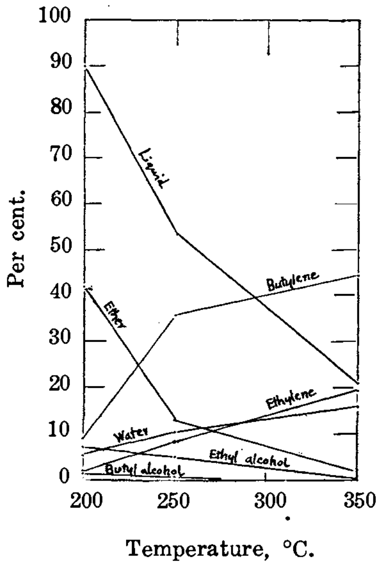


Fig. 10.

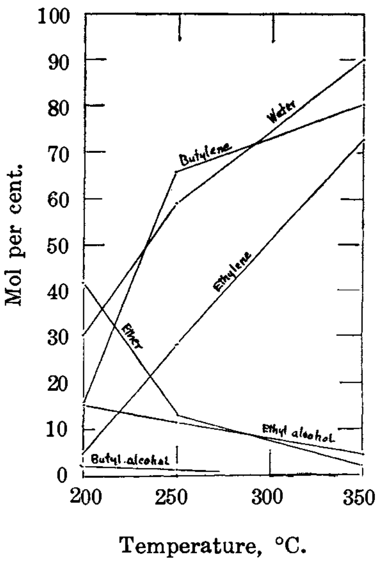


Fig. 11.

***n*-Amyl Alcohol.** Pure product of Eastman Kodak Co. and of Kahlbaum is used after distilling over powdered quick lime, boiling point of which being 137-138°. The experimental conditions, decomposition products and analytical results of the products are summarised in Tables 21, 22, 23 and 24, and the mutual relations of the main products are shown in Fig. 12.

Table 21.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Amylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
70	45	250	0.3	43.0	0.23	29.5	95.6
71	45	300	0.3	42.5	0.44	64.9	94.4
72	45	350	0.3	42.5	0.36	70.0	94.4

Table 22.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
70	250	0	1.2	0.8	21.1	4.6	0
71	300	1.4	0.2	2.4	19.5	4.0	0
72	350	5	0.4	1.0	18.7	2.6	3.8

Table 23.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water	Aldehyde
70	250	30.8	6.2	53.2	9.8	+
71	300	68.7	4.5	3.1	19.1	+
72	350	74.1	4.0	1.2	20.5	+

Table 24.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water %
70	250	37.1	3.3	50.8	45.7
71	300	81.6	2.4	2.9	88.1
72	350	88.0	2.1	1.1	94.5

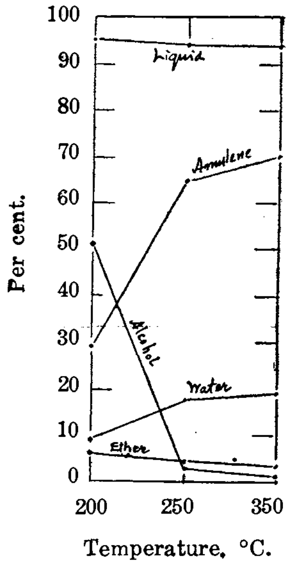


Fig. 12.

The writer wishes to express his thanks to Col. T. Hisamura and Prof. S. Komatsu for their having interest on the problem and also to Mr. H. Ishizawa for his assistance to complete the experiment.

November, 1929. Tokyo.

BEITRÄGE ZUR KENNTNIS DER ALLOTROPEN MODIFIKATIONEN VON SCHWEFEL.

II. KATALYTISCHE EINFLÜSSE.

Von C. R. PLATZMANN.

Eingegangen am 4. September 1929. Ausgegeben am 28. Februar 1930.

Nach den grundlegenden Arbeiten von Smith(1) und seinen Mitarbeitern wird die Einstellung des Schmelzpunktsgleichgewichts durch Schwefeldioxyd verzögert und durch Ammoniak beschleunigt, eine Beobachtung, die durch folgende, eigene Versuche bestätigt und erweitert wurde.

Je 25 gr. aus Schwefelkohlenstoff kristallisierten und vom Lösungsmittel, durch Erwärmen im Vakuum, befreiten Schwefels wurden in zwei gleichen Gefrierrohren bei einer Aussenbadtemperatur von 120°, also 0.75° oberhalb des idealen Schmelzpunktes (119.25°) geschmolzen, während gleichzeitig in das eine Gefrierrohr SO_2, in das andere NH_3 eingeleited wurden. Bei vier solchen Parallelversuchen trat das Schmelzen des Schwefels wie folgt ein:

Versuchs Nr.	Geschmolzen nach:	
	bei NH_3-Einleiten	bei SO_2-Einleiten
1	$1^h\ 15^m$	$3^h\ 15^m$
2	1 20	3 30
3	1 15	3 25
4	1 15	3 15

Bei den Versuchen Nr. 3 und 4 wurden sofort nach eingetretenem völligen Schmelzen folgende Erstarrungspunkte festgestellt:

Versuchs Nr	Erstarrungspunkt	
	bei NH_3-Einleiten	bei SO_2-Einleiten
3	114.5°	118.0°
4	114.7°	118.7°

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(1) Smith und Holmes, *Z. physik. Chem.*, **42** (1903), 469; **54** (1906), 257; Smith, Holmes und Hall, ibid., **52** (1905), 602; Smith und Carson, ibid., **57** (1907), 688; **61** (1908), 200; **77** (1911), 661; Smith und Brownlee, ibid., **61** (1908), 209.

Es war also bei NH_3-Einwirkung in $1^1/_4$ Stunden der natürliche Schmelzpunkt von 114.5° erreicht worden, während SO_2 die Einstellung desselben sehr stark verzögerte. Wurde indessen weiter erhitzt, so stellte sich auch bei SO_2-Behandlung mit der Zeit der natürliche Schmelzpunkt ein.

Nach den Untersuchungen von Smith soll die Senkung des Schwefelschmelzpunktes darauf beruhen, dass sich amorpher, in Schwefelkohlenstoff unlöslicher Schwefel (S_μ) bildet. In der Tat konnte festgestellt werden, dass mit dem Sinken des Erstarrungspunktes von 119.25° auf 114.5° der Gehalt an amorphem Schwefel (S_μ) proportional anstieg und beim natürlichen Schmelzpunkt von 114.5° dann etwa, in Uebereinstimmung mit Smith bis zu 3.6% betrug, wenn die erkaltete Schmelze nach 24 Stunden mit Schwefelkohlenstoff extrahiert wurde.

Eigem Versuche ergaben: 25 gr. Schwefel wurden jeweilig bis zur Konstanz des natürlichen Schmelzpunkts erhitzt.

Versuchs Nr.	Extrahiert an S_μ					
	sofort	6h	16h	22h	24h	12 Tage
	nach dem Erkalten					
1	0.02%	–	–	–	3.16%	–
2	0.07%	–	2.07%	–	–	2.78%
3	0.31%	1.90%	–	3.36%	–	–

Die Bestimmung des amorphen Schwefels liefert direkt nach dem Erkalten der Schmelzen keine oder nur sehr geringe Mengen an S_μ, was Smith mit der öligen Form, in der S_μ zunächst noch anwesend ist, erklären will.

Nach Smith ist beim natürlichen Schmelzpunkt stets die gleiche Menge an amorphem Schwefel vorhanden, unabhängig davon, ob SO_2 oder NH_3-Einleiten stattfand.

Beim Schmelzen in Luft bildet sich stets etwas SO_2 und entsprechend verhalten sich in der Luft bezw. SO_2 geschmolzener Schwefel insofern gleich, als sie die gleichen dem jeweiligen Erstarrungspunkt proportionalen Mengen an S_μ enthalten.

Wenn dagegen unter NH_3-Einwirkung geschmolzen wird, lässt sich, auch wenn bis zur Erreichung des natürlichen Erstarrungspunktes erhitzt war, bei der Behandlung mit Schwefelkohlenstoff 24 Stunden nach dem Erkalten, so gut wie kein amorpher Schwefel feststellen, trotzdem die kryoskopischen Konstanten bei der mit SO_2 bezw. NH_3 behandelten

Schmelze im Rahmen der experimentellen Fehlergrenzen übereinstimmen. Entsprechende Versuche ergaben:

Schwefel in gr.	Diphenyl gr. Einzelmengen	Erniedrigung	K
1. Nach Durchleiten von SO_2			
25.3	0.1223	0.706	225.1
	0.1245	0.671	210.1
	0.1364	0.712	203.5
		Mittel:	212.9
2. Nach Durchleiten von NH_3			
25.4	0.1264	0.716	220.8
	0.1390	0.736	206.4
	0.1433	0.712	193.7
		Mittel:	207.0

Neben der anfänglichen Ueberhitzung, über welche in Teil I dieser Abhandlung berichtet wurde, besteht auch durch das Einleiten von Ammoniak eine Möglichkeit, die Einstellung des natürlichen bei 114.5° liegenden Gefrierpunkts zu beschleunigen, während SO_2 das Bestreben hat den jeweiligen Schmelzpunkt eine Zeitlang zu fixieren.

Die Wirkung von NH_3 bei Einleiten in der Hitze lässt sich durch nachfolgende SO_2-Einwirkung wieder aufheben und umgekehrt, was Smith dahingehend zu erklären versucht, dass der nach Vorbehandlung mit SO_2 gebildete S_μ nach dem Abschrecken erhalten bleibt, während nach Vorbehandlung mit NH_3 der beim gleichen Gefrierpunkt in gleichter Menge gebildete amorphe Schwefel beim Erkalten in löslichen S_λ übergeht.

Als Beweis für diese Annahme führt er die Wahrnehmung öliger Tropfen von S_μ an, welche er nach dem Erkalten des SO_2-Schwefels bei sofortigem Extrahieren mit Schwefelkohlenstoff feststellte. Eigene Versuche ergaben dagegen lediglich, dass solcher Schwefel sich nach dem direkten Ausgiessen in eine kalte Porzellanschale fettig anfühlte und besonders fest an der Schale haftete. Seine Farbe war sattgelb. Nach längerem Stehen wird er heller, verliert den fettigen Griff und löst sich leichter von der Schale.

Demgegenüber fühlte sich der NH_3-Schwefel nicht fettig an, löste sich sofort unter Knistern von der Schale und besass eine weisslichgelbe, sehr helle Farbe.

Die Unstimmigkeiten lassen sich beheben, wenn man statt des angenommenen öligen amorphen Schwefels die Modifikation S_π von Aten⁽¹⁾ einführt. S_π besitzt sattgelbe Farbe, ist in Schwefelkohlenstoff löslich und geht bald in S_μ über, der seinerseits unter NH_3-Einwirkung die Tendenz besitzt, sich in löslichen S_λ zu verwandeln.

Amorpher Schwefel wird selbst in festem Zustande durch Ammoniakgas oder Pottaschelösung in löslichen S_λ verwandelt; das Verschwinden bei Gegenwart dieser Stoffe findet daher seine natürliche Erklärung.

Es drängte sich nunmehr die Frage auf, wie sich die zur Bestimmung der kryoskopischen Konstante $K=213$ benutzten organischen Substanzen in katalytischer Hinsicht verhalten würden, ob indifferent, ob analog der SO_2-order der NH_3-Einwirkung.

Da bei keiner derselben abnorm erscheinende kryoskopische Konstanten erhalten wurden, erscheint die Annahme berechtigt, dass an dem Erstarrungsgemisch nichts wesentliches geändert und der Erstarrungspunkt nicht durch Auftreten von Fremdmolekülen verschoben worden ist.

Dagegen stellte sich bei der Extraktion der erkalteten Schmelzen mittels Schwefelkohlenstoff zwecks Bestimmung von amorphem Schwefel heraus, dass ähnliche Unterschiede bestehen, wie sie bei Vorbehandlung mit SO_2 bezw. NH_3 vorhanden sind. So z. B. ergab sich:

Substanz	Prozent	S_μ in %
Diphenyl	0.70	4.71
α-Thiophencarbonsäure	0.34	3.49
Pyridin	0.72	0.003
Chinolin	0.46	0.0
Anilin	0.50	0.02

Es führen also Substanzen von indifferentem oder saurem Charakter wie Diphenyl oder α-Thiophencarbonsäure zu Mengen von amorphem Schwefel wie bei der Erhitzung in Luft oder SO_2, während Stoffe basischen Charakters (Pyridin, Chinolin, Anilin) sich in ihrem Verhalten dem der Ammoniakwirkung anschliessen.

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(1) A. H. W. Aten, *Z. physik. Chem.*, **81** (1912), 257; **83** (1913), 442; **86** (1913), 1; **88** (1914), 321.

Zusammenfassung.

1. Die von Smith beobachtete katalytische Wirkung von SO_2 und NH_3 auf die Geschwindigkeit der Einstellung des Schmelzpunktes sowie deren Einfluss auf die Entstehung von amorphem Schwefel (S_μ) in den erkalteten Schmelzen wurde nachgeprüft und bestätigt.

2. In letzterer Hinsicht zeigten organische Substanzen indifferenten oder sauren Charakters Analogie mit Schwefeldioxyd, während Stoffe basischen Charakters sich wie NH_3 verhielten.

3. In den kryoskopischen Konstanten treten diese Unterschiede nicht hervor, weshalb angenommen werden kann, dass sich der amorphe Schwefel (S_μ) erst sekundär aus zunächst entstehendem S_π nach Aten bildet.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. V.

By Tetsuya ISHIKAWA.

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Ideal Solutions of Solids in Liquids. Proposed formulas for the viscosities of ideal or chemically indifferent solutions of solids in liquids are numerous, among which, however, one attempt only at rational treatment has been made by Einstein.(1) According to him the viscosity η of a suspensoid increases linearly with the concentration expressed in a volume fraction z_v of the dispersion medium per unit volume of the solution.

$$\eta=\eta_0\,(1+2.5\,z_v),$$

where η_0 is the viscosity of the pure solvent. He deduced the formula from the hydrodynamical equation of motion by assuming (i) the particles are rigid spheres, (ii) the particles are few in number and (iii) the particles are great in comparison with the action spheres of molecules. Hatschek found the constant to be 4.5 instead of 2.5, but his procedure of calculation is false, so that his formula is considered to have no general meaning.(2)

A similar form of Einstein's formula is expressed by

$$\eta=\eta_0\,(1+c\,z_v),$$

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(1) A. Einstein, *Ann. d. Physik*, **19** (1906), 289; **34** (1911), 591; *Kolloid-Z.*, **27** (1920), 137.

(2) M. v. Smoluchowski, *Kolloid-Z.*, **18** (1916), 194.

where c is a constant which depends only upon the form of particles.

Though the above formula is theoretically interest, its validity is limited for very dilute solutions.

With the object of testing that Kendall's cube-root equation for a chemically indifferent binary mixture, $\eta^{\frac{1}{3}}=(1-z_m)\eta_1^{\frac{1}{3}}+z_m\eta_2^{\frac{1}{3}}$ (where η_1, η_2 and η are respectively the viscosities of components 1, 2 and the mixture, and z_m is a molar fraction of component 2) has applicability to ideal solutions of solids in liquids, Kendall and Monroe⁽¹⁾ carried out the viscosity measurements on solutions of naphthalene and of diphenyl in benzene and in toluene. The calculated values of η_2, by the formula, for either solute give good results for any system, those for benzene solutions are, however, different from the corresponding values for toluene solutions, namely, for naphthalene 2.25 in benzene and 1.825 in toluene, for diphenyl 3.44 in benzene and 2.82 in toluene. The authors pointed out that the ratio [η_2 on benzene basis]/[η_2 on toluene basis] is practically identical for the two solutes. While this agreement is of interest, it is difficult to accept the cube-root formula as anything but a further interpolation formula, considering that these solutions are undoubtedly ideal.

Application of the Writer's Formula to Ideal Solutions of Solids in Liquids. The writer has shown in the foregoing papers⁽²⁾ that his viscosity formula for a binary mixture where there form no new molecular compounds:

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z_m}$$

(where a and k with suffixes 1 and 2 denote the association degrees and the field-constants of components 1 and 2, and other symbols have the same meaning as above) affords the satisfactorily concordant results with the experimental data available in the literature. The next problem is whether or no the formula has validity for ideal or chemically indifferent solutions of solids in liquids.

For this purpose a transformation is made as in the following:

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{k_2a_2}{k_1a_1}.$$

For a chemically indifferent mixture $\frac{k_2a_2}{k_1a_1}$ is a constant independent of concentration, and we have, for two arbitrarily chosen concentrations z_m and z'_m and the respective viscosities η and η',

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(1) J. Kendall and K. P. Monroe, *J. Am. Chem., Soc.*, **39** (1917), 1802.

(2) This Bulletin, **4** (1929), 5; **4** (1929), 25; **4** (1929), 149; **4** (1929), 288.

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}=\frac{(1-z'_m)(\eta'-\eta_1)}{z'_m(\eta_2-\eta')} .$$

Now, consider component 1 to be the pure solvent. Component 2 being a solid, η_2 is here of course the unknown. Yet an estimation of it can be made as follows:

Rewrite the above expression in the form,

$$\frac{(1-z_m)\,z'_m\,(\eta-\eta_1)}{z_m(1-z'_m)(\eta'-\eta_1)}=\frac{\eta_2-\eta}{\eta_2-\eta'} .$$

The left-hand side of the expression consists of the factors all experimentally measurable and let it be denoted by q, then we have

$$\frac{\eta_2-\eta}{\eta_2-\eta'}=q \qquad \text{or} \qquad \eta_2=\eta'+\frac{\eta'-\eta}{q-1} .$$

The above method of calculation can be also applied for any solution in which no abrupt change in molecular state occurs, by taking two concentrations close to each other. For the verification of the writer's formula, Kendall and Monroe's data will be adopted below.

Table 1.

Naphthalene in Benzene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2 a_2}{k_1 a_1}$
0.0000	0.006048	1.002	
0.0510	0.006565	1.052	0.482
0.1121	0.007261	1.017	0.498
0.1538	0.007707	1.043	0.485
0.1979	0.008263	1.014	0.491
0.2398	0.008764		0.484
0.2693	0.009178	1.026	0.489
			0.488

Table 2.

Naphthalene in Toluene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2 a_2}{k_1 a_1}$
0.0000	0.005526	1.033	
0.0419	0.005848	1.026	(0.356)
0.1026	0.006394	1.029	0.377
0.1533	0.006866		0.377
0.2127	0.007470	1.029	0.378
			0.377

Since the values of q in each system and also in both the systems happen to be a constant within the limits of experimental error, I have taken $q=1.027$ as the mean value, with which calculated η_2 for successive two concentrations and obtained the mean value of them to be 0.02653. From the η_2 thus found $\left(\frac{k_2a_2}{k_1a_1}\right)$ can be calculated for each concentration, the values being recorded in the fourth column in each table. The constancy of $\left(\frac{k_2a_2}{k_1a_1}\right)$ is quite satisfactory.

Next consider $\frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}}$ from the two systems.

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}}=\frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}}$$

$$=\frac{(ka)_{\mathrm{solute}}}{(ka)_{C_6H_6}}\times\frac{(ka)_{C_6H_5CH_3}}{(ka)_{\mathrm{solute}}}=\frac{0.488}{0.377}=1.29.$$

This value is in good agreement with the already obtained value 1.23.

Table 3.

Diphenyl in Benzene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2\,a_2}{k_1\,a_1}$
0.0000	0.006051		
0.1006	0.007585	1.033	0.295
0.1824	0.009014	1.096	0.294
0.3638	0.01298		0.295
			0.295

Table 4.

Diphenyl in Toluene, 25°C.

z_m-Solute	$\eta_{obs.}$	q	$\frac{k_2\,a_2}{k_1\,a_1}$
0.0000	0.005520		
0.1398	0.007335	1.025	0.244
0.2197	0.008587	1.012	0.239
0.2761	0.009627		0.242
			0.242

In these cases the concentrations measured are not so regularly chosen as those in the preceding solutions and the following calculations have been taken.

For diphenyl in benzene

$$\eta_2 = 0.009014 + \frac{0.009014 - 0.007585}{1.033 - 1} = 0.05231$$

$$\text{or} \quad = 0.01298 + \frac{0.01298 - 0.009014}{1.096 - 1} = 0.05433 \text{ ,}$$

and for diphenyl in toluene

$$\eta_2 = 0.008587 + \frac{0.008587 - 0.007335}{1.025 - 1} = 0.05867$$

$$\text{or} \quad = 0.009627 + \frac{0.009627 - 0.008587}{1.025 - 1} = 0.05123 \text{ .}$$

$\left(\frac{k_2 a_2}{k_1 a_1}\right)$ calculated from the mean value of the four, 0.05413, are shown in the fourth column in each table, the constancy of which is also satisfactory.

From these systems we get as above

$$\frac{(ka)_{C_6H_5CH_3}}{(ka)_{C_6H_6}} = \frac{(k)_{C_6H_5CH_3}}{(k)_{C_6H_6}} = \frac{0.295}{0.242} = 1.22 \text{ ,}$$

which is very satisfactory result.

Quite recently, Herz and Scheliga⁽¹⁾ made the viscosity determinations of the solutions of solids such as iodine, naphthalene and phenanthrene in benzene, toluene, carbon tetrachloride, carbon bisulphide and aceton, but attempted no stoichiometrical discussion, probably because of no suitable formula to represent their results.

It is interesting to see whether the calculated viscosity of the solutions of naphthalene in benzene and in toluene by the formula, whose empirical constants η_2 and $\left(\frac{k_2 a_2}{k_1 a_1}\right)$ are the same values obtained above, are concordant or not with the experimental data given by these authors.

A further verification can also be tried with their results of naphthalene in carbon tetrachloride and in carbon bisulphide, the association degrees and the field-constants of these solvents having been known, for whether the following conditions required by the theory are realized or not:

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(1) W. Herz and G. Scheliga, *Z. anorg. allg. Chem.*, **169** (1928), 161.

$$\frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{CCl}_4}}=\frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{C}_6\text{H}_6}}\times\frac{(ka)_{\text{C}_6\text{H}_6}}{(ka)_{\text{CCl}_4}},$$

and
$$\frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{CS}_2}}=\frac{(ka)_{\text{naphthalene}}}{(ka)_{\text{C}_6\text{H}_6}}\times\frac{(ka)_{\text{C}_6\text{H}_6}}{(ka)_{\text{CS}_2}}.$$

In these calculations it must be remembered that between a weight fraction z and a molar fraction z_m there exists a relation:

$$\frac{1-z}{z}=\frac{1-z_m}{z_m}\frac{M_1}{M_2},$$

where M_1 and M_2 are the formal molecular weights of components 1 and 2 respectively. So that

$$\left(\frac{k_2a_2}{k_1a_1}\right)=\frac{(1-z_m)}{z_m}\frac{(\eta-\eta_1)}{(\eta_2-\eta)}=\left(\frac{k_2a_2}{k_1a_1}\right)_z\frac{M_2}{M_1},\quad\left(\frac{k_2a_2}{k_1a_1}\right)_z=\frac{(1-z)(\eta-\eta_1)}{z(\eta_2-\eta)}.$$

Table 5.

Naphthalene in Benzene, 20°, 40° and 60°C.

z-Solute	η_{20}		η_{40}		η_{60}	
	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.00645	—	0.00495	—	0.00395	—
0.0102	653	650	501	500	399	401
0.0198	660	655	505	506	401	406
0.0403	674	660	514	515	408	418

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z=0.488\times\frac{78.08}{154.1}=0.247,\quad\text{and}\quad\eta_2=0.02653.$$

Table 6.

Naphthalene in Toluene, 20°, 40° and 60°C.

z-Solute	η_{20}		η_{40}		η_{60}	
	obs.	calc.	obs.	calc.	obs.	calc.
0.0000	0.00584	—	0.00468	—	0.00386	—
0.0103	591	590	474	474	388	392
0.0200	596	595	478	480	392	398
0.0392	608	607	487	492	399	411

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = 0.377 \times \frac{92.10}{128.1} = 0.271\,, \quad \text{and} \quad \eta_2 = 0.02653\,.$$

Table 7.

Naphthalene in Carbon Tetrachloride, 20° and 40°C.

z-Solute	η_{20}		η_{40}	
	obs.	calc.	obs.	calc.
0.0000	0.00968	—	0.00745	—
0.0104	979	979	754	757
0.0209	991	990	768	770
0.0412	1011	1012	777	795

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = \left\{\frac{k_2a_2}{(ka)_{C_6H_6}}\right\}_z \times \left\{\frac{(ka)_{C_6H_6}}{(ka)_{CCl_4}}\right\}_z = 0.247 \times \frac{1}{0.63 \times 1.24} \times \frac{153.8}{78.08}$$
$$= 0.623\,, \quad \text{and} \quad \eta_2 = 0.02653\,.$$

Table 8.

Naphthalene in Carbon Bisulphide, 20° and 40°C.

z-Solute	η_{20}		η_{40}	
	obs.	calc.	obs.	calc.
0.0000	0.00389	—	0.00344	—
0.0102	392	395	345	350
0.0201	395	401	349	356
0.0391	404	413	355	359

$$\left(\frac{k_2a_2}{k_1a_1}\right)_z = \left\{\frac{k_2a_2}{(ka)_{C_6H_6}}\right\}_z \times \left\{\frac{(ka)_{C_6H_6}}{(ka)_{CS_2}}\right\} = 0.247 \times \frac{1}{0.76 \times 1.20} \times \frac{76.14}{78.08}$$
$$= 0.264\,, \quad \text{and} \quad \eta_2 = 0.02653\,.$$

As seen from each table, fair agreement between the observed and calculated values is interesting. The most discrepancy among them is observed in the case of carbon bisulphide solutions.

According to Thorpe and Rodger(1) the viscosities at 20° and 40°C. of benzene, toluene, carbon tetrachloride and carbon bisulphide are 0.00649,

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(1) T. E. Thorpe and J. W. Rodger, *Phil. Trans.*, **185** (1894), 397.

0·00492; 0·00586, 0·00466; 0·00969, 0·00738; and 0·00367, 0·00319 respectively. Judging from these data in comparison with those obtained by Herz and Scheliga, the above discrepancy comes probably, in the writer's opinion, from the purity of carbon bisulphide used by these authors.

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A NOTE ON NEGATIVE INDUCED REACTIONS.

By Susumu MIYAMOTO.

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The rate of change of a chemical reaction may sometimes be greatly diminished in the presence of quite an independent chemical reaction, when they are carried out simultaneously in a same vessel. The phenomenon may probably be called negative induced reactions, corresponding to the term induced reactions, in the case of which a chemical reaction exhibits an accelerating action on quite an independent chemical reaction, whose reaction velocity is extremely small, when it is carried out separately.

The simultaneous oxidations of the two substances, given in the following equations, by means of air were studied by the author and it was reported that the experimental results obtained can be explained as examples of some kind of negative induced reactions.

$$\text{A.}\left\{\begin{array}{ll} O_2+2Sn(OH)_2+2H_2O=2Sn(OH)_4 \;\cdots\cdots\cdots\cdots & (1) \\ O_2+2Na_2SO_3=2Na_2SO_4 \;\cdots\cdots\cdots\cdots\cdots\cdots & (2) \end{array}\right.$$

in sodium hydroxide,⁽¹⁾ or in sodium carbonate solution.⁽²⁾

$$\text{B.}\left\{\begin{array}{ll} O_2+4Fe(OH)_2+2H_2O=4Fe(OH)_3 \;\cdots\cdots\cdots\cdots & (1) \\ O_2+2Na_2SO_3=2Na_2SO_4 \;\cdots\cdots\cdots\cdots\cdots\cdots & (2) \end{array}\right.$$

in sodium hydroxide solution.⁽³⁾

The primary reaction in A or B exhibits a great inhibiting action on the velocity of the secondary reaction. It was also confirmed by the

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(1) S. Miyamoto, this Bulletin, **2** (1927), 191; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 195.

(2) S. Miyamoto, this Bulletin, **3** (1928), 95; *Scientific Papers of the Institute of Physical and Chemical Research*, **8** (1928), 237.

(3) S. Miyamoto, this Bulletin, **4** (1929), 132; *Scientific Papers of the Institute of Physical and Chemical Research*, **11** (1929), 81.

previous studies⁽¹⁾ that each of these reactions proceeds a most at the same rate, when they are carried out separately under the conditions of the author's investigations.

The terms actor, inductor, and acceptor are usually employed for the specialization of the reacting substances contained in ordinary induced reactions. For the oxidizing or the reducing agent, which is common in both reactions, the term *actor* can also be employed in negative induced reactions. In the place of the term inductor, the term *inhibitor* may be employed in the case of negative induced reactions for the substance, which can easily react with the actor, when the two reactions are carried out simultaneously. The substance, the reaction velocity of which with the actor is greatly diminished in the presence of the primary reaction, may be called *acceptor*.

In the cases, above described, oxygen may be called the actor, stannous hydroxide and ferrous hydroxide the inhibitors and sodium sulphite the acceptor respectively.

Corresponding to the term induction factor, which is used for the value of the ratio of the amount of the actor reacting with the acceptor to the amount of the actor reacting with the inductor, the term *inhibition factor* may be employed for the quantity,

$$\frac{A_{a.o} - A_a}{A_i}$$

where $A_{a.o}$ is the amount of the actor reacting with the acceptor in the absence of the inhibitor, A_a the amount of the actor reacting with the acceptor in the presence of the inhibitor, and A_i the amount of the actor reacting with the inhibitor.

W. D. Bancroft has given the following classification of induced reactions.⁽²⁾

(1) The inductor displays a catalytic action on the secondary reaction.
(2) The acceptor may react with a reduced stage of the actor.
(3) The acceptor may react with an oxidized stage of the inductor.
(4) The formation of a complex compound between the inductor and the acceptor.
(5) Combinations of the cases (1), (2), (3) and (4).

As for the classification of negative induced reactions, the following three cases were already described by the author⁽³⁾ with examples.

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(1) S. Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **3** (1928), 76; **3** (1928), 137; *Scientific Papers of the Institute of Physical and Chemical Research,* **7** (1917), 40; **7** (1927), 189; **8** (1928), 230; **9** (1928), 203.

(2) W. D. Bancroft, *J. Phys. Chem.*, **33** (1929), 1184.

(3) S. Miyamoto, this Bulletin, **4** (1929), 133; *Scientific Papers of the Institute of Physical and Chemical Research,* **11** (1929), 82.

(1) The inhibitor displays a negative catalytic action on the secondary reaction. In this case the reaction velocity between the actor and the acceptor will be extremely small in the beginning, but it will gradually increase with time as the concentration of the inhibitor decreases.

The simultaneous oxidation of stannous hydroxide and sodium sulphite in sodium hydroxide solution or sodium carbonate solution by means of air was found to be an example of this kind of negative induced reactions, as was already explained in the previous papers.

(2) The reaction product of the inhibitor exhibits a negative catalytic action on the secondary reaction. In this case the velocity of the secondary reaction will be un-affected at the starting point in the presence of the primary reaction, but it will decrease rapidly with time as the concentration of the reaction product of the inhibitor increases.

The simultaneous oxidation of ferrous hydroxide and sodium sulphite was found to be explained as an example of this type of negative induced reactions; ferric hydroxide, the reaction product of the inhibitor, acts as a negative catalyser on the oxidation velocity of sodium sulphide, the acceptor.

(3) Both of the inhibitor and its reaction product act as negative catalysers on the secondary reaction. This type of negative induced reactions can be regarded as a special case of the type (7), which will be described later, and it will scarcely occur in the actual cases, as the negative catalytic action should be regarded to depend upon the mutual specific nature of the two substances.

As the possible kinds of negative induced reactions, the following three cases may probably be added to the types above described, although the examples are not yet obtained.

(4) The reaction product of the actor of the primary reaction acts as a negative catalyser on the secondary reaction. It is quite clear that this case is only possible to occur, when the reaction product of the actor of the primary reaction is not the same as that of the secondary reaction, as the reaction product of the actor exhibits no inhibiting action on the velocity of the secondary reaction, when it is carried out separately.

(5) The inhibitor reduces the oxidation product of the acceptor. This is a kind of consecutive reactions and the induced reaction of the type (3) of Bancroft's classification may be regarded to be negative induced reaction of this type in special cases, if we consider the inductor as the acceptor and the acceptor as the inhibitor.

(6) Formation of a complex compound between inhibitor and acceptor.

(7) Combinations of the cases (1), (2), (4), (5) and (6).

The author has proposed, as a kind of possible mechanisms of catalysis, induced reactions(1) and negative induced reactions,(2) the process of the transference of active states. According to this idea, the transference of the active states of the molecules of the acceptor to the molecules of such substances as the inhibitor, the reaction product of the inhibitor and the reaction product of the actor of the primary reaction, may explain the mechanism of negative induced reactions of the types (1), (2) and (4), above described.

Summary.

(1) The possibility of the existence of negative induced reactions are described with examples, studied by the author.

(2) The definition of the terms actor, inhibitor and acceptor are given in the case of negative induced reactions.

(3) Corresponding to the term induction factor, the term inhibition factor was introduced in the case of negative induced reactions, although its value was not yet calculated in the actual cases.

(4) A classification of negative induced reactions was proposed. The classification will be unable to be confirmed thoroughly by experimental facts, as the examples of negative induced reactions are very few.

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(1) S. Miyamoto, *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 259.

(2) Loc. cit.

UEBER DIE AUFLÖSUNGSGESCHWINDIGKEIT DER METALLE.

Von M. TARLÉ.

Eingegangen am 20. Dezember 1929. Ausgegeben am 28. Februar 1930.

Ueber den Mechanismus der Auflösung unedler Metalle bestehen trotz mannigfacher Untersuchungen noch ziemliche Meinungsverschiedenheiten. Ein Uebersicht über die diesbezüglichen Arbeiten befindet sich in den Abhandlungen von Ericson-Aurén und Palmaer,(3) und Centnerszwer.(4)

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(3) *Z. physik. Chem.*, **39** (1902), 1; **45** (1903), 182.

(4) *Z. physik. Chem.*, **141** (1929), 297.

Die vorliegenden Versuche sind vor mehreren Jahren ausgeführt worden und hatten hauptsächlich zum Ziele die Untersuchung des Zusammenhanges zwischen der Dissoziation der Säuren und der Auflösungsgeschwindigkeit. Der Apparat, in welchem die Versuche ausgeführt worden sind, bestand aus einem runden Kolben von ca. 250 c.c. Inhalt, mit einem breiten Hals, welcher einen eingeschliffenen Stöpsel hatte. Durch diesen Stöpsel gingen das Rohr, in welchem der Glasrührer sass, und das Gasableitungsrohr. Der Kolben hatte ferner ein seitliches Rohr, ebenfalls mit eingeschliffenem Stöpsel, durch welches die Zinkstückchen hineingeworfen wurden. Die Verbindungsstellen des Gasableitungsrohres und der Gasbürette waren mit Quecksilber abgedichtet. Vor jedem Versuch musste durch die ganze Anordnung Wasserstoff durchgeleitet werden, weil das Gummifett, mit welchem der Rührer und die Schliffe abgedichtet waren, beträchtliche Mengen Wasserstoff absorbierte, und da die sich entwickelnde Wasserstoffmenge gemessen wurde, konnte diese Absorption Fehler verursachen.

Das Zink, mit welchem die Versuche ausgeführt worden sind, wurde in Stäben von 5 mm. Durchmesser bezogen und war chemisch rein. Die kleinen Zinkzylinder wurden glatt poliert, mit Schmirgelpapier abgerieben, mit Salzsäure angeätzt und schliesslich mit der Versuchslösung abgespült. Das verwendete Magnesium enthielt etwas Blei, Eisen und Kieselsäure (spurenweise). Es scheint, dass diese Beimischungen nicht viel schaden, da bei einem Versuch, wo Magnesium, mit Platindraht verbunden, verwendet wurde, d.h. wo die Bedingungen für die raümliche Trennung der Bildung von Metall-, und der Entladung von Wasserstoffionen von vornherein gegeben sind, der Wasserstoff sich nicht am Platin, sondern am Magnesium abschied und ferner die Gegenwart von Platin keine erkennbare Vergrösserung der Auflösungsgeschwindigkeit verursacht. Uebrigens tritt, wenn 30–40% der Säure verbraucht sind, auch am Platindraht eine Gasentwicklung ein.

Gerührt wurde mit 300 Touren in der Minute. Das Auflösungsgefäss befand sich im Thermostat bei 25°. Es wurden immer 100 c.c. der Lösung angewendet. Alle Voluminadaten sind auf 760 mm. und 20° reduziert. Da das Zink mit den schwachen Säuren ziemlich träge reagiert, wurde das Verhalten des Magnesium gegen Säuren verschiedener Dissoziationskonstanten untersucht. Die Auswahl der Säuren, welche ich gebrauchen konnte, war nicht gross, da dieselben im Wasser löslich sein müssen und durch Wasserstoff nicht reduziert werden dürfen. Aus diesen Gründen mussten z. B. die Versuche mit den Chloressigsäuren, Citronensäure, Adipinsäure ausfallen. Verwendet wurden 1 : 2 : 5-Dioxybenzoesäure, beta-Resorcylsäure, Tricarballylsäure, Essigsäure und Salzsäure. Diese Stoffe geben eine gute Skala von Säuren mit verschiedenen Dissoziationskonstanten. Der kinetische Verlauf der Auflösung lässt sich durch die bekannte Formel ausdrücken:

$$\frac{dx}{dt}=K(a-x) \qquad \ldots\ldots\ldots\ldots \qquad (1)$$

Es bedeuten: t=Zeit in Minuten, x=das entwickelte Wasserstoffvolumen in c. c., a=das Wasserstoffvolumen, welches durch die angewendete Säuremenge bei $t=\infty$, entwickelt wird.

Falls die menge der Säure im Verhältniss zur Menge des sich lösenden Zinks im grossen Ueberschuss vorhanden ist, so bekommen wir

$$\frac{dx}{dt}=K_1\,, \qquad \ldots\ldots\ldots\ldots \qquad (2)$$

was mit den Versuchen von Ericson-Aurén(1) gut übereinstimmt.

Bei unseren Versuchen war die Menge des Metalls gross im Verhältniss zu der Säuremenge. Dies hatte den Vorteil, dass die Grösse der Oberfläche des Metalls während des Versuchs praktisch konstant blieb.

Tabelle 1.

Magnesium. 0.02 n. Salzsäure.

t	x	K
20	5.4	0.0127
40	9.8	0.0131
60	12.8	0.0125
80	15.3	0.0126
100	17.2	0.0127
120	18.7	0.0125
150	20.5	0.0128
∞	24.04	—
	Mittelwert	0.0127

Tabelle 2.

Magnesium. 0.02 n. Tricarballylsäure.

t	x	K
10	1.3	0.00557
20	2.2	0.00480
40	4.2	0.00481
60	6.0	0.00478
80	7.7	0.00487
100	9.1	0.00477
∞	24.04	—

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(1) *Z. anorg. Chem.*, **27** (1901), 209.

Tabelle 3.

Magnesium. 0.02 n. 2:5-Dioxybenzoesäure.

t	x	K
20	3.4	0.00762
40	6.4	0.00774
60	8.9	0.00770
80	11.0	0.00793
100	12.8	0.00768
120	14.5	0.00768
150	16.7	0.00791
∞	24.04	—

Tabelle 4.

Magnesium. 0.02 n. 2:4-Dioxybenzoesäure.

t	x	K
20	2.5	0.00549
40	4.6	0.00531
60	6.5	0.00525
80	8.3	0.00528
100	9.7	0.00516
120	11.0	0.00509
160	13.3	0.00503
200	15.4	0.00511
∞	24.04	—
	Mittelwert	0.00518

In der Tabelle 6 sind die Reaktionsgeschwindigkeitskonstanten und die entsprechenden Dissoziationskonstanten zusammengestellt. Wie wir sehen, gehen die Auflösungsgeschwindigkeitskonstanten den Diss.-konstanten parallel. Eine Proportionalität besteht nicht. Die Dissoziationskonstante wächst viel schneller, als die Auflösungsgeschwindigkeit.

Tabelle 5.

Magnesium. 0.02 n. Essigsäure.

t	x	K
20	2.3	0.00503
40	4.1	0.00467
60	5.8	0.00460
80	7.3	0.00452
100	8.6	0.00443
120	9.8	0.00436
160	12.0	0.00432
200	14.8	0.00432
300	17.5	0.00434
∞	24.04	—
	Mittelwert	0.00449

Tabelle 6.

	K	Dissoziat.-konstante
Salzsäure	0.0125	?
2:5-Dioxybenzoesäure	0.0077	0.00108
2:4-Dioxybenzoesäure	0.0051	0.000515
Tricarballylsäure	0.0049	0.000220
Essigsäure	0.0045	0.0000186

Der Parallelismus besteht, aber, auch bei anderen Konzentrationen.

Tabelle 7.

Säure	Auflösungsgeschwindigkeitskonstante		
	Konzentration		
	0.1 n.	0.05 n.	0.02 n.
Salzsäure	0.0112	0.0114	0.0127
Essigsäure	0.00405	0.00436	0.00449
Tricarballylsäure	0.00436	0.00482	0.00493

Die Auflösungsgeschwindigkeit ist nicht unabhängig von der Konzentration. Dies kann durch die Beeinflussung des Vorgangs durch das sich bildende Salz erklärt werden. Auch der schwache Gang der Konstante, welcher in einigen Fällen (Tab. 2 und 5) auftritt, lässt sich durch diese Beeinflussung erklären. Die Wirkung der Neutralsalze ist recht kompliziert und setzt sich aus verschiedenen Faktoren verschiedenen Vorzeichens zusammen. Die wichtigsten Faktoren sind vermutlich: (1) Beeinflussung des Dissoziationszustandes der Saüre (2) Beeinflussung der Löslichkeit des sich bildenden Salzes (3) Auflösende Wirkung der Neutralsalzlösung.

Die nachstehende Tabelle 10 giebt die Resultate der Versuche mit den Neutralsalzen wider. Um (bei den Versuchen mit Zink) die Induktionsperiode auszuschliessen und die Reaktionsgeschwindigkeitsformel anwenden können, wurde Zink, verbunden mit Platindraht aufgelöst. Der Platindraht war 12 cm. lang, 2 mm. stark, als Spirale gebogen, hatte an einem Ende ein Gewinde und mittelst dessen wurde er in den Zinkzylinder fest eingeschraubt. Der Platindraht musste vor jedem Versuch mit Chromsäure gewaschen und frisch platiniert werden, wobei darauf zu achten war, dass das Platinieren immer dieselbe Zeit (1-2 Min.) dauerte. Das Zink wurde aus einer $HgCl_2$-Lösung amalgamiert. Dass Amalgamieren hatte den Vorteil, dass immer eine konstante und reine Zinkoberfläche vorhanden war.

Tabelle 8 zeigt die Anwendung der Formel (1) auf die Auflösung von Zink mit Platin, sowie von reinem Zink, nachdem das Maximum der Auflösungsgeschwindigkeit erreicht ist.

Tabelle 8.

0.1 n. Salzsäure.

Zeit	Zink mit Pt. c.c. Wasserstoff	*K*	Zink ohne Pt. c.c. Wasserstoff	*K'*
10	4.2	0.00355	—	—
50	18.9	0.00342	—	—
100	35.2	0.00346	—	—
150	47.1	0.00391	—	—
200	58.5	0.00358	—	—
300	78.0	0.00349	39.0	0.00131
400	91.1	0.00355	46.9	0.00124
500	98.3	0.00341	58.2	0.00132
600	103.3	0.00307	68.4	0.00140
800	—	—	80.5	0.00138
1000	—	—	90.1	0.00138
1500	—	—	102.9	0.00129

Aehnliche Versuche mit Magnesium zeigten, dass der Wasserstoff sich nicht am Platin, sondern am Magnesium abshied und ferner die Gegenwart von Platin keine erkennbare Vergrösserung der Auflösungsgeschwindigkeit verursacht, wie die Tabelle 9 zeigt.

Tabelle 9.

0.1 n. Salzsäure.

Zeit	Magnesium ohne Pt. c.c. Wasserstoff	Magnesium mit Pt. c.c. Wasserstoff
10	5.2	5.0
20	9.4	9.4
60	26.0	26.1
100	40.0	39.7

Nun zeigte es sich dass die Neutralsalze KCl, $ZnCl_2$ und $MgCl_2$ in den Konzentrationsbereich 0.1 – 0.7 n. beeinflussen die Auflösung der Zn-Pt Zylinders nicht wesentlich. Bei Magnesium ist der Einfluss von diesen und anderen Neutralsalzen viel stärker.

Tabelle 10.

Magnesium.

Säure	Salz	K
0.1 n. HCl	—	0.0112
,, ,,	0.1341 n. $MgCl_2$*	0.0125
,, ,,	0.2682 n. $MgCl_2$	0.0131
0.1 n. Essigsäure	0.1 n. Mg-acetat	0.00366
,, ,,	0.2 n. ,,	0.00326
,, ,,	0.2 n. $MgSO_4$	0.00416
,, ,,	0.2 n. Na_2SO_4	0.00454
,, ,,	0.2 n. Na-acetat	0.00441
0.1 n. H_2SO_4	—	0.0115
,, ,,	0.1341 n. KCl	0.0143
,, ,,	0.1341 n. KBr	0.0164
,, ,,	0.1341 n. KI	0.0148

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* Die Lösung war in Bezug auf 1/2 $MgCl_2$ 0.1341 normal.

Die Anionen in Konzentration 0.1–0.2 n. wirken also in der Reihenfolge $Br' > J' > Cl' > SO_4'' > CH_3COO'$.

Der eigentümlicher Einfluss des Br' entspricht der stark beschleunigender Wirkung von HBr-säure auf die Auflösung des Zinks, welche von Spring und Aubel beobachtet wurde(1).

Zur Zeit sind die Neutralsalzeffekte noch nicht hinreichend aufgeklärt als dass schon eine bestimmte Vorstellung über den Mechanismus der Auflösung entwickelt werden können. Auch die Versuche von W. Wittand(2) über den Einfluss von Säureanionen auf die Lösungsgeschwindigkeit des Aluminiums lassen sich vorläufig nicht in einer eindeutiger Weise erklären. Es ist, aber, unzweifelhaft dass eine gewisse Analogie zwischen den Einfluss der Neutralsalze auf die Auflösung der Metalle einerseits, und auf die Löslichkeit der Metallhydroxyde anderseits, vorhanden ist. Die Auflösung von Metallen in Neutralsalzlösungen verläuft vermutlich in zwei Stufen. Das Metall reagiert zunächst mit Wasser, indem eine Hydroxydschicht sich auf seiner Oberfläche bildet; hiernach wird das gebildete Hydroxyd durch die Neutralsalzwirkung weggelöst. Es scheint nicht ausgeschlossen zu sein, dass dieselbe Auffassung auch auf andere Fälle (z.B. Auflösung von Aluminium und Zink in Alkalilösungen) ausgedehnt werden könnte.

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(1) *Z. physik. Chem.*, **1** (1887), 477.

(2) M. Centnerswer, *Z. Elektrochem.*, **35** (1929), 695.

BIOCHEMICAL STUDIES ON RICE STARCH. I.
THE CHEMICAL CHANGES OF THE STARCH DURING THE GERMINATION OF RICE IN DARKNESS.

By Wei Sun TAO.

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The rice which is the chief food stuff of the Orient, is widely planted and regarded as one of the most important plants in the East.

In the cultivation of rice, the grains are usually germinated in spring, after flowering and ripening, the crops are harvested in autumn. The physiological development during the germination of the grain greatly arouses our interest, especially from the biochemical point of view. According to the authorities, the requirements for germination are sufficient water and a suitable temperature; under these conditions the embryo absorbs water and swells as other grains do, and the shoot and root sprout out through the crack of the hull. The temperature at which the grains are germinated, is said to be an optimum at 30°–35°C., while 10°C. to 13°C., and 40°C. are the lowest and highest limits.(1) Under the most favourable conditions the germination of rice becames externally evident after about two days. But the chemical changes which take place in the substance of the kernel during this process, have not yet been investigated.

The germination of other seeds was studied by many investigators from the point of view of plant physiology, and the results arrived at were summarized in the elaborate work "Vergleichende Physiologie des Keimungsprocesses der Samen (1880)" by W. Detmer. M. Berthelot's(2) investigations on this subject were carried out in collaboration with M. Andre during the periods 1883-1885, 1893-1896, following the investigations of M. Boussingault & A. Müntz.(3)

According to these investigations, the germination of seeds in darkness, which is distinct from the vegetation of plants growing in light, it was regarded that the stored substances alone were utilized, while in the latter case the transformation of the reserve materials was usually accompanied by the assimilation which results in the formation of new substances from the carbon dioxide and water in the atmosphere.

The chemical processes of germination are, therefore, not identical in different kinds of seeds as already indicated by Palladin(4) and they depend largely upon the chemical nature of the reserve materials; the loss of weight in starchy seeds such as maize and barley, during germination was explained as occurring through loss of carbohydrates. The chemical transformation of the starch in barley in the process was precisely investigated by H. T. Brown & H. Morris, estimating the products in the plant tissues by the method recommended by O'Sullivan,(5) and stated in their classical work: "Researches on the germination of some of the Gramineoe"(6) that the starch reserved in the embryo was converted into transitory starch by the hydrolytic enzymes accumulated in the germinated seeds, which by the same agency was converted into simpler sugars. Moreover, they noticed the formation of sucrose in the barley embryo together with the production of maltose, dextrose and laevulose, which was previously observed by O'Sullivan in his experimental research on barley-malt.

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(1) M. Akemine, *Landw. Z.*, **63** (1914), 78; and refer, I. Nagai, "Cultivation of Rice in Japan" (1925, Japanese), 378.

(2) M. Berthelot, "Chimie vegetable et Agricole," II (1899), 7–371.

(3) M. Boussingault, "Agronomie, Chimie Agricole et Physiologie," V (1874), 50.

(4) B. E. Livingston, "Palladin's plant physiology," (1917), 175.

(5) *J. Chem. Soc.*, **45** (1884), 1.

(6) *J. Chem. Soc.*, **57** (1890), 458.

O'Sullivan has stated that the maltose is derived from the starch which unquestionably disappears during germination, but he gave no opinion as to the origin of the cane-sugar and its products of inversion.

Brown & Morris have, however, offered the suggestion for the origin of the sugar that the transformed starch is absorbed from the endosperm by the columnar epithelium of the embryo in the form of maltose which is by the more or less complicated metabolic processes of the living cells of the embryo rapidly converted into cane-sugar, and they have demonstrated the suggestion in a very striking manner, showing the ability of the growing tissue of the embryo to convert maltose into cane-sugar.

If this view is correct, we have still some difficulty in explaining in what manner the maltose is converted into sucrose.

However, there is no question as to the intimate connection between cane-sugar and starch in seeds which has been known to exist, but no chemist has made any statement concerning the conditions under which the conversion of starch into sucrose takes place.

The writer, therefore, has taken it on herself to investigate the chemical changes which may be expected to take place in the reserve starch during the germination of the rice in darkness.

I. The Germination of the Rice at 20°C.

Preparation of Materials. The seeds used in this experiments were called Asahi, produced in Zeze, near Otsu 1928 and harvested in that year and stored carefully in a straw rice-bag in our laboratory.

The grains were ground in a stone mill in the laboratory, and the resulting flour was sifted through a $\frac{1}{23}$ cm. sq. mesh sieve.

The rice seedlings were prepared by steeping the seeds in distilled water for two days at room temperature until they had absorbed about 50 per cent in weight of moisture, and were left to germinate for seven days at 20°C. in darkness. After germination had proceeded to the extent that the shoots were half an inch long, they were dried in an air current at room temperature, and ground in a stone mill until all of them were sifted through a $\frac{1}{23}$ cm. sq. mesh sieve.

Proximate Analysis. The content of moisture, the total reducing sugar, the soluble starch, (or soluble polysaccharide), starch, cellulose, pentosan (hemicellulose), the total nitrogen, the total fat and ash of each sample were determined in the following ways, and the results are shown in the table, both seeds and seedlings having a mean weight of 100 grains.

1. **Moisture.** 2 to 3 grams of each sample were dried at 105°C. in an air bath to a constant weight, the loss of weight being designated as the moisture content.

2. **Alcohol Extract.** An 80% solution of alcohol was added to 2 to 3 gr. of each sample, and allowed to stand overnight and then heated at 70°C. in a water-bath for four hours, filtered, washed, and this process was repeated till the washings contained no more reducing sugar. The filtrate and washings combined together and concentrated under diminished pressure to a small volume, which brought down the final volume to 100 c.c.

(a) Total Reducing Sugars. Of 50 c.c. of the solution, the total reducing sugar was estimated by determining the reducing power of the solution and calculated as *d*-glucose on an ash and moisture free basis.

(b) Soluble Polysaccharides. After 50 c.c. of the extract above mentioned was heated with a 3 % sulphuric acid solution on a direct flame for 3 hours, diluted to 100 c.c., neutralized with sodium carbonate and filtered. The reducing sugars in this filtrate were estimated by determining the reducing power of Fehling's solution and calculated as *d*-glucose on an ash and moisture free basis. The difference between the content of the reducing sugars in the solution after and before the hydrolysis was designated as a soluble polysaccharide.

3. **Starch.** About 0.2 to 0.4 gram of the sample which might be expected to contain reducing sugar, soluble polysaccharide and starch were heated to hydrolyse the starch and polysaccharides into *d*-glucose by using 50 c.c. of 3 % sulphuric acid for 4 hours on a direct flame. The acid solution was diluted to exactly 100 c.c., neutralized with sodium carbonate and filtered, The content of reducing sugars in the filtrate was estimated in the usual way, from which the content of reducing sugars and soluble polysaccharides was subtracted and the remainder was assumed to be the starch-content.

4. **Pentosans.** The presence of pentosans in the seeds and seedlings was confirmed by transforming them into furfural; for the estimation of the sugar 1 to 2 grams of the sample were subjected to distillation with 12 % HCl, and the content of furfural distilled was determined by means of phloroglucin.

5. **Cellulose.** The amount of cellulose was determined by the method of Cross and Bevan.

6. **Total Fat.** The content of the fat in the samples was determined by the usual way by extracting it with petroleum ether.

7. **Total Nitrogen and Protein.** The total nitrogen of 0.1 to 0.2 gr. of the sample was estimated by Kjeldahl's method, and the protein content in the samples was calculated by multiplying 6.25 with the total nitrogen content.

8. **Total Ash.** The samples were ignited carefully at a low temperature and the crude ash, thus obtained, was dissolved in water, filtered, and the residue was heated in an electric furnace to a constant weight. The filtrate was dried in a water-bath, and then to constant weight at 105°C. The two ashes combined together were designated as the total ash content.

The analytical results of the seeds and seedlings are shown in the following table:

	Seeds	Seedlings	Gain or loss during germn.
Dry wt. of 100 grains	3.1 gr.	2.3 gr.	—.8 gr.
Ash	.136	.098	—.038
Total nitrogen	.039	.031	—.008
Fat	.066	.042	—.024
Protein	.255	.200	—.055
Reducing sugars	0	.088	+.088
Soluble polysaccharides	.048	.220	+.172
Starch	2.184	1.234	—.950
Cellulose	.213	.224	+.011
Pentosan	.162	.123	—.039

In the above table, the content of fat, protein, reducing sugar, soluble polysaccharides, starch, cellulose and pentosan was calculated on a moisture and ash free basis.

Discussion.

As will be seen by the results shown in the above table, the loss of weight occurs during the germination of rice seeds as other investigators have already observed in experiments on the germination of other seeds, due to the transformation of the reserve starch into other substances while the amount of total fat remains almost unchanged.

As a matter of fact, 0.950 gr. of starch were lost per 100 grains of rice seeds on the one hand, and on the other 0.260 gr. of soluble sugars calculated as *d*-glucose were found to be formed during germination, and accordingly 0.716 gr. of the starch had disappeared from the seeds; in other words, they are consumed by being converted into carbon dioxide and water for the germination. Thus, the fate of the starch in the seeds during germination would be considered in the following manner; one part of starch was transformed by hydrolysis into soluble polysaccharides and simple sugars of unknown nature, and one part of the sugars was then decomposed by oxidation into carbon dioxide and water, similar to the function of respiration.

$$(C_6H_{10}O_5)_n \xrightarrow{+H_2O} C_6H_{12}O_6 \xrightarrow{+O} CO_2+H_2O.$$

The energy liberated in these transformations of starch was evidently utilized for the germination of the seeds. The main source of the energy would be supplied by the complete combustion of the simple sugar molecule in the plant tissues since the heat of formation of both the soluble polysaccharides and the simple sugars would be negligibly small compared with that of the combustion of the sugar molecule, as will be seen in the following equations:

$$C_6H_{12}O_6+6\ O_2=6\ CO_2+6\ H_2O+674{,}000\ \text{cal.}$$

$$C_{12}H_{22}O_{11}+12\ O_2=12\ CO_2+10\ H_2O+1{,}350{,}000\ \text{cal.}$$

$$C_6H_{10}O_5+H_2O=C_6H_{12}C_6+5{,}900\ \text{cal.}$$

Thus, the energy which was required for the germination of one grain was estimated approximately from the quantity of diminished starch based on the assumption stated above to be 3000 cal.

July, 1928. Laboratory of Organic- & Bio-Chemistry,
Kyoto Imperial University.

BIOCHEMICAL STUDIES ON RICE STARCH. II. TEMPERATURE EFFECTS ON THE GERMINATION OF RICE SEEDS IN DARKNESS.

By **Wei Sun TAO.**

Received December 26, 1929. Published February 28, 1930.

In the previous experiment, the chemical changes of rice starch during germination were studied. In the experiment, the germination of seeds was operated at 20°C. In practice, however, the most favorable temperature for the germination is said to be 35°C. for the purpose of obtaining strong and healthy seedlings.

So the writer now has studied further, the germination of seeds under different temperatures, viz., 20°C., 35°C. and 40°C. in order to observe the temperature effects on the chemical transformations of starch during the process.

The rice seeds were soaked in water for 2 days and allowed to germinate in darkness at the different temperatures above-mentioned, till the shoots were half an inch long. Then they were dried in an air current at room temperature and ground in a stone mill. The content of moisture, reducing sugars, soluble polysaccharides and starch was determined by the usual methods and the results are shown in the following table:

Table 1.

	Germinated at	Dry wt. per 100 grains gr.	Loss	Reducing sugars %	Soluble polysacch. %	Starch %	Loss in starch %
Seeds		3.1		0	1.6	73	0
Seedlings	20°C.	2.3	0.8 gr. (26%)	3.9	10.0	56	- 3
	35°C.	2.2	0.9 gr. (30%)	2.7	7.3	53	-10
	40°C.	2.3	0.8 gr. (26%)	2.5	3.5	58	- 9

As will be seen in the above table, the weight loss was most noticeable in the seedlings, the loss differing with the temperature of germination, and greater at 35°C. than at either 20°C. or 40°C. When the chemical constituents of seeds and seedlings were compared, the content of simple sugars and soluble polysaccharides in the seedlings of the three cases was all found to have increased inversely to the decrease of the starch-content. The loss of starch among the seedlings was greatest in the seedlings germinating at 35°C., while the loss among those germinating at 40°C. and at 20°C. is quite regular.

The fact that the proportion of soluble polysaccharides and reducing sugars in seedlings which germinated under different temperatures is not the same, indicates that the hydrolysis of starch into sugars in seedlings depends greatly upon the surrounding conditions, especially the temperature under which the seeds were germinated. The formation of reducing sugars and soluble polysaccharides from starch is favonrable at 20°C., while the inversion of polysaccharides into simple reducing sugars is comparatively great at 40°C.

In order to learn the chemical nature of the sugars which occur in seedlings, by the transformation of starch during the germination, the separation and identification of these sugars, if possible, were undertaken.

About 500 grams of the rice seedlings ground in a stone mill, were steeped in 80% alcohol for about 12 hours then diluted with distilled water to make a 50% alcohol solution, and heated in a water bath at 70°C. for 5 hours with occasional stirring. After cooling, it was filtered and the residue was again treated with 50% alcohol in a water bath. This process was repeated 5 or 6 times till the filtrate contained no more reducing sugar. The extracts and washings were combined together and then concentrated under diminished pressure to small volume, and a sufficent quantity of basic lead acetate was added, the precipitate thus formed was filtered off and to the filtrate hydrogen sulphide gas was passed to remove the excess of lead in the solution. After filtering off the lead sulphide, the solution was concentrated to small volume and alcohol was added to make an 80% alcohol solution. The precipitate (A) thus formed was separated by decantation, dissolved again in a little water, and reprecipitated with an 80% alcohol solution, washed with absolute alcohol and ether, and dried in a desiccator over sulphuric acid.

The clear decanted liquid and the washings were combined together and concentrated to small volume under reduced pressure and the precipitate (B) was obtained by means of a 90% alcohol solution.

The filtrate separated from the precipitate (B), was evaporated to a thick syrup, absolute alcohol was added, on which the precipitate (C) was formed, and this was washed with ether and dried in a desiccator.

The alcoholic filtrate was evaporated to a syrup in vacuo, dissolved in methyl alcohol and ether was added to form the precipitate (D). Thus, the soluble dextrins, mono- and poly-saccharides, which occur in the seedlings, were extracted and separated approximately by fractional precipitation into the four crops of the following properties:

The first precipitate (A) or the 80% alcohol precipitate was a lustrous white powder, easily soluble in cold water. The second precipitate (B) or the 90% alcohol precipitate was a slightly yellowish white powder, easily soluble in cold water. Both the third precipitate (C) or the absolute alcohol precipitate, and the fourth precipitate (D) or the ether precipitate was a light yellowish powder with a sweet taste, and easily soluble in cold water.

Of these crops, the rotatory power and reducing power of the aqueous solution were determined on the one hand, and on the other the colour reaction with iodine, the ketose test and the formation of osazone with phenyl hydrazine were studied, and the experimental results are shown in the accompanying table:

Table 2.

	Germinated at	$(\alpha)_D$	R.P.	Iodine test	Pinoff's test	Osazone test
(A)	20°C.	163-164	4-5	Red Brown		
	35	173	5	,,		
	40	173	6	,,		
(B)	20°C.	159	10	Brown		
	35	163	22	,,		
	40	123	23	,,		
(C)	20°C.	59	25	Nil	+	Malto- and gluco-osazones
	35	86	42	,,	+	
	40	50	49	,,	+	
(D)	20°C.	56	29	,,	+	Malto- and gluco-osazones.
	35	78	55	,,	+	
	40	38	50	,,	+	

As will be seen in the above table, the first precipitate (A) from three cases, seem to consist equally of a mixture of dextrins which usually can be obtained from starch by hydrolysis with acids or diastase. The second of the precipitates (B) were ascertained from their properties to consist of dextrin with some maltose, the proportion of the latter in the precipitate was increased with the germinating temperature. The third and fourth precipitates (C & D) were supposed to consist mostly of simple sugars with some maltose. To our interest, these two precipitates in each case, contain some cane sugar its occurrence being indicated by the rotatory power and reducing power and also the Pinoff test. According to the literature, Kuhneman has isolated sucrose from germinated barley and the same sugar was also confirmed by O'Sullivan and Brown & Morris to occur in the same germinating seeds, though the mechanism for the formation of the sugar was obscure. As a matter of fact, the content of sucrose was rich in the seedlings at 20°C. among three cases, glucose and fructose were predominant in the other cases which germinated at the highest temperature, and the formation of the disaccharide such as maltose was favoured at the middle temperature, 35°C.

According to Brown & Morris, the growing tissues of the barley embryo has the ability to convert maltose into cane-sugar but not glucose into sucrose. It seems, therefore, that maltose formed by the action of the hydrolytic enzymes from starch, will convert into sucrose by the intramolecular transformation on the one hand, and on the other, into glucose and fructose by inversion, and the former reaction is favoured at the lower temperature, and at the higher the latter reaction prevails.

In closing the writer would like to express her hearty thanks to Prof. Komatsu of Kyoto Imperial University, for these experiments were performed under his kind direction and never-failing encouragement.

October, 1929.

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SINOMENINE AND DISINOMENINE PART XIV. ON BROMO-SINOMENINONE.

By **Kakuji GOTO** and **Taro NAMBO.**

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In the 12th communication(1) of this study, one of the authors (K.G.) has reported the formation of sinomenine hydrate by heating the latter with 2 n. hydrochloric acid. The assumption of a semiacetal constitution of this hydrate was there supported with several facts.

As this formation of sinomenine hydrate is, however, rather remarkable, it is desirable to repeat the same reaction with other phenanthrene alkaloid and enforce the author's conception. Thebainone may seem at first sight to be fitted for the purpose, but actually it is not, .since its preparation involves the heating with conc. hydrochloric acid at 100°C. It seems, therefore, that there is no other easily accessible alkaloid than bromo-sinomenine in this respect. That the bromo-sinomenine has exactly the same constitution with sinomenine, except one bromine atom at C_1, was indirectly proved by its catalytic reduction by K. Goto and T. Nakamura.(2) The action of hot dilute hydrochloric acid was, therefore, proved on bromo-sinomenine. The results of the experiment were, however, somewhat different from those with sinomenine. The easily crystallizable substance

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(1) Goto and Sudzuki, this Bulletin, **4** (1929), 244.

(2) This Bulletin, **4** (1929), 195.

from bromo-sinomenine, when the latter was heated two hours with 2n. hydrochloric acid, was not bromo-sinomenine hydrate, but bromo-sinomeninone itself. It has the molecular formula $C_{18}H_{19}NO_4Br$, one methoxyl group and two ketone groups, forming a dioxime and a disemicarbazone. That this bromo-sinomeninone must be corresponding to the sinomeninone, which would be formed by the hydrolysis of the semi-acetal group of sinomenine hydrate or the hydrolysis of the dioxime of sinomenine hydrate (though these reactions are not yet realised), is proved by the fact that the dioxime of the sinomenine hydrate gave on bromination the same bromo-sinomeninone dioxime as obtained from bromo-sinomeninone.

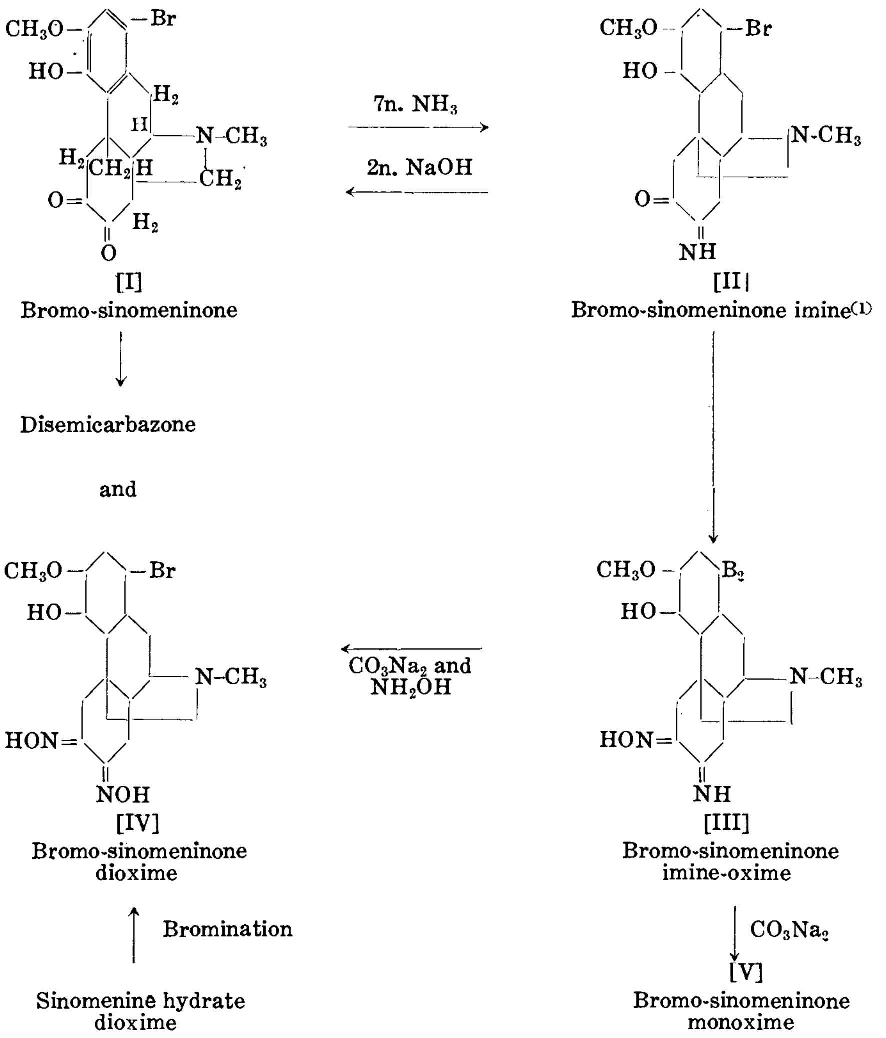
When bromo-sinomeninone was treated with 7 n. ammonia, it did not gave the expected condensation product, but a monomolecular imine $C_{18}H_{20}N_2O_3Br$. That here we treat actually an imine is shown from the following two facts. First, this bromo-sinomeninone imine is easily hydrolyzed by caustic alkali on its imino-group and gives bromo-sinomeninone and ammonia in a nearly quantitative yield. Secondly, the oxime of bromo-sinomeninone imine is easily attacked even by sodium carbonate and gave bromo-sinomeninone monoxime. This monoxime could be turned into the above bromo-sinomeninone dioxime by treating again with hydroxylamine.

The properties of the bromo-sinomeninone and its imine are summarised in the following table and the relation of these substances are shown in the annexed diagrams.

Table 1.

	Bromo-sinomeninone	Bromo-sinomeninone imine
Yield	50~70%	50°
Crystal form	long prisms	short prisms
M.p.	227°	208°
$[\alpha]_D$	+54.52°	+110.19°
M.p. of oxime	189° (dioxime)	208° (monoxime)
M.p. of iodomethylate	244°~246°	not yet crystallized
Methoxyls	one	one
$FeCl_3$ - reaction	violet (in alc.)	weak (in alc.)
Diazo - reaction	(+1,000,000th dil.)*	+50,000th dil.
$K_3Fe(CN)_6$ - reaction	no	no
Formaline - SO_4H_2	yellowish brown	yellowish brown

* This strong diazo-reaction may be due to the two methylene groups, vicinal to the 1, 2-diketone.



[I] Bromo-sinomeninone

Disemicarbazone and

[II] Bromo-sinomeninone imine(1)

[IV] Bromo-sinomeninone dioxime

[III] Bromo-sinomeninone imine-oxime

Sinomenine hydrate dioxime

[V] Bromo-sinomeninone monoxime

Experimental.

Bromo-sinomeninone (I)—Bromo-sinomenine bromohydrate (20 gr.) is heated with 2 n. HCl (200 c.c.) in a steam-bath for two hours. It is precipitated with sodium carbonate and extracted with chloroform. The bromo-sinomeninone can be recrystallised from methyl alcohol in long prisms. M.p. 227° (dec.). Yield 50%. From the free base of bromosinomenine the substance was obtained in a somewhat better yield (70%). For the properties, see the Table 1.

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(1) Mutual position of the ketone and imine groups is not yet determined.

Anal. Found: C=54.71; H=5.52; N=3.20; Br=19.62; Methoxyl=7.90%. Calc. for $C_{18}H_{20}NO_4Br$=394: C=54.82; H=5.55; N=3.28; Br=20.30; CH_3O-=7.87%.

Sp. rotatory power. 0.2421 gr. subst. was dissolved into 10 c.c. alcoholic solution. l=1dm; $\alpha=+1.32°$. $[\alpha]^{16}_{D}=+54.52°$.

Iodomethylate. Recrystallised from water; m.p. 244~246°; yield 50% (Found I=23.23%; Calc. I=23.69%).

Semicarbazone. Recrystallised from acetone. It decomposes at 118°, sintering at 98°. Yield not good. (Found: N=18.01%; Calc. for disemicarbazone: N=19.29%).

Dioxime. Prepared in ordinary way and extracted with ether, after the precipitate was dissolved in methyl alcohol and water. Beautiful prisms. M.p. 189° (dec.) Yield good. (Found: N=9.33%. Calc. for dioxime: N=9.91%).

Bromination of Sinomenine Hydrate Dioxime (IV). Sinomenine hydrate dioxime (1 gr.), dissolved in glacial acetic acid (20 c.c.) is brominated by bromine (0.5 gr.) in glacial acetic acid (5 c.c.) at the freezing point of the solvent. After being made alkaline with sodium carbonate solution, it is extracted with chloroform and obtained in crystals, when methyl alcohol is added to the residue of the chloroform evaporation. Yield almost quantitative. M.p. 189° (dec.) Admixture with bromo-sinomeninone dioxime did not lower the m.p.

Bromo-sinomeninone Imide (II). Bromo-sinomeninone (1 gr.) is dissolved in 1% hydrochloric acid (10 c.c.) and added with conc. ammonia (10 c.c.; d=0.9). After standing overnight, the precipitate is collected and dissolved in chloroform. It crystallises out in prisms, when methyl alcohol is added to the residue of the chloroform evaporation. Yield 50%. It darkes at 228°, sinters at 233°, but does not melt completely until 300°. For the properties, see Table 1.

Anal. Found: C=54.83; H=5.45; N=7.05, 7.19; Br=20.16; Methoxyl=8.01%. Calc. for $C_{18}H_{21}N_2O_3Br$=393: C=54.96; H=5.34; N=7.11; Br=20.35; CH_3O-=7.89%.

Sp. rotatory power. 0.3158 gr. subst. was dissolved into 10 c.c. chloroform solution. l=1dm; $\alpha=+3.48$. $[\alpha]^{16}_{D}=+110.9°$.

Mol. wt. Found (in glacial acetic acid): 244. (Remarkably low value is perhaps due to the partial decomposition of the imino-group).

Oxime (III). Prepared in ordinary way, and extracted without the use of sodium carbonate, i.e. methyl alcohol is added to the reaction mixture just enough to dissolve the precipitate and is shaken with ether several times, until the oxime crystallises out in colourless prisms. It sinters at 208°, but does not decomposes until 300°. (Found: N=10.23%. Calc. for $C_{18}H_{22}N_3O_3Br$: N=10.29%).

In the above reaction, when sodium carbonate is used to precipitate the oxime, sometimes bromo-sinomeninone dioxime, and sometimes bromo-sinomeninone monoxime is obtained, according to the conditions. Dioxime obtained in this case is quite identical with that obtained from bromo-sinomeninone directly. The mixed melting point remained unaltered. (Found: N=9.49%. Calc. for dioxime: N=9.88%).

Monoxime is long needles and melts at 199°, sintering first at 191°. (Found: N=7.59, 7.40%. Calc. for monoxime: N=6.83%).

Hydrolysis of Bromo-sinomeninone Imine. Bromo-sinomeninone imine is easily hydrolysed on its imino-group by warm caustic soda (10%), and bromo-sinomeninone is recovered in an almost quantitative yield by extracting with ether. By micro-Kjeldahl, the ammonia was determined up to 80% in this reaction.

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BEITRÄGE ZUR KENNTNIS DER ALLOTROPEN MODIFIKATIONEN VON SCHWEFEL. III. UEBER DAS VERHALTEN VON JOD ZU SCHWEFEL UND SELEN.

Von C. R. PLATZMANN.

Eingegangen am 6. November 1929. Ausgegeben am 28. März 1930.

Nach den bekannten Untersuchungen gibt es bisher keine Beweise für die Existenz von Jod-Schwefelverbindungen, zumal sich Jod kryoskopisch gegen Schwefel ebenfalls völlig indifferent verhält, wofür die nachstehenden Versuche—Schwefel in Jod und Jod in Schwefel gelöst—auch als Beweis angeführt werden mögen:

1. Kryoskopische Bestimmungen von präzipitiertem, löslichen Schwefel in Jod (Smp. 114°, K=204)(1)

Jod in gr.	Schwefel, Einzelmengen, gr.	Erniedrigung in grad.	Mol.-Gew.	Atome.
50	0.1338	0.214°	255	8.0
	0.1915	0.319	245	7.7
	0.1597	0.269	242	7.6

Auch plastischer, unlöslicher Schwefel lieferte unter Rückbildung identischer Lösungen, die gleichen Werte von normalem, S_8 entsprechendem Molekulargewicht.

2. Kryoskopische Bestimmungen von Jod in Schwefel (Smp. 114.5°, K=213)(2)

Schwefel in gr.	Jod, Einzelmengen, gr.	Erniedrigung in grad	Mol.-Gew.	Atome
25.0	0.2390	0.780	261	2.05
	0.2303	0.729	269	2.12
	0.2317	0.776	254	2.00
	0.2252	0.748	257	2.02

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(1) E. Beckmann und R. Hauslian, *Z. anorg. allg. Chem.*, **80** (1913), 223.

(2) Vgl. die erste Abhandlung dieser Serie, dieser Bulletin, **4** (1929), 235.

Die experimentell ermittelte und offenbar für schmelzenden Schwefel allgemein gültige Konstante K=213 hat sich also auch in diesem Falle als brauchbar erwiesen und man kann demzufolge aus dieser Tatsache schliessen, dass durch Fremdmoleküle keine Veränderungen des Gleichgewichts beim Schmelzpunkt stattgefunden haben. Wenn trotzdem nach 24 Stunden in der erkalteten Schmelze, wenn diese Jod enthielt, mehr amorpher Schwefel gefunden wurde, als wenn diese jodfrei war, so wird man diese Erscheinung ebenso erklären können, wie das nachträgliche Verschwinden von amorphem Schwefel aus solchem, der mit NH_3 behandelt war und sekundäre Verschiebungen bei bezw. nach dem Erkalten annehmen dürfen.

Nach E. Beckmann besitzt Selen analog dem Schwefel in organischen Lösungsmitteln grosse Moleküle Se_8, die sich indessen in schmelzendem Jod bis zu Se_2 und Se_1 aufspalten, was angesichts der kleinen, 3-4 betragenden Dielektrizitätskonstante des Jods, nach welcher Jod nur geringen dissoziierenden Einfluss haben sollte, überraschend ist, um so mehr, als auch eine chemische Jod-Selen-Verbindung nicht hat nachgewiesen werden können.

Die Kryoskopie eröffnete hinsichtlich des Schwefels die Möglichkeit einer Nachprüfung des Verhaltens von Selen zu Jod und von Selen zu Schwefel.

Nach den Arbeiten von Bettendorf und vom Rath,⁽¹⁾ Muthmann⁽²⁾ und Ringer⁽³⁾ scheiden sich aus Selen-Schwefellösungen Mischkristalle aus monoklinem Schwefel und monoklinem Selen aus. Entsprechend wurden bei kryoskopischen Versuchen statt Erniedrigungen Erhöhungen des Gefrierpunkts beobachtet.

Bei der vermutlich vorhandenen Isomorphie ist anzunehmen, dass die Mischkristalle aus S_8 und dem analog zusammengesetzten Se_8 bestehen. Gleiche Molekulargrösse des Selens in der festen wie flüssigen Lösung setzt voraus, dass zwischen Gefrierpunkts- und Konzentrationsänderung eine feste Proportion besteht, für die in der Tat die folgenden Versuche als Bestätigung angesehen werden können, wenn man die schwere Löslichkeit des Selens und die verhältnismässig unsichere Einstellung des Gefrierpunktes berücksichtigt. Um das Selen schneller und leichter zu lösen, erwies es sich als vorteilhaft, Selen mit der vierfachen Menge Schwefel zusammenzuschmelzen und kurze Zeit bis zum Sieden zu erhitzen, worauf man die erkaltete Schmelze zu den Einzelbestimmungen benutzt, bei denen oft erst nach längerer Zeit Gefrierpunktskonstanz erreicht wird. Die kryoskopischen Versuche ergaben folgende Werte.

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(1) *Poggendorfs Annalen*, **139** (1870), 129.

(2) *Z. Kristallographie*, **17** (1890), 4.

(3) *Z. anorg. allg. Chem.*, **32** (1902), 183.

Vers. Nr.	Schwefel in gr.	Selen in %	Erhöhung nach Konstanz	Erhöhung auf 1% Se.
1	25.00	1.270	0.275	0.216
2	25.00	0.608	0.173	0.285
3	25.00	0.605	0.148	0.245
4	25.00	1.580	0.366*	0.230
5	25.00	1.283	0.303**	0.234

*Nach 2 Tagen. **Nach 1 Tag.

Obwohl die Konzentration bis zum Verhältnis 1:2.5 wechselt, bleibt die Enderhöhung ziemlich proportional und beträgt für 1% Selen im Mittel 0.242°. Das Molekulargewicht des Selens dürfte daher in der festen wie flüssigen Phase gleich gross sein und Se_8 in Analogie mit S_8, dem Molekül des isomorphen, monoklinen Schwefels.

Wenn die vorstehenden Annahmen richtig sind, so lässt sich mittels der in der ersten Abhandlung ermittelten kryoskopischen Konstante des Schwefels K=213 der relative Gehalt der festen Phase an Selen berechnen. Nach E. Beckmann und seinen Mitarbeitern(1) besteht bei ebullioskopischen Bestimmungen, wenn Substanz mit dem Lösungsmittel verdampft, folgende Beziehung:

$$\varDelta=\frac{K\times\%}{m}(1-a)\ ,$$

wobei a das Konzentrationsverhältnis des gelösten Stoffes im Dampf einerseits, in der Flüssigkeit andererseits bedeutet. Diese Formel ist auch bei der Kryoskopie anwendbar, wenn gelöstes Material in die kristallinische Abscheidung des Lösungsmittels als feste Lösung mit übergeht. a bedeutet dann das Konzentrationsverhältnis des gelösten Stoffes in der Abscheidung einerseits in der Lösung andererseits. Im vorliegenden Falle sind

$\varDelta$ berechnet auf 1% Se	-0.242°
m berechnet auf Se_8	633.6
K Mittelwert	213

Aus $\varDelta=\frac{K\times\%}{m}(1-a)$ berechnet sich für:

$$1-a=-0.718$$

$$a=1.718$$

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(1) *Z. physik. Chem.*, **17** (1895), 110; **58** (1907), 543; **86** (1914), 339.

In den Kristallen befindet sich also 1.7 mal mehr Selen als in der Lösung, aus der es abgeschieden ist.

Trägt man in eine geschmolzem Selen-Schwefelmischung Jod ein, ohne dass eine Aenderung der Selenmoleküle erfolgt, so muss bei der kryoskopischen Bestimmung die normale Molekulargrösse des Jods $J_2=254$ resultieren. Würden die Selenmoleküle indessen zu Se_2 oder Se_1 durch das Jod aufgespalten, so müsste sich eine grössere als vorauszusehende Gefrierpunktserniedrigung ergeben, ganz abgesehen von der in solchem Falle gänzliche ausfallenden Isomorphie und Mischkristallbildung. Entsprechende Versuche ergaben.

Konstantenbestimmung in Schmelzen von selenhaltigem Schwefel.

(a) Selengehalt, 1.58% ; Erhöhung, 0.366° nach 2 Tagen.

Schwefel gr.	Gelöst gr. Einzelmengen	Erniedrigung	Badtemperatur beim		K Einzel best.
			Erstarren	Schmelzen	
1. Gelöst Jod, M (J_2)=254					
26.58	0.1361	0.362	114	116	179.6
	0.0984	0.318	113.7	115.6	218.2
	0.0947	0.304	113.7	115.2	216.7
2. Gelöst Diphenyl, M=154.1					
26.58	0.1355	0.675	112.6	115.2	204.0
	0.1125	0.555	112.6	114.5	202.1
	0.0842	0.408	111.6	114.0	198.5

(b) Selengehalt, 1.283% ; Erhöhung, 0.303° nach 24 Stunden.

Schwefel gr.	Gelöst gr. Einzelmengen	Erniedrigung	Badtemperatur beim		K Einzel best.
			Erstarren	Schmelzen	
1. Gelöst Jod, M (J_2)=254					
26.28	0.0890	0.278	113.	116.0	208.5
	0.1013	0.346	113.3	115.7	228.0
	0.1139	0.371	113.0	115.3	217.4
2. Gelöst Diphenyl, M=154.1					
26.28	0.1144	0.611	112.4	115.0	216
	0.1358	0.694	111.7	114.4	207

Da die Konstanten nach den vorstehenden Versuchen sowohl bei Gegenwart von Selen mit Jod wie auch die mit Diphenyl zur Kontrolle erhaltenen um K=213 liegen, deutet nichts auf eine Verschiebung des Gleichgewichts bezw. Aufspaltung des Selens durch Jod.

Zur weiteren Prüfung dienten umgekehrt die verwendeten Jod-Selen-Mischungen zur Bestimmung der Konstanten in Schwefel.

Melokulargewicht von Jod-Selen-Schmelzen beim Eintragen in geschmolzenen Schwefel.

Annahmen:—1. 1.283% Se=0.303° Erhöhung,
2. Schwefel K=213,
3. Jod, Mol. Gew.=254.

(a) Verwendete Schmelze von 74.23 Jod und 25.77 Selen.

Vers. Serie	Schwefel gr.	Schmelze, gr. Einzelmengen	Gefundene Erniedrigung	Mittleres Mol. der Schmelze
A_1	25.00	0.2501	0.580	367
		0.2512	0.614	347
		0.2546	0.627	347
		0.2495	0.577	369
A_2	25.00	0.2482	0.590	358
		0.2497	0.616	345
		0.2509	0.598	356

Kontrolle der Konstanten mit Diphenyl.

Schwefel gr.	Gelöst, gr. Einzelmengen	Erniedrigung	K
25.00	0.1378	0.789	221
	0.1338	0.679	196

(b) Verwendete Schmelze von 60.17 Jod und 39.83 Selen.

Vers. Serie	Schwefel gr.	Schmelze, gr. Einzelmengen	Gefundene Erniedrigung	Mittleres Mol. der Schmelze
B_1	25.00	0.2553	0.404	537
		0.2520	0.429	501
		0.2509	0.427	499

Kontrolle der Konstanten mit Diphenyl.

Schwefel gr.	Gelöst Einzelmengen	Erniedrigung	*K*
25.00	0.1427	0.806	218
	0.1024	0.510	192

Vers. Serie	Schwefel gr.	Schmelze Einzelmengen	Gefundene Erniedrigung	Mittleres Mol. der Schmelze
B_2	25.00	0.2546	0.405	536
		0.2496	0.470	452
		0.2509	0.496	429

Kontrolle der Konstanten mit Diphenyl.

Schwefel gr.	Gelöst Einzelmengen	Erniedrigung	*K*
25.00	0.1408	0.781	213.7
	0.1267	0.651	197.9

Es ergibt sich demnach, dass das Schmelzpunktsgleichgewicht des Schwefels durch den Gehalt an Selen und Jod nicht verändert wird, da die Kontrollen mittels Diphenyl allgemein normale Schwefelkonstanten lieferten. Die eingetragenen Selen-Jodmischungen lieferten höhere Molekulargewichte und es wurden mit der an Selen reicheren Mischung die relativ höchsten Molekularwerte erhalten, wie es auch der Annahme von Se_8=633.6 entspricht.

Der erste Wert jeder Serie möge deswegen etwas genauer untersucht werden, weil durch das Vorerhitzen über Nacht die hierbei erzielte Einstellung des Gleichgewichts besonders präzis erscheinen muss. Wäre das Selen in der jodhaltigen Schwefellösung wie in seiner Lösung in blossem Schwefel als monoklines Se_8 vorhanden, so müsste die gefundene kryoskopische Erniedrigung sich aus der dem Selengehalt (Se_8=633.6) entsprechenden Erhöhung

$$\varDelta_1 = \frac{213 \times \% Se_8}{633.6}(-0.718) \quad \text{oder} \quad -\frac{213 \times \% Se_8 \times 0.718}{633.6}$$

und der dem Jodgehalt entsprechenden Erniedrigung

$$\Delta_2 = \frac{213 \times \% J_2}{254}$$

additiv als $\Delta_1 + \Delta_2 = \Delta$ berechnen lassen. Die entsprechende Rechnung ergibt für die ersten Werte der Serien A_1, A_2, B_1 und B_2.

Vergleich der gefundenen Erniedrigung mit der berechneten.

Versuch	Gefundene Erniedrigung	Berechnete Erniedrigung
A_1	−0.580°	−0.622+0.061=−0.561
A_2	−0.590°	−0.618+0.060=−0.558
B_1	−0.404°	−0.515+0.097=−0.418
B_2	−0.405°	−0.515+0.096=−0.419

Mit Rücksicht auf die labilen Gleichgewichtsverhältnisse ist die Übereinstimmung im Rahmen der unvermeidlichen Fehlergrenzen als ausgezeichnet anzusehen.

Man muss also nunmehr als richtig unterstellen, dass Selen, welches in schmelzendem Jod zu Se_1 und Se_2 aufspaltet, durch Auflösen der Jodselenschmelze in Schwefel grosse Moleküle Se_8 zurückbildet, was um so interessanter ist als Jod und Schwefel hinsichtlich Schmelztemperatur und Dielektrizitätskonstante, wie folgt übereinstimmen.

	Schmelztemperatur	Dielektrizitätskonstante
Jod	114°	4.0
Schwefel	114.5°	3−4

Es müssen also noch andere Einflüsse spezifischer Art in diesem Falle die Verschiedenheit von Jod bezw. Schwefel gegenüber bedingen. Dass es sich um einfache, leicht verschiebbere Dissoziation handelt, zeigt nicht nur die Veränderlichkeit des Moleküls mit der Natur des Lösungsmittels, sondern auch mit der Konzentration. Nachdem Olivari(1) in Jodlösung Moleküle Se_2 festgestellt hatte, konnten E. Beckmann und R. Hanslian(2) nachweisen, dass bei grösserer Verdünnung in Jodlösung die Aufspaltung bis Se_1 geht, woran Temperaturerhöhungen bis 183° (Siedepunkt des Jods) nichts änderten.

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(1) *Rend. Acc. Lincei*, [5] **17** II (1908), 391.

(2) *Z. anorg. allg. Chem.*, **80** (1913), 224.

Kryoskopisch		Ebullioskopisch	
Konzentration	Molekül	Konzentration	Molekül
0.22–2.05%	$Se_{1.33-1.78}$	0.165–2.80%	$Se_{1.36-1.88}$

Nach Olivari liefert Selen sowohl in Quecksilberchlorid (Schmelzpunkt 277°)(1) wie in Quecksilberbromid (Schmelzpunkt 253°)(2) mit steigender Konzentration assoziierende Moleküle. Auch diese Beobachtung spricht dafür, dass es sich in Selen-Jod-Lösungen um einfache Dissoziationen unter dem spezifischen Einfluss des Lösungsmittel handelt. Das Schwefelmolekül S_8 ist hingegen auch bei diesen Lösungsmitteln und Temperaturen beständig. Immer wieder zeigt sich, dass der Einfluss des Lösungsmittels denjenigen der Temperatur erheblich übertreffen kann.

Zusammenfassung.

1. Selen liefert in Schwefel gelöst kryoskopische Erhöhungen infolge der Bildung von Mischkristallen aus Selen und Schwefel. Nach den mitgeteilten Versuchen sind diese aus isomorphen Mischungen von monoklinem Schwefel (S_8) und monoklinem Selen (Se_8) zusammengesetzt.

2. Selenhaltige Schwefellösungen geben sowohl mit Diphenyl wie mit Jod normale Konstanten so, dass also durch Selen die Gefrierpunktsverhältnisse nicht geändert werden, was als ein Beweis dafür zu werten ist, dass Selen und Jod eine Verbindung eingehen oder aber in der Schwefellösung eine Aufspaltung des Selenmoleküls herbeigeführt wird.

3. Das beobachtete kleine Selenmolekulargewicht (Se_2—Se_1) in Jodlösungen ohne Gegenwart von Schwefel, das grosse (Se_8) bei dessen Anwesenheit als Lösungsmittel erscheint um so interessanter, als Schmelztemperatur und Dielektrizitätskonstante bei Jod und Schwefel fast vollkommen übereinstimmen und nur geringe Dissoziation erwarten lassen.

Hamburg, Deutschland.

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(1) *Rend. Acc. Lincei,* [5] **18** II (1909), 94.
(2) *Rend. Acc. Lincei,* [5] **21** I (1912), 718.

BIOCHEMICAL STUDIES ON RICE STARCH. III.
THE ACTION OF ENZYMES ON RICE STARCH. I.

By Wei Sun TAO.

Received December 26, 1929. Published March 28, 1930.

The experimental results of researches into the complex metabolic processes which take place in the reserved starch during the germination of the seeds have been described briefly in the previous article, and the transformation of the starch molecule into simpler sugars was assumed to take place successively by the action of the hydrolytic enzymes such as amylase or diastase which, according to the opinion of Brown and Morris, seems to occur in the seedlings by a direct glandular secretion of the columnar epithelium of the embryo.

The idea that the conversion of starch into sugars by the action of the diastase formed and diffused slowly out of the epithelium during germination, was confirmed by the experiment upon rye by Haberlandt.⁽¹⁾ The process of germination thus shows that as it commences, active metabolism, synchronous with the dissolution of the cell-walls and the transformation of starch, goes on in the epithelium.

There are two kinds of vegetable diastase, one of which named translocation diastase acts on starch grains to convert them slowly into sugar, the optimum temperature being said to be 45–50°C., and the other one is "diastase of secretion," which corrodes starch grains and disintegrates them before dissolution, and the working temperature is around 50–55°C., and the latter enzyme plays an important part for the conversion of starch into sugars during the germination.

As a matter of fact, the diastase from germinated barley was found to be capable of corroding and dissolving the starch of barley, wheat, rice and maize but to have no evident action on that of the potato, and the kidney-bean.

The optimal temperature for the diastase in germinated grains is said to be 54–56°,⁽²⁾ and the activity of the enzymes is usualy increased or retarded by the presence of various salts.⁽³⁾

The optimum temperature for the germination of the rice grain is said to be 30° to 35°, and actually the transformation velocity of the starch in

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(1) *Ber. Deut. botan. Ges.*, **8** (1890), 40.

(2) J. Effront, *Compt. rend.*, **174** (1922), 18.

(3) C. Oppenheimer, "Die Fermente u. Ihre Wirkungen," (1924–6); H. C. Sherman and A. W. Thomas, *J. Am. Chem. Soc.*, **37** (1915), 623.

the plant tissues is noticed to be greatest at 35°, where the diastase occurs in the embryo, and this fact seems apparently to contradict the experimental results in vitro that the optimal temperature of diastase extracted from germinated grains is situated at 54–56°, and the discrepancy between the two cases will be attributed to the presence of some accelerating agents for the action of the enzymes in vivo.

The action of the diastases prepared from malted barley and rice on the starch solution in vitro was investigated.

In the experiments, diastatic enzymes were prepared by extraction with 100 c.c. of distilled water at room temperature for 3 hours from 5 grams of the malted barley and germinated rice which were previously powdered, the insoluble residue being filtered off, and the brown coloured filtrate was used.

The substrate which was used in studying the action of the enzymes, was prepared with many precautions, as the impurities associated with starch, such as protein, exert some influence on the diastatic action of enzymes.(1)

The various starch solutions were prepared as follows:

(1) The rice starch was prepared from ground rice-powder after treating with petroleum ether, and a 0.3% NaOH solution to remove the fat and the protein. The 1% solution of this starch was used, the reducing power of the solution is zero.

(2) Soluble starch was prepared by Lintner's method. Digest the starch with 7.5% HCl for 7 days at room temperature, wash with water till the washing shows a neutral reaction to litmus, filter and dry. The reducing power of this solution is 1.5.

(3) Amylose and amylopectin were prepared by the method proposed by Gatin and Gruzewska, from the rice starch by means of a 1% NaOH solution. The reducing power of amylose and amylopectin is 3.1 and zero respectively.

To 20 c.c. of the 1% starch solutions, 4 c.c. of the extracts were added, and the mixture was left to stand for 15 minutes at 20°C., 30°C., 40°C. and 50°C. respectively. After a certain time of reaction, the reducing power of each solution was determined on one hand, and on the other the colour test for the iodine solution was studied.

In the following tables, the reducing power of the starch solution examined was shown by subtracting the value original to the extracts from that of the whole of the reaction system. The conversion of the starch solutions into simpler sugars by the enzymes was carried out with progressive velocity at a higher temperature.

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(1) S. A. Waksman and W. C. Davison, "Enzymes," (1926), p. 154.

Rice Diastase.

		Rice starch		Soluble starch		Amylose		Amylopectin	
		I.	R.P.	I.	R.P.	I.	R.P.	I.	R.P.
Without enzymes		Blue	0	Blue	1.5	Blue	3.1	Blue	0
With enzymes	20°C.	blue	3.1	violet blue	5.5	purple	4.7	blue	3.9
	30°	violet blue	7.8	violet blue	9.5	purple	7.8	blue black	6.9
	40°	violet blue	9.5	red violet	16.4	red violet	16.4	blue	12.4
	50°	violet blue	17.3	red violet	25.0	red violet	21.0	blue	18.9

Barley Diastase.

		Rice starch		Soluble starch		Amylose		Amylopectin	
		I.	R.P.	I.	R.P.	I.	R.P.	I.	R.P.
Without enzymes		Blue	0.	Blue	1.5	Blue	3.1	Blue	0
With enzymes	20°C.	violet blue	42.9	violet blue	51.5	violet	39.9	blue	35.8
	30°	,,	46.1	,,	55.5	red violet	44.6	violet blue	42.7
	40°	,,	49.2	,,	59.3	light violet	45.2	,,	46.9
	50°	violet	52.6	violet	84.2	yellow	50.1	light violet	56.8

The malted rice acts on soluble starch more easily than on the other starch solutions, and this fact would be ascribed to the occurrence of a subtance promoting the enzyme activity in the soluble starch. The case is also noticed in the action of the malted barley extract on the starch solutions. However, there was noticed a marked difference between the two malt extracts in their hydrolytic action on the starch solution, especially in the temperature effect; the activity of the malted rice extract was increased markedly by increase of temperature, while the malted barley extract remains almost constant in its activity throughout the different temperatures. The optimal temperature for the action of these extracts in vitro seems to lie at about 50°, as is described in the literatures.

In the next experiment, both the rice amylase and the barley amylase were prepared in a purified state by the method of Sherman from both extracts, which show no reducing power, and acted on the starch solutions.

2.3 mg. of the barley diastase and 2.9 mg. of the rice diastase acted on the 1% solutions of 50 mg. of the starches for 15 minutes at 24°C., the reducing power of the solution, and the colour reaction for the iodine solution, were studied.

Rice Diastase.

Substrate	Rice starch solution		Soluble rice starch solution	
	Iodine-colour	R.P.	Iodine-colour	R.P.
	light violet	50.0	light violet	51.6

Barley Diastase.

Substrate	Rice starch solution		Soluble rice starch solution	
	Iodine-colour	R.P.	Iodine-colour	R.P.
	violet	57.8	violet	63.1

As will be seen from the above results, the hydrolytic action of the barley diastase on both the rice starch and the soluble starch shows no marked difference between them, and also the diastases prepared fairly in a pure state from both seeds show a similarity in the hydrolytic action on rice starch at 24°C., though they behave in their malt extracts with a different activity toward the same substrates.

In conclusion, the writer states that the diastases from different kinds of germinated grains behave in a different manner in their activity toward the same starch, and that the activity of the enzyme depends upon its purity.

July, 1928.

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BIOCHEMICAL STUDIES ON RICE STARCH. IV. THE ACTION OF ENZYMES ON RICE STARCH. II.

By Wei Sun TAO.

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In the first communication on this subject, the writer stated that the substances transformed from the reserve starch by germination were different, due to the influence of temperature on the reaction; when the seeds germinated at a low temperature, the simple sugars formed were composed mostly of sucrose with some maltose, and the formation of maltose is favorable at a high temperature. In the chemical reactions in vitro, the temperature is regarded as only changing the reaction velocity. Chemical reactions of combination and intramolecular transformation, in general, only take place within certain limits of temperature, and cannot be accomplished outside those limits. However, we can hardly believe that sucrose will form from starch at 20°, while maltose at a higher temperature.

The writer, therefore, took up the study of the reaction products from rice starch in vitro by the action of the rice diastase prepared from the germinated rice at 20°C. and 35°C. in order to learn what the chemical changes that occur in the plant tissues at different temperatures.

The rice diastase used in the present experiment was prepared from the rice seedlings by the method proposed by Sherman and Schlesinger and acted on the rice starch, both the rice diastase and the rice starch were obtained from the grains produced in the same rice field, 1928, which were used in the previous experiments.

In the experiment, the rice diastase acted on 15 gr. of the rice starch in 3% solution for 3 hours at 20° and 35°C. respectively. The reaction products were treated with 80%, 90% and absolute alcohols to separate by fractional precipitation as in the case of the rice seedlings, and the separated products were examined as to their rotatory power and reducing power in their aqueous solutions, and also the reaction for the iodine solution, and also for the Pinoff reagent, and the results are summarized in the following table:

Reaction Products at 20°C.

Fraction	Yield	$[\alpha]_D$	R.P.	Iodine test	Pinoff's test
80% alcohol ppt.	2.6 gr.	160	7	wine red	–
90% alcohol ppt.	1.0	137	23	brown	–
abs. alcohol ppt.	0.1	83	46	nil	–
Sum	3.7				

Reaction Products at 35°C.

Fraction	Yield	$[\alpha]_D$	R.P.	Iodine test	Pinoff's test
80% alcohol ppt.	3.6 gr.	179	74	wine red	—
90% alcohol ppt.	2.3	117	26	brown	—
abs. alcohol ppt.	1.2	95	43	nil	—
Sum	7.1				

In vitro, 50% of the starch by the rice diastase at 35° were converted into simpler sugars, and at 20°C. only 33% were transformed, while in the germinated seeds, 20% and 17%, of starch were converted into simpler substances; at the corresponding temperatures. From the comparison of these figures we have learned that the transformation of starch will be performed in a parallel way both in vitro and in vivo, and also that the disappearance of the sugar molecule by decomposing into carbon dioxide and water will happen in vivo while in vitro it is never met with.

The 80% alcohol precipitate in both cases as in vitro, which shows a wine red colour to iodine, and is judged to be composed mostly of dextrins from the data of the rotatory power and the reducing power, and these results agree quite well with these in the corresponding state in vivo.

The 90% alcohol precipitate was assumed also from its physical and chemical properties to be composed mostly of maltose with some glucose while the absolute alcohol precipitate was predominant in glucose in two cases, and both of the precipitates was lacking in sucrose as indicated in the Pinoff test.

The fact that the formation of reducing sugars is favorable at high temperature, was already noticed by the writer in the germination of seeds.

To the writer's interest, the formation of cane sugar was actually noticed in vivo, but not in vitro. We noticed further a great difference between in vivo and in vitro, in the chemical reactions which take place in the starch molecule, the decomposition of starch into carbon dioxide and water, the so-called respiration, prevailed in the case of in vivo.

In closing, the writer would like to offer her hearty thanks to Prof. Komatsu of Kyoto Imperial University, for these experiments were performed under his kind direction and neverfailing encouragement.

October 1929. Laboratory of Organic- and Bio-Chemistry,
Kyoto Imperial University.

SINOMENINE AND DISINOMENINE. PART XV. ON THE REDUCTION OF BROMO-SINOMENINE WITH NASCENT HYDROGEN.

By **Kakuji GOTO** and **Reikichi INABA.**

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In the XI communication,(1) one of the authors (K. G.) studied, in cooperation with H. Sudzuki, the reduction of sinomenine with nascent hydrogen and determined the following four facts.

1. Two molecules of sinomenine can be linked together with Na-amalgam reduction and give bis-8,8′-demethoxy-dihydrosinomenine.
2. Dihydrosinomenine gives by Na-amalgam reduction demethoxy-dihydrosinomenine, i.e., *d*-form of dihydrothebainone.
3. Sinomenine gives by Clemmensen's Zn-amalgam reduction in the hot demethoxy-desoxo-dihydrosinomenine, i. e., *d*-form of *β*-tetrahydro-desoxy-codeine.
4. The double linking of sinomenine can be reduced with nascent hydrogen, such as zinc and hydrochloric acid or Zn-amalgam and hydrochloric acid in the cold. The dihydrosinomenine thus obtained is identical with that produced by catalytic hydrogenation of sinomenine.

The research communicated in this report was carried out with the view to determine whether the bromo-sinomenine behaved in the same way as with sinomenine against these reducing agents. The results were completely affirmative as are shown in the following diagrams.

Properties of these substances may be summarised in the following table for convenience's sake.

Table 1.

	1. 1′-Dibromo-bis-8,8′-demethoxy-dihydro-sinomenine	1-Bromo-demethoxy-dihydro-sinomenine	1-Bromo-demethoxy-desoxo-dihydro-sinomenine	Brominated β-tetrahydro-desoxycodeine
Yield	20%	40%	30%	50%
Crystal form	granular	prisms	prisms	prisms
M.p.	227°	119°	127°	127°
$[\alpha]_D$	+19.02°	+57.57°	+40.44°	−39.52°
M.p. of oxime	237° (dec.)	263°	—	—
M.p. of iodomethylate	253–255°	119° (sinters) 127° (dec.)	253–255°	—
$FeCl_3$-react. in alcohol	green	green	green	green
Diazo-reaction	400,000*	200,000	50,000	10,000
$FeK_3(CN)_6$-reaction	no	+only in 1,000th	no	no
Formaline-SO_4H_2	greenish blue	greenish blue	yellowish brown	yellowish brown

* The figures show the dilution, at which the colour is still visible.

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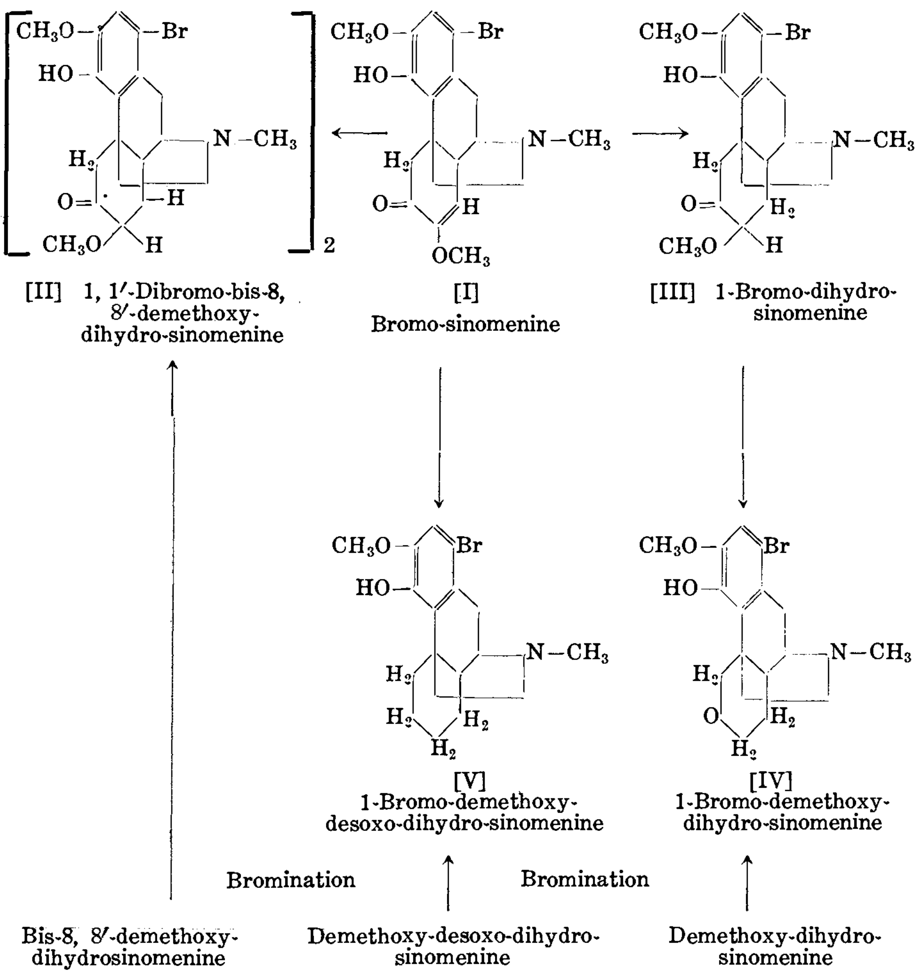
(1) This Bulletin, **4** (1929), 244.



By the reduction with Na-amalgam, bromo-sinomenine gave a substance of a bimolecular weight $(C_{18}H_{21}BrNO_3)_2$ in a yield about 20–40%, which melted at 227° and showed the properties given in the first column of the Table 1. Since the identical substance could be prepared by the bromination of bis-8,8'-demethoxy-dihydrosinomenine, it is clear that by the Na-amalgam reduction bromosinomenine is also linked together on its double linking. And from the same reasoning as was applied to the bis-8,8'-demethoxy-dihydro-sinomenine, it can be assumed that the linking point must be C_8 of each bromo-sinomenine molecule.

Secondly, bromo-dihydrosinomenine gave by the reduction with Na-amalgam, a substance $C_{18}H_{22}BrNO_3$ whose melting point was at 119°. Since the identical substance was also obtained by the direct bromination of demethoxy-dihydro-sinomenine, it is clear that the substance is nothing but brom-demethoxy-dihydro-sinomenine. Thus the action of Na-amalgam on bromo-dihydro-sinomenine is also the splitting off the methoxyl group, vicinal to the ketone, as was with dihydro-sinomenine.

Thirdly, by the Clemmensen's reduction of bromo-sinomenine, bromo-demethoxy-desoxo-sinomenine was obtained in 30% yield. The substance was checked by the bromination of demethoxy-desoxo-sinomenine, which gave the identical substance. The action of the zinc-amalgan and hydrochloric acid in the hot is, thus, the reduction of the double linking, the elimination of the methoxyl group and the reduction of the ketone to the methylene group. It is rather interesting to note that such complicated reactions could be effected in such a short lapse of time with tolerably good yield.

Moreover, the bromo-demethoxy-desoxo-dihydro-sinomenine ($[\alpha]_D = +40.44$) was racemised effectively with brominated β-tetrahydro-desoxy-codeine ($[\alpha]_D = -39.52$) prepared from codeine. This brings forward another evidence that the demethoxy-desoxo-dihydrosinomenine is the optical antipode of β-tetrahydro-desoxy-codeine. Hence, at least the three asymmetric carbon atoms C_{13}, C_{14} and C_9 of sinomenine must be arranged so as to form the image of the corresponding asymmetric carbon atoms of the reduced derivatives of codeine and thebaine.⁽¹⁾

Fourthly and lastly, bromo-sinomenine was reduced with granular zinc and hydrochloric acid in the cold. Yield of bromo-dihydro-sinomenine was here about 30%.

Experimental.

1,1′-Dibromo-bis-8,8′-demethoxy-dihydro-sinomenine [II]. (1) Bromo-sinomenine (5 gr.) was reduced in 2% caustic soda solution (50 c.c.) with 5% Na-amalgam (30 gr.). After 72 hours, the aqueous part, diluted with water (150 c.c.), was saturated with carbonic acid gas. The precipitate was dissolved in chloroform. The residue of the evaporated chloroform crystallised out on addition of acetone. The yield of the raw material was 1.2 gr., viz. 34.3% of the theoretical. It was redissolved in dilute caustic soda, precipitated with CO_2 and again recrystallised from acetone. The substance has a nice appearance of crystals, but, on examination with microscope, it consisted from granules, showing no angles. It melted at 227° and darkened at 274°.

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(1) Loc cit., p. 252.

(2) Bromination of bis-8,8′-demethoxy-dihydro-sinomenine (2 gr.) with bromine (1 gr.) in glacial acetic acid solution in the way already given, resulted in the same substance as above. The yield amounted to 70%. The melting point was at 227°, which was unaltered with the admixture of the substance obtained in the reaction (1).

As regards other properties of this substance, see the first column of the Table 1.

Anal. Found: C=56.77; H=5.56; N=3.42; Br=20.49, 20.61%. Calc. for $(C_{18}H_{23}BrNO_3)_2$=758: C=56.98; H=5.58; N=3.69; Br=21.08%.

Mol. wt. Found (in glacial acetic acid): 807. Calc.: 758.

Sp. rotatory power: 0.3549 gr. subst. was dissolved into 25 c.c. alcoholic solution. l=1 dm.; $\alpha=+0.27$; $[\alpha]_D^{13}=+19.02.°$

Oxim: M.p. 237 (dec.) Found: N=7.09%. Calc. for $(C_{18}H_{24}BrNO_4)_2$: N=7.10%.

Iodomethylate: M.p. 253～255°. Yield 80%. Crystallises in stout prisms, when aqueous solution is very slowly cooled. Found: J=24.33%. Calc.: I=24.36%.

1-Bromo-demethoxy-dihydro-sinomenine [IV]. (1) Bromo-dihydro-sinomenine (5 gr.) was reduced in 2% caustic soda solution (60 c.c.) with 5% Na-amalgam. (36 gr. divided in two portions). After five days, when the alkaloid was completely dissolved, the aqueous part was treated as was given with 1.1′-dibromo-bis-8,8-demethoxy-dihydro-sinomenine. The reduced substance can be recrystallised from a small quantity of acetone. M.p. 119°. Yield 1.2 gr., viz. 35% of the theoretical.

(2) Bromination of demethoxy-dihydro-sinomenine, in the same way as was given above, resulted in the same 1-bromo-demethoxy-dihodro-sinomenine, which melted at 119°. The admixture of this substance with that obtained by the above reduction (1) did not lower the melting point. The yield was almost quantitative.

The properties of 1-bromo-demethoxy-dihydro-sinomenine are given in the second column of the Table 1.

Anal. Found: C=56.70; H=5.77; N=3.30; Br=20.97%. Calc. for $C_{18}H_{22}BrNO_3$: C=56.83; H=5.83; N=3.68; Br=21.02%.

Sp. rotatory power: 0.2866 gr. subst. was dissolved into 10 c.c. alcoholic solution. l=1 dm.; $\alpha=+1.65$. $[\alpha]_D^{13}=+57.57°$.

Oxime: prepared in the ordinary way. Prisms, when precipitated with sodium carbonate from water. M.p. 263° (dec.) Found: N=6.98%. Calc.: N=7.08%

Iodomethylate: can be recrystallised from water very slowly. Fine prisms collected in globules, which sinter at 119° and decompose at 127°. Found: I=24.57%. Calc.: I=24.31%.

1-Bromo-demethoxy-desoxo-dihydro-sinomenine [V]. (1) Bromo-sinomenine hydrobromide (ca. 10 gr.) was added to Clemmensen's Zinc amalgam (a large quantity) and the mixture was first poured on with 20 c.c. hydrochloric acid (1 : 1). While the reaction mixture was heated in the boiling water bath for one and half hours, the fuming hydrochloric acid was added from time to time (30 c.c. in three portions).

The isolation took place as was given in the XI communication.⁽¹⁾ The bromo-demethoxy-desoxo-dihydro-sinomenine, thus obtained, can be recrystallised from acetone in prisms. M.p. 127°. Yield 2.2 gr. i.e. 30% of the theory.

(2) Bromination of demethoxy-desoxo-dihydro-sinomenine, in the way frequently cited, gave the above substance in 80% yield.

The mixed melting point of these two substances, prepared in the different way, remained unaltered (127°).

As regards the properties of this substance, see the third column of the Table 1.

Anal. Found: C=59.42; H=6.70; N=3.78; Br=21.08%. Calc. for $C_{18}H_{24}BrNO_2$: C=59.01; H=6.55; N=3.82; Br=21.83%.

Sp. rotatory power: 0.3066 gr. subst. was dissolved into 10 c.c. alcoholic solution. $l=5$ cm.; $\alpha=+0.62$. $[\alpha]_D^{12}=+40.44$.°

Racemisation of Bromo-demethoxy-desoxo-dihydro-sinomenine with Brominated β-Tetrahydro-desoxy-codeine. β-Tetrahydro-desoxy-codeine (0.5 gr.; m.p. 149°) was brominated in acetic acid (5 c.c.) with bromine (0.25 gr. in 5 c.c. acetic acid). The brominated substance melted at 127° and showed the properties given in the fourth column of the Table 1. Yield good. (Found: Br=21.94%. Calc. for $C_{18}H_{24}BrNO_2$: Br=21.83%).

Sp. rotatory power: 0.2935 gr. was dissolved into 10 c.c. alcoholic solution. $l=5$ cm.; $\alpha=-0.58$. $[\alpha]_D^{13}=-39.52$.°

Racemisation. The substances used in the above two estimations of the rotatory power were mixed together and, after evaporation of alcohol, recrystallised from a little acetone. Ca. 0.33 gr. of the substance was collected in this way. It sintered at 119° and decomposed at 122°. When 0.3213 gr. of this substance was dissolved into 10 c.c. alcoholic solution and examined on its rotatory power in the tube of 1 dm., it did not rotate the polarised light.

Reduction of Bromo-sinomenine with Zinc and Hydrochloric Acid [III]. Bromo-sinomenine (1 gr.) was suspended in 4% hydrochloric acid (30 c.c.) and reduced with granular zinc (5 gr.). At the interval of one hour, 10% HCl (10 c.c. each) was added five times. After 24 hours, the aqueous part was filtered and the reduced base was isolated in the ordinary way. As bromo-dihydro-sinomenine is very difficultly soluble in boiling

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(1) This Bulletin, **4** (1929), 252.

ethyl alcohol, it could be purified easily. M.p. 236°. Admixture with bromohydro-sinomenine (m.p. 237°) prepared by the bromination of dihydrosinomenine did not alter the melting point.

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THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART II.

By Toshizo TITANI.

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Experiments on the transpiration method have been continued for various organic gases, using the capillary viscosimeter recently devised by the writer.[1] As described in the preceding paper air has been taken as standard substance, its viscosity being assumed to be equal to Millikan's value 1823×10^{-7} at 23°C. ; and the values for other substances have been determined by relative measurement. Present work includes the measurements for seventeen gases at temperatures ranging between 20° and 120°C. and the computation of Sutherland's constants and molecular diameters for each of them. The gases used and their preparations are as follows:

Ethane: obtained by the electrolysis of potassium acetate, thoroughly washed with potassium hydroxide solution, condensed and then repeatedly fractionated.

Propane and isobutane: obtained by the action of Zn–Cu couple on dilute alcoholic solution of isopropyl- or isobutyl-iodide, condensed and fractionated.

Normal butane: prepared by the action ef sodium amalgam on ethyl-iodide and purified by fractional distillation.

Ethylene and propylene: obtained by dehydrating ethyl- or iso-propyl-alcohol with hot concentrated phosphoric acid.

α- and β-butylene: obtained by the action of alcoholic potash on n-butyl- or secondary butyl-iodide and puried by fractional distillation.

γ-butylene: obtained by dehydrating tertiary butyl alcohol with hot anhydrous oxalic acid and purified by fractional distillation.

Isoamylene (isopropyl-ethylene): obtained by the action of alcoholic potash on isoamyl-iodide prepared from Kahlbaum's isoamyl alcohol, shaken with two volumes dilute sulphuric acid at 0°C. for two hours[2] and then fractionated.

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(1) This Bulletin, **4** (1929), 277.

(2) Wischnegradsky, *Ann.*, **190** (1878), 353.

Acetylene: prepared from calcium carbide and water and purified after Vanino.(1)

Allylene: obtained by the action of alcoholic potash on propylene-bromide, precipitated as copper compound, regenerated by warm dilute hydrochloric acid and fractionated.

Trimethylene: prepared by the reduction of trimethylene-bromide with zinc dust and alcohol, washed with potassium permanganate solution and fractionated.

Methyl-ether: obtained by dehydrating methyl alcohol with hot concentrated phosphoric acid, alcohol vapour mixed having been absorbed with phosphorus pentoxide.

Methyl-chloride: obtained by the action of dry hydrogen chloride gas on the boiling mixture of methyl alcohol and zinc chloride, washed with dilute potassium hydroxide solution and fractionated.

Methyl-bromide: obtained by heating the mixture of methyl alcohol, potassium bromide and dilute sulphuric acid, washed with water and fractionated.

Sulphur-dioxide: taken from a steel bomb and dried with sulphuric acid.

The gases hardly soluble in water were all thoroughly washed with water and dried with calcium chloride before distillation.

The results of measurements are shown in the following tables. Sutherland's formula has been found to be applicable with satisfactory results for all gases. The viscosity values calculated by this formula are given in the third column. For the sake of comparison other observers' values are also cited, of which the figures with asterisk have been estimated graphically from original observed values.

Ethane.

$$\eta=107.15\frac{T^{3/2}}{T+287.3}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	863	855 (Vogel(2) 1914)
20	929	926	917*(Ishida(3) 1923)
40	986	989	—
60	1050	1050	—
80	1111	1110	—
100	1167	1169	—
120	1230	1227	—

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(1) Vanino, "Handbuch d. präparativen Chemie," II, 2. Aufl., (1923).

(2) Vogel, *Ann. Phys.*, **43** (1914), 1235.

(3) Ishida, *Phys. Rev.*, **21** (1923), 550.

Propane.

$$\eta=102.3\frac{T^{3/2}}{T+341.3}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Other observers' value
	Obs.	Calc.	
0	—	751	752 (Klemenc & Remi,⑴ 1923)
20	806	809	—
40	873	866	—
60	922	922	—
80	978	977	—
100	1029	1032	—
120	1082	1085	—

Normal butane.

$$\eta=98.27\frac{T^{3/2}}{T+377.4}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	682	852*(Kuenen and Visser,⑵ 1913)
20	739	735	—
40	787	789	—
60	839	841	—
80	885	893	—
100	947	944	1092 (,,)
120	998	994	—

Isobutane.

$$\eta=92.85\frac{T^{3/2}}{T+335.5}\cdot 10^{-7}$$

t°C.	$\eta\cdot 10^7$		Others observer's value
	Obs.	Calc.	
0	—	689	—
20	744	741	747*(Ishida⑶ 1923)
40	792	793	—
60	845	844	—
80	888	895	—
100	947	944	—
120	995	993	—

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(1) Klemenc and Remi, *Monatsh. Chem.*, **44** (1923), 307.

(2) Kuenen and Visser, *Verhandel. Akad. Wetenschappen Amsterdam*, **22** (1913), 336; *Comm. Phys. Lab. Univ. Leiden*, No. 138 a.

(3) Ishida, loc. cit.

Ethylene.

$$\eta = 107.0 \frac{T^{3/2}}{T + 259.1} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$		Other observers' values
	Obs.	Calc.	
0	—	907	966 (Graham,(1) 1846) 922 (v. Obermayer,(2) 1875) 961 (Breitenbach,(3) 1901) 907 (Zimmer,(4) 1911)
20	—	972	1090 (Graham) 987*(v. Obermayer) 1032*(Breitenbach) 974*(Zimmer)
22	970	979	—
40	1036	1036	—
60	$\left.\begin{matrix}1109\\1106\end{matrix}\right\}1108$	1098	1116*(v. Obermayer)
80	$\left.\begin{matrix}1155\\1153\end{matrix}\right\}1154$	1160	—
100	$\left.\begin{matrix}1223\\1217\end{matrix}\right\}1220$	1220	1280*(Breitenbach)
120	$\left.\begin{matrix}1278\\1280\end{matrix}\right\}1279$	1279	—

Propylene.

$$\eta = 103.2 \frac{T^{3/2}}{T + 321{\cdot}6} \cdot 10^{-7}$$

t°C.	$\eta \cdot 10^7$	
	Obs.	Calc.
0	—	783
20	835	842
21.5	856	847
40	893	901
60	959	958
80	1023	1015
100	1071	1070
120	1122	1125

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(1) Graham, *Phil. Trans.*, **3** (1846), 573.
(2) v. Obermayer, *Wien. Ber.*, **71** [2a], (1875), 281.
(3) Breitenbach, *Ann. Phys.*, **5** (1901), 166.
(4) Zimmer, Diss. Halle, (1911); *Verhandl. deut. physik. Ges.*, **14** (1912), 471.

α—butylene.

$$\eta=94.48\frac{T^{3/2}}{T+328.9}\cdot10^{-7}$$

t°C.	$\eta\cdot10^7$	
	Obs.	Calc.
0	—	708
20	761	762
40	819	815
60	863	868
80	922	919
100	971	970
120	1020	1020

β—butylene.

$$\eta=97.63\frac{T^{3/2}}{T+362.1}\cdot10^{-7}$$

t°C.	$\eta\cdot10^7$	
	Obs.	Calc.
0	—	694
25	761	761
40	796	801
60	858	854
80	905	906
100	961	957
120	1005	1008

γ—butylene.

$$\eta=99.21\frac{T^{3/2}}{T+339.0}\cdot10^{-7}$$

t°C.	$\eta\cdot10^7$	
	Obs.	Calc.
0	—	732
30	815	815
40	843	843
60	897	897
80	949	951
100	1006	1004
120	1056	1056

Isoamylene (Isopropyl-ethylene).

$$\eta=94.48\frac{T^{3/2}}{T+368.0}\cdot 10^{-7}$$

t° C.	$\eta\cdot 10^7$	
	Obs.	Calc.
0	—	665
22	714	722
40	771	769
50	793	794
60	829	819
80	871	869
100	915	919
120	967	968

Acetylene.

$$\eta=99.59\frac{T^{3/2}}{T+198.2}\cdot 10^{-7}$$

t° C.	$\eta\cdot 10^7$		Other observer's value
	Obs.	Calc.	
0	—	954	943 (Vogel,(1) 1914)
20	1020	1017	—
40	1079	1079	—
50	1113	1110	—
60	1131	1140	—
80	1198	1199	—
100	1254	1256	—
120	1318	1313	—

Allylene.

$$\eta=98.35\frac{T^{3/2}}{T+276.5}\cdot 10^{-7}$$

t° C.	$\eta\cdot 10^7$	
	Obs.	Calc.
0	—	808
10	—	837
20	867	866
30	895	895
40	925	924
50	952	953
60	977	981
70	1009	1009
80	1039	1036
90	1066	1064
100	1090	1091

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(1) Vogel, loc. cit.

Trimethylene.

$$\eta=115.3\frac{T^{3/2}}{T+372.0}\cdot 10^{-7}$$

t°C.	$\eta\cdot10^7$	
	Obs.	Calc.
0	—	807
20	876	870
40	923	933
50	960	964
60	999	994
80	1057	1055
100	1113	1115
120	1179	1175

Methyl-ether.

$$\eta=116.4\frac{T^{3/2}}{T+344.9}\cdot 10^{-7}$$

t°C.	$\eta\cdot10^7$		Other observers' values
	Obs.	Calc.	
0	—	850	905 (Graham,⁽¹⁾ 1846)
19.5	909	914	—
20	—	915	1020 (,,)
40	984	980	—
60	1044	1043	—
80	1109	1106	—
100	1167	1168	1190 (Pedersen,⁽²⁾ 1907)
120	1228	1229	—

Methyl-chloride.

$$\eta=142.3\frac{T^{3/2}}{T+380.1}\cdot 10^{-7}$$

t°C.	$\eta\cdot10^7$		Other observers' values⁽³⁾
	Obs.	Calc.	
0	—	983	1025 (Graham, 1846) 989 (Breitenbach, 1901) 978 (Vogel, 1914)
10	—	1022	—
20	1061	1061	1160 (Graham) 1072*(Breitenbach)
30	1101	1099	—
40	1140	1137	—
50	1175	1175	—
60	1209	1213	—
70	1250	1251	—
80	1287	1288	—
90	1323	1325	—
100	1357	1362	1388*(Breitenbach)
110	1400	1398	—
120	1440	1434	—
130	1471	1470	—

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(1) Graham, loc. cit. (2) Pedersen, *Phys. Rev.*, **25** (1907), 225. (3) Loc. cit.

Methyl-bromide.

$$\eta=177.5\frac{T^{3/2}}{T+379.2}\cdot 10^{-7}$$

$t°$ C.	$\eta\cdot 10^7$	
	Obs.	Calc.
0	—	1228
10	1277	1277
20	1327	1325
21	1333	1330
30	1378	1373
40	1420 1412 } 1416	1421
50	1457	1468
60	1512 1522 } 1517	1515
120	1797	1791

Sulphur-dioxide.

$$\eta=173.6\frac{T^{3/2}}{T+395.8}\cdot 10^{-7}$$

$t°$ C.	$\eta\cdot 10^7$		Other observers' values.
	Obs.	Calc.	
0	—	1171	1225 Graham,(1) 1846) 1183 (Vogel,(2) 1914) 1168 (Smith,(3) 1922)
20	1266	1265	1380 (Graham) 1263* (Smith) 1250* (Trautz and Weizel,(4) 1925)
40	1352	1357	1345* (,,)
60	1455	1448	—
80	1540	1538	1533* (Trautz and Weizel)
100	1622	1627	1630 (Smith) 1625* (Trautz and Weizel)
120	1716	1715	1720* (,,)

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(1) Graham, loc. cit.

(2) Vogel, loc. cit.

(3) Smith, *Phil. Mag.*, [vi], **44** (1922), 508.

(4) Trautz and Weizel, *Ann. Phys.*, [4], **78** (1925), 305.

Sutherland's constants C for various gases are said to be proportional to the critical point T_K or the boiling point T_S expressed in absolute scale, being equal to $\frac{T_K}{1.12}$ according to Rankine⁽¹⁾ or to $1.47T_S$ according to Vogel.⁽²⁾ The above results show that the relations do not hold strictly and the discrepancy from the rules is often remarkable, as is seen from the next table.

Sutherland's Constants.

Substance	$C_{\text{obs.}}$	$\frac{T_K}{1.12}$	$1.47\,T_S$	Other observers' values⁽³⁾
Ethane	287	275	272	—
Propane	341	330	335	323.7 (Klemenc and Remi)
Normal butane	377	380	400	349 (Kuenen and Visser)
Isobutane	336	363	387	—
Ethylene	259	253	249	272 (Sutherland) 226 (Breitenbach) 272 (O. E. Meyer and Zimmer)
Propylene	322	326	332	
α-butylene	329	372	393	
β-butylene	362	382	403	
γ-butylene	339	372	391	
Isoamylene	368	—	432	
Acetylene	198	276	278	
Allylene	277	360	366	
Trimethylene	372	—	350	
Methyl-ether	345	360	368	
Methyl-chloride	380	371	366	454 (Breitenbach)
Methyl-bromide	379	417	409	
Sulphur-dioxide	396	384	386	416 (Smith)
Air	113	118	119	Cf. the Part I of this paper

Mean free pathes (l) and collision diameters (σ) of molecules were calculated by the kinetic theory of gases using the following equations, where $\bar{u}$ expresses mean velocity, M molecular weight and n the number of molecules in one cubic centimeter, all referred to 0°C. and one atmospheric pressure.

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(1) Rankine, *Proc. Roy. Soc. London*, [A], **84** (1910), 181.

(2) Vogel, loc. cit.

(3) Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," I, 5. Aufl., (1923).

$$\bar{u}^2=\frac{8}{\pi}\frac{p}{d}=\frac{8}{\pi}\times 1\,013\,250\times\frac{22\,412}{M}$$

$$l=\frac{32\eta}{5\pi d\bar{u}}=\frac{\eta\times 22\,412}{0.49\times M\times\bar{u}}$$

$$\sigma^2=\frac{1}{\sqrt{2}\,n\pi l\left(1+\frac{C}{T}\right)}\cdot \qquad (n=2.7\times 10^{19})$$

The next table contains the results of calculation :

Substance	M	$\bar{u}$	$\eta\cdot 10^7$	$l\cdot 10^8$	C	$\sigma\cdot 10^8$
Ethane	30.05	43 870	863	299	287	3.68
Propane	44.06	36 230	751	215	341	4.15
Normal butane	58.08	31 550	682	170	377	4.53
Isobutane	58.08	31 550	689	172	336	4.66
Ethylene	28.03	45 420	907	326	259	3.62
Propylene	42.05	37 090	783	230	322	4.08
α-butylene	56.06	32 120	708	180	329	4.58
β-butylene	56.06	32 120	694	176	362	4.51
γ-butylene	56.06	32 120	732	186	339	4.47
Isoamylene	70.08	28 730	665	151	368	4.84
Acetylene	26.02	47 150	954	356	198	3.68
Allylene	40.03	38 010	808	243	277	4.13
Trimethylene	42.05	37 090	807	237	372	3.86
Methyl-ether	46.05	35 440	850	238	345	3.93
Methyl-chloride	50.48	33 850	983	263	380	3.64
Methyl-bromide	94.94	24 680	1 228	240	379	3.81
Sulphur-dioxide	64.06	30 040	1 171	278	396	3.49
Air	28.99	44 660	1 711	604	113	3.12

The molecular diameters (σ_η) thus calculated from viscosity agree generally with those (σ_b) from van der Waals' b, deduced from critical data(1) as is seen in the following table.

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(1) Valentiner, Landolt-Börnstein-Roth, "Physikalisch-chemische Tabellen," I, 5. Aufl., (1923), 253; Pickerring, *J. Phys. Chem.*, **28** (1924), 97.

Molecular diameters.

Substance	$\sigma_\eta \cdot 10^8$	$\sigma_b \cdot 18^8$	$\sqrt[3]{V_S}$
Ethane	3.68	3.70	3.84
Propane	4.15	4.05	4.21
Normal butane	4.53	4.59	4.58
Isobutane	4.66	4.48	4.57
Ethylene	3.62	3.56	3.54
Propylene	4.08	4.02	4.05
α-butylene	4.58	—	4.46
β-butylene	4.51	—	4.46
γ-butylene	4.47	—	4.45
Isoamylene	4.84	4.80	4.79
Acetylene	3.68	3.44	3.33
Allylene	4.13	—	3.90
Trimethylene	3.86	—	3.92
Methyl-ether	3.93	3.85	3.97
Methyl-chloride	3.64	3.71	3.69
Methyl-bromide	3.81	-	3.82
Sulphur-dioxide	3.49	3.55	3.53
Air	3.12	3.06	3.11

The figures in the last column express the cube root of the molecular volumes at boiling points. These values shall be proportional to the actual diameters of molecules according to the theory of corresponding state and it seems to be actually the case. Indeed, if 10^{-8} be affixed to the figures in the last column, they express the actual dimensions of molecules. This result shows the molecular volumes at boiling points being about three times as large as the actual volume of molecules :

$$6.06 \times 10^{23} \cdot \frac{\pi}{6} \sigma^3 \fallingdotseq 0.318 V_s \, .$$

In ,conclusion the writer wishes to express his cordial thanks to Prof. M. Katayama for this kind guidance and encouragement throughout this experiment.

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A SERIES OF CONDENSATIONS PRODUCING THE ESTERS OF ACETYL-PROPYLENE-CARBOXYLIC ACIDS.

By Yoshiyuki URUSHIBARA.

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In the previous paper on "peculiarity in the formation of the nitrile-esters of dicarboxyglutaconic acid"(1) the author pointed out the fact that in the condensation of the ethoxymethylene-compound $XYC=CHOC_2H_5$ with the sodio-methylene-compound $CHNaX'Y'$, if it is carried out in the ethereal medium, the following four products are possible:
$XYC=CH-CNaX'Y'$; $X'Y'C=CH-CNaXY$; $X'Y'C=CH-CNaX'Y'$; $XYC=CH-CNaXY$.

That paper mainly dealt with the cases where each of X, X′, Y, and Y′ was either CN or $COOC_2H_5$. In the present paper the results of the condensations where the acetyl-group acts in place of the nitrile-group will be reported.

As a whole, similar results have been obtained, which are shown in the table. The found products are placed in the forms of the sodium derivatives under the general formulae showing the kinds, the blank spaces corresponding to those which could not be found inspite of their formation being possible.

But, unfortunately, the products of the first and the second kinds must be considered under the following unfavourable conditions: There have been no method to determine the positions of the sodium atom and the double union; there was no condensation in which both the first and second products were found; and moreover, as shown in the experimental part, it was impossible to determine whether the products of a pair of condensations were identical or not, except condensations 1 and 2. These conditions make the results somewhat indefinite, for it is impossible to determine whether a product belongs to the first kind or the second. In the table such compounds are placed in partly expanded formulae. Nevertheless, the author believes that four products are also theoretically possible in each of these condensations.

Experimental Part.

Experimental Procedure in General. The methylene compound is converted into the sodium derivative by adding it to finely granulated metallic sodium covered with pure ether. To the sodio-methylene compound in ether a

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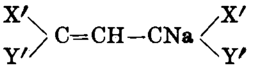
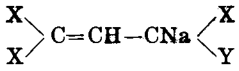
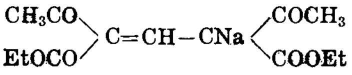
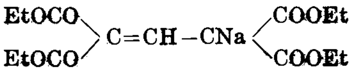
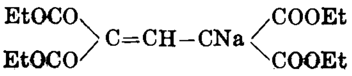
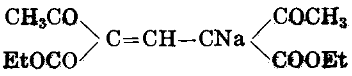
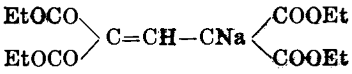
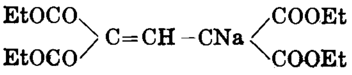
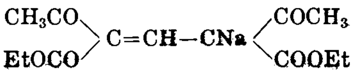
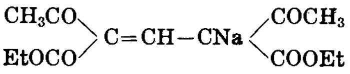
(1) This Bulletin, 5 (1930), 1.

	Condensations.	Products	
		The first kind	The second kind
	$\begin{matrix}X\\Y\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}X'\\Y'\end{matrix}$	$\begin{matrix}X\\Y\end{matrix}\!>C{=}CH-CNa<\!\begin{matrix}X'\\Y'\end{matrix}$	$\begin{matrix}X'\\Y'\end{matrix}\!>C{=}CH-CNa<\!\begin{matrix}X\\Y\end{matrix}$
1	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COCH_3\\COOMe\end{matrix}$	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!>C{=}CH-CNa<\!\begin{matrix}COCH_3\\COOMe\end{matrix}$	
2	$\begin{matrix}CH_3CO\\MeOCO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	$\begin{matrix}CH_3CO\\MeOCO\end{matrix}\!>C{=}CH-CNa<\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	
3	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!>(C_3HNa)<\!\begin{matrix}COCH_3\\COOEt\end{matrix}$	
4	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COOEt\\COOEt\end{matrix}$	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!>(C_3HNa)<\!\begin{matrix}COOEt\\COOEt\end{matrix}$	
5	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$	$\begin{matrix}EtOCO\\EtOCO\end{matrix}\!>(C_3HNa)<\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$	
6	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COOEt\\COOEt\end{matrix}$	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>(C_3HNa)<\!\begin{matrix}COOEt\\COOEt\end{matrix}$	
7	$\begin{matrix}CH_3CO\\EtOCO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COCH_3\\COCH_3\end{matrix}$		
8	$\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>C{=}CHOEt+CHNa<\!\begin{matrix}COCH_3\\COOEt\end{matrix}$		

The third kind	The fourth kind
 $\begin{matrix}X'\\Y'\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}X'\\Y'\end{matrix}$	 $\begin{matrix}X\\X\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}X\\Y\end{matrix}$
 $\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}$	 $\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$
 $\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$	 $\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}$
	 $\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$
 $\begin{matrix}\mathrm{EtOCO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COOEt}\\\mathrm{COOEt}\end{matrix}$	
	 $\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}$
 $\begin{matrix}\mathrm{CH_3CO}\\\mathrm{EtOCO}\end{matrix}\!\!>\mathrm{C{=}CH{-}CNa}<\!\!\begin{matrix}\mathrm{COCH_3}\\\mathrm{COOEt}\end{matrix}$	

calculated amount of the ethoxymethylene compound diluted with pure ether is added gradually under constant stirring. The mixture is kept at the room temperature for a length of time, during which the colour of the mass grows from yellow to red, and, after relatively long standing, to dark red. Then water is added to the mass. If the sodium derivative of tetraethyl dicarboxyglutaconate is present in a large quantity, it crystallises from the aqueous solution after a short time. If such is the case, the crystals are collected, and treated separately. The aqueous solution is acidified with dilute hydrochloric or sulphuric acid, and the separating substance is extracted with ether. If any solid substance difficulty soluble in ether be present, it is filtered. The ethereal solution is shaken many times with small volumes of a ten percent aqueous solution of sodium carbonate, and in this way the substance in ether is fractionated into several parts in the grade of acidity. Most of the red colouring matter is taken in the first few fractions. If tetraethyl dicarboxyglutaconate be present, its sodium derivative separates out in yellow crystals towards the end of the fractional extraction with sodium carbonate, and then this is collected. These fractions are separately acidified with hydrochloric acid, when oil or crystals separate out. Here, if it can be considered that some numbers of successive fractions are of the same nature, they are united together, and afterall the whole is divided into five or six fractions. Crystalline substances are purified by recrystallisation from carbon bisulphide and ligroin; oils are extracted with ether and the ethereal solutions are washed with water, dried, and evaporated in vacuum. These purified substances are subjected to analysis and identification. If necessary, oils are dissolved in ether, again fractionated with soda solutions, and the seemingly purest part is analysed.

The red substance in the condensation mass, the crystalline substance separating on acidifying the aqueous solution of the condensation mass and difficulty soluble in ether, and the red colouring matter taken into the soda extracts, are all of the similar nature. These are probably xanthophanic acids(1) or similar compounds; but as they are not the objects of the present investigation, no experiment on these substances was carried out.

1. *Condensation of ethyl ethoxymethylene-acetoacetate with methyl sodio-acetoacetate.*(2) α-Methyl γ-ethyl α,γ-diacetylglutaconate was isolated. The substance, obtained by recrystallising the crude product three times from carbon bisulphide and once from ligroin, melted at 74°. After it was recrystallised twice more from carbon bisulphide and once from ligroin, it melted at 76°, but the melting point was, none the less, unsharp. According-

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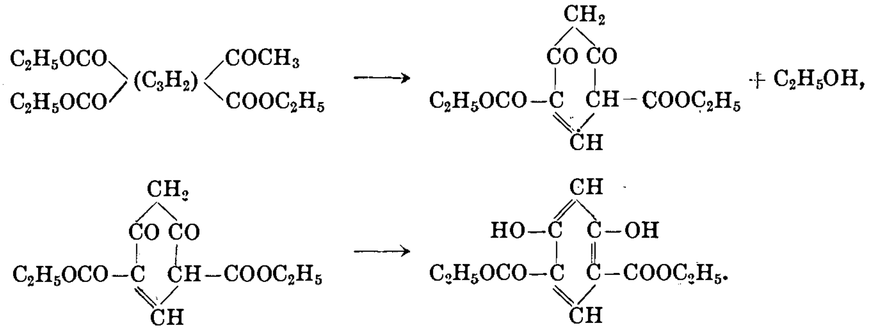
(1) Claisen, *Ann.*, **297** (1897), 48.
(2) Cf. Feist, *Ber.*, **59** (1926), 2958.

ing to Feist this compound melts at 73°, and, as he states, it seems difficult to purify it.

2. *Condensation of methyl ethoxymethylene-acetoacetate with ethyl sodio-acetoacetate.*(1) γ-Methyl α-ethyl α,γ-diacetylglutaconate was isolated. The substance, recrystallised three times from carbon bisulphide and once from ligroin, melted at 85°, and after it was recrystallised further twice from carbon bisulphide and once from ligroin, it melted sharply at 90°. According to Feist the melting point of this substance is 87°.

3. *Condensation of diethyl ethoxymethylene-malonate with ethyl sodio-acetoacetate.* An oily fraction, on standing, changed into a crystalline mass. This was recrystallised from carbon bisulphide. Anal. Found: C=56.83; H=5.53%. Calc. for $C_6H_7O_3$: C=56.67; H=5.55%. Melting point: 77°. Molecular weight: about 220. If $C_{12}H_{14}O_6$ be the molecular formula of the substance, it is less C_2H_6O or C_2H_5OH than a triethyl acetyl-carboxy-glutaconate $C_{14}H_{20}O_7$, one of the expected products of this condensation. It is, therefore, most natural to suppose the formation of a triethyl acetyl-carboxy-glutaconate, the product of the first or the second kind, and to consider the substance $C_{12}H_{14}O_6$ a derivative of resorcine produced by the following reactions:



Besides the above substance, diethyl α, γ-diacetyl-glutaconate was isolated. Anal. Found: C=57.67, 57.59; H=6.69, 6.70%. Calc. for $C_{13}H_{18}O_6$: C=57.78; H=6.67%. Melting point: 93°. The melting point observed by Claisen is 96°.

Further tetraethyl α,γ-dicarboxyglutaconate was isolated. Anal. Found: C=54.68; H=6.74%. Calc. for $C_{15}H_{22}O_8$: C=54.51; H=6.72%.

4. *Condensation of ethyl ethoxymethylene-acetoacetate with diethyl sodio-malonate.* From the fraction which was expected to be consisted of diethyl diacetylglutaconate an oil giving the following analytical results

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(1) Cf. Feist, loc. cit.

was obtained. Anal. Found: C=57.57; H=6.39%. This seems to have been impure diethyl diacetyl-glutaconate.

The same resorcine derivative as obtained in condensation 3 was isolated. Anal. Found: C=56.75; H=5.63%. This indicates the formation of a triethyl acetyl-carboxy-glutaconate; but, as the isolated substance $C_{12}H_{14}O_6$ is not the direct product, it is impossible to determine whether this triethyl acetyl-carboxy-glutaconate is the first kind or the second, and whether it is identical with the triethyl acetyl-carboxy-glutaconate of condensation 3.

Further tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.42; H=6.73%.

5. *Condensation of diethyl ethoxymethylene-malonate with sodio-acetylacetone.* An oily compound giving an analytical result corresponding to diethyl α,α-diacetyl-propylene-γ,γ-dicarboxylate or to diethyl γ,γ-diacetyl-propylene-α,α-dicarboxylate was isolated. Anal. Found: C=57.61, 57.13; H=6.63, 6.66%. Calc. for $C_{13}H_{18}O_6$: C=57.78; H=6.67%.

Tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.76; H=6.76%.

6. *Condensation of ethoxymethylene-acetylacetone with diethyl sodiomalonate.* An oil corresponding in analysis to diethyl α,α-diacetyl-propylene-γ,γ-dicarboxylate or to diethyl γ,γ-diacetyl-propylene-α,α-dicarboxylate was isolated. It could not be determined whether this was identical with the substance obtained in condensation 5 or not. Anal. Found: C=57.61, 57.43; H=6.66, 6.66%.

Tetraethyl dicarboxyglutaconate was isolated. Anal. Found: C=54.22; H=6.66%.

7. *Condensation of ethyl ethoxymethylene-acetoacetate with sodio-acetylacetone.* Diethyl α,γ-diacetylglutaconate was isolated. Anal. Found: C=57.80; H=6.66%.

8. *Condensation of ethoxymethylene-acetylacetone with ethyl sodioacetoacetate.* Diethyl α,γ-diacetylglutaconate was isolated. Anal. Found: C=57.76; H=6.55%. Melting point: about 92°.

The same condensation as condensation 4, that is the condensation of ethyl ethoxymethylene-acetoacetate with diethyl sodio-malonate, was carried out in alcohol. Diethyl α, γ-diacetylglutaconate (C=57.80; H=6.63%), the product of the fourth kind, and tetraethyl α, γ-dicarboxyglutaconate (C=54.37; H=6.69%), the product of the third kind, were isolated. This experiment shows that there is no fundamental difference between the condensations in alcohol and those in ether.

The author expresses his hearty thanks to Prof. K. Matsubara for his kind inspection of this paper.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. VI.

By **Tetsuya ISHIKAWA.**

Received February 15, 1930. Published April 28, 1930.

In an earlier paper,(1) the writer reduced Dunstan and Wilson's equation connecting logarithms of the absolute viscosity and the molecular weight into a form:

$$\log\eta = -3.22 + bM$$

(where η and M are the viscosity coefficient and the molecular weight of a liquid, and b is a particular constant for the particular liquid, depending upon the temperature) and showed that the values of b and the field-constant k are practically the same when both are compared with those for benzene.

Other formulas showing the relation between the viscosity coefficient and the molecular weight have been proposed by Gartenmeister(1) and Macleod.(3)

Gartenmeister deduced the following relation from his careful determinations of the absolute viscosity of various liquids:

$$\eta = k_G\ M, \quad\dots\dots\dots\dots(1)$$

where k_G is a particular constant within the observed temperature range for chlorine, bromine and iodine substitution compounds.

For those which do not obey the rule such as homologous series in which successive members differ by CH_2, he took M^2 in place of M, but the constancy of their proportional constants are not satisfactory.

Macleod, having drawn attention to the fact that the relation between the viscosity of liquids and their coefficients of expansions and densities can be explained on the assumption that the viscosity is a simple function of the free space within the liquid, proposed the expression:

$$\eta_t x_t^A = C,$$

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(1) This Bulletin, **4** (1929), 149.

(2) R. Gartenmeister, *Z. physik. Chem.*, **6** (1890), 524.

(3) D. B. Macleod, *Trans. Faraday Soc.*, **19** (1923), 6; **21** (1925), 145 and 151.

where η_t is the viscosity at a temperature t, x_t the free space at that temperature, C is a constant for the particular liquid, and A is approximately unity for unassociated substances. In this calculation he assumed that the expansion is wholly confined to the free space and the volume of the molecules remains constant, and put

$$x_t = x_0 + \frac{v_t}{v_0} - 1,$$

in which x_0 is the free space at 0°; v_t and v_0 are the specific volumes at t° and 0° respectively.

Macleod further observed that by putting A as unity (which causes no serious error in finding x_0 for normal liquids) C is proportional to the molecular weight. He applied this method of calculation to any liquid, in this case, however, the discrepancy of the proportional constant from the value obtained for such a normal liquid as octane he attributed to the molecular complexity of the liquid and put forward the expression:

$$\eta = \frac{k_M a_M}{x}, \quad \dots\dots \quad (2)$$

where a is the degree of association and k_M is a constant for all liquids.

Comparing the equal terms in expressions (1) and (2), we get

$$k_G x = k_M a$$

With the object of testing which of the values k_G or $k_G\ x$ gives more constancy, the present writer will make use of the values at 0°C. tabulated by Macleod in his paper.(1)

Table 1.

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot k_G \cdot x_0$
C_2H_5Br	0·00478	109·0	0·1080	4·39	4·74
C_3H_7Br	0·00645	123·0	0·0908	5·24	4·76
i-C_3H_7Br	0·006045	123·0	0·0923	4·92	4·54
i-C_4H_9Br	0·008235	137·0	0·0829	6·01	4·98
CH_3I	0·005945	142·0	0·0967	4·19	4·05
C_2H_5I	0·00719	156·0	0·0907	4·61	4·18
C_3H_7I	0·00938	170·0	0·0782	5·52	4·31
i-C_3H_7I	0·008785	170·0	0·0836	5·17	4·32

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(1) D. B. Macleod, *Trans. Faraday Soc.*, **21** (1925), 154–155.

Table 1.—(*Continued*)

Substance	η_0	M	x_0	$10^5\cdot k_G$	$10^6\cdot x_0$
C_5H_{12}	0·00283	72·1	0·1207	3·93	4·74
i-C_5H_{12}	0·00273	72·1	0·1202	3·79	4·55
C_6H_{14}	0·003965	86·1	0·0979	4·60	4·51
i-C_6H_{14}	0·00371	86·1	0·1054	4·31	4·54
C_7H_{16}	0·00519	100·1	0·0863	5·19	4·48
i-C_7H_{16}	0·00477	100·1	0·0883	4·77	4·21
C_8H_{18}	0·00703	114.1	0·0744	6·16	4·58
CH_3OH	0·00813	32·0	0·0580	25·4	14·7
C_2H_5OH	0·01770	46·0	0·0450	38·5	17·3
C_3H_7OH	0·03882	60·0	0·0233	64·7	15·1
i-C_3H_7OH	0·04564	60·0	0·0252	76·0	19·1
C_4H_9OH	0·05185	74·0	0·0248	70·0	17·4
i-C_4H_9OH	0·08038	74·0	0·0243	108·6	26·4
$HCOO\cdot CH_3$	0·00429	60·0	0·0994	7·15	7·11
$HCOO\cdot C_2H_5$	0·00505	74·0	0·0936	6·83	6·39
$HCOO\cdot C_3H_7$	0·00668	88·0	0·0768	7·59	5·83
$CH_3CO_2\cdot CH_3$	0·00478	74·0	0·0974	6·46	6·29
$CH_3CO_2\cdot C_2H_5$	0·00578	88·0	0·0820	6·57	5·39
$CH_3CO_2\cdot C_3H_7$	0·00770	102·0	0·0700	7.55	5·28
$H\cdot COOH$	0·02245	46·0	0·0356	48·8	17·4
$CH_3\cdot COOH$	0·01219	60·0	0·0564	20·3	11·5
$CH_3\cdot CH_2\cdot COOH$	0·01519	74·0	0·0563	20·5	11·5
$CH_3(CH_2)_2\cdot COOH$	0·02284	88·0	0·0417	26·0	10·8
$(CH_3)CH\cdot COOH$	0·01885	88·0	0·0463	21·4	9·92
$CH_3\cdot CO\cdot CH_3$	0·00394	58·0	0·1134	6·79	7·70
$C_2H_5\cdot CO\cdot CH_3$	0·005385	72·0	0·0827	7·48	6·19
$C_2H_5\cdot CO\cdot C_2H_5$	0·00595	86·1	0·0800	6·91	5·53
$C_3H_7\cdot CO\cdot CH_3$	0.00644	86·1	0·0754	7·48	5·64
C_6H_6	0·009025	78·0	0·0585	11·6	6·77
$C_6H_5CH_3$	0·007685	92·0	0·0642	8·35	5·36
$C_6H_5C_2H_5$	0·00874	106·0	0·0545	8·24	4·49
o-$C_6H_4(CH_3)_2$	0·011025	106·0	0·0486	10·4	5·06
m-$C_6H_4(CH_3)_2$	0·00802	106·0	0·0597	7·57	4·52

Table 1.—(*Continued*)

Substance	η_0	M	x_0	$10^5 \cdot k_G$	$10^6 \cdot k_G \cdot x_0$
CS_2	0·004295	76·0	0·1206	5·65	6·81
$(CH_3)_2S$	0·00354	62·0	0·1150	5·71	6·57
$(C_2H_5)_2S$	0·00559	90·0	0·0863	6·21	5·36
$C_2H_5 \cdot O \cdot C_2H_5$	0·00286	74·1	0·1234	3·86	4·76
$C_3H_7 \cdot O \cdot CH_3$	0·00307	74·1	0·1272	4·14	4·86
$C_3H_7 \cdot O \cdot C_2H_5$	0·003965	88·0	0·0994	4·50	4·48
$C_3H_7 \cdot O \cdot C_3H_7$	0·00540	102·0	0·0816	5·29	4·32
i-$C_4H_9 \cdot O \cdot CH_3$	0·00381	88·0	0·1018	4·33	4·41
i-$C_4H_9 \cdot O \cdot C_2H_5$	0·00482	102·0	0·0887	4·73	4·19

It is easily understood from the above table that Gartenmeister's exceptional cases, to which homologous series such as alcohols and acids belong, are sufficiently expressed by the formula $\eta = KM$, K being corrected for Macleod's free space and that for some substitution compounds such as formates and ketones more constancy of the values of the proportional constants is obtained by Gartenmeister's formula than by Macleod's. In short, it being difficult to justify which is the superior of the two so far as the present data are concerned, it seems highly probable, in accordance with the physical meaning that the viscosity is due to a transport of momentum, (i) that the viscosity η is proportional to the molecular weight M and (ii) that the proportional constant K in the expression $\eta = KM$ is a particular constant which plays a very important part.

Brillouin,⁽¹⁾ who made a success to interpret the negative temperature coefficient of viscosity of liquids from a theoretical standpoint of view, assumed that in liquids where the molecules are continually in collision and where the transfer of matter (diffusion) is ordinarily insignificant, when a molecule strikes all of the molecules in the vicinity are shaken and an elastic wave is found which is propagated through the medium, or, in other words, the molecules of liquids are never free and always under strong forces.

This intensity of attraction field must of course be taken into consideration in studying the viscosity of liquids. If the viscosity of a liquid is stoichiometrically related with the molecular weight as in the expression :

$$\eta = KM$$

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(1) L. Brillouin, *J. phys. radium* [6] **3** (1922), 326 and 362.

the factor depending on the intensity of attraction field may be included in no other than the constant K.

According to Macleod's idea the constant K depends on the free space and the relative value K of a liquid to K of octane is simply equal to the degree of association of the liquid, for which, however as stated above, his deduction formula $\eta\ x=$const. (x being the free space) does not hold true.

For a further test the comparison among the particular constants at 0°C. (relative to those for benzene) calculated from the three formulas of Dunstan and Wilson, of Gartenmeister and of Macleod will be made in the following.

Table 2.

Substance	$\frac{(b)C_6H_6}{b}$	$\frac{(k_G)C_6H_6}{k_G}$	$\frac{(k_G\cdot x)C_6H_6}{k_G\cdot x}$
C_6H_6	1	1	1
$C_6H_5CH_3$	1·25	1·39	1·26
$CH_3GO_2C_2H_5$	1·35	1·76	1·26
$CHCl_3$	1·69	1·98	1·22
CCl_4	1·72	1·32	1·29
CS_2	1·34	2·05	0·99
CH_3OH	0·43	0·46	0·46
C_2H_5OH	0·47	0·30	0·39
H_2O	0·18	0·12	0·33
CH_3COOH	0·69	0·57	0·59

Though a quite satisfactory coincidence among the constants may not be hoped for, yet it is probable that they are the equivalent quantities with one another and are consequently the corresponding factors with the writer's field-constant k.(1) Similar consideration as above shown, if it extends to binary mixtures, accords with the writer's theory.(2)

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Tokyo.

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(1) This Bulletin, **4** (1929), 149.
(2) This Rulletin, **4** (1929), 5.

COLLOIDAL SYNTHESIS OF CERTAIN READILY CRYSTALLIZABLE ORGANIC COMPOUNDS.(1)

By Nadine von WEIMARN.

Received March 2, 1930. Published April 28, 1930.

Compounds Studied up to the Present. The Methods of Preparation of their Colloidal Solutions.

The colloidal synthesis of those organic compounds, which are obtained under ordinary conditions in crystals clearly seen by the naked eye, has not been extensively studied.(2)

Below are summed up the general results of the colloidal synthesis of eight organic compounds (naphthalene, papaverine, camphor, salol, benzophenone, anthracene, anthraquinone and phenanthrene). In the near future the list will be enlarged.

Two methods of colloidal synthesis were employed: A. The cooling of a solution.(3) B. The replacing of one dispersion medium by another.(4)

General Results.

1. The first of the above five organic compounds give *stable* colloidal solutions only at *low* temperatures (e.g.–80°C.), in dispersion media consisting of concentrated (e.g. 68 per cent.) aqueous sucrose solutions congealed to glasses.

2. Colloidal anthracene solutions stable for not less than several months, are easily obtained e.g. by pouring into large volumes (99–495 c.c.) of distilled water of room temperatures, from one to several c.c. of alcoholic anthracene solutions (0.005–0.25 per cent).

3. Colloidal anthraquinone solutions obtained by pouring its alcoholic solutions into distilled water of room temperatures, are less stable than colloidal anthracene solutions. Colloidal phenanthrene solutions are very unstable at room temperatures, owing to the greater solubility of phenanthrene in water. Colloidal solutions of anthraquinone and phenanthrene of a markedly longer stability may be obtained at low temperatures, at about

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(1) For more details, see *Kolloid-Z.*, **50–51** (1930), 164 etc.

(2) P. P. von Weimarn, "Die Allgemeinheit des Kolloidzustandes," I (1925), 228.

(3) P. P. von Weimarn, "Grundzüge der Dispersoidchemie," (1911), 69.

(4) P. P. von Weimarn, "Grundzüge der Dispersoidchemie," (1911), 67.

0°C. or lower, with water or weak aqueous sucrose solutions as dispersion media.

4. Anthracene and phenanthrene readily form disperse systems, the particles of the disperse phases of which are not three-dimensionally colloid, as is usual, but *monodimensionally* colloid, because the lengths and breadths of the disperse particles, crystalline lamellae, are of microscopical dimensions. Anthraquinone gives easily disperse systems, the disperse particles of which are *bidimensionally* colloid. The lengths of the disperse particles, crystalline needles, considerably exceed the ultramicroscopic size. The structure of these disperse particles was defined by ultramicroscopical observations of P.P. von Weimarn.

5. Micro-and ultramicroscopic observations by P.P. von Weimarn on benzophenone and salol disperse systems, obtained at room temperatures, have shown that these disperse systems, in the first stage of their existence, are emulsoids or emulsions ; later on they pass into suspensoids and suspensions. These observations can be generalized for the colloidal systems of other organic substances with relatively low melting points.

I wish to express here my gratitude to my husband, Prof. Dr. P.P. von Weimarn for suggesting the theme of this investigation as well as for his guidance and help in every way during the work.

My acknowledgements are due also to Dr. Eng. I. Shoji, President of the Imperial Industrial Research Institute of Osaka.

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART I.

By Susumu MIYAMOTO and Tetsuo KAYA.

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Introduction. One of the authors(1) had studied the oxidation velocities of sodium sulphite, stannous hydroxide and ferrous hydroxide in alkaline or in acidic solutions by means of air and found that the observed velocities

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(1) S. Miyamoto, this Bulletin, **2** (1927), 74; **2** (1927), 155; **2** (1927) 259; **3** (1928), 76; **3** (1928), 137; **4** (1929), 48. *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40; **7** (1927), 189; **8** (1928), 93; **8** (1928), 230; **9** (1928), 203; **10** (1929), 7.

were independent of the concentrations of these oxidizable substances under the conditions of the author's experiments. The results were interpreted by the consideration that the dissolution velocity of oxygen is much slower than the true reaction velocity and the observed value will mean the dissolution velocity of oxygen into the liquid.

The phenomenon is a special case of the heterogeneous reaction between gaseous and liquid phases and the mechanism can be explained by the following considerations.

The difference between the number of molecules of a gas which enter into the liquid phase and the number of molecules of the gas which leave the liquid phase through definite boundary surface area per unit of time can be called the dissolution velocity of the gas into the liquid at the given temperature and pressure. It is evident that the dissolution velocity of a gas into a liquid depends upon the partial pressure of the gas and the nature of the boundary surface. We can then expect that the dissolution velocity of a gas into a given liquid at the given temperature and pressure will have a maximum value when the concentration of the gas in the boundary surface is kept zero.

This state can be maintained if the sufficient quantity of a substance be present in the surface layer to react with all of the molecules of the gas which enter into the liquid phase per unit of time. Under this condition, the dissolution velocity of the gas will be independent of the concentration of the reacting substances, if the presence of the necessary quantity of the latter in the surface have not much effect upon the nature of the boundary surface. The reaction velocity of the substance with the gas will also be maximum under this condition, and it can not increase however its concentration is increased, as the reaction velocity with the gas can not be greater than the maximum dissolution velocity of the gas into the liquid.

The phenomenon is in some degree analogous to that of the saturation current conducted by electrons emitted by a heated body in an electric field. The current can not be greater than a definite value however the strength of the field is increased, if the temperature of the heated body be kept constant.

Under the conditions of the present research, the oxidation velocity of sodium sulphite solution by means of air is independent of its concentrations. According to the viewpoint, above described, the result should mean the maximum reaction velocity of the solution with air at the given temperature, and the dissolution velocity of oxygen into water, obtained from the result, should mean the maximum dissolution velocity of oxygen into water at the given temperature and pressure.

Mitsukuri(1) has explained the dissolution velocity of carbon dioxide into sodium hydroxide solution by the consideration that the reaction takes place in the thin liquid surface layer. The result of this investigation will also be able to interprete by Mitsukuri's theory, if we only consider the thickness of the diffusion layer of oxygen is extremely small and the concentration of the reacting substance is sufficiently great. It will be impossible to decide whether it is necessary to assume the existence of the liquid film at the surface in order to interprete the present results.

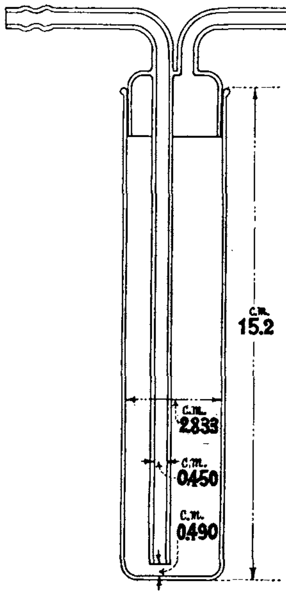

Fig. 1

Experimental. The oxidation velocities of sodium sulphite solution were observed when air is passed at various velocities. The experimental procedure is quite the same as that described in the previous papers.(2) The reacting vessel employed is shown in Fig. 1. Air, washed by acidified potassium bichromate solution and alkali, was passed at uniform velocity into the solution of sodium sulphite of known concentration, the total volume of the solution being made to 40 c.c. in each case. After t-minutes, the air current was stopped and the total quantity of the solution was poured into a known quantity of iodine solution, acidified with hydrochloric acid, and the excess of iodine was titrated back by means of sodium thiosulphate solution, v in the following tables, being the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite.

The values of k are calculated by $k=\frac{1}{t-t_0}(v_0-v)$, v_0 being the value of v at $t=t_0$. The values of $v_{calc.}$ given in the tables were obtained by the equation $v_{calc.}=v_0-k\ (t-t_0)$, using the mean value of k.

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(1) S. Mitsukuri, *The Science Reports of the Tohoku Imperial University*, Series 1, Vol. 18, No. 2. (June 1929).

(2) Loc. cit.

Table 1.

Temp. = 25°C.

Velocity of air c.c. / min.	*t* min.	*v* c.c.	$v_{calc.}$ c.c.	*k*.
30.5	3	19.83	—	—
	23	17.54	17.63	0.115
	43	15.21	15.43	0.116
	3	27.71	—	—
	23	25.39	25.51	0.116
	43	23.31	23.31	0.110
	3	33.68	—	—
	24	31.21	31.37	0.118
	43	29.17	29.28	0.113
	3	38.32	—	—
	23	36.10	36.12	0.111
	43	34.01	33.92	0.108
	3	47.50	—	—
	21	45.65	45.52	0.103
	41	43.39	43.32	0.108
	3	52.37	—	—
	23	50.49	50.17	0.094
	43	48.19	47.97	0.105
			Mean	0.110
60.3	3	19.45	—	—
	23	16.23	16.11	0.161
	43	12.99	12.77	0.162
	3	27.58	—	—
	23	24.24	24.24	0.167
	43	20.97	20.90	0.165
	3	34.49	—	—
	23	31.01	31.15	0.174
	43	27.67	27.81	0.171
	3	40.66	—	—
	23	37.14	37.32	0.176
	43	33.83	33.98	0.171
	3	47.60	—	—
	23	44.24	44.26	0.168
	43	41.11	40.92	0.162
	3	54.03	—	—
	23	50.80	50.69	0.162
	43	47.42	47.35	0.165
			Mean	0.167

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v. c c.	$v_{calc.}$ c.c.	k.
86.7	3	16.32	—	—
	23	12.24	12.14	0.204
	43	7.49	7.96	0.221
	3	17.66	—	—
	43	9.16	9.30	0.213
	3	18.89	—	—
	23	14.95	14.71	0.197
	43	9.91	10.53	0.225
	3	20.01	—	—
	23	15.76	15.83	0.213
	43	11.70	11.65	0.208
	3	23.82	—	—
	23	19.82	19.64	0.200
	43	15.40	15.46	0.210
	3	26.53	—	—
	23	22.27	22.35	0.213
	43	18.62	18.17	0.198
	3	27.52	—	—
	23	23.59	23.34	0.197
	43	19.25	19.16	0.202
	3	30.21	—	—
	23	26.06	26.03	0.208
	43	22.18	21.85	0.202
	3	33.21	—	—
	23	28.95	29.03	0.213
	43	24.58	24.85	0.216
	3	33.68	—	—
	7	32.84	32.84	0.210
	28	28.21	28.45	0.219
	3	41.46	—	—
	23	37.68	37.28	0.189
	43	33.18	33.10	0.207
	3	46.60	—	—
	23	42.27	42.42	0.217
	43	38.01	38.24	0.215
	3	51.26	—	—
	23	46.99	47.08	0.214
	44	42.20	42.69	0.221
			Mean	0.209

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
111.7	3	16.60	—	—
	23	11.77	11.58	0.242
	43	7.07	6.58	0.238
	3	18.91	—	—
	23	14.11	13.89	0.240
	43	8.49	8 87	0.261
	3	22.20	—	—
	43	12.57	12.16	0.241
	3	22.58	—	—
	23	17.43	17.56	0.258
	43	12.20	12.54	0.260
	3	24.82	—	—
	23	19.80	19.80	0.251
	43	14.27	14.78	0.264
	3	28.64	—	—
	23	23.78	23.62	0.243
	43	18.47	18.60	0.254
	3	28.87	—	—
	23	24.04	23.85	0.242
	43	18.40	18.83	0.262
	3	32.70	—	—
	23	27.77	27.68	0.247
	43	21.98	22.66	0.268
	3	40.01	—	—
	23	35.06	34.99	0.248
	43	30.00	29.97	0.250
			Mean	0.251
137.0	3	20.90	—	—
	43	8.54	9.06	0.309
	3	23.00	—	—
	23	17.16	17.08	0.292
	43	11.87	11.16	0.278
	3	31.01	—	—
	23	24.95	25.09	0.303
	43	18.48	19.17	0.313
	3	35.16	—	—
	23	29.40	29.24	0.288
	43	23.70	23.32	0.287
	3	39.77	—	—
	43	28.16	27.93	0.290
	3	44.93	—	—
	43	33.29	33.09	0.291
	3	45.13	—	—
	23	39.25	39.21	0.294
	43	33.07	33.29	0.302
	3	52.15	—	—
	23	46.22	46.23	0.297
	43	40.37	40.31	0.295
	3	58.72	—	—
	23.5	52.58	52.65	0.300
	43.5	46.52	46.73	0.301
			Mean	0.296

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
160.8	3	21.80	—	—
	43	8.34	8.48	0.337
	3	22.50	—	—
	23	16.19	15.84	0.316
	43	9.90	9.18	0.315
	3	31.17	—	—
	23	24.61	24.51	0.328
	43	17.69	17.85	0.337
	3	33.43	—	—
	43	20.41	20.11	0.326
	3	38.75	—	—
	23	32.29	32.09	0.323
	43	24.89	25.43	0.347
	3	43.33	—	—
	43	29.97	30.01	0.334
	3	45.51	—	—
	23	38.75	38.85	0.338
	43	32.13	32.19	0.335
	3	55.96	—	—
	23	49.17	49.30	0.340
	43	42.46	42.64	0.338
	3	57.22	—	—
	42	43.44	44.23	0.353
			Mean	0.333
182.8	3	31.29	—	—
	43	17.07	17.01	0.356
	3	31.67	—	—
	43	17.30	17.39	0.359
	3	52.78	—	—
	43	38.80	38.50	0.350
	3	58.22	—	—
	43	43.51	43.94	0.368
	3	68.88	—	—
	43	54.72	54.60	0.354
			Mean	0.357

Table 1.—(*Continued*).

Velocity of air c.c. / min.	t min.	v c.c.	$v_{calc.}$ c.c.	k.
201.8	3	34.20	—	—
	23	26.40	26.22	0.390
	43	17.77	18.24	0.411
	3	42.41	—	—
	43	26.09	26.45	0.408
	3	45.65	—	—
	23	37.85	37.67	0.390
	43	29.82	29.69	0.396
	3	45.76	—	—
	43	29.72	29.80	0.401
	3	50.26	—	—
	23	42.12	42.28	0.407
	43	34.51	34.30	0.394
	3	50.94	—	—
	43	34.36	34.98	0.415
	3	58.41	—	—
	23	50.64	50.44	0.389
	43	42.17	42.46	0.406
	3	66.93	—	—
	43	51.66	50.97	0.382
			Mean	0.399

Table 2.

Temp.=25°C.

V (Velocity of air) c.c./min.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles/min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles/min.
30.5	0.110	0.115	2.75×10^{-6}	2.89×10^{-6}
60.3	0.167	0.165	4.18 „	4.12 „
86.7	0.209	0.208	5.23 „	5.20 „
111.7	0.251	0.249	6.28 „	6.23 „
137.0	0.296	0.291	7.40 „	7.28 „
160.8	0.333	0.330	8.33 „	8.26 „
182.8	0.357	0.366	8.93 „	9.16 „
201.8	0.399	0.398	9.98 „	9.95 „

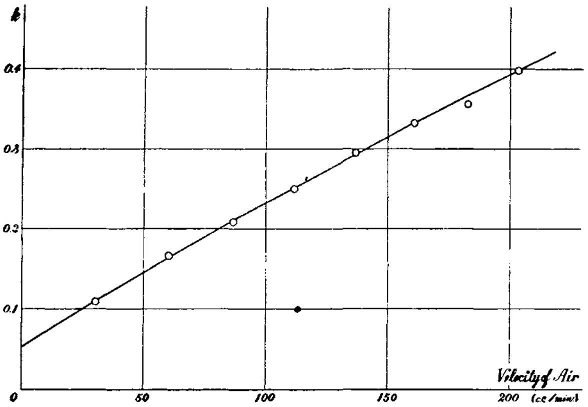

Fig. 2.

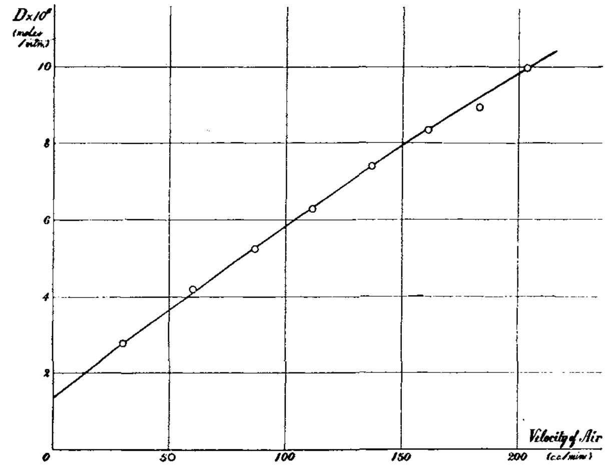

Fig. 3.

The oxidation velocity observed is thus independent of the concentration of sodium sulphite. According to the viewpoint above described, the observed value is the maximum oxidation velocity of sodium sulphite by means of air.

From the results it can be seen that the velocity constant is a linear function of the velocity of air passed, as is shown graphically in Fig. 2. The values of $k_{calc.}$ given in the third column of Table 2, were calculated by

$$k_{calc.}=0.001648V+0.0652 \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where V is the velocity of air passed.

The observed velocity constant k means the volume of sodium thiosulphate solution of 0.1000 normal equivalent to the amount of sodium sulphite oxidized per minute. Then the dissolution velocity of oxygen into water under this special condition can be expressed by

$$D_{obs.}=\frac{1}{4}k_{obs.}\times 10^{-4} \text{ moles per minute.} \quad\ldots\ldots\ldots\ldots \quad (2)$$

The calculated values of D by this equation are given as $D_{obs.}$ in the fourth column of Table 2. It is evident that $D_{obs.}$ is a linear function of the velocity of air passed in this case. It is shown graphically in Fig. 3. The values of $D_{calc.}$ given in the last column of Table 2 are those calculated by

$$D_{calc.}=4.121\times 10^{-8}V+1.630\times 10^{-6} \quad\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Theoretical. According to the kinetic theory of gases, total number of molecules which collide with unit boundary surface area per unit of time can be expressed by

$$\frac{NP}{\sqrt{2\pi MRT}} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where N = Avogadro's constant,
P = partial pressure of the gas,
M = molecular weight of the gas,
R = the gas constant,
T = absolute temperature.

Total number of molecules which enter into the liquid phase per unit of time through unit boundary surface area can be expressed by

$$\frac{\alpha NP}{\sqrt{2\pi MRT}} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where α is a quantity which depends upon the nature of the gas and the liquid and the partial pressure of the gas. With regard to one liquid, in the surface of which the concentration of the gas is kept zero, α may be represented by

$$\alpha=f(P) \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Under this condition α may be taken to be constant if the partial pressure of the gas be constant.

The total boundary surface area which is in contact with the gas can be represented in the present experiment by

$$4\pi r^2 n\frac{l}{u}+s_0 \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (7)$$

where r=radius of a bubble,
n=number of bubbles passed per second,
l=the depth of the center of a bubble when it just leaves the exit,
u=the ascending velocity of the bubble,
s_0=the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

From (5) and (7) we can represent the total number of molecules which enter into the liquid phase per second by

$$\frac{aNP}{\sqrt{2\pi MRT}}\left(4\pi r^2 n\frac{l}{u}+s_0\right) \quad\dots\dots\dots\dots\dots\dots \quad (8)$$

The dissolution velocity of the gas can then be represented by

$$D=\frac{60aP}{\sqrt{2\pi MRT}}\left(4\pi r^2 n\frac{l}{u}+s_0\right) \text{ moles per minute.} \quad\dots\dots \quad (9)$$

when the concentration of the gas in the surface layer is kept zero.
Now,

$$n=\frac{1}{60}\,\frac{V}{\frac{4}{3}\pi n^3} \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (10)$$

where V denotes the volume of the gas passed per minute.

Then,

$$D=\frac{60aP}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \text{ moles per minute.} \quad\dots\dots \quad (11)$$

Under the conditions of this research, the dissolution velocity of oxygen should be regarded as the maximum value, and the value of a can be considered to have a definite maximum value. As the values of P, T, r, and u are constant, from the equation (11) we have,

$$D=AV+B \quad\dots\dots\dots\dots\dots\dots\dots\dots \quad (12)$$

where A and B are constants.

From (2) and (11) we have,

$$k=\frac{24aP\times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad\dots\dots\dots\dots\dots\dots \quad (13)$$

Under the present conditions,

$$k=A'V+B' \qquad (14)$$

where A' and B' are constants.

The equations (12) and (14) are in good agreement with the experimental facts, above described.

The calculation of the values of α *and* s_0. The value of α in the above equations depends upon the condition of the boundary surface and the partial pressure of the gas. If the concentration of the gas in the surface layer be kept zero, α will have a definite specific value with regard to the liquid and gas. From the present experimental results we can calculate the maximum value of α concerning water and oxygen, whose partial pressure is 15.96 cm. Hg.

From the equations (3) and (11) we obtain,

$$\frac{3\alpha Pl}{r\,u\sqrt{2\pi MRT}}=4.121\times10^{-8} \qquad (15)$$

If we know the values of l, r, and u we can calculate the value of α from the equation (15).

The value of r was obtained by the following process. Air was passed into the reacting vessel from a gas burette at uniform velocity. From the volume of air passed, we can calculate the radius of one bubble by counting the number of bubbles. A slight difference of the radius of the bubble was observed, when we change the velocity of air passed. The mean value of the radius of a bubble was found to be 0.334 cm. when the mean value of the velocity of air passed is about 19.64 c.c. per minute. This value was employed for the calculation as an approximate value of the radius of a bubble.

According to the study on the motion of an air bubble rising in water by O. Miyagi,(1) the ascending velocity of an air bubble attains an uniform value almost immediately when it leaves the exit, and the ascending velocity is 23.1 cm. per second when the radius of the bubble is 0.334 cm. As the viscosity of sodium sulphite solution of such concentration as that employed in the present research is not much different from that of pure water, it can be expected that the ascending velocity of the air bubble in the solution will nearly be the same as that in pure water. The value 23.1 cm. per second was employed as an approximate value of u in the following calculations.

The value of l was observed directly to be 6.20 cm.

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(1) *Phil. Mag.*, **50** (1925), 112.

By introducing these values in the equation (15) we have,

$$\alpha=\frac{4.121\times10^{-8}r\,u\sqrt{2\pi MRT}}{3Pl}=1.794\times10^{-7}$$

This value means the ratio of the total number of the molecules of oxygen which enter into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time when the partial pressure of oxygen is about 0.21 atmosphere, the concentration of oxygen in the surface being maintained to be zero. The obtained value of α is the definite specific value with regard to water and oxygen at the given temperature and pressure.

The present chemical method will be able to employ in order to calculate the value of α with regard to various liquids and gases.

From the equations (3) and (11) we have,

$$\frac{60\alpha P}{\sqrt{2\pi MRT}}s_0=1.630\times10^{-6}$$

By introducing the value of α above obtained,

$$s_0=1.59\text{ cm.}^2$$

The calculated value of s_0 from Fig. 1 is about 5 cm.^{2} It is not curious that the calculated value of s_0 is much smaller than this value, for the most part of the upper surface of the liquid is occupied by the surface of the bubbles passed incessantly.

Summary.

(1) The oxidation velocity of sodium sulphite solution was observed when air is passed at various velocities.

(2) It was found that the oxidation velocities are independent of the concentration of sodium sulphite and the velocity constant was expressed as a linear function of the velocity of air passed.

(3) The dissolution velocity of oxygen into water when the concentration of oxygen in the surface layer is kept zero, was calculated from the obserbed reaction velocity, and it was found to be expressed as a linear function of the velocity of air passed.

(4) An interpretation of the mechanism of this reaction under the observed conditions was given.

(5) The maximum value of the ratio of the total number of molecules of oxygen which enter into water to the total number of molecules of oxygen which collide with the unit boundary surface per unit of time at 25° C. was calculated from the observed results.

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ON THE THERMAL DECOMPOSITION OF CRESOLS.

By Risaburo NAKAI.

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It is a well known fact that the constituents of coal tar vary with the conditions under which coal is treated; the tar obtained from coals by low temperature carbonisation contains much cresol and no phenol nor benzene or merely traces, while the tar produced by high temperature distillation has less cresol but much phenol, benzene and toluene.[1] These facts suggest that at a high temperature, cresol should decompose into benzene, toluene and phenol as illustrated in the following scheme:

$$
\begin{array}{lll}
 & \nearrow C_6H_5OH + CH_3 \quad \text{demethylation} & (1) \\
C_6H_4CH_3OH & \rightarrow C_6H_5CH_3 + H_2O \quad \text{dehydration} & (2) \\
 & \searrow C_6H_6 + H_2O + CH_3 \quad \text{dehydration \& demethylation} & (3)
\end{array}
$$

On referring to the literature on the present subject, we noticed that J. Kraemer[2] has confirmed phenol by passing it through a glass or iron tube heated to a red heat, and it was decomposed into benzene and higher aromatic hydrocarbons. The removal of oxygen from phenol was also noted by W. Smith,[3] when phenol or cresol was introduced into a glowing glass tube, filled with charcoal or iron filings, a small amount of benzene or toluene was produced together with a large amount of gaseous substances. On bringing phenol vapour into contact with a heated platinum wire, H.

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[1] A. Warnes, "Coal tar distillation" (1923), 65; C. Lander and R. MacKay, "Low temperature carbonisation" (1924), 71, 79; H. Strache und R. Lant, "Kohlenchemie" (1924), 381; F. Wirth, "Brennstoff Chemie" (1926), 396.

[2] J. Kraemer, *Ann.*, **189** (1877), 129.

[3] W. Smith, *J. Soc. Chem. Ind.* **9** (1890), 447.

Meyer⁽¹⁾ has identified benzene in the reaction product. Demethylation of cresol was reported by F. Fischer⁽²⁾; according to his report, cresol vapour passed with hydrogen or carbon monoxide through a tube heated to 700°–800°C., yields phenol as well as benzene. E. Müller⁽³⁾ has reported that cresol, when passed through an iron tube heated to 700°–800°C., was found to decompose chiefly into methane, carbon monoxide, hydrogen and carbon, and a small amount of benzene and tarry matter were also produced, and that the proportion of the chief reaction products is as follows:

$$C_6H_4CH_3OH \longrightarrow CO+CH_4+2H_2+5C.$$

1. The Thermal Decomposition of *m*-Cresol. The writer's supposition for the thermal decomposition of the cresol, which was mentioned above, was partly confirmed by the experiments of many investigators in subjecting phenol to a high temperature with or without catalysts. However, the mechanism and conditions for the formation of benzene, toluene and phenol from cresol remained in a state of uncertainty. The present research was undertaken with the intention of obtaining confirmation of the true nature of the pyrogenic decomposition of cresols and also to settle the conditions under which the hydrocarbons and phenol are formed.

The best method of utilizing the tar acids composing the major part of the tar formed by the low temperature carbonization of coals, a matter which concerns the important problem of the economical uses of coals as fuel, will naturally be acquired from the study of the pyrogenic reaction of cresols.

In the experiment, *o*-, *m*-, and *p*-cresols were passed, at the rate of 3.5–4.5 gr. per hour into a glass tube heated to 600°, 650°, and 700° respectively, in a combustion furnace. The temperature of the reaction tube was measured by means of a thermocouple inserted into the tube, and the reaction products—gas and tar, were separately collected in receivers connected by means of a delivery tube to one end of the tube, as may be seen in Fig. 1 mentioned in the experimental part.

The gaseous product was analysed with the Bone-Wheeler gas analysis apparatus, of methane, hydrogen, carbon monoxide, and carbon dioxide. The tar separated from water, was analysed for hydrocarbon, phenols and polymers; the phenol and the cresol which were separated from the hydrocarbons by means of an 8% caustic soda solution, had their content

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(1) H. Meyer und A. Hofmann, *Monatsh.*, **38** (1917), 343.
(2) F. Fischer, *Abh. d. Kohle*, **4** (1919), 373; **5** (1920), 413.
(3) E. Müller, *J. prakt. Chem.*, [2] **58** (1898), 1.

estimated by the aid of density with reference to that of a mixture of a known quantity of two phenols.

When 20 gr. of *m*-cresol were passed in 5 hours through a glass tube heated to 600°, a gaseous product was noticed to be produced in the first few minutes, and then followed the tar-formation with diminution of the gas-production in process of time, and only 15.5% of the cresol decomposed, and the product was composed mostly of a polymer of high boiling point with 160 c.c. of gas composed of methane, carbon monoxide, carbon dioxide, and hydrogen. The formation of phenol and hydrocarbons was noticed to increase with the rise of the reaction temperature as will be shown in the Table.

The yield of gaseous substances from *m*-cresol at 650° was very meagre, but increased pari passu with the rate of decomposition of the cresol with the rise of the reaction temperature. The composition of the gas formed at 600° being rich in CO_2 and poor in H_2, is quite different from that generated at 650°, in which hydrogen is predominant, and the content of CO and CH_4 shows but slight variation through the whole range of the reaction temperatures. Phenol and benzene began to appear in a measurable quantity at 650°, and at high reaction temperature the yield of both phenol and benzene increased, viz., the formation of phenol is favourable at a low temperature; while the production of benzene and carbon monoxide was increased with the rise of the reaction temperature.

From this fact, it will be understood that the formation of phenol and benzene is due to the thermal decomposition of the polymer which is produced as a primary reaction product. As to this polymer, we have many evidences for considering it a mixture of some diphenyl ether derivatives. P. Sabatier(1) has reported that phenols when heated to 400°–500° in the presence of alumina yield chiefly aromatic ethers, and diphenyl ether according to the writer's experiment was decomposed by passing it through a glass tube heated to 700° into water, benzene, phenol, some polymers and carbon, and the gaseous products were composed mainly of carbon monoxide and hydrogen, and an inferior content of methane and carbon dioxide. Similar statements about the decomposition of phenyl ethers under different conditions were previously made by C. Graebe(2) and W. Ipatiew(3).

Taking these facts into account, the thermal decomposition of phenols would be represented in the following schemes:

$$(1)\quad ROH \longrightarrow ROR + H_2O$$

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(1) P. Sabatier, "Die Catalyse in der Organischen Chemie" (1927), 281.

(2) C. Graebe, *Ber.* **29** (1896), 1877.

(3) W. Ipatiew, *Ber.* **60** (1927), 1963.

$$\text{(2)}\quad \text{ROR}\longrightarrow\begin{cases}\text{R}'+\text{H}_2\text{O}\\ \text{ROH}+\text{RH}\\ \text{polymer}\\ \text{CO, H}_2\text{, CH}_4\text{, H}_2\text{O and carbon}\end{cases}$$

phenol, for example, is condensed first by splitting off one mol of water from two mols of phenol into phenyl ether which then decomposes into benzene and phenol on the one side, and on the other polymerises into complex compounds and eventually into carbon, liberating such simple substances as water, carbon monoxide, carbon dioxide, hydrogen and methane.

In the thermal decomposition of cresol, besides toluene, benzene and phenol would be produced, as the result of demethylation happening simultaneously with the formation and decomposition of cresylether. The rate of detachment of the methyl group from the cresol molecule is assumed to depend mostly on the relative position of the methyl group visa vis the hydroxyl group.

As a matter of fact, the formation of hydrocarbon and phenol from cresol predominates at low temperatures, while the decomposition of the phenol into hydrocarbon is favorable at high temperatures with the formation of carbon monoxide and water, and the writer has noticed diphenyl occurring in the reaction product.

2. The Comparison of the Thermal Decomposition of *m*-, *o*-, and *p*-Cresols. When *o*- and *p*-cresols were treated at 700° in a glass tube, under conditions similar to those of *m*-cresol, the decomposition of the substances proceeded in a similar manner to the isomeric substance but differing in the proportionate quantities of the reaction products as may be seen in the following Table.

Cresol		*m*	*o*	*p*
Decomposed cresol	%	51.0	88.0	93.5
Benzene hydrocarbon	%	8.0	11.5	13.0
Phenol	%	9.5	22.5	20.0
Polymer	%	17.5	24.5	21.5
Water	%	1.5	3.5	3.0
Gas	c.c./gr.	108	165	150
(Vol. %)	CO	40.5	29.3	36.7
	CH_4	35.8	47.6	45.6
	H_2	23.2	22.2	17.1

The rate of decomposition of the cresols is in the order *p*, *o* and *m*, but the formation of the gaseous products is greatest with the ortho compound and least with the meta, and the para-compound stands between those two.

The proportions of CO, CH_4 and H_2 in the gaseous product from the meta-compound is different from that produced from the ortho and the para-isomers, and this fact will afford some notion of the composition of the liquid products from *m*-cresol, in which hydrocarbons of a low boiling point such as benzene and toluene compose the major part, but phenol is the chief reaction constituent from other cresols. Such a difference in the reaction products from the three isomers of cresol is partly due to the easiness by which the elimination of the methyl group from the cresol molecule will take place according to the position combined the group to the carbon atom of the benzene nucleus.

As a matter of fact, the methyl group situated in ortho or para position to the hydroxyl group in the cresol molecule is easily removed in course of the pyrogenesis of the substances, and consequently the phenol-yield is great in *o*- and *p*-cresols, and it is established that *m*-cresol is the most stable and *p*-cresol the most unstable toward thermal treatment.

3. **Effect of the Material of the Reaction Tube.** In order to investigate the catalytic effect of the wall-materials of the reaction tube on the thermal decomposition of cresols, porcelain, copper and iron tubes were employed, through which *m*-cresol was passed under similar experimental conditions as described in the experimental part, and the amount of cresol affected by the reaction was greatest with the copper tube; and the effect of the material is in the order: copper, iron, porcelain, and glass; while for the formation of gaseous products, the order is iron, copper, porcelain, and glass.

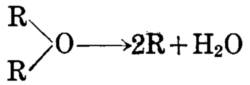
The gas from *m*-cresol which is passed into an iron tube, is chiefly composed of hydrogen and CO, with a small amount of methane, a result quite different from what happens when glass, porcelain or copper tubes are employed. In the latter three cases the constituents of the gaseous products are similar, the chief constituents being CO and methane, and glass and porcelain seem to affect the cresol catalyticaly as may be assumed from the gaseous constituents, in a similar manner, to the decomposition of cresol. This assumption of the catalytic effect of the tube materials is evidently approved on examination of the liquid reaction products which are composed of benzene hydrocarbon (H.C.) and phenol in the following ratio with the several tubes:

Material of tube		Glass	Porcelain	Copper	Iron
Decomposed cresol	%	41	75.5	92.5	77.5
$\frac{\text{H.C.}}{\text{Phenol}}$		$\frac{8.0}{9.5}$	$\frac{13.5}{8.0}$	$\frac{20.5}{5.5}$	$\frac{8.5}{4.5}$
Cresol changed into gas & carbon	%	14.5	33.5	46.5	53.0
Decomposed *m*-cresol	%	51.0	75.5	92.5	77.5
Benzene hydrocarbon	%	8.0	13.5	20.5	8.5
Phenol	%	9.5	8.0	5.5	4.5
Polymer	%	17.5	18.0	16.5	6.5
Water	%	1.5	2.5	3.5	5.0
Gas	c.c./gr.	108	183	314	342
(Vol. %)	CO	40.5	41.0	43.1	22.1
	CH_4	35.8	34.5	33.5	7.0
	H_2	23.2	22.9	18.3	67.7

The relative amount of the hydrocarbon and phenol in the reaction product is the same whether porcelain or iron tubes be employed, though the copper tube shows a different result. The formation of phenol and the hydrocarbon being attributed to the decomposition of the polymer is supposed to proceed equally in glass or porcelain tubes, according to the following scheme:

$$R\text{–}O\text{–}R \longrightarrow R + ROH$$

but the formation of the hydrocarbon is facilitated with the iron and copper tubes, as may be manifest in the scheme:



$$\begin{matrix} R \\ R \end{matrix}\!>\!O \longrightarrow 2R + H_2O$$

When the iron tube was employed the gaseous substances were predominant in the reaction product, which formed at the expense of the polymer, and the latter was partly transformed into the hydrocarbon and phenol.

From these facts it may be concluded that the materials used for the reaction tube will promote catalytically any one of the reactions occurring in the thermal treatment of cresols, and the formation of phenol and polymers from cresols is favoured by the use of a glass or porcelain tube, and the production of benzene is promoted with the use of a copper tube; but with the employment of an iron tube a complete decomposition into gas, water and carbon is accelerated.

4. Effect of Catalysts. The occurrence of benzene, toluene and phenol in the coal tar by the high temperature distillation of coals was attributed in the foregoing paragraph to the fact that the tar acids formed as one of the primary reaction products in the tar generated by the carbonization are cracked to form these substances in passing the heated zone of coke or coal in a retort, which consists of the mineral matter together with some organic substances of complex nature. The thermal decomposition of cresols in the presence of some catalysts which are similar in composition to coal ash is very important in order to learn the mechanism of the reaction of the formation of the light fractions of the tar from coal materials.

There is some resemblance between the composition of some Japanese coal ash and of Japanese acid earth, both containing alumina and silica as a chief constituent as shown in the following Table :(1)

	Shimbara coal ash	Japanese acid earth
SiO_2	59.2	65.19
Al_2O_3	26.2	16.36
Fe_2O_3	5.6	
MnO_2	trace	—
CaO	4.8	0.73
MgO	1.2	2.72
Na_2O+K_2O	1.7	0.11

It is, therefore, not inconceivable that the catalytic action of the Japanese acid earth and alumina are analogous to that of coal ash. *o*-Cresol was passed into glass tube which contains Japanese acid earth or alumina, to see the catalytic effect on the decomposition of the substance.

In each case, the formation of a polymer and phenol is evidently favoured at a low temperature, and the yield of benzene hydrocarbon and carbon monoxide is increased with the rise of the reaction temperature due to the cracking of the polymer.

To discover a special feature of the catalysts for the decomposition of the cresol, the reaction products at 700° were studied.

The rate of decomposition of cresol is increased in the presence of the catalysts, and the alumina tends to promote the gasification of the substance. The hydrogen content in the produced gas increased with alumina, due to the expense of methane by the action of water in the presence of the

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(1) *Research Report of the Naval Fuel Depot, Japan,* **1** (1926), 40.

catalyst. The decomposition of polymers into hydrocarbons is obviously accelerated in presence of these catalysts, in which some difference was noticed when the liquid product was examined precisely according to the difference in the chemical constituents of the catalysts.

		Blank	Acid earth	Al_2O_3
Changed cresol	%	88.0	91.5	94.0
Benzene hydrocarbon	%	11.5	13.5	13.0
Phenol	%	22.5	16.5	12.5
Polymer	%	24.5	18.5	12.5
Water	%	3.3	5.0	4.0
Gas	c.c./gr.	165	198	327
(Vol. %)	CO	29.3	28.5	22.3
	CH_4	47.6	46.8	33.7
	H_2	22.2	24.0	36.9

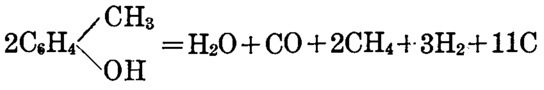
5. Effect of Deposited Carbon. In the course of the pyrogenetic reaction of cresols, the writer has noticed that in the first several minutes of the reaction, gaseous substances only are produced, followed by the formation of tar, the nature of the latter substance would not be the same as passing of time of reaction.

These observations led the writer to the notion that in the beginning of the process of pyrogenesis, the complete decomposition of cresols into gaseous compounds and carbon will prevail, and the latter substance accumulated in the reaction tube will retard the gasification, but promote the oxidation or removal of hydrogen from cresols to a polymer which will in turn change into phenol and benzene.

In passing *p*-cresol into the glass tube with alumina at 700°, the main reaction products in the first hour consisted of hydrogen, methane, carbon monoxide and water, with some quantities of carbon and some polymers. The composition of the gaseous products was determined to be

$$CO\ (CO_2),\ 1;\quad CH_4,\ 1.5;\quad H_2,\ 3.8.$$

The formation of these substances is supposed to occur by the reaction represented by the equation which differs slightly from that reported by E. Müller⁽¹⁾



$$2C_6H_4\begin{matrix}\diagup CH_3 \\ \diagdown OH\end{matrix} = H_2O + CO + 2CH_4 + 3H_2 + 11C$$

In the latter phase of the reaction, polymers and phenol are the chief reaction product, and their formation will be connected with the deposition of carbon in the reaction tube. The physical and chemical properties of carbon produced by the thermal decomposition of organic compounds, vary with not only the nature of the substance from which the carbon is produced, but the external conditions such as the temperature and the pressure⁽²⁾ under which the carbonization takes place, also the physical nature of the surface⁽³⁾ of the tube on which the carbon is precipitated. In fact, some differences have been noticed in the appearance of the carbon deposited on the surface of glass, porcelain, copper and iron tubes, and the difference in composition of the reaction products from cresols is partly due to the physical and chemical nature of the carbon deposited on the tube-walls.

Experimental Part.

Cresols from Kahlbaum, distilled for purification after being treated with anhydrous sodium sulphate, show the following physical constants :

Cresol	B. p.	$d_{4°}^{25°}$	$n_{D}^{25°}$
o–	187.5°–183.3°	1.0426	1.5398
m–	198.5°–199.5°	1.0304	1.5350
p–	197.5°–198.5°	1.0310	1.5335

A reaction tube of 2 cm. in diameter and 1 m. in length, made of glass, porcelain, copper, or iron, was heated in a combustion furnace, and the

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(1) E. Müller, loc. cit.

(2) W. J. Mellor, "Comprehensive treaties on inorganic and theoretical chemistry," V, (1924).

(3) K. A. Hofmann und U. Hofmann, *Ber.*, **59** (1926), 2433.

temperature of the inside of the tube was measured by means of a thermocouple; the cresols were gradually dropped into a reaction tube by means of a capillary tube attached to the tube, and the reaction product was collected in a receiver which was cooled with a freezing mixture of ice and salt, and the generated gas which escaped from the receiver was collected on a 10% sulphuric acid solution in a bottle. (Fig. 1).

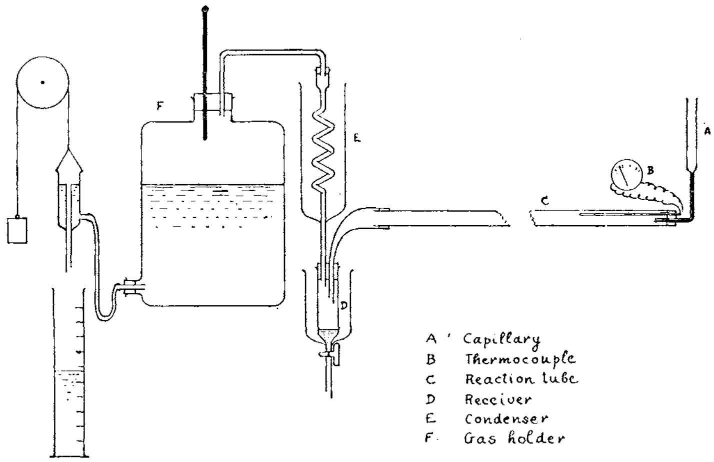

Fig. 1

The gas produced was analysed with a Bone-Wheeler(1) gas analysis apparatus, and the content of CO_2, CO, CH_4 and H_2 specially estimated in each experiment. The tarry matter condensed in the receiver was subjected to fractional distillation after water was separated, into three parts; the first part boiled from 78° to 120°, the second part b.p. 120°–200°, the residue b.p. up 200°, and each fraction was treated with 8% caustic soda solution to separate the phenolic substances from the neutral ones and redistilled. The main fractions were estimated to be composed of the following constituents.

1. The neutral fraction b.p. (79°–120°) benzene and toluene
2. ,, acidic ,, b.p. (178°–200°) phenol and cresols
3. ,, residue ,, b.p. (200° —) polymer

The phenol-content in the acidic fraction (178°–200°) was calculated by weight from its density by consulting the following Table and Fig. 2.

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(1) C. Grice and W. Paymann, *Fuel in Science and Practice* (1924), 236.

o-Cresol		*m*-Cresol		*p*-Cresol	
Phenol %	$d^{25°}_{4°}$	Phenol %	$d^{25°}_{4°}$	Phenol %	$d^{25°}_{4°}$
0	1.0426	0	1.0304	0	1.0310
8.4	1.0448	18.6	1.0377	17.7	1.0380
14.9	1.0470	25.9	1.0406	25.4	1.0408
26.4	1.0501	44.7	1.0480	35.9	1.0454
47.8	1.0565	50.2	1.0502	51.7	1.0514
67.7	1.0623	65.4	1.0565	72.7	1.0601
76.7	1 0651	76.7	1.0610		

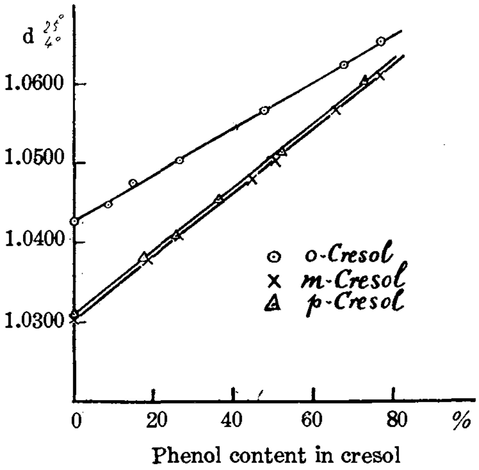

Fig. 2.

The data shown in the Table was obtained by the writer by mixing the known weight of two substances.

Benzene and toluene which occur in the neutral fraction were identified by transforming them into their amino derivatives by the usual method, and also phenol was confirmed by converting into the diazo-derivative.

1. Experiment with a Glass tube. *m*-, *o*- and *p*-cresols were passed at the rate of 3.6–4.2 gr. per hour, into a glass tube heated to 600°, 650° and 700° respectively. At the beginning of the reaction, some gaseous product only was formed, followed by the formation of a liquid substance. The products were analysed and the results are shown in Tables 1, 2 and 3. It was noticed that the inner surface of the tube was covered by a film of carbon, and the higher the reaction temperature the greater the thickness of the carbon film. The appearance of the carbon film is black at 600°, bluish black at 650°, with a grey and dull metallic lustre at 700°.

Table 1.

m-Cresol

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°, 760 mm.	Carbon
600°C.	20.0	4.0	18.7	160	+
650°	20.0	4.0	18.1	620	+
700°	20.0	4.0	17.5	2150	+

Liquid

Reaction temp.	Neutral (79°-120°)			Acidic (178°-200°)			Residue (200°-)	Water
	gr.	$d_{4^\circ}^{25^\circ}$	$d_{D}^{25^\circ}$	gr.	$d_{4^\circ}^{25^\circ}$	$n_{D}^{25^\circ}$	gr.	gr.
600°	trace	—	—	16.9	1.0307	1.5322	0.9	trace
650°	0.3	—	1.4911	14.9	1.0328	1.5334	1.9	0.2
700°	1.6	0.8672	1.4903	11.7	1.0368	1.5356	3.5	0.3

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	84.5	trace	trace	4.5	trace	—
650°	70.0	1.5	4.5	9.5	1.0	2.1/5.0=0.42
700°	49.0	8.0	9.5	17.5	1.5	11.1/10.6=1.05

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	8	35.6	22.5	36.6	5.2
650°	31	0.9	34.9	42.1	22.1
700°	108	0.5	40.5	35.8	23.2

Table 2.

o-Cresol

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760mm.	Carbon
600°C.	20.0	4.0	18.9	340	+
650°	20.0	3.8	17.5	1560	+
700°	20.0	3.6	15.1	3300	+

Liquid

Reaction temp.	Neutral (79°-120°)			Acidic (178°-200°)			Residue (200°—) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	$n_D^{25°}$		
600°	0.1	—	1.4892	16.3	1.0444	1.5412	2.0	0.1
650°	1.1	0.8709	1.4964	11.2	1.0495	1.5404	4.0	0.4
700°	2.3	0.8756	1.4946	6.9	1.0615	1.5432	4.9	0.7

(Yield in % for sample)

Reaction temp.	*o*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	76.0	0.5	5.5	10.0	0.5	0.7/ 6.1=0.11
650°	42.5	5.5	13.5	20.0	2.0	7.6/15.8=0.48
700°	12.0	11.5	22.5	24.5	3.5	15.5/25.7=0.62

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	17	2.9	18.6	64.1	14.4
650°	78	2.1	22.5	63.8	11.6
700°	165	0.8	29.3	47.6	22.2

Table 3.

p–Cresol

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760mm.	Carbon
600°C.	20.0	3.8	18.3	410	+
650°	20.0	3.8	15.7	2840	+
700°	20.0	4.2	13.1	3000	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°—) gr.	Water gr.
	gr.	$d^{25°}_{4°}$	$n^{25°}_{D}$	gr.	$d^{25°}_{4°}$	$n^{25°}_{D}$		
600°	0.2	—	1.4889	15.5	1.0373	1.5327	1.8	0.1
650°	1.4	0.8691	1.4959	9.4	1.0490	1.5374	3.7	0.5
700°	2.6	0.8711	1.4911	5.4	1.0610	1.5400	4.3	0.6

(Yield in % for sample)

Reaction temp.	*p*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	72.5	1.0	5.0	9.0	0.5	1.3/5.9=0.23
650°	26.0	7.0	21.0	18.5	2.5	9.7/25.8=0.37
700°	6.5	13.0	20.5	21.5	3.0	18.0/23.7=0.76

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	20	1.7	20.3	62.0	16.0
650°	142	0.9	28.4	57.5	13.5
700°	150	0.7	36.7	45.6	17.1

2. Experiment with Porcelain, Copper and Iron Tubes. Three tubes made of porcelain, copper and iron was used instead of the glass tube, in the experiment with *m*-cresol which was carried out under the conditions shown in the Table, and the results are as follows :

Table 4.

(A) Porcelain tube

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760 mm.	Carbon
600°C.	20.0	4.0	17.2	140	+
650°	20.0	3.6	17.0	680	+
700°	20.0	3.6	14.0	3670	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–) gr.	Water gr.
	gr.	$d^{25°}_{4°}$	$n^{25°}_{D}$	gr.	$d^{25°}_{4°}$	n^{25}_{D}		
600°	trace	—	—	14.7	1.0310	1.5330	1.2	0.1
650°	0.5	0.8630	1.4936	13.4	1.0328	1.5353	2.0	0.2
700°	2.7	0.8684	1.4920	6.5	1.0400	1.5366	3.6	0.5

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	72.0	trace	1.5	6.0	0.5	trace/1.7
650°	62.5	2.5	4.5	10.0	1.0	3.5/5.0=0.70
700°	24.5	13.5	8.0	18.0	2.5	18.6/9.4=1.97

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	7	29.8	24.8	40.5	4.9
650°	34	4.2	35.7	37.9	22.2
700°	183	1.7	41.0	34.5	22.9

Table 5.

(B) Copper tube

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c c. at 0°, 760 mm.	Carbon
600°C.	20.0	4.7	18.2	950	a few
650°	20.0	4.0	15.2	3260	a few
700°	20.0	3.8	11.6	6280	a few

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–) gr.	Water gr.
	gr.	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$	gr.	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$		
600°	0.1	—	—	15.8	1.0313	1.5320	1.0	0.1
650°	1.9	0.8694	1.4930	9.4	1.0367	1.5348	2.9	0.6
700°	4.1	0.8704	1.4900	2.6	1.0472	1.5375	3.3	0.7

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	76.5	0.5	2.5	5.0	0.5	0.7/2.6=0.27
650°	39.5	9.5	7.5	14.5	3.0	12.1/8.2=1.48
700°	7.5	20.5	5.5	16.5	3.5	28.5/6.2=4.60

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	43	21.4	37.2	39.8	1.5
650°	163	4.6	40.0	29.8	25.6
700°	314	5.2	43.1	33.5	18.3

Table 6.

(C) Iron tube

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760 mm.	Carbon gr.
600°C	20.0	3.5	12.9	4080	+
650°	20.0	4.0	12.8	5430	2.5
700°	20.0	3.8	10.0	6850	5.0

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°) gr.	Water gr.
	gr.	$d^{25°}_{4°}$	$n^{25°}_{D}$	gr.	$d^{25°}_{4°}$	n^{25}_{D}		
600°	0.4	0.8663	1.4870	10.4	1.0313	1.5328	1.0	0.3
650°	0.4	0.8704	1.4914	9.6	1.0328	1.5334	1.3	0.7
700°	1.7	0.8726	1.4930	5.4	1.0367	1.5350	1.3	1.0

(Yield in % for sample)

Reaction temp.	*m*-Cresol	Hydrocarbon	Phenol	Polymer	Water	Hydrocarbon (mol %) / Phenol (mol %)
600°	50.5	2.0	1.5	5.0	1.5	2.8/1.8=1.56
650°	44.5	2.0	3.5	6.5	3.5	2.8/3.8=0.74
700°	22.5	8.5	4.5	6.5	5.0	11.8/5.3=2.26

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	204	6.2	25.4	11.3	57.1
650°	271	4.9	25.0	4.3	65.9
700°	342	3.2	22.1	7.0	67.7

3. Experiment with Catalysts. Japanese acid earth or alumina was used in the thermal decomposition of *o*-cresol as a catalyst to investigate their effect on the reaction. Commercial Japanese acid earth was washed repeatedly with water, dried at 100° and then heated to 500°, and alumina from the market was used.

In the experiment, 10 grams of the catalysts, thus prepared, were spread to a length of 70 cm. in the glass tube and heated to the desired reaction temperature for one hour in a current of air, and then *o*-cresol was passed at the rate of 3.3–4.2 gr. per hour through the tube. After the reaction, the surface of the catalyst was noticed to be covered with carbon. The experimental result are shown in Tables 7 and 8.

Table 7.

Japanese acid earth

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°,760 mm.	Carbon
600°C.	20.0	3.4	16.9	970	+
650°	20.0	4.2	16.4	380	+
700°	20.0	4.0	12.9	3970	+

Liquid

Reaction	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°—) gr.	Water gr.
	gr.	$d_{4°}^{25°}$	$n_D^{25°}$	gr.	$d_{4°}^{25°}$	$n_D^{25°}$		
600°	0.7	0.8787	1.4952	13.3	1.0456	1.5400	2.0	0.6
650°	1.3	0.8732	1.4949	11.6	1.0504	1.5412	2.7	0.6
700°	2.7	0.8748	1.4944	5.0	1.0618	1.5428	3.7	1.0

(Yield in % for sample)

Reaction temp.	*o*-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	59.5	3.5	7.0	10.0	3.0	4.9/ 7.9=0.62
650°	42.0	6.5	16.0	13.0	3.0	9.0/18.5=0.49
700°	8.5	13.5	16.5	18.5	5.0	18.7/18.9=0.99

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	48	0.7	11.6	43.3	44.3
650°	19	0.5	15.3	47.4	36.9
700°	198	0.7	28.5	46.8	24.0

Table 8.

Alumina

Reaction temp.	Sample used gr.	Passing rate of sample gr./hour	Decomposition products		
			Liquid gr.	Gas c.c. at 0°, 760 mm.	Carbon
600°C.	20.0	3.3	13.8	2690	+
650°	20.0	4.0	12.3	2990	+
700°	20.0	4.2	10.2	6530	+

Liquid

Reaction temp.	Neutral (79°–120°)			Acidic (178°–200°)			Residue (200°–) gr.	Water gr.
	gr.	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$	gr.	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$		
600°	0.7	0.8760	1.4900	10.2	1.0483	1.5404	1.7	0.8
650°	1.5	0.8743	1.4947	7.2	1.0537	1.5423	2.6	0.8
700°	2.6	0.8750	1.4935	3.7	1.0623	1.5430	2.5	0.8

(Yield in % for sample)

Reaction temp.	o-Cresol	Hydrocarbon	Phenol	Polymer	Water	$\frac{\text{Hydrocarbon (mol \%)}}{\text{Phenol (mol \%)}}$
600°	41.0	3.5	10.0	8.5	4.0	4.5/11.2=0.40
650°	22.0	7.5	14.0	13.0	4.0	10.4/16.3=0.64
700°	6.0	13.0	12.5	12.5	4.0	18.0/14.1=1.28

Gas

Reaction temp.	Yield c.c./gr.	Composition (in vol. %)			
		CO_2	CO	CH_4	H_2
600°	135	3.0	8.6	35.9	52.6
650°	150	7.3	14.9	44.4	33.2
700°	327	7.1	22.3	33.7	36.9

Table 9.

No. of interval	Time hour	Sample passed gr.	Decomposition products	
			Liquid gr.	Gas c.c. at 0°,760 mm.
I	1	10.7	2.8	4690
II	$3\frac{2}{3}$	39.2	32.9	5232
III	$4\frac{1}{2}$	49.1	40.7	4185

Liquid

No. of interval	Fraction	gr.	$d_{4^\circ}^{25^\circ}$	$n_{D}^{25^\circ}$
I	Neutral (79°-120°)	0.3	—	1.4881
	Acidic (178°-200°)	0.7	1.0500	1.5377
	Residue (200° ——)	1.2		
	Water	0.6		
II	Neutral (79°-120°)	1.8	0.8677	1.4924
	Acidic (178°-185°)	3.2	1.0608	1.5439
	,, (185°-190°)	2.3	1.0483	1.5375
	,, (190°-195°)	9.8	1.0347	1.5345
	,, (195°-200°)	4.5	1.0330	1.5341
	Residue (200° ——)	4.7		
	Water	0.5		
III	Neutral (79°-120°)	1.9	0.8684	1.4903
	Acidic (178°-185°)	3.0	1.0546	1.5391
	,, (185°-190°)	4.0	1.0462	1.5366
	,, (190°-195°)	13.0	1.0347	1.5356
	,, (195°-200°)	7.8	1.0326	1.5349
	Residue (200° ——)	5.5		
	Water	0.3		

Liquid (% for sample)

No. of interval	*p*-Cresol	Hydrocarbon	Phenol	Polymer	Water
I	3.8	3.8	2.8	11.2	5.6
II	39.0	4.6	11.5	12.0	1.3
III	46.8	3.8	9.8	11.2	0.6

Table 9.—(*continued*).

Gas (composition in vol. %)

No. of interval	CO_2	CO	CH_4	H_2	C_nH_{2m}
I	3.4	10.8	23.6	59.6	2.8
II	3.4	21.2	33.0	39.6	2.6
III	3.1	24.3	39.5	30.1	2.5

4. Experiment on the Effect of the Deposited Carbon. 99 grams of *p*-cresol were passed in 9 hours into a glass tube with three porcelain boats which were situated separately at certain intervals in the tube, each containing about 10 gr. of alumina. The reaction products, gas and tar were collected successively in three intervals ; the first one hour, then 3.5 hours for the second fraction, and finally 4.5 hours for the third, and each collection was analysed, and the results are shown in Table 9.

In order to learn the chemical nature of the carbon deposited on the catalyst in the boats, the whole content of these boats was subjected to combustion, and carbon and hydrogen were estimated as in the elemental analysis of an organic compound.

Position in reaction tube	Capillary side	Centre	Receiver side
C %	97.3	95.3	92.5
H %	2.0	3.1	3.1
O %	0.7	1.6	4.4
C/H	4.05/1	2.56/1	2.48/1

As will be seen from the above Table, the so-called carbon deposited on alumina is mostly composed of carbon, and its composition varies with the position in which the boat is situated in the tube. When cresol comes into contact with the heated surface of alumina, it would undergo repeated polymerisations and decompositions, splitting off oxygen and hydrogen, and producing such a carbon-rich substance as the so-called carbon(1).

5. Diphenyl Ether. Diphenyl ether prepared from chlorobenzene and sodium phenolate, showed b.p.$=(97.5°-98.5°)_{3mm.}$ $d_{4°}^{25°}=1.0716$, $n_D^{25°}=1.5782$, was passed into a glass tube heated to 700°, at the rate of 15.4 gr. per hour, and thus, 30.8 gr. of diphenyl ether yielded 27.0 gr. of the tarry substance, 0.3 gr. of water, 1900 c.c. of gas and some carbon. Analytical results of the tar are shown in the following Table.

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(1) M. Berthelot, "Essai de mecanique chimique", II, (1879), 137.

The neutral fraction.

Fraction	gr.	%		
1. 78°—100°	3.5	11.4	$d_{4^\circ}^{25^\circ}=0.8753$, $n_D^{25^\circ}=1.4974$	benzene (24.7 mol %)
2. 220°—260°	5.8	18.8	$d_{4^\circ}^{25^\circ}=1.0734$, $n_D^{25^\circ}=1.5958$	mainly diphenyl ether
3. 260°—330°	1.9	6.2		,, diphenylene oxide
4. residue	3.6	11.8		

The acidic fraction.

Fraction	gr.	%		
1. 178°—185°	4.1	13.3	m.p. [39.5°—40.5°]	phenol (34.1 mol %)
2. 280°—290°	0.4	1.3		
3. residue	0.2	0.6		

Benzene in the neutral fraction was confirmed by the usual chemical method. The fraction b.p. 220°–260° of the neutral part was assumed to be a mixture of diphenyl ether and diphenyl from the physical constants. From the fraction b.p. 260°–330° of the neutral part, a substance of m.p. 80°–81° by recrystallisation from alcohol was isolated, which was identified as diphenylene oxide by converting it into picrate with a m.p. of 96°–97°.

The composition of the gas was determined and shown by volume.

CO	H_2	CH_4	C_nH_{2m}	C_2H_4	CO_2
51.9	38.9	7.6	0.7	0.4	0.5

In conclusion,the writer wishes to express his hearty thanks to Vice-Admiral K. Yamashita and Engineer-Captain Viscount M. Kawase who have taken a kindly interest in the problem, and given him permission to publish this paper, also to Professor Shigeru Komatsu who has given kind guidance and invaluable advice.

October, 1927.

The Scientific Research and Experimental Branch,
Imperial Naval Fuel Depot Tokuyama.

STUDIES ON THE ENZYMES OF SILKWORM. I.

By Motohichi MORI.

Received March 24, 1930. Published May 28, 1930

For the properties of enzymes of silkworm we have yet only a few reports, so I intended to study the properties of enzymes of various organs of silkworm. At first the enzymes of the intestine has been studied. In the present paper some properties of amylase in the middle intestine are described.

Preparation of Enzyme. The intestinal tube from 1000 matured silkworms has been collected by dissolution, and washed thoroughly by distilled water. The organ is then ground up in an ordinary mortar with sands. The mass is then treated with acetone, acetone-ether and lastly with ether, then spread out on filter paper in the air for 30 minutes to evaporate the ether. The preparation is dried in vacuo over sulphuric acid, powdered and preserved.

The active enzyme is obtained by extraction of the powder with water, glycerin solution or buffer solution (for example glycocoll-NaCl-NaOH mixture $P_H = 9.62$). From extracted solution the enzyme have been precipitated with acetone or alcohol, the precipitate is washed with absolute alcohol, then with ether and lastly is dried in vacuo over sulphuric acid. For the further purification the resulting precipitate is redissolved in water and absorbing the amylase with kaolin (at $P_H = 9.62$). Absorbed amylase can be washed out with ammonium-phosphate mixture solution. The elution is then diluted with water and the phosphate is precipitated with magnesium mixture and again precipitated.

The amylase which is obtained in this way has the activity (saccharifying action) $\overset{25^\circ C}{\underset{24\ \text{hour}}{D}} = 1500$, per gram in wohlgemuth unit.

Optimal Temperature. The velocity of the amylase reaction is accelerated as the temperature is raised until 60°C. On further elevation of the temperature the reaction velocity begins to diminish until it cease completely (80°C).

It is generally believed that each enzyme has an optimal temperature characteristic of that enzyme. This optimum is, however, greatly influenced by its concentration, the nature and concentration of substrate upon which the enzyme acts, the reaction of medium, and the period of action, etc.

In the case of this amylase, the optimal temperature observed are as follows, the value of P_H being 9.6.

Table 1.

Optimal Temp.	Period of action
55–60°C.	6 hours or less
55°C.	10 hours
50–55°C.	20 hours
50°C.	24 hours

Reaction velocity, temperature coefficient and temperature constant are shown in Table 2 and Fig. 1.

Table 2.

The rate of saccharifying of soluble starch by amylase at various temperature ($P_H=9.6$).

	Sugar produced (mg.)							Velocity constant $k=\frac{1}{t}\log\frac{a}{a-x}$	Temperature coefficient $k_{t+10}:k_t$	Temperature constant $A=\frac{\log k_2-\log k_1}{0.4343}R\frac{T_2 T_1}{T_2-T_1}$
Time (hour) / Temp.	1/2	1	2	3	4	5	24			
80°C.	0	0	0	—	—	—	—	—	—	—
70	1.2	1.6	2.6	3.4	4.0	4.4	7.4	—	—	—
65	1.25	2.9	5.7	7.5	9.0	11.4	15.0	0.00150	—	—
60	1.5	3.3	6.7	9.0	11.4	13.0	20.0	0.00217	—	—
55	1.3	3.0	5.2	7.5	9.5	12.2	21.0	0.00151	1.85	13271
50	1.0	2.1	4.1	6.3	7.8	9.4	21.7	0.00117	1.94	13486
40	0.6	1.1	2.0	3.7	5.2	6.3	17.4	0.00060	2.00	13088
30	—	0.55	1.3	2.4	3.0	3.6	15.8	0.00030		

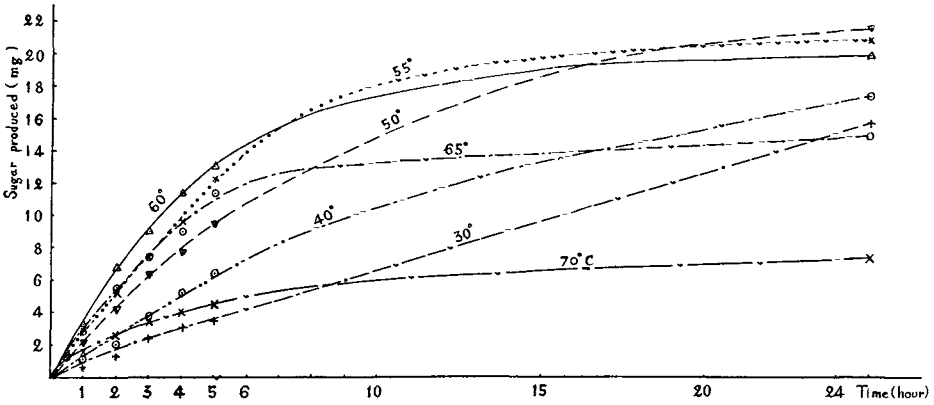

Fig. 1.

Optimal Hydrogen Ion Concentration for the Amylase Action. Most enzymes are greatly influenced by the concentration of hydrogen ion of the medium in which they act. That is, there is an optimal hydrogen ion concentration for the action of each enzyme.

The intestinal amylase of silkworm has an optimal hydrogen ion concentration at $P_H=9.4$ to 11. This result has been obtained by comparing the activity at various values of P_H, other conditions being held constant, and at lower temperature 30°C., so as to avoid the destruction of the enzyme. The activity has been measured by determining the reducing action of the decomposed starch, e.g. with respect to Fehling's solution according to Bertrand. The results of experiments for the optimal P_H are as follows. (Table 3, Fig. 2).

Table 3.

Milli-grams of sugar produced by the action of amylase at various values of P_H. (Period of action=10 hours)

P_H / Temp.	5.3	5.9	6.8	7.4	8.04	8.6	9.4	9.7	11.3	12.9
30°C.	2.4	2.6	2.9	3.5	4.5	5.1	9.1	9.0	9.1	1.4
40	2.6	2.9	3.2	3.8	5.0	5.6	10.3	10.1	10.2	1.5

Thus, the P_H optimum of the amylase lies between 9.4–11.3. The optimal P_H for an enzyme action often depend upon the type of buffer solution used, so the several types of buffers, have been examined, for example, phosphate mixture, glycocoll-NaOH mixture and ammonium mixture, etc. and it was observed that the P_H optimum for this amylase is independent of the nature of buffer solution used.

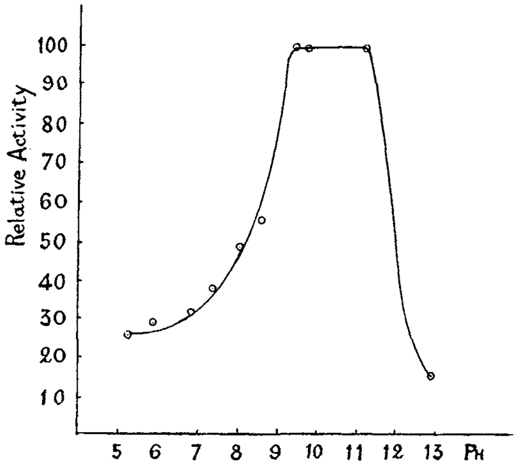

Fig. 2.

Isoelectric Point of the Amylase. Amphoteric substances, such as proteins, to which most enzymes are probably related, are charged positively or negatively depending upon the ion with which they are combined or upon the reaction of the solution in which they are suspended. These colloid particles travel toward the pole of opposite sign to that of the charge.

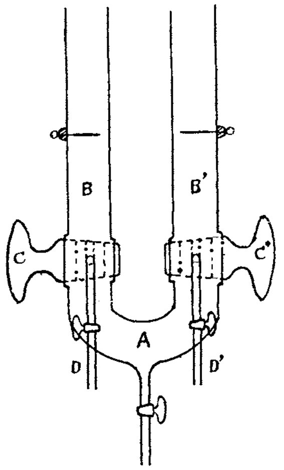

Fig. 3

In the case of this amylase, I observed that the enzyme travel toward the negative pole in alkaline solution and toward the positive pole in acid reaction, and neither negative nor positive pole at about $P_H=5.7$.

The apparatus for this experiment is shown in Fig. 3. The middle part (50 c.c.) of U shaped tube is filled by the enzyme solution (A). After closing the cocks C and C′ each limbs of U-tube is filled with 50 c.c. of distilled water. When the water has settled, the cocks C and C′ are slowly opened and connect the electrodes with the circuit of 100 volt direct current. The whole apparatus should be kept as free from shaking as possible. After one hour, the cocks C and C′ are closed and the solutions at B and B′ are drawn out by the cocks D and D′, and determined the enzymatic activity of each solution.

Table 4 shows the number of milli-grams of sugar produced by the action of 5 c.c. of the solution at B and B′ with 10 c.c. of 1% soluble starch solution at 40°C. ($P_H=9.7$ for 4 hours). The enzymatic power of the original enzyme solution (A) is 51 under the same condition.

From the result of the observation one can conclude that the amylase is positively charged in alkaline reaction, and negatively charged in acid reaction, and its isoelectric point is at about $P_H=5.7$.

On the other hand it was observed that the amylase is absorbed quantitatively by kaolin, and not by infusorial earth in alkaline solution. On the contrary, the amylase is absorbed by infusorial earth, and not by kaolin in acid solution (P_H is less than 5.7), and is absorbed both by kaolin and by infusorial earth at $P_H=5.7$. This result coincide with the observation of cataphoresis.

Table 4.

Cataphoresis of amylase.

P_H	Positive pole B	A	Negative pole B′
9.7	0.0	7.1	39.5
7.2	0.0	15.2	30.4
6.6	0.0	39.7	6.2
5.7	trace	50.0	0.0
3.9	4.0	42.0	0.0

Summary.

1. The optimal temperatures for the action of amylase obtained from the middle intestine of silkworm have been determined.
2. The optimal hydrogen ion concentration for the amylase action has been determined to be $P_H=9.4-11.3$ at 30–40°C.
3. The amylase charges positively in alkaline reaction, and negatively in acid reaction, the isoelectric point being at about $P_H=5.7$.

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NOTE ON ANOMALOUS DISPERSION AND ABSORPTION OF ELECTRIC WAVES.

By San-ichiro MIZUSHIMA

Received April 21, 1930. Published May 28, 1930.

The writer has published several reports⁽¹⁾ in this journal on anomalous dispersion and absorption of electric waves for the wave-lengths between 50m. and 3m. In comparing his results with the dipole theory, the writer

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(1) Mizushima, this Bulletin, **1** (1926), 47, 83, 115, 143 and 163.

referred to an older paper⁽¹⁾ of Debye in which only the plane motion of molecule is considered, and compared ϵ simply with n^2 (ϵ : dielectric constant; n : refractive index). It may not be out of place to notice that quite recently he supplemented his former results with the data which he obtained for a still shorter wave-length (60 cm.).⁽²⁾ This time the writer used the following formula derived in a recent paper⁽³⁾ of Debye :

$$\epsilon=\frac{\epsilon_0+\left(\frac{\epsilon_0+2}{\epsilon_\infty+2}\right)^2\left(\frac{4\pi\eta a^3}{kT}\right)^2\omega^2\epsilon_\infty}{1+\left(\frac{\epsilon_0+2}{\epsilon_\infty+2}\right)^2\left(\frac{4\pi\eta a^3}{kT}\right)^2\omega^2}$$

in which ϵ is the dielectric constant measured for the frequency $\frac{\omega}{2\pi}$, ϵ_0 the static dielectric constant, ϵ_∞ the optical dielectric constant, η the viscosity, a the molecular radius, k Boltzmann's constant, and T the absolute temperature. The results obtained for monovalent alcohols (CH_3OH, C_2H_5OH, C_3H_7OH, iC_4H_9OH, $iC_5H_{11}OH$) were in good agreement with the above formula; i.e. the molecular radii calculated from the experimental values of ϵ and η were found to have reasonable values. The results with glycerine, however, are not in accordance with the theory. The discrepancy would be accounted for, if glycerine be a colloidally dispersed system so that the effective viscosity acting against the rotation of molecule is quite different from the viscosity of the liquid in bulk.

In the recent book of Prof. Debye on "Polar Molecules," only my former papers are quoted. In this book, Prof. Debye not only recalculated the data just as I had done in my new paper, but also gave further valuable explanations of them.

Leipzig, Germany.

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(1) Debye, *Verh. Deut. Phys. Gesel.*, **15** (1913), 777.

(2) Mizushima, *Scientific Papers of the Institute of Physical and Chemical Research, Tokyo*, **9** (1928), 209.

(3) Debye, "Handbuch der Radiologie," VI, (1925).

SINOMENINE AND DISINOMENINE. PART XVI.

ON ISOBROMO-SINOMENINE (OR BROMO-SINOMENEINE).

By **Kakuji GOTO** and **Taro NAMBO.**

Received April 22, 1930. Published May 28, 1930.

Isobromo-sinomenine is always produced in minor, but varying quantities when sinomenine hydrochloride is brominated in glacial acetic acid. The properties of the chief product, bromo-sinomenine, had been greatly elucidated by the studies, published in the former three papers.⁽¹⁾ This communication deals with the formation and the transformation of isobromo-sinomenine.

The properties of bromo-sinomenine and isobromo-sinomenine was contrasted in the Table 1 of the 13th communication of this study. The most striking differences are, for convenience's sake, here again pointed out.

	Bromo-sinomenine	Isobromo-sinomenine
Specific rotation	−	+
$FeCl_3$ reaction	Strong as with sinomenine	Very weak
$FeK_3(CN)_6$ reaction	Strong as with sinomenine	No
M.p. of bromo-sinomeninone derived from them	227°C.	197°C.

The research had been made first on the following two assumptions, which were, however, quickly to be given up by the reasons annexed to them.

1. Bromo-sinomenine might have been hydrated on its double linking by the action of hydrobromic acid gas generated in the process of bromination. Isobromo-sinomenine might be, therefore, bromo-sinomenine hydrate.⁽²⁾ But, this assumption collided with the fact that isobromo-sinomeninone, derived from isobromo-sinomenine, was quite different from bromo-sinomeninone produced from bromo-sinomenine.

2. Isobromo-sinomenine might be acetylated bromo-sinomenine, the acetylation being effected by the catalysis of hydrobromic acid gas in the

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(1) K. Goto and T. Nakamura, this Bulletin, **4** (1929), 195; K. Goto and T. Nambo, ibid., **5** (1930), 73; K. Goto and R. Inaba, ibid., **5** (1930), 93.

(2) Compare sinomenine hydrate, this Bulletin, **4** (1929), 271.

glacial acetic acid. The elementary composition of isobromo-sinomenine resp. isobromo-sinomeninone and supposed acetylated bromo-sinomenine resp. bromo-sinomeninone is very similar, and the elemental analysis alone could not decide this problem.

Yet, with all effort we could not prove the acetyl radical by the hydrolysis, the attempted transformation of bromo-sinomenine or its ketone into isobromo-sinomenine or its ketone and the transformation vice versa could not be realised. Moreover, the fact that the bromination of sinomenine in propionic acid (Kahlbaum) afforded also isobromo-sinomenine at last decided the case in the negative sense.

Then we came to suspect the oxidative action of bromine. In the course of bromination, we always notice the formation of red syruppy substance, which is dissolved later and whose quantity is increased according to the velocity of the addition of bromine. If this syruppy substance is a perbromide of brominated sinomenine, then the sinomenine molecule will be oxidised, when the perbromide is decomposed. This supposition agrees well with the elemental analysis of isobromo-sinomenine and of its ketone. If isobromo-sinomenine contains two atoms of hydrogen less than bromo-sinomenine, it is no wonder that isobromo-sinomeninone is totally different from ordinary bromo-sinomeninone.

Hereupon, sinomenine was brominated with 2 mol. of bromine and the isobromo-sinomenine was obtained in 40% yield in three experiments. As is seen from the example of nicotine perbromide,(1) sinomenine perbromide has probably the formula $C_{19}H_{22}Br\ NO_4.\ BrH.\ Br_2$, and the number of hydrogen atoms taken away at the decomposition of this perbromide would be two.

From these facts and arguments, the names isobromo-sinomenine and isobromo-sinomeninone would be inappropriate, and the authors wish to replace them by bromo-sinomeneine and bromo-sinomeneine ketone.(2) But the points, from which these two atoms of hydrogen were taken away, can not be decided at present.

When the brominating mixture (bromine 2 atoms) was left stand for a long time, bromo-sinomenine disappears slowly and bromo-sinomeninone appears in its place. Thus from the mixture left stand for a weak, bromo-sinomeninone was isolated in 40% yield. Thus, the hydrobromic acid gas generated in glacial acetic acid, at the concentration of 1/2~1/3 normality, could effect the hydrolysis of the enolic methoxyl of sinomenine at ordinary

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(1) Pinner, *Ber.*, **26** (1893), 292; M. Freund, *Ber.*, **39** (1906), 847.

(2) The name bromo-dehydro-sinomenine would be preferable, but the name dehydro-sinomenine was given to the other substance.

temperature. Sinomenine hydrochloride was also transformed into its hydrate by the same treatment, the necessary hydrochloric acid gas being liberated from acetyl chloride.

Experimental.

Bromo-sinomenine. Sinomenine hydrochloride (10 gr.), dissolved in glacial acetic acid (50 c.c.), is slowly added with bromine (5 gr.; 1 mol.) in glacial acetic acid solution (25 c.c.) at 15°C. When the precipitate of the perbromide was dissappeared, the bases are isolated in the ordinary way. The yield of the bromo-sinomenine (m.p. 153°) is 80% and that of isobromo-sinomenine varies 2~20%.

Anal. of bromosinomenine. Found: C=55.38, 56.09; H=5.71, 5.71; N=3.27; Br=19.91; CH_3O-=14.86%. $C_{19}H_{22}NO_4Br$=408 requires C=55.82; H=5.39; N=3.52; Br=19.61; CH_3O-=15.19%.

Mol. wt. Found (in glacial acetic acid): 425, 443.

Sp. rotatory power: $[\alpha]^{6}_{D}=(-0.354\times10)\div(0.3989\times1.0)=-8.87°$ in chloroform.

Hydrochloride (with 3 aq.): m.p. 116°. (Solubility in water 0.66%).

Hydrobromide: m.p. 232° (from methyl alcohol). Solubility in water 0.632%.

The both show beautiful silky lustre, when suspended in water.

Oxime: Dec. p. 211° (softening at 168°) Found: N=6.35%. Calc. for $C_{19}H_{23}N_2O_4Br$: N=6.62%.

Iodomethylate: m.p. 80°. Found: I=39.37, 30.12, 31.46%. Calc.: 23.08%. These extremely high values of iodine perhaps show the mobility of bromine atom against $AgNO_3+HNO_3$ at the ordinary temperature.

Isobromo-sinomenine (or Bromo-sinomeneine). Bromination is effected in the same way as above, only 2 mols. of bromine being used. Yield about 40%. The base is recrystallisable in long prisms from 100 parts of boiling alcohol. M.p. 217°.

Anal. Found: C=56.44, 55.97, 55.94; H=5.29, 4.91, 5.35; N=3.57; Br=19.30, 18.73; CH_3O-=15.29%. $C_{19}H_{20}BrNO_4$=408 requires C=56.16; H=4.92; N=3.45; Br=19.71; CH_3O-=15.27%.

Mol. wt. Found (in glacial acetic acid): 406, 414.

Sp. rotatory power: $[\alpha]^{9}_{D}=(+3.23\times10)\div(0.3890\times10)=-83.03$ in chloroform.

Hydrochloride: m.p. 231° (dec.) Solubility in water 2.96%.

Hydrobromide: m.p. 229°. Solubility in water 0.84%.

Oxime: m.p. 162°; hydrochloride m.p.>280°, softening at 236°. Found: N=6.04%. $C_{19}H_{20}BrN_2O_4.HCl$ requires N=6.12%.

Iodomethylate: m.p. 211-212°. Found: I=22.03%. Calc.: I=23.77%.

Isobromo-sinomeninone (or Bromo-sinomeneine Ketone). Prepared by heating isobromo-sinomenine (5 gr.) in 2n.HCl (25 c.c.) at 100° for one hour. Fine needles, melting at 198°. Very soluble in methyl alcohol, but recrystallisable from chloroform.

Anal. Found: C=55.01, 54.88, 55.23; H=4.98, 5.18, 4.94; N=3.27; Br=20.68; CH_3O- =7.93, 8.03%. $C_{18}H_{18}NO_4Br$ requires C=55.01; H=4.59; N=3.55; Br=20.30; CH_3O-= 7.87%.

Sp. rotatory power: $[\alpha]^{9}_{D} = (1.60\times10.0)\div(0.2666\times0.5) = +119.89°$.

Dioxime: m.p. 173.5° (dec.); hydrochloride, m.p. 212°, softening at 208°. Found: N=9.12%. $C_{18}H_{20}N_3O_4$ Br. HCl=458 requires N=9.12%.

Iodomethylate: m.p. 195° (dec.), softening at 190°. Found: I=22.03%. Calc.: 23.69%.

Bromo-sinomeninone. Brominating mixture as was described with bromo-sinomenine was left stand for some weeks, from which at several intervals brominated bases were isolated. The chief product was bromo-sinomeninone, melting at 227°. The yield was tolerably good, when the isolation was carried out after one week's standing.

Anal. Found: C=55.19, H=5.10, Br=20.24, CH_3O-=8.02%. Calc. for $C_{18}H_{20}NO_4Br$: C=54.82, H=5.07, Br=20.30; CH_3O-=7.86%.

Oxime: m.p. 189°. Found: N=9.47%. Calc.: N=9.90%.

Iodomethylate: m.p. 246° (mixed m.p. with that prepared in ordinary way 245°).

These results show clearly that bromo-sinomenine is transformed into bromo-sinomeninone in the brominating mixture. Moreover, the bromo-sinomenine itself was transformed into the bromo-sinomeninone in glacial acetic acid at ordinary temperature by the hydrobromic acid at the concentration as was attained in the bromination.

Sinomenine Hydrate. From the following mixtures, which were prepared to imitate the contents of hydrobromic acid gas in the brominating mixture, sinomenine hydrate was isolated in the annexed yield.

1. When the mixture was composed of sinomenine (free) 33 gr., glacial acetic acid 50 c.c., hydrobromic acid (48%) 20 c.c. and acetic anhydride (to destroy water) 50 c.c. the yield of sinomenine hydrate was: 4.5% after 24 hours, 15% after 48 hours and 45% after 2 weeks.
2. When the hydrobromic acid was replaced by acetyl-chloride, (sinomenine hydrochloride 40 gr., glacial acetic acid 100 c.c., acetyl anhydride 10 c.c. and acetyl chloride 7.8 gr.), the yield of sinomenine hydrate was 10% after 48 hours, but much better after 2 or 3 weeks.

The sinomenine hydrate was identified by the following properties.

M.p. 157° (twice recrystallised from ethyl alcohol.)(1)

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(1) When sinomenine hydrate was isolated from the 2 n. HCl, it melts generally at 138° thereabout. Recrystallisation elevates the melting point slowly and 157° is the most reliable, though it may not be the highest.

Anal. Found: $C=65.68$; $H=7.29$; $N=4.03$; $CH_3O-=17.72\%$. Calc. for $C_{19}H_{25}NO_5$: $C=65.70$; $H=7.20$; $N=4.03$; $CH_3O-=17.86\%$.

Sp. rotatory power: $[\alpha]_D^7=+41.85$. Oxime: m.p. 231°.

Iodomethylate: Melting and decomposing into yellow bubbles at 192–195°. (The dec. point 264° formerly given was regretfully based on some accidental error. The new dec. point 192–195° was checked by three different preparations, obtained from different lots of sinomenine hydrate). Found: $I=24.56\%$. Calc.: $I=25.97\%$.

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RESEARCHES ON CHEMICAL CHANGES UNDER A STRONG ELECTRIC FIELD.

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Introduction. Many reports on the studies of the chemical changes and equilibria between different gasses due to high tension electric discharges such as silent-, brush-, point-, spark-, and arc discharge, etc. are found in every periodical of that part. But those studies between gases and liquids are rare, and the results are divergent. In this experiment a new method was devised to apply extremely strong electric field to the reacting substances both safely and efficiently.

Principles and Methods. When a small gas bubble (dielectric constant $=\epsilon_g$) was placed in a dielectric liquid, which is under the action of uniform electric force E_l, the force on the bubble is given by the equation

$$E_g = \frac{3}{2+\frac{\epsilon_g}{\epsilon_l}} E_l$$

It is general that $\epsilon_g/\epsilon_l < 1$, therefore the force acting on the gas bubble is stronger than that on the surrounding dielectric liquid, or, when a certain electric potential is applied between the electrodes, the force acting on the gas bubble must be stronger than that when the whole dielectric is a gas. As the dielectric strength of a liquid is generally stronger than that of a gas, it is able to generate a corona discharge in a gas in this way without causing any breaking down of the materials.

Now, let the distance between the two parallel electrodes be L, the potential difference of the electrodes V, and the space be filled with a gas $(\epsilon_a=1)$, then the electric displacement is

$$D = \frac{V}{4\pi L},$$

and the electric force

$$E_a = 4\pi \frac{D}{\epsilon_a} = \frac{V}{L},$$

Divide the space between the two electrodes into several layers (a, b, c, etc.) of thickness l_a, l_b, l_c, etc., and fill the each layer with different dielectric material of dielectric constant ϵ_a, ϵ_b, ϵ_c, etc. respectively, then the force in (a) becomes

$$E_a = 4\pi \frac{D'}{\epsilon_a} = \frac{V}{l_a + \frac{l_b}{\epsilon_b} + \frac{l_c}{\epsilon_c} + \ldots}$$

Comparing E_a and E_a' we have

$$E_a' = E_a \frac{L}{l_a + \frac{l_b}{\epsilon_b} + \frac{l_c}{\epsilon_c} + \ldots}$$

If $\epsilon_b > 1$, $\epsilon_c > 1, \ldots\ldots$, then $E_a' > E_a$.

This indicates that, selecting proper materials, the force on a special layer (here a gas) is able to make stronger than usual. It is also able to increase the electric strength of the layer in this way, and we can safely raise the applied voltage to a higher value than usual.

In this experiment, several reaction vessels were devised, but the concentric cylindrical tubes, consisting of layers of glass wall and dielectric liquids, showed to be the most convenient for the purpose. The innermost tube and outermost glass vessel, containing electrolyte solution, play the rôle of the electrodes. The reaction vessel is made of four concentric tubes A, B, C and D. The innermost tube A, containing an electrolyte solution, is used as the inner electrode. The second tube B, surrounding A, gives a passage to the reacting gases. The third tube C, surrounding B, contains the reacting liquids through which the reacting gas is bubbled up. The outermost protective tube D contains dielectric liquids such as liquid paraffine, nitrobenzene or some oils. The cylinder D is placed in water, in which the outer electrode is put.

If there are no liquids in C- and D-tube of this apparatus, the corona discharge in B will occur only when the electric force (in KV.) on the surface of A reaches the following value:

$$E = 30 + \frac{9}{\sqrt{r}} \quad (r: \text{ radius of A in cm.})$$

In this experiment the applied voltage was 40–60 KV. and the reaction tubes were made of proper sizes to produce corona discharge in B, which activates the reacting gas in it. When the corona sets in, the value of ϵ of that part becomes very great and the whole voltage distributes mainly between C and D. It is evident that the distribution of the force is inversely proportional to ϵ_c and ϵ_d.

The gas, formerly activated in this way, then comes into C and mixes with the liquid in it. Here the gas, being still acted by the strong electric force, which is very irregular in C, becomes very fine particles in some cases and readily reacts with the surrounding liquid. When it is observed in the dark, every particle has pale light and some of them are scintillating. This dispersion of the gas will partly be due to the heterogeneous distribution of the electric force and partly due to the change of surface tension of the liquid film enclosing the gas bubbles. The dispersion of the gas bubbles will also be affected by the dielectric constant, viscosity and temperature of the dielectrics. In this experiment it was observed in the cases of unsaturated oils, and not in the cases of nitrobenzene and acetic acid.

Experimental Results. The cases studied in this experiment are:

1. reduction of nitrobenzene, methylene blue and benzaldehyde,
2. hydrogenation of oleic acid, silkworm pupa oil, cod-liver oil, fish oil, soy-bean oil and olive oil with hydrogen,
3. ozonisation of oleic acid and olive oil with oxygen,
4. chlorination of acetic acid with chlorine,
5. reaction of nitrogen and hydrogen to ammonia in oleic acid,
6. also the effect of temperature and that of the presence of metallic powder (catalyser) on the hydrogenation of oils.

The results are summarized in Table 1. The products were chemically tested in some cases (iodine value and solubilities, etc.), and physically in other cases (refractive indices, microscopic study, etc.) The rate of reduction was calculated by measuring the change of iodine value. The index of refraction ($n_D^{25°}$) was also measured in most cases. From these results it will not be too much to say that this is not only a new method of hydrogenation and ozonization of some organic dielectrics, but also a new method of ammonia synthesis by electric discharge. The effect of temperature elevation or addition of metallic powders such as Cu, Al, Fe (till 100°C.) is not eminent in this method, but the presence of reduced Ni is somewhat effective, especially when the temperature was elevated up to 100–120°C. These effects were studied in cases of hydrogenation of oils, but the details will be omitted here.

The following interest phenomenon has, however, to be mentioned, which was observed when the electric force was applied on the reacting system of oil and hydrogen in the tube with the metallic catalyser of Cu or Al powder. The metallic powders arrange themselves under the electric field along the wall of the glass cylinder in beautiful figures very much like the common cypress leaves. In the case of Fe powder, the figure was quite different, a ring of scintillating zone of Fe powder was observed in the upper part of the reaction tube. The width of the zone was seemed to grow inversely with the elevation of applied voltage. The appearance, growth and extinction of these dust figures are very interesting, and it will give some suggestion to experimental crystal-physics.

Table 1.

No. of Exp.		Substance	Gas	Time in hours	Amount of reduction	Reduction per hour	Results
I	a	Nitrobenzene	H_2	25			Change of colour, formation of a resinous and cryst. matter, pale yellow rhombic needle (probably azoxybenzene)
	b	Methylene blue (chloroform)	,,	5			No appreciable change
	c	Benzaldehyde	,,	29			Change was not determined
	d	Silkworm pupa oil	,,	36.5	12.7%	0.35%	Discoloration, red to white, formation of white turbidity
	e	Cod-liver oil	,,	68.5	29.9%	0.44	Increase of viscosity, formation of semitransparent solid
	f	Fish oil	,,	ca. 60	19.4	0.35	Discoloration, crystalline ppts.
	h	Olive oil	,,	26.5	8.9	0.34	Reduction prod. of 5 kinds
	i	Oleic acid	,,	39.5	21.2	0.54	Formation of stearic acid
	i′	,,	,,	48	16.3	0.34	
II	a	Aniline	O_2	15	n_D^{25} 1.58328 →	1.58304	No appreciable change
	b	Oleic acid	O_2	24	1.46034 →	1.46510	Formation of ozonide, increase of viscosity and odour
	c	Olive oil	O_2	7			Ozonized
III	a	Oleic acid	N_2	17			No change
	b	,,	$2H_2+N_2$	1.5			Some change occurred but undetermined. Formation of NH_3
IV	a	Acetic acid	Cl_2	2.5			No appreciable change
V	a	Soy-bean oil	H_2	0.5			Undetermined, 180°C.
	b	Oleic acid	,,	24	8.8	0.37	100–200°C.

In order to explain whether the chief cause of activation of the reaction is the strong electric force or the ultraviolet light produced thereby in the gas bubbles in the reaction tube, some experiments were carried out by means of an ultraviolet light generator (Acme's Sun Light), and it was verified that the ultraviolet light had also the effect of the like but the quantitative comparison has been a matter of very difficult.

Summary.

1. A new method was devised to apply extremely strong electric force to gases and dielectric liquids, and accelerate their reactions.
2. Using this method, many reactions between gases and liquids under the action of strong electric force were studied. Thereby the effect of temperature elevation and presence of metallic powders (catalyser) were also studied.
3. In connecting with the electric discharge some interesting phenomena were observed.

The most part of this experiment was carried out about four years ago (1925-26) as the graduation thesis of the Tokyo Imperial University, Faculty of Science, under the guidance of Dr. Y. Yamaguti, to whom the author expresses his best thanks. This sort of experiments should be continued by the author, but his condition is now to give up his hope for some time, and he has been obliged to write the report still on its middle way.

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SORPTION OF AMMONIA BY CHARCOAL.

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The author studied the sorption phenomena by charcoal⑴ and chabazite⑵ of carbon dioxide, etc., and concluded that the gas molecules enter into the molecular cavities in the solid body and form a homogeneous solid solution.⑶

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(1) Sameshima, this Bulletin, **2** (1927), 1 and 246; Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289.

(2) Sameshima, this Bulletin, **4** (1929), 96.

(3) Sameshima, this Bulletin, **4** (1929), 125; *Chem. News*, **139** (1929), 61.

In the present paper, the result of investigation of the sorption of ammonia by charcoal is reported. The sorption amount by charcoal of ammonia was already measured by numerous authors.(1) A few reports are found on the velocity of sorption of ammonia by charcoal,(2) which, however, are not so exact and the observations did not continued sufficiently long period of time.

The present experiment was undertaken, at first, for the purpose to compare the sorption amounts and velocities of ammonia by granular and by powder charcoals, just as reported in the case of carbon dioxide.(3) But by the experiment, it has been known that the sorption amount by charcoal of ammonia cannot be measured exactly for the equilibrium state cannot be attained even after several months. The measurement has been continued for six months, but the charcoal was still absorbing the gas in considerable velocity. This is a very remarkable fact. So it is almost impracticable to measure the sorption amount of ammonia by charcoal exactly.

Experimental. The apparatus and the method of measurement are quite the same with those which were described already.(4) The charcoal has been made by heating the pure saccharose from Merck in a porcelain crucible to red heat and then transferred into a quartz tube and again heated in vacuo to ca. 1000°C. for 30 minutes. The ammonia was prepared from ammonium chloride and lime, and dehydrated by potassium hydroxide, frozen and fractionated twice with liquid air.

In the experiment, 0.3550 gram of charcoal has been used. The volume of ammonia in the apparatus has always been read after the temperature of charcoal was adjusted to 25.00°C., and the pressure of gas to 760 mm. The volume of gas absorbed can be calculated and then reduced to that at normal temperature and pressure. The results are shown in Table 1.

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(1) Hunter, *Phil. Mag.*, **29** (1865), 116; *J. Chem. Soc.*, **24** (1871), 76; Joulin, *Ann. chim. phys.*, **22** (1881), 398; Kayser, *Wied. Ann.*, **12** (1881), 526; **14** (1881), 450; Chappuis, *Wied. Ann.*, **19** (1883), 21; Vaubel, *J. prakt. Chem.*, **74** (1906), 232; Titoff, *Z. physik. Chem.*, **74** (1910), 668; Hempel, *Z. Elektrochem.*, **18** (1912), 724; Richardson, *J. Am. Chem. Soc.*, **39** (1917), 1828; Firth, *J. Chem. Soc.*, **119** (1921), 926; Ruff, *Z. angew, Chem.*, **38** (1925), 1164; Henglein and Grzenkowski, *Z. angew. Chem.*, **38** (1925). 1186; Magnus and Cahn, *Z. anorg. allg. Chem.*, **155** (1926), 205; Ruff and Hohlfeld, *Kolloid-Z.*, **36** (1925), 23; Ruff and Roesner, *Ber.*, **60** (1927), 411.

(2) Giesen, *Ann. Physik*, **10** (1903), 842; Pickles, *Chem. News*, **121** (1920), 25.

(3) Sameshima, this Bulletin, **2** (1927), 1.

(4) Sameshima, this Bulletin, **2** (1927), 1 and 246.

Table 1.

Date D. H. M. S.	Time duration from the beginning in minutes	Apparent volume of NH_3 absorbed by 0.3550 gr. of charcoal in c.c. (N.T.P.)	Leak estimated by blank experiment in c.c.	Corrected volume of HN_3 absorbed by 0.3550 gr. of charcoal in c.c. (N.T.P.)
1928, July 18, 10-30-0 A.M.	0	0	0	0
10-30-20 A.M.	0.33	22.317	0	22.317
10-30-46 A.M.	0.77	24.345	0	24.345
10-31-16 A.M.	1.27	32.305	0.01	32.29
10-31-50 A.M.	1.83	34.120	0.01	34.11
10-32-20 A.M.	2.33	35.040	0.01	35.03
10-33-54 A.M.	3.90	35.937	0.02	35.92
10-40-50 A.M.	10.83	36.528	0.045	36.483
10-51 A.M.	21	36.846	0.070	36.776
11-37 A.M.	67	37.326	0.143	37.183
12-50 P.M.	140	37.578	0.196	37.382
3-36 P.M.	306	37.927	0.235	37.692
July 19, 10-10 A.M.	1420	38.681	0.325	38.356
19, 2-10 P.M.	1660	38.733	0.332	38.401
20, 1-35 P.M.	3065	39.032	0.357	38.675
21, 12-15 P.M.	4425	39.197	0.360	38.837
23, 11-50 A.M.	7280	39.416	0.367	39.049
24, 12-10 P.M.	8740	39.508	0.370	39.138
25, 11-50 A.M.	10160	39.591	0.373	39.218
27, 1-30 P.M.	13140	39.685	0.380	39.305
30, 11-0 A.M.	17310	39.813	0.390	39.423
Aug. 1, 10-10 A.M.	20140	39.912	0.397	39.515
3, 2-20 P.M.	23270	39.993	0.404	39.589
6, 12-0 M.	27450	40.082	0.414	39.668
8, 10-15 A.M.	30225	40.147	0.421	39.726
13, 11-15 A.M.	37485	40.249	0.438	39.811
16, 11-15 A.M.	41805	40.313	0.448	39.865
22, 1-0 P.M.	50550	40.419	0.468	39.951
27, 1-30 P.M.	57780	40.518	0.485	40.033
31, 10-30 A.M.	63360	40.575	0.498	40.077
Sept. 7, 12-20 P.M.	73550	40.666	0.522	40.144
17, 11-15 A.M.	87885	40.790	0.556	40.234
28, 2-20 P.M.	103910	40.960	0.594	40.366
Oct. 13, 10-40 A.M.	125290	41.084	0.644	40.440
30, 1-40 P.M.	149950	41.233	0.702	40.531
Nov. 19, 1-50 P.M.	178760	41.347	0.770	40.577
Dec. 10, 1-30 P.M.	208980	41.427	0.841	40.586
24, 2-30 P.M.	229200	41.491	0.888	40.603
1929, Jan. 28, 12-10 P.M.	279460	41.618	1.006	40.612

The charcoal in the apparatus was heated to 300°C. evacuating by a mercury diffusion pump for 30 minutes. Then keeping the temperature of charcoal to 25.00°C., the gas was introduced into it and the sorption began to take place. The contaction of charcoal and gas took place at half past ten before noon on July 18th, 1928. The observation continued, then, to the end of January 1929, extending more than six months. The first column of Table 1 shows the date and time, the second column the time duration in minutes of contact of charcoal and gas, the third column the volume of ammonia absorbed by 0.3550 gram of charcoal calculated by the manner described already,(1) the fourth column the amount of leak of the apparatus estimated by a blank experiment which is described below, the fifth column the corrected volume of ammonia absorbed by 0.3550 gram of charcoal.

After the sorption experiment by charcoal had been finished, the blank experiment has been done without the charcoal, other conditions remaining unchanged. The blank experiment was continued three and half months as shown in Table 2.

Table 2.

Date D. H. M.		Time duration from the beginning in minutes	Volume of NH_3 decreased in c.c. (N.T.P.)
Feb. 1, 11-40	A.M.	0	0
11-46	A.M.	6	0.029
11-58	A.M.	18	0.067
1- 4	P.M.	84	0.163
2-21	P.M.	161	0.204
3, 3-40	P.M.	3120	0.348
5, 2-30	P.M.	5930	0.352
7, 3-40	P.M.	8880	0.359
10, 1-10	P.M.	13050	0.405
15, 12- 0	M.	20180	0.419
19, 1-10	P.M.	26010	0.414
25, 2-20	P.M.	34720	0.423
Mar. 4, 2-40	P.M.	44820	0.456
14, 4-50	P.M.	59350	0.488
28, 2-50	P.M.	79390	0.532
Apr. 12, 1-30	P.M.	100910	0.582

The decrease of volume of ammonia in the apparatus was read and is shown in the third column of Table 2. There was a considerable decrease of volume at the first day of observation, which is probably due to the sorption of ammonia by the glass wall and the grease on the stop-cocks. From the third day forward (reading was not taken on the second day) the

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(1) Sameshima, this Bulletin, **2** (1927), 246.

amount of decrease was nearly in linear relation with time, being about 0.1 c.c. per month. This may be the leakage through the grease of stopcocks.

Now by the method of least square applying to the values below 3120 minutes in the table, we obtain the following linear equation.

$$l=0.00000235\ t+0.350$$

where l denotes the volume of leakage in c.c. and t the time in minutes.

The values below 0.357 (corresponds to 3065 minutes) in the fourth column of Table 1 have been calculated by this equation, while those above 0.332 (corresponds to 1660 minutes) in the same column have been obtained by interporation from the leakage curve depicted by the values of Table 2.

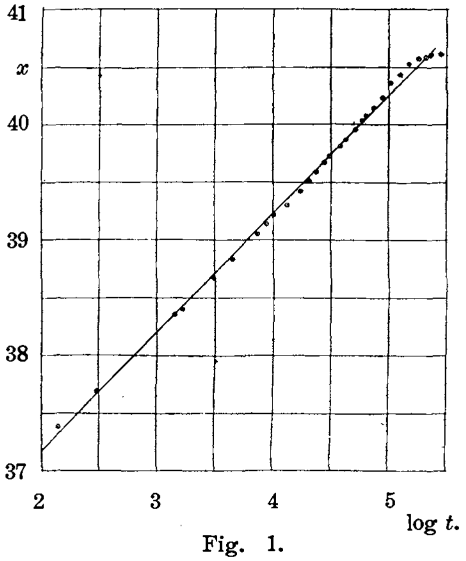

Fig. 1.

Now putting the volumes of gas sorped against the logarithms of time we obtain Fig. 1. This is nearly a straight line. The values above 67 minutes in Table 1 are not shown in the figure, for this part does not lie on the straight line.

It is very remarkable fact that the charcoal absorbs ammonia for such a long period. What is the cause of this phenomenon? Does a chemical reaction takes place between charcoal and ammonia? It is described in early literatures⁽¹⁾ that the carbon react with ammonia at the elevated temperature forming ammonium cyanide and hydrogen. Thus,

$$C + 2NH_3 = NH_4CN + H_2.$$

If this reaction proceeds at room temperature in a measurable velocity, however slow it may be, the volume of gas must decrease. To decide this point the following experiments have been undertaken.

After the sorption experiment had been finished, the gas remaining in the apparatus and that absorbed by charcoal was pumped out and collected into a gas burette using an apparatus shown in Fig. 2.

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(1) Kuhlmann, *Lieb. Ann.*, **38** (1841), 62; Langlois, ibid., **38** (1841), 64; Weltzien, ibid., **132** (1864), 224.

A is the bulb containing charcoal, E the burette to measure the volume change of ammonia and F the niveau tube just as described already.⁽¹⁾ H is a Töpler pump and K a gas burette. At first the gas space, J, in the Töpler pump is well evacuated, and the burette K is filled with mercury. Then by opening the stop-cock C ammonia enters into J, which is then transferred into K by elevating I. This is repeated many a times until most of the gas, absorbed and unabsorbed, collects in K. During this process the bulb A is heated to 100°C. By this manner, the volume of gas collected in K was 46.3 c.c. at N.T.P., while the ammonia initially introduced was 50.50 c.c. at N.T.P.

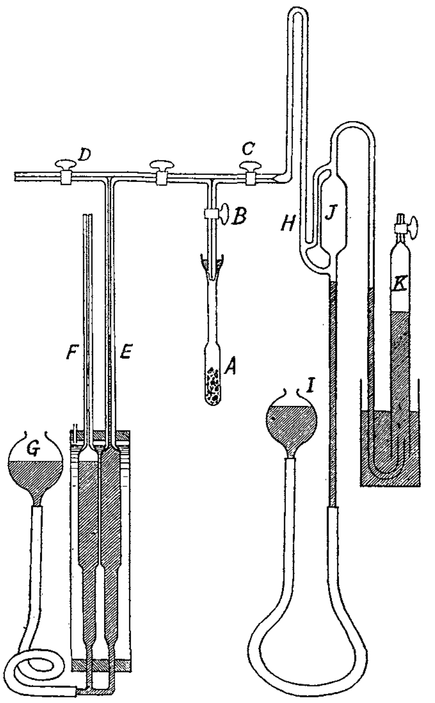

Fig 2.

This gas was almost completely absorbed by introducing 17 c.c. of dilute sulphuric acid (0.2 n.) into the tube K. The gas remained unabsorbed by sulphuric acid was only 0.3 c.c. It was known, therefore, that there was no hydrogen in the gas.

Now, the bulb A was detached from the apparatus and the charcoal was transferred into a glass tube, which was subsequently heated, evacuated, sealed and weighed. By subtracting the weight of glass tube, the exact weight of the charcoal can be known. The weight of charcoal thus determined was 0.3541 gram. As the charcoal initially taken for the experiment was 0.3550 gram, the loss is only 0.0009 gram which can be attributed to the experimental error.

Thus it was ascertained that there was no perceptible chemical reaction between charcoal and ammonia at room temperature, and the slow decrease of the volume of ammonia must be attributed to some physical cause such as diffusion or sorption into the deep part of charcoal body.

Theoretical. The diffusion velocities of a substance, say gas, into solid bodies of simple shapes are calculated. Let x be the quantity of gas

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(1) Sameshima, this Bulletin, **2** (1927), 2.

absorbed by the solid body of definite surface area, t the time, and a, b, c, etc. the constants. Then the diffusion into a plate of finite thickness is given by an equation of the following form.⁽¹⁾

$$x=a\left(\frac{1}{2}-\frac{4}{\pi^2}e^{-bt}-\frac{4}{9\pi^2}e^{-9bt}-\ldots\ldots\right)$$

By a similar calculation, using Fourier's theorem, we obtain a formula for the diffusion into a plate of infinite thickness, thus,

$$x=a\sqrt{t}\,.$$

Moreover, we can deduce the formula for the diffusion into a sphere,

$$x=a-b\left(e^{-ct}+\frac{1}{4}e^{-4ct}+\frac{1}{9}e^{-9ct}+\ldots\ldots\right)$$

All these formulas, however, are not applicable to the values of Table 1. A porous substance like charcoal has a very complicated surface, so the diffusion velocity may not be calculated exactly. But at any rate, in the present case, there is neither evidence nor numerical support of the diffusion theory.

Now the sorption theory will be examined. Here "sorption" means the entering of the gas molecules into the molecular cavities and forming a solid solution.⁽²⁾ The entering of gas molecules into relatively large openings among solid molecules are accomplished easily. So the sorption process of the main part of gas is finished in relatively short time. In the present experiment it takes about one hour. About 37 c.c. of ammonia has been absorbed during this period as shown in Table 1. This part of the sorption curve cannot yet be treated quantitatively.

Then the gas molecules begin to enter into more narrow cavities among solid molecules. The narrower the cavity, the greater the resistance. Let us assume that the resistance encounters in entering into a narrow molecular cavity is proportional to the time required for it. Thus,

$$R=a\,t,$$

where R denotes the resistance, t the time and a a constant.

On the other hand, we may assume that the velocity of sorption is inversely proportional to the resistance, So

$$\frac{dx}{dt}=\frac{b}{R}$$

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(1) McBain, *Z. physik. Chem.*, **68** (1910), 477.

(2) Sameshima, this Bulletin, **4** (1929), 127.

where x is the quantity of gas sorped, and b another constant. Therefore we have,

$$\frac{dx}{dt}=\frac{b}{at}$$

More precise explanation may be necessary. Assume an ammonia molecule attacks on a narrow channel to enter itself, encountering a great resistance. When the attack has been continued for t minutes the molecule enters itself to a certain depth in the solid. Namely, it takes t minutes for the dissolution of the ammonia molecule in charcoal. Then a space has been cleared where another ammonia molecule can settles. This results the sorption of one molecule of ammonia. Thus the sorption velocity depends upon the dissolution velocity.

Now the above equation is integrated,

$$\int dx=\frac{b}{a}\int\frac{1}{t}dt+k$$

or

$$x=\frac{b}{a}\ln t+k,$$

where k is the integration constant. Using another constant K, we have

$$x=K\log t+k.$$

So the sorption amount, x, and the rogarithm of time, $\log t$, is in a linear relation, which has been observed in the present experiment as shown in Fig. 1.

Summary.

1. The sorption velocity of ammonia by sugar charcoal has been measured, extending over six months.
2. It was known that the charcoal absorbs ammonia for a very long time, taking more than several months to arrive at the equilibrium condition.
3. The sorption velocity from one hour forward can be expressed by an equation.

$$x=K\log t+k,$$

where x is the sorption amount, t the time, and K and k are the constants.

4. The mechanisms of sorption have been discussed.
5. The sorption velocity depends upon the dissolution velocity of ammonia molecules into the narrow molecular cavities of charcoal.

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EQUILIBRIA IN THE SYSTEM: $Ca(ClO_3)_2 + 2\,KCl \rightleftarrows 2\,KClO_3 + CaCl_2$ at 15° and 45°C.

By **Yukichi OSAKA** and **Hideo NISHIO**.⁽¹⁾

Received April 26, 1930. Published June 28, 1930.

In the old process for manufacture of potassium chlorate, chlorine is passed into milk of lime and then potassium chloride is added to the solution thus formed to produce potassium chlorate by double decomposition. The reactions involved in this process are represented by the equations:

$$6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O, \quad \ldots\ldots\ldots\ldots(1)$$
$$2KCl+Ca(ClO_3)_2=2KClO_3+CaCl_2. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

We have studied the equilibria of the second reaction at 15.0° ± 0.1° and 45.0° ± 0.1°C. One of us, Nishio, by whom the experiments were being carried out, had to leave the Laboratory and so we report here very briefly the results so far obtained.

The materials used were carefully purified and the method was the ordinary one.⁽²⁾

The compositions of the liquid phases are expressed according to the general formula:

$$100mH_2O,\ xK,\ (100-x)(\tfrac{1}{2}Ca),\ yCl,\ (100-y)ClO_3.$$

The results are given in Tables 1 and 2 and graphically in Figs. 1 and 2.

The data with asterisk were calculated from the values interpolated from the data found in the International Critical Tables, Vol. IV.

As seen from the diagrams, potassium chlorate and calcium chloride are the stable pair in these temperatures, and this fact is fundamentally important for the process of manufacture of potassium chlorate.

The solution obtained by the reaction (1) is expressed by

$$100mH_2O,\ 100(\tfrac{1}{2}Ca),\ 83.3Cl,\ 16.7ClO_3,$$

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(1) This report has been already published by one of us under his former name Hideo Takesuye in the Report of the Imperial Industrial Laboratory in Osaka where the work was carried out.

(2) For the details, see the Report, above cited, Vol. **10** (1929), No. 11.

Table 1.

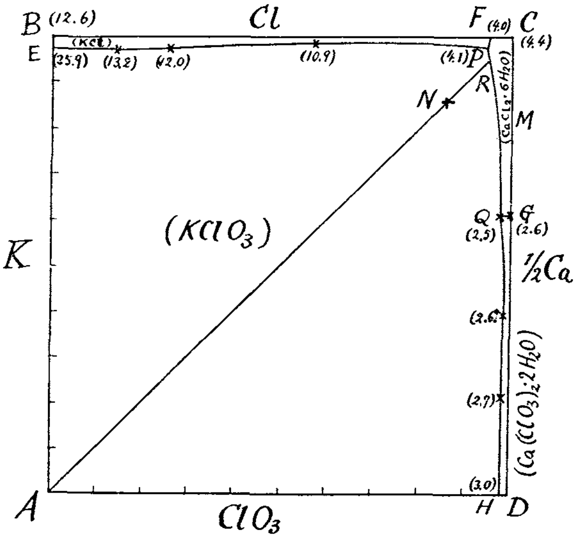
Temperature: 15.0°C.

No.	x	y	m	Residue.
1	100	100	12.6*	KCl
2	100	0	111 *	$KClO_3$
3	0	100	4.4*	$CaCl_2.6H_2O$
4	0	0	—	$Ca(ClO_3).2H_2O$
5	100	97.09	25.68	$KCl+KClO_3$
6	85.39	97.05	13.23	,, + ,,
7	74.26	97.20	12.04	,, + ,,
8	42.33	97.97	10.90	,, + ,,
9	17.28	98.20	7.14	,, + ,,
10	4.71	100.	4.02	,, $+CaCl_2.6H_2O$
11	0	61.17	2.56	$CaCl_2.6H_2O+Ca(ClO_3)_2.2H_2O$
12	3.40	85.77	3.91	,, $+KClO_3$
13	1.27	0	2.99	$KClO_3+Ca(ClO_3)_2.2H_2O$
14	1.08	21.59	2.88	,, + ,,
15	1.09	39.64	2.57	,, + ,,
16	5.01	97.55	4.10	$KCl+KClO_3+CaCl_2.6H_2O$
17	2.01	60.88	2.46	$KClO_3+Ca(ClO_3)_2\cdot2H_2O+CaCl_2\cdot6H_2O$

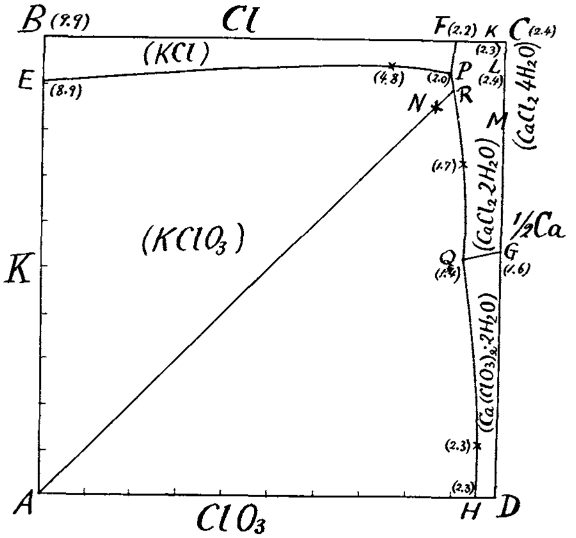
Table 2.

Temperature: 45.0°C.

No.	x	y	m	Residue.
1	100	100	9.9*	KCl
2	100	0	40.5*	$KClO_3$
3	0	100	2.4*	$CaCl_2.4H_2O$
4	0	0	—	$Ca(ClO_3)_2.2H_2O$
5	100	90.43	8.94	$KCl+KClO_3$
6	24.72	94.81	4.85	,, + ,,
7	10.61	100	2.17	,, $+CaCl_2.2H_2O$
8	1.63	100	2.35	$CaCl_2.2H_2O+CaCl_2.4H_2O$
9	0	98.57	2.36	,, + ,,
10	0	54.22	1.56	,, $+Ca(ClO_3)_2.2H_2O$
11	8.47	73.07	1.69	$KClO_3+CaCl_2.2H_2O$
12	4.53	0	2.28	,, $+Ca(ClO_3)_2.2H_2O$
13	4.27	11.50	2.27	,, + ,,
14	11.70	92.99	1.99	$KCl+KClO_3+CaCl_2.2H_2O$
15	8.13	52.38	1.42	$KClO_3+Ca(ClO_3)_2.2H_2O+CaCl_2.2H_2O$



Temperature: 15.0°C.
Fig. 1.



Temperature: 45.0°C.
Fig. 2.

and represented by the point M in the diagrams. When potassium chloride equivalent to the chlorate is added, the solution before separation of any solid phase is expressed by

$100mH_2O$, 14.3K, 85.7($\frac{1}{2}$Ca), 85.7 Cl, $14.3ClO_3$,

and represented by the point N in the diagrams.

The straight line drawn from A through N meets the curve PQ at R. The line NR represents the change of the composition of the solution as potassium chlorate crystallizes out, and when it reaches R, calcium chloride begins to crystallize out together with potassium chlorate.

When the two diagrams are compared, it may be concluded that the lower the temperature the more potassium chlorate crystallizes out before the deposition of calcium chloride.

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THE ELECTROLYTIC REDUCTION OF PHTHALIMIDES.
PART I.

By Buhei SAKURAI.

Received May 14, 1930. Published June 28, 1930.

The electrolytic reduction of phthalimide was undertaken by T. Shimamoto, S. Araki and M. Hanawa at suggestion of Professor M. Matsui in his laboratory, but they could not continue the work to completion. I, therefore, took up the problem as a part of a general theme dealing with the electrolytic reduction of cyclic imides and tried to make the progress of the reaction clear, freely consulting the results obtained by the above mentioned colleagues.

So far as my experiments were concerned the electrolytic reduction was observed to proceed only to the stage of pyrrolidone, the further reduction to the pyrrol or the pyrrolidine stage having been unattainable in all cases. By properly controlling the electrolytic condition I could always isolate hydroxyimidines as the intermediate reduction product which could not hitherto be prepared by a purely chemical process.

Free phthalimide was electrolytically reducible only in an acid solution, and changed into oxyphthalimidine or phthalimidine according to the electrolytic conditions. In an alkaline solution phthalimide was chiefly hydrolysed into phthalamic acid and phthalic acid and gave no reduction-product. In the case of methyl or ethyl phthalimide intermediate oxyimidines were obtained when electrolysis was conducted in their acid solution with the copper cathode. With the lead cathode reduction went further on so as to produce phthalimidine.

It is here to be noted that so-called oxyphthalimidine prepared purely chemically by A. Reisert(1) differs from that which I prepared by the electrochemical method. While my oxyphthalimidine melts at 105°, that obtained by Reisert is reported to melt at 171°. In studying how they differ from each other it was found that the former can be transformed into the latter, when it was dissolved in 6N-H_2SO_4 at about 75° and then precipitated again by neutralizing sulphuric acid with caustic soda. The substance thus formed crystallized in needles and melted at 170–171°. Its properties were identical with Reisert's oxyphthalimidine in all respects and its melting point showed no depression when mixed with some oxyphthal-

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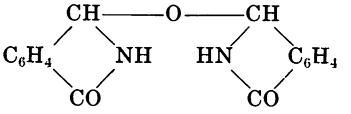
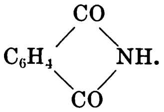
(1) *Ber.*, **46** (1913), 1488.

imidine prepared by reducing phthalimide with zinc and caustic soda. Reisert describes that his oxyphthalimidine changes into an anhydride  by the action of glacial acetic acid. Oxyphthalimidine prepared electrolytically was also found to behave similarly. Now it was made clear from the result of the molecular weight determination that oxyphthalimidine prepared by me is the normal compound, while that obtained by Reisert is a polymerized substance consisting of two molecules.

I. Phthalimide,  By reducing phthalimide chemically with tin and hydrochloric acid C. Graebe(1) could only isolate phthalimidine as the reduction product. But by electrolytic chemical method I could isolate the intermediate reduction product which is to be named hydroxy- or oxyphthalimidine, as is described below.

To an alcoholic hydrochloric acid solution consisting of 50 c.c. of alcohol, 10 c.c. of hydrochloric acid (sp. gr. 1.2) and 50 c.c. of water, 3 grams of phthalimide were added, and the mixture was used as the catholyte. As electrodes lead was used and a current of 2 amp./100 sq. cm. was passed at 20°–30°, maintaining the solution always in agitation. After 4 hours' electrolysis the catholyte coloured greenish yellow was made slightly alkaline by adding a caustic soda solution and cautiously evaporated under a reduced pressure, when a substance which was afterward confirmed to be oxyphthalimidine separated out in a needle form. Exactly the same result was also obtained with an alcoholic sulphuric acid solution in which copper was observed to act as the cathode with similar effect.

The substance separated out as needle crystals was soluble in hot water and alcohol, and difficultly so in benzene and ether. It melted at 105° and was easily transformed into the original substance when oxidized with potassium permanganate and sulphuric acid, and was also reducible further to phthalimidine when a current of a greater density was passed into a more strongly acidic solution. The results of the elementary analysis and of the molecular weight determination were found as follows:

Anal. Subst. = 0.0680; CO_2 = 0.1610; H_2O = 0.0296 gr. Found: C = 64.51; H = 4.84%. Calc.: C = 64.43; H = 4.73%.

0.3630 gr. substance produced ammonia which required 6.4 c.c. of 0.3879 N-HCl. Found: N = 9.38%. Calc.: N = 9.40%.

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(1) *Ann.*, **247** (1888), 288.

Its molecular weight was determined by the ebullioscopic method using ethyl alcohol as the solvent.

Subst. = 0.253, solvent = 15.382 gr.; elevation of b.p. = 0.080°. Mol. wt., found: 155, calc.: 149.

Another experiments was next tried making the cathode solution about 5 times more acidic and passing a current of 6 amp./100 sq. cm. for 6-7 hours. The temperature was maintained between 30° and 40°. When the electrolysis was over the electrolytic solution, coloured greenish yellow, was evaporated under a reduced pressure to remove alcohol, and left to stand for a day after having been made slightly alkaline, whereupon phthalimidine separated out as long needle crystals. A sulphuric acid solution consisting of equal volumes of water, alcohol and concentrated sulphuric acid also gave nearly the same results. It is a rather remarkable fact that even the copper cathode produced the same reduction product, but not intermediate oxyphthalimidine, when worked with a strongly acidified cathode solution.

Phthalimidine was purified by recrystallizing it from alcohol and obtained as colourless needles melting at 149°. Its hydrochloride combines with gold trichloride to form a double salt, melting point of which was determined to be 195°. For analysis the gold content of this double chloride was estimated.

0.1590 gr. substance gave on ignition 0.0515 gr. Au. Found: Au = 32.40%. calc.: Au = 32.48%.

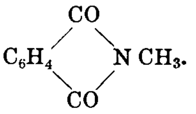
As was stated before, oxyphthalimidine prepared electrochemically changes into the so-called oxyphthalimidine obtained by Reisert by a purely chemical method. Though the latter has higher melting point its chemical properties are nearly the same with those of the former, changing to phthalimide on oxidation and to phthalimidine on reduction. On determining its molecular weight by the ebullioscopic method it was found to be a polymerized substance consisting of two molecules, thus:—

Subst. = 0.256, solvent = 19.05 gr.; elevation of b.p. = 0.052°. Mol. wt., found: 302, calc.: 298.

Reisert states that his oxyphthalimidine changes into an anhydride melting at 240° when boiled with glacial acetic acid. It was now found that normal oxyphthalimidine, just like the polymerized substance, may also be transformed into the same anhydride when treated with 6 normal sulphuric acid heated above 75°. The molecular weight of the anhydride was also determined by the boiling point method as follows:

Subst.=0.110, solvent=15.33 gr.; elevation of b.p.=0.030°. Mol. wt., found: 280, calc.: 281.

A series of experiments were carried out electrolytically to reduce phthalimide in a solution of about 2 normal caustic soda, but in no case reduction products could be isolated. It was observed that phthalimide easily undergoes hydrolysis and changes into phthalamic acid and further to phthalic acid.

II. Methyl Phthalimide,  $C_6H_4\begin{matrix}CO\\ CO\end{matrix}NCH_3$. The electrolytic reduction of methyl phthalimide in a sulphuric acid solution was first undertaken using lead as the cathode. As the catholyte a mixture of 50 c.c. of water, 40 c.c. of absolute alcohol and 10 c.c. of 95% sulphuric acid was used, and for 2 gr. of the imide a current of 3 amp./100 sq. cm. was passed for 3 hours at 25°. When the electrolysis was over, the cathode solution was evaporated to drive off alcohol and made alkaline by adding a caustic soda solution, whereupon a reduction-product separated out in an oily form. It was extracted with ether and recrystallized from alcohol. It crystallized in plates having a characteristic odour and melting at 45°. It was analysed as its gold double chloride which melted at 145°.

0.1215 gr. substance gave 0.0492 gr. gold on ignition. Found: Au=40.5%. calc.: Au=40.6%.

The reduction product was thus confirmed to be methyl phthalimidine.

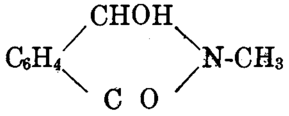
When copper was used as the cathode maintaining other conditions the same no imidine was formed, but a quite new reduction product was obtained. It crystallized in a short prismatic form from hot water and melted at 129°. It was soluble in alcohol, ether, acetone and benzene. It was reducible into corresponding phthalimidine electrolytically with the lead cathode and chemically with zinc and sulphuric acid, and was oxidizable to methyl phthalimide by the action of potassium permanganate and sulphuric acid. The result of the elementary analysis was found to be as follows:

Anal. Subst.=0.0880; CO_2=0.2140; H_2O=0.0435 gr. 0.4014 gr. substance produced ammonia, neutralization of which required 6.5 c.c. of 0.3879 N-HCl. Found: C=66.34; H=5.53; N=8.67%. calc. for $C_9H_9O_2N$: C=66.26; H=5.52; N=8.59%.

Its molecular weight was determined by the ebullioscopic method using alcohol as the solvent.

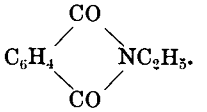
Subst.=0.2276, alcohol=16.237 gr.; elevation of b.p.=0.105°. Mol. wt., found: 157, calc.: 163.

From these results it may be concluded that the reduction product is nothing but oxyphthalimidine having the formula



The electrolytic reduction in a hydrochloric acid solution was observed to proceed in the similar way and perhaps more easily.

No reduction product could be isolated in the electrolysis conducted with an alkaline solution, in which all phthalimide completely hydrolysed into phthalic acid and methylamine.

III. Ethyl Phthalimide,  The electrolytic reduction of ethyl phthalimide in an alcoholic sulphuric acid solution was carried out in the manner just analogous to the case of methyl phthalimide. By using lead as the cathode ethylphthalimidine was obtained as a colourless oil having a characteristic odour. It was analysed as gold double chloride melting at 145°. When copper or nickel was used as the cathode no ethyl phthalimidine was formed, but ethyloxyphthalimidine was produced instead of it. It is soluble in water, alcohol, ether, acetone and benzene, and melts at 106°. It was analysed with the following results:

Anal. Subst.=0.1060; $CO_2=0.2635$; $H_2O=0.0600$ gr. 0.3982 gr. substance gave ammonia which required 4.15 c.c. of 0.5447 N-HCl for neutralization. Found: C=67.78; H=6.33; N=7.93%. calc. for $C_{10}H_{11}O_2N$: C=67.80; H=6.27; N=7.91%.

The molecular weight was determined with the ebullioscopic method using benzene as the solvent.

Subst.=0.1375, benzene=21.70 gr.; elevation of b.p.=0.090°. Mol. wt., found: 184, calc.: 177.

It was transformed into ethyl phthalimidine when further reduced with a lead cathode in a sulphuric acid solution, and into ethyl phthalimide when electrolytically oxidized with a platinum anode in an acetone sulphuric acid solution.

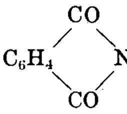
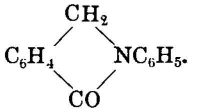
The electrolysis in a caustic soda solution gave no reduction product and produced ethyl phthalamic acid as a product of hydrolysis. It was isolated from the cathode solution by acidifying it with hydrochloric acid. It crystallized in needles and melted at 136°. It was soluble in hot water, sparingly so in cold. For confirmation its elementary analysis and molecular weight determination were conducted, and the following results were obtained:

Anal. Subst.=0.1368; CO_2=0·3110; H_2O=0.0704 gr. 1.3291 gr. substance produced ammonia which required 12.90 c.c. of 0.5447 N-HCl for neutralization. Found: C=62.02; H=5.76; N=7.40%. Calc. for $C_{10}H_{11}O_3N$: C=62.14; H=5.74; N=7.25%.

The molecular weight was determined ebullioscopically using alcohol as the solvent.

Subst.=0.0534, alcohol=17.48 gr.; elevation of b.p.=0.018°. Mol. wt., found: 199, calc.: 193.

Phthalic acid and ethylamine were also formed as the products of hydrolysis.

IV. Phenyl-phthalimide,  $C_6H_4{<}^{CO}_{CO}{>}NC_6H_5$. The electrolytic condition was maintained nearly the same as in the previous electrolysis, except that the temperature of the bath was kept a little higher, that is, at 85°. After the electrolysis the solution was filtered while hot and left to cool, when shining scaly crystals separated out. The crystal was insoluble in water and ether, but soluble in hot alcohol and benzene, and it was confirmed to be phenyl phthalimidine  $C_6H_4{<}^{CH_2}_{CO}{>}NC_6H_5$.

Several trials were made to isolate oxyphenylphthalimidine as the intermediate reduction-product by changing the conditions of electrolysis in different ways, but all was fruitless.

The electrolysis in an alkaline solution yielded no reduction product, phenylphthalimide hydrolysing easily and completely into phthalic acid and aniline.

My hearty thanks are due to Professor Motooki Matsui, under whose kind guidance and encouragement the work was carried out.

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SORPTION OF VAPOUR BY CHABAZITE.

By Tositomo BABA.

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The fact that a partially dehydrated chabazite has the striking property of sorbing a very considerable amount of gases such as ammonia, carbon dioxide and ethylene, etc., has already been examined and confirmed by many investigators.(1) In the case of vapours, however, it was reported by O. Weigel and E. Seinhoff,(2) and O. Schmidt(3) that this property was not so much marked as in the case of gases, and moreover in certain cases, say ether and benzene, etc., it could not be observed entirely. Schmidt concluded in his paper that this unexpectancy might be due to the great magnitude of their molecular dimentions comparing with the small pores or cavities presumably existing in the crystal of a dehydrated chabazite, into which gases and vapours are sorbed. Further studies on the sorptions of vapours by chabazite may decide whether his conclusion be right or not, and may give us some information about the mechanism of sorption by solid adsorbent. In the present experiments both the sorption amounts and velocities of the vapours of some organic substances have been measured.

Material. The mineral, chabazite, from Izu in Japan(4) has been crashed into small pieces together with mother rock, and the transparent well defined crystals of 0.5~1.5 mm. have been carefully picked up. After dehydration by heating to 370°C. and highly evacuating, the crystals have kept their appearance unaltered, 0.5736 gr. of air-dry sample gave 0.4640 gr. of dehydrated substance, so the water evaporated was 19.1%.

Experimental Procedure. The apparatus used for this experiment is schematically shown in Fig. 1. The whole apparatus is made of glass, and the cocks are of mercury sealed type. Part A is the same with the apparatus ordinarily used for the volumetric measuring of both the sorption amount and velocity at constant pressure,(5) bulb E, cock K_3, burettes B_1 and B_2, and mercury reservoir H_1 being provided for this purpose. In order to overcome the difficulties which are met with, when we treat liquid vapour instead of gas, – preventions of condensation and leaking through the cocks of vapour – parts B and C are attached. Part B, nothing but a manostat which keeps the whole apparatus at a constant low pressure, consists of a manometer M, a large bottle V, a cock K_5 and a mercury reservoir H_2 etc. M serves not only as U-formed manometer but also as the pressure regulator

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(1) R. Seeliger, *Physik. Z.*, **22** (1921), 563; F. Simon, *Z. physik. Chem.*, **132** (1928), 456; O. Schmidt, *Z. physik. Chem.*, **133** (1928), 263; J. Shameshima, this Bulletin, **4** (1929), 96.

(2) O. Weigel and E. Steinhoff, *Z. Krist.*, **61** (1924), 125.

(3) Loc. cit.

(4) K. Jimbo, *J. Coll. Sci. Imp. Univ. Tokyo*, **11** (1899), 279.

(5) For example, Sameshima, this Bulletin, **2** (1927), 2.

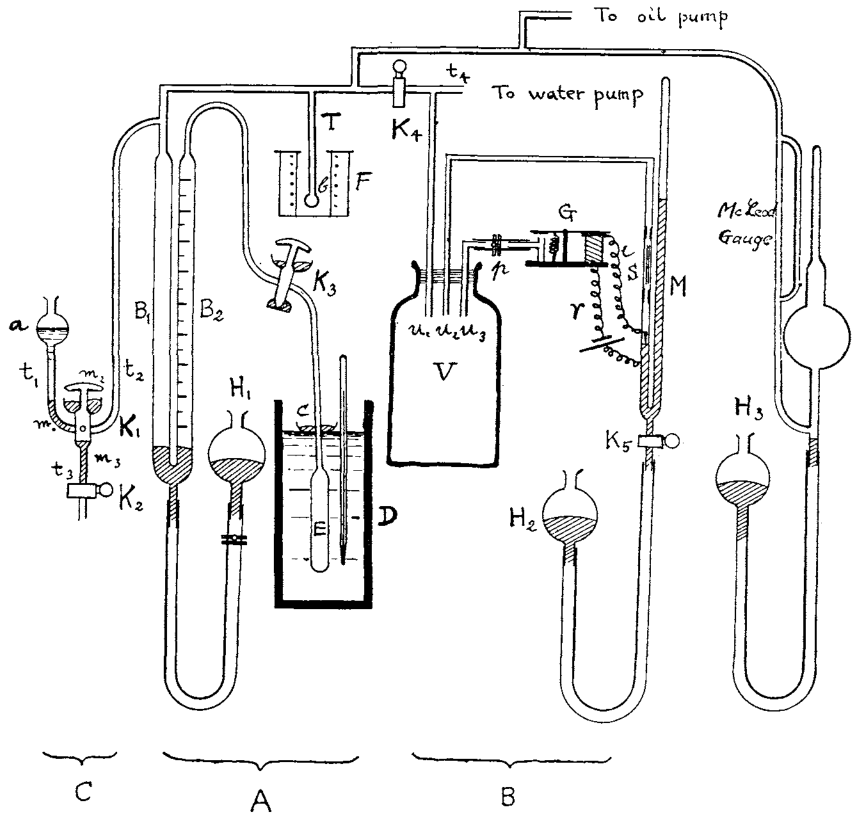

Fig. 1.

in which the quantity of mercury can arbitrarily be adjustable by the use of K_5 and H_2. The bottle V has a capacity of about 10 litres and serves as a preventer of a sudden change of pressure, the pressure in which is kept constant automatically by means of a device composed of a lever G, an electro-magnet i and an accumulator r. The lever G has an iron stick on one end and a rubber piece on the other and can open or close the mouth of bottle by the action of electric current which may be self-explainable by the figure.

The bottle is constantly evacuated by a water pump through tube t_4. By the proper adjustment of the power of water pump and screw cock p, the pressure has been able to keep constant within 0.1–0.2 mm. Hg. S is a safety device which consists of a glass tube packed with copper wires of about 20 cm. long for the accidental explosion causing from the electric sparks between the mercury surface and the platinum pointer.

An attached part designated by C is a specially deviced introducer for liquid vapours, which is a bottomless hollow cock K_1 with one hole, a turning of which causes communication of tubes t_1 to t_3, or t_2 to t_3, but not

t_1 to t_2. At first the parts m_1, m_2 and m_3 are sealed with mercury, and cock K_1 is evacuated together with the whole apparatus through tube t_2. Then the liquid under investigation is poured into bulb a, and cock K_1 is turned to tube t_1, when the liquid partially rushes into the hollow space of cock K_1 with the mercury in m_1. On turning cock K_1 to tube t_2 again, the liquid in the cock vapourizes at once into the whole apparatus through tube t_2. This method enables us to introduce liquid vapours into the apparatus without any difficulty or trouble even in the case of methyl amine whose boiling is -6°C., by the use of solid carbon dioxide.

To carry out the experiment, ground joint c is disconnected, the weighed fresh crystals of chabazite are placed in sorption bulb E, then the ground joint is restored to the former position. The mercury level in the burettes B_1 and B_2 is opened, cock K_4 being closed, cock K_1 is turned to tube t_2 and mercury-sealed. Now, electric furnace F is brought around the bulb E and heated to 350~370°C. and then all the parts of the apparatus are highly evacuated by an oil pump. Both heating and evacuating are continued for two hours. Then electric furnace F is substituted by thermostat D, the temperature of which being always kept at 25.0°C. and the manostat is also brought into action at the same time. Cock K_3 is then closed, the mercury level in the burettes is raised a little and the liquid vapour is introduced into the apparatus for the first time. Cock K_4 is opened and the reading of burette B_2 is recorded, keeping the mercury level in burettes B_1 and B_2 at the same height, and then opening cock K_3, the changes of readings are recorded with the time and the room temperature, the latter being necessary for the corrections of the readings afterwards.

Tube T is used for the measuring of the water content of the mineral, and in this case, the weighed sample in bulb b is heated to 360~370°C. in a high vacuum for two hours as before, hermetically sealed, and the net decrease of the weight of the mineral is measured as usual. This tube T is also used for the introduction of carbon dioxide by connecting it with the gas generator.

Experimental Results. The sorption amounts and velocities of the following fifteen substances have been measured: pentane, benzene, ether, chloroform, carbon tetrachloride, acetone, ethyl acetate, methyl alcohol, ethyl alcohol, methyl amine, ethyl amine, propyl amine, butyl amine, carbon bisulphide, and carbon dioxide(1). The last have been measured for the purpose of comparison with the results obtained by Prof. Sameshima recently. The results obtained by the author are shown in Table 1.

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(1) In the cases of methyl amine and carbon dioxide the atmospheric pressure served conveniently as the natural manostat.

Table 1

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vapour at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Pentane C_5H_{12} $p=404$	0	0.0
	10	0.0
	40	0.0
Benzene C_6H_6 $p=71$	0	0.0
	60	0.0
	120	0.0
Ether $(C_2H_5)_2O$ $p=374$	0	0.0
	20	0.0
	40	0.1
	60	0.1
Chloroform $CHCl_3$ $p=120$	0	0.0
	0.5	0.1
	1.5	0.2
	10	0.2
	20	0.2
Carbon tetrachloride CCl_4 $p=76$	0	0.0
	0.5	0.1
	30	0.1
Acetone $(CH_3)_2CO$ $p=116$	0	0.0
	10	0.0
	30	0.0
Ethyl acetate $CH_3COOC_2H_5$ $p=60$	0	0.0
	0.5	0.2
	1.5	0.3
	3.5	0.4
	5	0.4
	10	0.5
	15	0.6
	31	0.6
	42	0.7
	60	0.7
Methyl alcohol CH_3OH $p=73$ (1st observation)	0	0.0
	0.33	3.5
	1	5.3
	3	9.0
	5	13.0
	10	27.1
	21	60.8
	41	107.9
	60	129.9
	95	144.9
	120	148.2
	180	149.5
Methyl alcohol CH_3OH $p=73$ (2nd observation)	0	0.0
	0.5	5.7
	1	7.0
	3	11.4
	5	1.51
	10	28.5
	20	57.7
	40	101.5
	60	122.6
	90	131.3
	120	134.8
Ethyl alcohol C_2H_5OH $p=35$	0	0.0
	0.5	1.1
	1	1.4
	3	1.6
	5	1.6
	10	1.7
	20	2.3
	30	2.7
	40	3.1
	62	4.0
	100	5.2
	162	5.8

Table 1.—(*Continued*)

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vapour at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Methyl amine CH_3NH_2 p=754	0	0.0
	0.5	4.7
	1	5.8
	2	6.9
	3	8.8
	5	10.2
	10	12.8
	15	14.6
	21	16.4
	30	19.0
	40	20.8
	60	24.5
	120	31.3
	180	37.5
	300	44.8 (p=755)
	2549	74.4 (p=763.5)
Ethyl amine $C_2H_5NH_2$ p=585	0	0.0
	0.5	2.2
	1.33	2.5
	2	2.8
	5.25	3.1
	11	4.2
	20	4.5
	40	5.6
	60	6.2
	120	7.0
	256	7.6
Propyl amine $C_3H_7NH_2$ p=174	0	0.0
	0.5	0.5
	1	0.8
	2	1.1
	3	1.2
	5	1.6
	10	1.9
	20	2.3
	40	2.7
	60	2.9
	90	3.2
	180	4.2
	250	5.2
	1215	7.2
Butyl amine $C_4H_9NH_2$ p=52	0	0.0
	0.58	1.0
	1	1.1
	2.17	1.2
	4	1.3
	8	1.5
	18	1.7
	30	2.0
	61	2.6
	120	3.3
	192	4.2
	320	4.9
	1295	5.5
Carbon dioxide CO_2 (1st sorption) Case I p=768.8	0	0.0
	0.42	23.3
	1	36.8
	1.5	41.6
	2	44.1
	3	45.9
	5	47.8
	10	51.0
	20	54.3
	42	59.1
	60	60.9
	120	64.2

Table 1.—(*Continued*)

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vaponr at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Carbon dioxide CO_2	0	0.0
	0.45	38.6
(2nd sorption)		57.2
Case II	2	70.4
p=772	3	75.1
	5	77.6
	10	80.2
	20	82.4
	45	85.3
	80	87.8
	120	89.3
	180	90.8
	1200	96.2 (p=764)
Carbon dioxide CO_2	0	0.0
	0.45	45.2
(3rd sorption)	1	60.2
Case III	2	69.6
p=760.9	3	74.0
	5	76.9
	10	79.8
	20	81.9
	40	84.9
	80	86.0
	120	88.2 (p=760)
	2640	102.8 (p=760)

Substance and pressure of vapour in mm. Hg	Time in min.	Sorbed volume of vapour at 25.0°C. by 1 gr. dehydrated chabazite in c.c. (N.T.P.)
Carbon dioxide CO_2	0	0.0
	0.33	68.1
Another sample of chabazite	0.75	81.3
	1.5	96.6
Case IV	2.25	98.5
p=762	3	101.1
	5	103.5
	10	104.5
	15	104.7
	20	105.2
	40	106.0
	65	106.3
Carbon bisulphide CS_2	0	0.0
	0.5	41.3
p=200	1	51.1
	2	59.5
	3	63.0
	5	67.1
	10	70.9
	15	72.5
	20	73.4
	42	75.3
	100	77.4
	2440	85.1

As seen from the above table, chabazite has almost no tendency to sorb pentane, benzene, ether, chloroform, carbon tetrachloride, acetone and ethyl acetate, while it sorbs methyl-, and ethyl alcohol, methyl-, ethyl-, propyl-, and butyl amine. By the first sorptions of alcohols, amines and carbon dioxide, chabazite seems to have little change in its transparent and colourless appearance, but to become more or less fragile in its crystal structure. If these fragile crystals again or repeatedly sorb methyl alcohol, methyl amine or ethyl alcohol, sorption amount of which being considerable, they show a tendency to collapse partially into small pieces even in the course of sorption, and if we try to drive off these vapours from the crystals by heating and evacuating, they readily become fine powders. This phenomenon, however, is not observed in the case of carbon dioxide.

Differing from these substances, carbon bisulphide is found to be a very interesting substance against chabazite because the mineral, strange to observe, takes appearance of pure yellow colour on the sorption of this vapour, evolving simultaneously hydrogen sulphide which is easily detectable from its characteristic addled egg-like odour and the sensitive reaction with lead salts. It is evident that carbon bisulphide is decomposed catalyticaly on the course of sorption by chabazite, free sulphur and hydrogen sulphide being produced as some of the decomposition products. Though the true mechanism of this decomposition may not be hoped for until the other decomposition products have been brought to light, it is highly probable that the other reactant is the water in crystals which cannot be expelled by the above mentioned treatment of dehydration, the hydrogen in the hydrogen sulphide having been considered not to come from any other source than the water.

Theoretical Consideration of the Mechanism of Sorption. Consistent with Schmidt's idea, it may be plausible to consider that vapours which have large molecular volumes are, in, general, impossible or difficult to be sorbed by chabazite, comparing with those which have small molecular volumes. Thus pentane, benzene, chloroform, etc. which are nearly not sorbed have molecular volumes greater than 70 except acetone, while alcohols, amines, carbon bisulphide, carbon dioxide, etc, which are more or less considerably sorbed, have molecular volumes smaller than 70 except higher homologous of amines. Though any definite relation is not as yet found between the sorption amount and molecular volume, the sorption amount may decrease distinctly with the increase of molecular volume or molecular weight in homologous compounds, and it is very noteworthy that the substitution of methyl group by ethyl group causes instantaneously a remarkable decrease in the sorption amount as in the cases of alcohols and amines.

As regards the sorption velocities, it was already pointed out by Prof. Sameshima that carbon dioxide and ammonia are sorbed very rapidly, while ethylene is sorbed rather slowly. These characteristic sorption phenomena against different substances have also been observed in the present experiment; the sorption velocities of methyl amine, methyl alcohol, and ethyl alcohol, etc. are very small in comparison with those of carbon dioxide, and of carbon bisulphide. These circumstances are more distinctly shown in the following graphs in which the sorption amount x at time t has been plotted against t.

Any mathematical formula to express these curves will be hoped for, yet unfortunately, this has been done only in the cases of alcohols where the velocity curves are not fully but approximately expressible by the equations somewhat like those of autocatalytic reactions.

$$\log\frac{b+x}{a-x}=kt+h \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(A)}$$

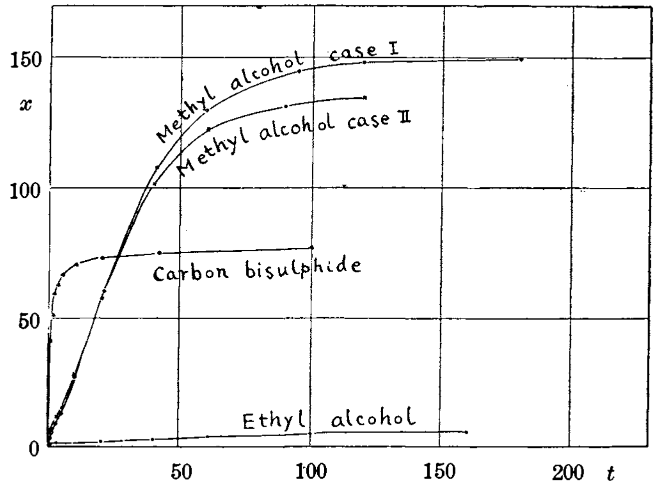

Fig. 2.

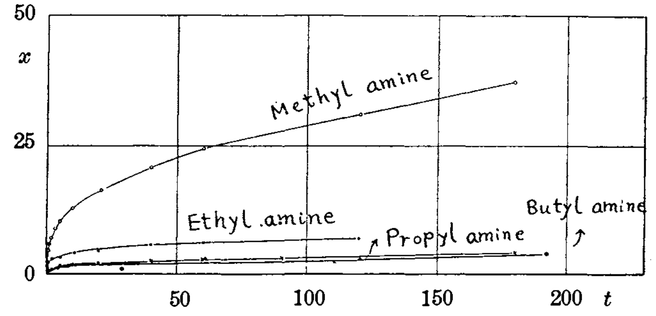

Fig. 3.

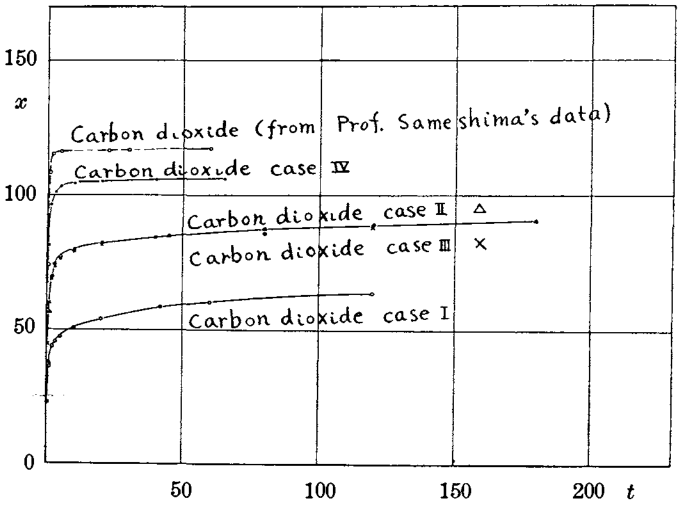

Fig. 4.

where x is a sorption amount at time t; and a, b, k, and h are empirical constants. Fig. 5 shows the linear relationship between $\log\frac{b+x}{a-x}$ and t, the constancy of k being also shown in Table 2.

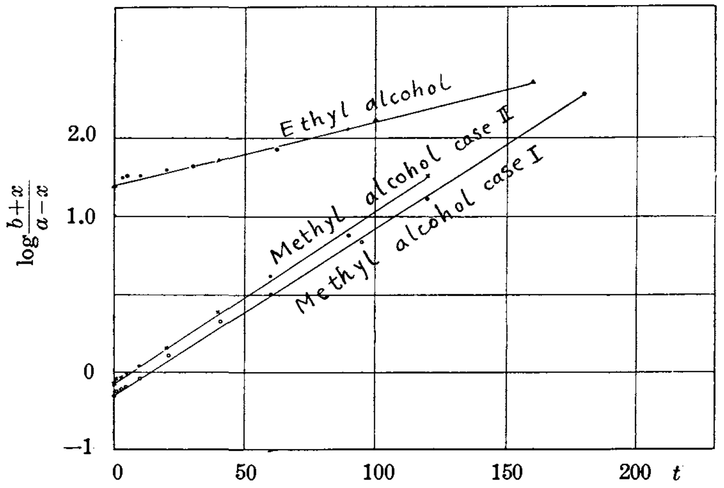

Fig. 5.

Table 2.

Vapour	Time in min.	Sorbed vol. of vapour at 25° by 1 gr. dehydr. chabazite in c.c. (N.T.P.)	Constant k
Methyl alcohol (1st observation) $a=149.56$ $b=77.0$	0	0.0	—
	1	5.3	(0.0355)
	5	13.0	0.0214
	10	27.1	0.0218
	21	60.8	0.0228
	41	107.9	0.0221
	60	129.9	0.0218
	95	144.9	0.0207
	120	148.2	0.0209
	180	149.5	0.0215
			mean 0.0216
Methyl alcohol (2nd observation) $a=135.5$ $b=100$	0	0.0	—
	1	7.0	(0.0524)
	5	15.1	0.0224
	10	28.5	0.0211
	20	57.7	0.0219
	40	101.5	0.0226
	60	122.6	0.0228
	90	131.3	0.0208
	120	134.8	0.0211
			mean 0.0215
Ethyl alcohol $a=6.1$ $b=150$	0	0.0	—
	1	1.4	(0.1172)
	5	1.6	(0.0253)
	10	1.7	0.0137
	20	2.3	0.0106
	30	2.7	0.0087
	40	3.1	0.0079
	62	4.0	0.0077
	100	5.2	0.0084
	160	5.8	0.0082
			mean 0.0092

To deduce the above formula following two assumptions have been made.

(i) The sorption velocity is proportional to the area of the entrances of pores or cavities into which vapours are sorbed, and to the degree of unsaturation of sorption capacity, namely, the amount sorbed after infinite time minus the present amount sorbed.

(ii) The area of the entrances of pores or cavities is enlarged by their collision with the vapour molecules passing through them in such a way that the area increase per unit time is, for the first approximation, proportional to the number of molecules which pass through the pores or cavities per unit time.

Granting the above two assumptions, we obtain two equations.

$$\frac{dx}{dt}=kA(a-x) \quad \text{(I)}$$

$$\frac{dA}{dt}=c\cdot\frac{dx}{dt} \quad \text{(II)}$$

where x is sorption amount at time t as above; A the area of the entrances of pores or cavities; a the saturation value of x; k and c proportional constants.

Integrating equation (II)

$$A=cx+A_0\ , \quad \text{(III)}$$

where A_0 is the initial value of A, that is, the area of the entrances of the pores or cavities in the crystal, on which any vapour molecules have not yet been sorbed.

Eliminating A from equations (I) and (III)

$$\frac{dx}{dt}=k(cx+A_0)(a-x). \quad \text{(IV)}$$

This becomes by integration

$$\log\frac{\frac{A_0}{c}+x}{a-x}\cdot\frac{ac}{A_0}=\left(\frac{A_0}{c}+a\right)kct\ ,$$

which can be easily rewritten in the form of equation (A).

In the case of carbon dioxide the variation of the sorption velocities in the alternative repetition of sorption and desorption has been observed. As Table 1 and Fig. 4 show, the sorption velocity accelerates about twice, when desorption and sorption have been repeated again (Case I and Case II), but further repetition causes no further increase (Case III). The large velocity in Case IV is probably due to the different treatment of the mineral before the experiment was commenced; or more correctly speaking, instead of taking the fresh mineral, the writer employed the mineral which had been exposed to the open atmosphere for several hours after the first dehydration, where it seems probable that a previous sorption of air and moisture occurs and consequently has a change of the sorption velocity in the next sorption of carbon dioxide. It is easily understood here that these facts are well consistent with the writer's assumptions made above, which indicate that the changes of the velocity are due to the enlargement of the pores or cavities in the mineral by the shock of bombardments of the sorbing gas or vapour molecules, and in the cases of alcohols and methyl amine, this enlargement of the pores or cavities is more conspicuous than in the case of carbon dioxide, so that in the former cases the crystal of chabazite may be much weakened in its structural nature, while in the latter case it is apparently unchanged, but vary in the sorption velocity when they sorbs the gas again.

In conclusion, the precise mechanism of sorption by chabazite might not be accounted for by mere consideration of the molecular volume of sorbing gas or vapour molecules as well as of the sorption velocity, however it may be sure that the sorption is much more related to the volume absorption than to the surface adsorption, otherwise disintegration of chabazite crystals or acceleration of sorption velocity would not take place in the above cases.

The present work has been done all through the experiments under the kindest guidance of Prof. J. Sameshima, to whom the writer wishes to express his hearty thanks.

Summary.

1. The sorption amounts and velocities by chabazite of fifteen substances have been measured at 25.0°C. by a statical method.

2. The sorption amounts of the vapours of pentane, benzene, ether, chloroform, carbon tetrachloride, acetone, and ethyl acetate have been found to be negligibly small, while those of methyl alcohol, methyl amine, carbon dioxide and carbon bisulphide have been found to be great. Ethyl alcohol, ethyl amine, propyl amine and butyl amine have been slightly sorbed.

3. No change in appearance of the mineral has been observed by the first sorption of alcohols, amines and carbon dioxide, but in the case of carbon bisulphide the crystal of chabazite have becomes yellow in colour,

probably indicating catalytic decomposition of this vapour into free sulphur, hydrogen sulphide and other decomposition products.

4. By the repeated sorptions of methyl amine, methyl alcohol and ethyl alcohol, the crystals of chabazite have become more or less fragile, and by heating and evacuating these fragile crystals have disintegrated themselves into fine powders.

5. The vapours which have large molecular volumes are generally difficult, if not impossible, to be sorbed by chabazite. The large gaps in sorption amounts between methyl and ethyl compounds in alcohol and amine series may be attributed to the same reason.

6. With regard to the sorption velocities of alcohols, the following formula has been applied which has some theoretical meaning:

$$\log\frac{b+x}{a-x}=kt+h$$

where x is the sorption amount at time t, and a, b, k and h the empirical constants.

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STUDIES ON THE PHOSPHORESCENCE OF GELATINE AND FLUORESCEIN AT LOW TEMPERATURES.

By Kazuo OCHIAI.

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It is already known that many organic compounds are phosphorescent at low temperature, first discovered by Dewar(1) and further studied by Nichols, Meritt(2) and Kowalski(3) and others.(4) Chemically pure substances show, generally, after-glow of very short duration at low temperature, while they show after-glow of rather long duration (say more than 1 sec.) when dissolved or suspended in a suitable medium and are exited by a ray of suitable wave-length at suitable temperature. Gelatine itself shows brilliant phosphorescence at the temperature of liquid air as shown by Dewar. Moreover, gelatine prolongs duration of after-glow of some substances mixed with it. Though it is not sure whether " pure " gelatine is phosphorescent or not, its phosphorescence depends largely upon the temperature and the water content.

It was also known that fluorescein is phosphorescent when it is dissolved (or suspended) in boric-(5) tartaric-(6) and citric acid.

Experiments on the phosphorescence of gelatine are described in the first part of this paper, and of fluorescein in various mediums are described in the second part.

Part 1. Phosphorescence of Gelatine. As gelatine is phosphorescent only at low temperature, it was sealed in a small test-tube and laid in a cryostat during the experiment. The cryostat was composed of a Dewar's vessel containing pentane or petroleum ether and cooled by a regulating flow of liquid air in a spiral tube within the vessel. A 100 volt, 250 watt incandescent lamp was used as the light source and the light was condenced and filtered by a flask containing ca. 1% cupric sulphate solution before entering the Dewar's vessel.

Time duration of after-glow, denoted by t in the following, was determined subjectively, the accuracy of which was ca. 1 second even when the eyes were rested fully in the darkness.

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(1) Dewar, " Collected Papers ", Vol. I (1927), p. 409.

(2) Kayser, " Handbuch der Spektroskopie ", Vol. IV, p. 1027.

(3) Kowalski, *Physik. Z.*, **12** (1911), 956.

(4) For instance, Pringsheim, " Fluorescenz und Phosphorescenz ", 3ed. (1928).

(5) E. Tiede and P. Wuff, *Ber.*, **55** (1922), 588; R. Tomaschek, *Ann. Physik*, **76** (1922), 612.

(6) B. Batscha, *Ber.*, **58** (1925), 187.

Nelson's No. 2 Photographic Gelatine was used in the experiments. Gel was prepared in the following manner: gelatine was swelled for about an hour in distilled water, and then warmed to 30–40°C. until it dissolve into a sol. Now one part was sealed off in a small test-tube for using in the experiment, while another part was dried at 110°C. in an air bath to determine the composition of the gel. A gel thus dried was noted as 100% gelatine. The composition of the ordinary gelatine was found to be 82%. It coloured slightly yellow and contained ca. 3.5% ash.

When gel of 15 to 12% gelatine was frozen, test-tube was broken frequently, probably due to expansion of gel as it frozen. If carefully cooled from the bottom of tube, breakage might be got rid off, but even if bear surface of a gel came in contact with the liquid of the bath (pentane or petroleum ether) no change in t was observed.

Colour of the phosphorescence is white, but in cases of 82% and 100% gels, bluish green colour appeares distinctly. Change of colour in the course of after-glow cannot be observed definitely.

Before measuring t, we must know its relation to the time of excitation. General behaviour is shown in Fig. 1. Thus if excited longer than 5 seconds a constant value of t is obtained. Excitation more than 5 minutes showed no change of the value of t. In the following experiments, therefore, the time of excitation was always 5 to 10 seconds. The results of the experiments are shown in Table 1 and Fig. 2. The hysteresis of these after-glow duration, t, is small and if the sample be kept 10 minutes or more in the cryostat t-value becomes quite constant.

Table 1.

T=temperature in absolute scale. t=duration of after-glow in seconds.

100%		82%		58.5%		35%	
T	t	T	t	T	t	T	t
290	12	265	8	233	6	225	3
265	15	260	13	213	18	220	6
244	21	242	17	203	27	213	15
233	23	235	20	193	30	205	20
213	26	219	25	183	32	190	30
203	27	205	30	173	34	170	34
175	27	185	33			146	34
158	29	173	30			128	32
131	30	136	26			84	35
123	31	123	25				
84	35	84	35				

18.6%		4%		0.8%		0.04%	
T	t	T	t	T	t	T	t
213	13	213	5	204	2		
203	19	203	7	183	27	203	7
193	24	188	27	174	29	193	12
183	29	174	30	166	29	183	15
173	31	166	33	155	29	173	22
		159	34	152	32		
		140	34	135	29		
		131	32				
		84	34				

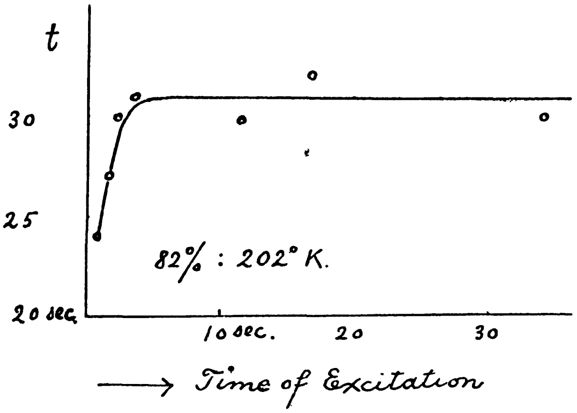

Fig. 1

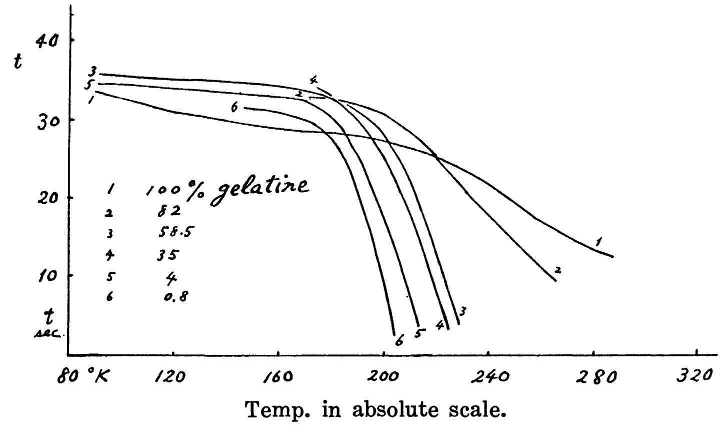

Fig. 2

The t-value of the gels containing less than 20% gelatine varies markedly by the heat treatment of them. It was observed that a dilute gel (gelatine content less than 20%) is heated for several hours at 80° to 90°C. after the preparation as described before, the value of t changes markedly. The gel was again melted and heated, then again different t-value will be obtained. This cannot be explained as a result of change in composition due to evaporation. Gel of initial composition 20% showed hardly the heating effect.

Some examples of t-values when excited by a 100 volt, 1000 watt lamp are shown in Table 2.

Table 2.

Excited by a 1000 watt lamp.

T	35%	82%	100%
250	—	15	22
233	—	26	29
220	15	—	—
213	—	—	33
195	32	—	34
183	—	41	—
155	46	—	—
150	—	36	30

It is clear from Fig. 2, etc. that, as a rule, t suddenly increases at about 220°K., and further cooling has no remarkable effect on it. Moreover, as concentration increases, the temperature where it begins to be phosphorescent becomes higher and, besides, t gradually decreases from its nearly constant value as the temperature rises.

Then, to answer the question about the relation between phosphorescence and composition of gels, it seems best to compare the temperature and the inclination of t-temperature curves of Fig. 2 where t increases suddenly. As a rough approximation we may take the temperature where t takes a half of its maximum value. Because it may be considered that these temperature is rather independent of the quantity, form of surface, etc. of the gel. Fig. 3 shows the results thus obtained.

Frozen gels can be divided into three classes from their appearances: gels containing 4 to 5% or less geletine separates laminae of ice and gelatine alternately which reminds of Liesegang's ring, more concentrated but less

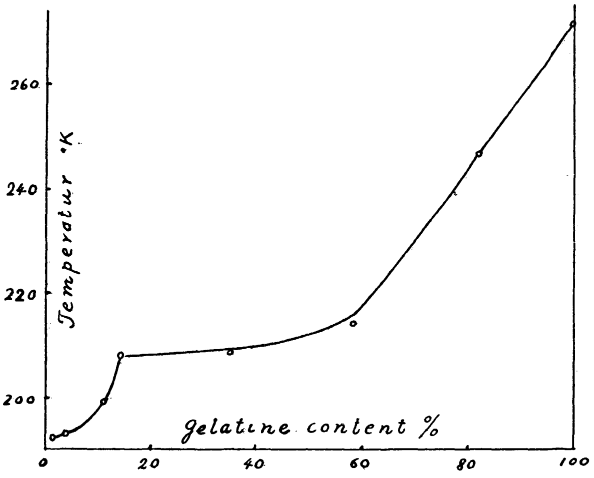

Fig. 3.

than about 60% gelatine freeze to a white solid probably due to irregularly separated small flocks of ice, and more concentrated gels retain their appearance at the room temperature even in the liquid air.

Returning to the present problem, we see here also analogous phenomena. Nearly horizontal part in the middle of the curve in Fig. 3 may be attributed to the separation of gelatine of constant structure, say identical degree of hydration, etc. The inclination in the right side of the curve may be explained as the change in structure, say degree of hydration decreases and thus disturbance of water molecule to the mechanism of phosphorescence is removed. Rather sharp "Knick" in the left side of the curve may be undue, but it is probable that in this region the structure of the gel is distinctly different from the gels containing more than 15% gelatine. Remarkable heating effect may partly due to chemical change like hydrolysis and partly due to the change of degree of dispersion of hydrated gelatine. Of cource the extreme left side of the curve must fall to very low temperature because distilled water is not phosphorescent even in the liquid air in the region of wave length of this experiment.

Part 2. Phosphorescence of Fluorescein. It is well known that fluorescein is phosphorescent when it is buried in boric-, tartaric- and citric acid, and grape sugar containing several organic acids in it. Fluorescein may be dissolved in these substances or in a state of colloidal suspension but we are not sure to which it belongs. B. Batscha(1) has suggested that fluorescein is phosphorescent only when substances of acidic nature co-

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(1) Loc. cit.

exists with it. The writer found that fluorescein is also phosphorescent when it is buried in sulphuric acid, hydrogen chloride, nitric-, formic, acetic-, butylic-, oxalic-, and succinic acid at low temperatures. All these acids give coloured solid matter.

Experiment is described in the followings. Exciting light is the same which was used in Part 1. Fluorescein is dissolved in concentrated sulphuric acid considerably. The solution shows slight surface fluorescence and is light to dark orange in colour and when cooled below -37°C. it freezes to yellow silky crystal or brown glassy mass as the quantity of fluorescein increases. 0.005, 0.05 and 2.6 mol/litre solutions of fluorescein were frozen and found to be intensively phosphorescent. Colour and duration of afterglow was nearly the same for them all. Duration was about 15 seconds at -37°C., but if it is cooled below -100°C., then after the cease of orange yellow intense phosphorescence, very weak phosphorescence lasts more than 3 minutes.

Next, a small quantity of sulphuric acid is added to ca. 0.0001 mol/litre aqueous fluorescein solution. On freezing this solution a brilliant phosphorescence was appeared. To the same 0.0001 mol/litre solution hydrochloric-, nitric-, acetic-, formic-, and butylic acid were added respectively and again found to be phosphorescent below their freezing temperature, Fluorescein is soluble in liquid hydrogen chloride to a small quantity and by cooling it gives yellow transparent solid. This is also phosphorescent but the colour of it is rather yellowish.

It was known that fuming nitric acid gives tetra-nitro-fluorescein. This substance was prepared and dissolved in water and frozen, but the result was negative, showing that the substitution cannot be the cause of phosphorescence.

Oxalic- and succinic acid containing fluorescein showed very weak phosphorescence even at the temperature of liquid air in contrast with the result of Batscha, where oxalic acid gave rather intense phosphorescence (in grape sugar). Molten succinic acid dissolves fluorescein and gives coloured crystal but showed none.

Some salts of the above mentioned acids like KCl, $CaCl_2$, $Ca(CH_3CO_2)_2$, etc. and some alkalies like NH_4OH, NaOH, KOH, $Ba(OH)_2$ were added to the aqueous fluorescein solution and frozen, but the result was rather negative, neverthless some of them seem to show phosphorescence of short duration. The same for picric acid, acid potassium phthalate, benzoic acid and glycerine.

Substances like acids probably go into complex molecule (even if lablie as a complex compound) with fluorescein, and in this complex molecule the positive part of the polar group is directed to fluorescein. In a complex molecule we understand that molecules of acid and fluorescein are situated so near that the polar group serves nearly as a positive charge to fluorescein. In the interior of this complex molecule the mechanism analogous to that of "crystalo-phosphore"(1) may occur and the phosphorescence is observed. As formerly described NaCl, etc. show no phosphorescence with fluorescein. This may partly due to spare solubility of fluorescein in them or the formation of complex molecule is difficult, but even these conditions are fulfilled large ionic volume of sodium, etc. compared with that of hydrogen ion may give a negative result. Further the structure of the fluorescein in the phosphorescent state should be akin to that in the ionized state in liquid solution, and the spectra of phosphorescence may be in the same system of that of fluorescence, because the positive part of the polar group situated so nearly as supposed above will force fluorescein to take analogous structure as in a ionized state.

In conclusion the writer wishes to express his cordial thanks to Prof. J. Sameshima for his kind guidance throughout this experiment.

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(1) R. Tomaschek, *Ann. Physik*, **76** (1922), 612.

BIOCHEMICAL STUDIES ON RICE STARCH. V. COMPARATIVE STUDIES ON RICE, BOILED RICE AND MOCHI.

By Wei Sun TAO.

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In our daily life, in the Orient, it is our custom to eat rice at every meal, the best of food, after it is boiled with water, or steamed and pounded into a cake called mochi (usually prepared from glutinous rice). Mochi is said to be much more digestible for the digestive organs than even boiled rice. Therefore, the chemical changes of the starch of rice in the process of boiling with water, and also in the trituration process of making mochi aroused our interest, and induced us to investigate the subject from the point of view of bio-chemistry, and the following experiments were undertaken.

Preparation of Materials and Their Analysis. 1. *Boiled rice*: The rice named Asahi, which was used in the previous experiments,(2) polished, and

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(2) This Bulletin, **5** (1930), 64, 69, 87 & 91.

boiled with water in the following quantities: 500 gr. of polished rice boiled with 750 c.c. of water at 105°C. for 25 min., then, taken off the fire but otherwise untouched left for about 10 min.

2. *Mochi*: 500 gr. of polished rice, washed and soaked in water over night, and steamed for 45 min. at 99°–110°C., triturated with a wooden pestle to make a sticky mass with the addition of a little water, and no more individual rice granules are to be seen.

In analysis, the boiled rice and mochi were soaked in cold acetone and let stand in a cold place for 3 days, filtered, and the filtrate was evaporated to dryness and the fat remaining in the residue was extracted with petroleum ether. With the residual substance the content of reducing sugars was determined as usual.

The insoluble residue in acetone was dried, ground into powder in a stone mill, treated with water at room temperature for a few hours, and filtered. The content of reducing sugars in the filtrates was estimated before and after the hydrolysis with 3 % H_2SO_4 as usual. The starch-content in the final residue was determined after it was hydrolysed with the mineral acid. The results are shown in the following table with the data for polished rice in comparison.

	Rice		Mochi	Seedlings
	Polished	Boiled		
H_2O	13.6%	62%	55%	—%
Starch	76	67	68	56
Red. sugars	0	0.7	0.7	4
Sol. polysacch.	0	9	9	10

As may be seen from this table, the polished rice contained no reducing sugar or soluble polysaccharides, but they were found in boiled rice and mochi, and their formation was assumed to occur from the hydrolysis of starch. When the chemical changes which happen to the rice starch during cooking are compared with those in the germination of seeds, it may be noticed that hydrolysis of starch occurs in both cases, but the complete decomposition of the sugar molecule into CO_2 and H_2O, is to be found only in the germination.

To learn the difference in digestibility of two kinds of cooked rice—boiled rice and mochi—which would arise due to the differentiation of their physical state, the action of diastase and saliva under various P_H on the freshly prepared boiled rice and mochi was investigated. In the experiment, they were ground in a mortar and suspended in water, and 100 gr. of the sample, 500 c.c. of water, 4 gr. of Taka-diastase, and 20 c.c. of the writer's saliva were mixed separately. The mixtures were allowed to stand at 35°C. for 3 hours, and the colour test with iodine, and determination of the content of soluble sugars by means of Fehling's solution were made, and the results are shown in the table below.

	Boiled rice		Mochi	
	Diastase	Saliva	Diastase	Saliva
Rotatory power	19	15	23	19
Red. sugars	17	12	12	15
Sol. polysacch.	26	17	45	15

	Rice starch	
	Rice diastase	Saliva
Red. sugars	25	38
Sol. polysacch.	25	39
Starch	46	20

As will be seen in the table, the conversion of rice starch by saliva into soluble sugars is greater than that by rice diastase, but the reaction to starch of boiled rice and of mochi is reciprocated with diastase and saliva in each case. In any way, starch in mochi seems easy to convert into soluble sugars by means of the hydrolytic enzyme in diastase and saliva.

In order to learn more precisely the chemical nature of the reaction products which were produced by the action of diastase and of saliva from boiled rice and from mochi, the water soluble substance separated from the reaction products was treated with basic lead acetate, and filtered, H_2S gas was passed to remove the lead in the solution, and the filtrate was concentrated into a small volume. Alcohol was added to make 80% of an alcohol solution. The first precipitate thus formed was separated, and the filtrate was concentrated and the second precipitate was formed with 90% of alcohol. Finally, the filtrate was evaporated to a thick syrup and treated with absolute alcohol to form the third precipitate. Of these precipitates, the rotatory power and reducing power of the Fehling solution were determined, and confirmed for the occurrence of glucose and maltose in the products by the osazone test. The results are shown in the following table.

Boiled rice

	Diastase				Saliva			
	Yields %	$[\alpha]_D$	R.p.	Osazone test	Yields %	$[\alpha]_D$	R.p.	Osazone test
A	26	136	32	M	17	168	30	M
B	11	109	52	M	—	—	—	
C	6	107	58	M+G	12	138	40	M

Mochi

	Diastase				Saliva			
	Yield %	$[\alpha]_D$	R.p.	Osazone test	Yield %	$[\alpha]_D$	R.p.	Osazone test
A	45	145	38	M	15	169	26	M
C	12	112	56	M+G	15	139	47	M

where: A=80 % alcohol precipitate,
B=90 % ,, ,,
C=absolute ,, ,,
M=moltosazone,
G=glucosazone,
R.p.=Reducing power indicated as the percentage of d-glucose.

By the action of diastase on boiled rice and mochi, maltose as well as glucose were produced, but with saliva only maltose was noticed to form.

In mochi, the reaction product consisted mostly of soluble polysaccharides, and the production of reducing sugars and soluble polysaccharides from boiled rice by diastase and saliva is proportionately similar.

The action of diastase and saliva on boiled rice and mochi seems to differ in their reaction products from each other due to the differentiation of the physical state of these two preparations.

Of these reaction products, the distribution of dextrin, maltose and glucose were also determined by Wiley's method(1); the reducing sugars in

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(1) Wiley, "Agricultural Analysis" (1897) Vol. III, p. 288.

the products are removed by fermentation with yeast, and dextrin and maltose were determined separately. The results are as follows :

	Boiled rice		Mochi	
	By diastase	By saliva	By diastase	By saliva
Dextrin	37	38	35	37
Maltose	30	62	46	63
Glucose	23	—	12	—

As will be seen in this table, when saliva acted on both boiled rice and mochi, maltose and dextrin were formed, and with diastase some glucose was noticed as a reaction product. Mochi is easily converted by diastase into maltose ; but in boiled rice conversion of the starch into simpler sugar takes place.

When foods with saliva come into the stomach their digestion was said to proceed in an acidic medium of the gastric juice which usually shows $P_H=1.7$, and therefore, the chemical changes in the constituents of boiled rice and of mochi by diastase and by saliva were investigated under conditions similar to the fluid of the digestion organ, namely at $P_H=1.7$, using KCl—HCl for buffer. The results are shown in the following table.

	Diastase		Saliva	
	$P_H=1.7-2.3$	$P_H=7.8$	$P_H=1.7$	$P_H=6.2-6.5$
Mochi	1.6	23	0.9	19
Boiled rice	1.1	19	0.8	15
Starch	—	50	0.4	28

The numbers indicate the percentage of reducing sugars calculated as d-glucose.

The action of diastase and saliva on the starch of boiled rice and mochi proceeded in a little acid side, $P_H=6\sim7$ to form simpler sugars but no action was observed in an acidic medium such as $P_H=1.7$.

Discussion. As a whole, the action of water on starch at 105°C. will result to produce soluble sugars by hydrolysis, and the beating of rice starch with a wooden pestle in presence of water will also promote in some degree the hydrolysis of the starch, converting it into soluble polysaccharides and reducing sugars. When diastase or saliva acts on mochi and boiled rice, the formation of soluble polysaccharides and reducing sugars is much more intensive.. The chemical change of the starch in rice by cooking with boiled water and trituration resembles, in some respects, the germination of rice seeds ; the difference is that the velocity in the conversion of starch into soluble sugars is greater in the former, but the conversion of starch into carbon dioxide and water takes place in the latter.

When comparing the action of amylase which occurred in diastase or saliva in boiled rice and mochi, the latter is more affected by the enzyme.

In closing, the writer would like to offer her hearty thanks to Professor S. Komatsu of Kyoto Imperial University, for the experiments were performed under his kind direction and never failing encouragement.

April, 1930.

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THE ACTION OF PERBENZOIC ACID ON GLUCAL AND ITS DERIVATIVES.

By Choji TANAKA.

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M. Bergmann(1) has already observed that when the glucal derived from glucose was oxidised with perbenzoic acid in acetic acid ethyl ester, it was almost completely converted into mannose and thus he discovered a new way for the transformation of glucose into mannose, and such a conversion of sugar was previously regarded as being effected by intramolecular conversion in an aqueous alkali solution.(2) The mechanism of the new transformation was explained by assuming a transitory formation of 1–2 anhydromannose from glucal, which will then be resolved by taking one molecule of water into the mannose.

The present writer has undertaken the experiment in order to study whether the conversion of glucal into mannose will take place not only in glucal but also in its derivatives, such as triacetyl glucal, and diacetyl pseudo-glucal or not, by oxidation with perbenzoic acid in a chloroform solution.

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(1) Bergmann & Schotte, *Ber.*, **54** (1921), 440.

(2) Lobry de Bruyn & van Ekenstein., *Rec. Trav. Chim.*, **14** (1895), 1010-1023.

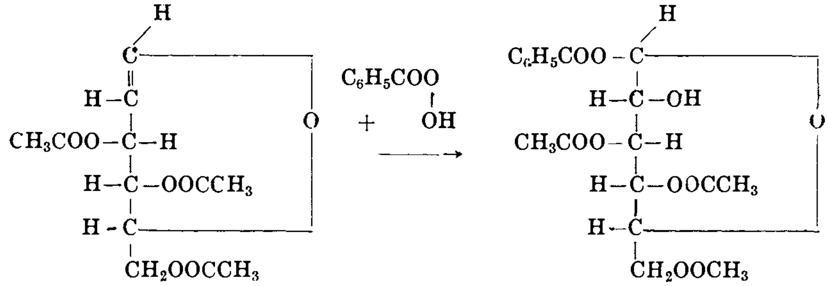
Glucal as Bergmann has stated, was oxidised instantly by perbenzoic acid, and converted into mannose. While, the oxidation of triacetyl glucal with perbenzoic acid was very slow, taking about four days, and diacetyl pseudo-glucal was noticed to undergo in oxidation with much difficulty.

In the latter case, contrary to our expectation, the addition of 1 mol of perbenzoic acid to the sugar will cause the formation of mono-benzoyl triacetyl compound (m.p.=141°–142°). The determination of the constitution of the addition compound established it as 1-benzoyl 2, 4, 6-triacetyl glucose (II), by the study of its chemical reactions (1) it yields neither hydrazone nor semicarbazide, (2) the benzoyl group in the molecule was very easily removed by treating with dilute alkali, (3) when the compound treated with phenyl-hydrazine and acetic acid at room temperature after being hydrolysed with N/5 barium hydroxide solution, gives almost quantitatively phenyl-glucosazone but no crystals of mannose-phenylhydrazone. For the confirmation of the structure, the substance was benzoylated and the product was identified with 1, 2-dibenzoyl 3, 4, 6-triacetyl glucose (m.p.=149°) prepared from 3, 4, 6-triacetyl glucose(1) with benzoyl chloride and pyridine, and their specific rotatory power shown in Table 1 was studied for comparison.

Table 1.

Glucose derivatives	$[\alpha]_D$
1-benzoyl 3, 4, 6-triacetyl glucose	+18.35° (in benzene)
1, 2-dibenzoyl 3, 4, 6-triacetyl glucose	−15.7° (in chloroform)
1-benzoyl 2, 3, 4, 6-tetra-acetyl-glucose	−24.43° (in chloroform)

Thus, in the conversion of 1-benzoyl triacetyl β-glucose from triacetyl glucal, the trans-addition of perbenzoic acid to the double bond of the



(I) Triacetyl glucal

(II) 1-Benzoyl 3, 4, 6-triacetyl β-glucose

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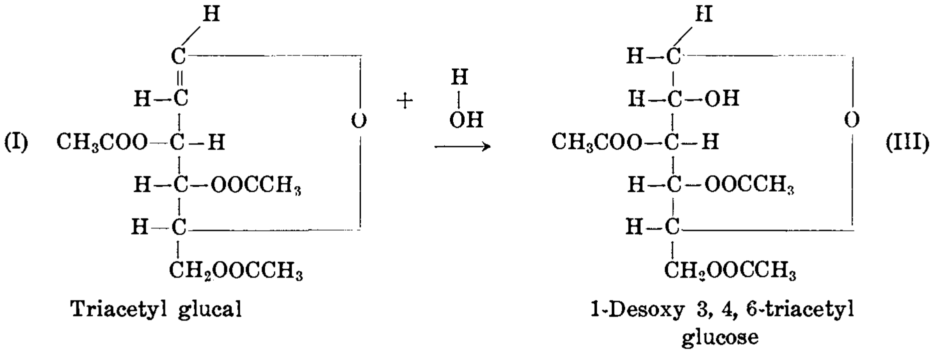
(1) P. Brigl, *Z. Physiol. Chem.*, **122** (1922), 245.

glucal molecule was assumed to occur, but theoretically the cis-addition is possible in the reaction, by which a new isomeric substance should occur in the reaction product. As a matter of fact, an isomeric substance of m.p.=168° was noticed to arise in the reaction product, but its physical and chemical properties were hardly to be determined owing to the meagreness of the sample.

In the meantime, a third new substance of the formula $C_{12}H_{18}O_8$, m.p.=122°, was isolated from the reaction product, which was supposed to be derived by the addition of H_2O to the triacetyl glucal, this differed in properties from the 2-desoxy glucose prepared by Bergmann⁽¹⁾ from glucal by treating with dilute acid when cold, and did not reduce Fehling's solution and form any oxide, semicarbazone or phenylhydrazone. As a consequence the constitutional formula (III) as 1-desoxy 3,4,6-triacetyl glucose was given for this compound.



Experimental Part

Triacetyl Glucal.⁽²⁾ Twenty gr. of β-acetobromo glucose⁽³⁾ (m.p. 87°–88°) which were previously cooled to 0°C., were treated with 40 gr. of zinc powder in 200 c.c. of a 50% acetic acid solution. When all of the β-acetobromo glucose was dissolved, the zinc power was filtered and the filtrate was concentrated to a small volume under reduced pressure to remove acetic acid. The syrup was diluted with 100 c.c. of water, the sugar substance was extracted with ether, neutralized with sodium bicarbonate, washed with water, dried with calcium chloride, and the ether was distilled. The colourless syrup which remained in the flask was changed on standing to white crystals, the yield was about 11.8 gr. This was purified by recry-

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(1) *Ber.*, **55** (1922), 158.

(2) E. Fischer, *Ber.*, **47** (1914), 196.

(3) E. Fischer, *Ber.*, **49** (1916), 584.

stallization from absolute alcohol-petroleum ether solution m.p.$=54°$–$55°$, $[\alpha]_D^{10}=\frac{-1.03+0.06}{6.298\times 1}\times 100=-15.4°$ in absolute alcohol.

This substance decolourizes bromine water immediately, gives a dark green colour by pine shaving reaction, and reduces Fehling's solution when hot.

Glucal.(1) This substance prepared from triacetyl glucal by following directions of Bergmann & Schotte, was slightly yellow-coloured and is very hygroscopic, melts at 60°–62°, $[\alpha]_D^{9}=\frac{+0.25-0.45}{0.258\times 1}=-7.8°$ in aqueous solution.

Diacetyl Pseudo-glucal. Triacetyl glucal, m.p.$=54°$–$55°$, was converted by the method of Bergmann and Ludewig(2) into a colourless syrup of diacetyl pseudo-glucal.

II. Oxidation of Glucal. A cold solution of 3.3 gr. of glucal dissolved in 30 c.c. of absolute methyl alcohol was added with vigorous agitation to an ice-cooled 280 c.c. of perbenzoic acid-chloroform solution (the amount of available oxygen in 1 c.c. of the solution corresponded to 3.40 c.c. of the N/10-$Na_2S_2O_3$ solution) which were prepared freshly by following the directions of J. Levy and R. Lagrave.(3)

Table 2.

Reaction temp.	Reaction time	C.c. of $\frac{N}{10}$ $Na_2S_2O_3$ required for 1 c.c. of the solution
0°	Soon after addition	3.07 c.c.
0°	0.5 h	1.70 „
0°	1.0 „	1.47 „
0°	2.0 „	1.47 „
9°	24.0 „	1.50 „

After the reaction was over, the product was treated with some distilled water to extract sugar compounds, and the aqueous solution was neutralized with calcium carbonate, evaporated up to a syrup under reduced pressure, 95% of alcohol was added to remove the salt remaining in the syrup, and

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(1) *Ber.*, **54** (1921) 440.

(2) *Ann.*, **434** (1923), 105.

(3) *Bull. soc. chim.*, **37** (1925), 1597.

filtered. When the filtrate was evaporated to a syrup in vacuo, about 3.5 gr. of the colourless syrup were obtained, which gave no Pinoff's reaction. The specific rotation of the syrup was as follows :

$$[\alpha]_D^8=\frac{1.74-0.45}{0.4238\times 1}\times 100=+30.4^\circ \text{ in aqueous solution.}$$

Mannose-phenylhydrazone was prepared in the usual way, melted at 195°–198°, $[\alpha]_D^8=\frac{+0.36-0.15}{0.0802\times 1}\times 100=+26.2^\circ$ in pyridine.

III. Action of Perbenzoic Acid on Triacetyl Glucal. A cold solution of 5.2 gr. of triacetyl glucal dissolved in 50 c.c. of chloroform was added drop by drop to an ice-cooled 140 c.c. of perbenzoic acid-chloroform solution (1 c.c. of the solution corresponding to 4.33 c.c. of the $\frac{N}{10}$ $Na_2S_2O_3$ solution). The progress of the reaction is shown in the following Table 3.

Table 3

Reaction temp.	Reaction time	C.c. of $\frac{1}{10}$ N-$Na_2S_2O_3$ to 1 c.c. of the solution	Blanc test. C.c. of $\frac{1}{10}$ N-$Na_2S_2O_3$ required to 1 c.c. of perbenzoic acid solution
0°	Soon after addition	3.40	4.33
,,	1.0 h ,, ,,	3.40	4.17
,,	2.0 h ,, ,,	3.20	4.33
,,	3.0 h ,, ,,	2.70	4.30
,,	4.0 h ,, ,,	2.65	4.33
9°	24.0 h ,, ,,	1.65	4.33
,,	48.0 h ,, ,,	1.20	4.15
,,	72.0 h ,, ,,	1.00	4.15
,,	96.0 h ,, ,,	0.90	4.15

After about four days, the theoretical amount of oxygen in the sugar solution having been consumed, the reaction product was neutralized with a sodium carbonate solution, washed with water, dried with anhydrous sodium sulphate, and concentrated to a small volume under diminished pressure to remove the chloroform and a colourless syrup was obtained, which changed to crystals on being left standing in an ice box, and weighed ca. 5 gr.

1-Benzoyl 3,4,6-Triacetyl Glucose. The crystals above mentioned were treated with absolute alcohol and 2.5 gr. of the glucose derivative were isolated from the solution. When recrystallized from hot absolute alcohol, it melts at 141°–142°, is soluble in ether and chloroform, slightly soluble in absolute alcohol, but insoluble in water.

The rotatory power in benzene solution shows $[\alpha]_D^8 = +18.35°$ The analytical results are as follows:

Anal. Subst.=0·1148; CO_2=0.2322; H_2O=0.0554 gr. Found: C=55.17; H=5.36%. Calc. for $C_{19}H_{22}O_{10}$: C=55.6; H=5.3%.

Cryoscopy. Subst.=0.2876, glacial acetic acid=15.1050 gr.; depression=0.179°. Mol. wt., found: 414. Subst.=0·4240, glacial acetic acid=15.9090 gr.; depression=0.249°. Mol. wt., found: 417. Mol. wt., calc. for $C_{19}H_{22}O_{10}$: 410.

It reduces Fehling's solution when hot, oxidises Schiff's reagent, and gives the silver mirror with ammoniacal silver nitrate solution, but does not show any mutarotation. When the alcohol solution was heated with dilute alkali, the liberation of the benzoic acid ethyl ester was recognized by its characteristic odour.

The acyl value of the substance was estimated by an N/14 HCl solution after hydrolysing with N/5.32 barium hydroxide solution, and the results agree with the theoretical value for one benzoyl group and three acetyl groups in the molecule.

A. *Hydrolysis of 1-Benzoyl 3,4,6-Triacetyl Glucose.* 1.7 gr. of 1-benzoyl 3,4,6, triacetyl glucose were dissolved in hot alcohol, and 340 c.c. of N/5 barium hydroxide were added, and let stand at room temperature over night. After the solution was neutralized with 1–N sulphuric acid, filtered and concentrated to a small volume under diminished pressure, acidified with some 1–N sulphuric acid, and benzoic acid was extracted with ether. Benzoic acid isolated was found to melt at 122° and confirmed to be so by elementary analysis and study of chemical properties. The yield was 0.5 gr.

Glucosazone. The acidic solution separated from benzoic acid was neutralized with dilute barium hydroxide solution, filtered off the barium sulphate and the filtrate evaporated to a small volume under reduced pressure. Then a mixture of phenylhydrazine and acetic acid, was added to the syrup and heated, and the osazone of m.p. 206° was obtained. The analysis of the substance gave N=15.52%, theory for $C_{18}H_{22}O_4N_4$, N=15.64%.

B. *1-Benzoyl 2,3,4,6-Tetra-acetyl Glucose.* 1.4 gr. of acetic acid anhydride was added to a solution of 0.7 gr. of 1-benzoyl 3,4,6-triacetyl glucose in 2.1 gr. of pyridine, the mixture was poured into ice water, whereon white crystals (ca. 0.7 gr.) were precipitated, and the substance purified from hot absolute alcohol solution, melts at 145°–146°.

This substance is soluble in chloroform, acetone, benzene, ether, slightly soluble in alcohol, petroleum ether, but insoluble in water.

Rotatory power in chloroform: $[\alpha]_D^4 = \frac{-0.45-0.12}{0.2158 \times 1} \times 100 = -26.43°$.

Anal. Subst.=0.1081; CO_2=0.2192; H_2O=0.0538 gr. Found: C=55.30; H=5.53%.

Calc. for $C_{21}H_{24}O_{11}$: C=55.8; H=5.3%.

Molecular weight by Rast's method shows 444, theory 452 for $C_{21}H_{24}O_{11}$.

C. *1,2-Dibenzoyl 3,4,6-Triacetyl Glucose.* 1.0 gr. of benzoyl chloride was added to a solution of 0.6 gr. of 1-benzoyl 3,4,6 triacetyl glucose dissolved in 2.5 gr. of pyridine, and the mixture was left to stand at room temperature for one day, and then poured into ice water, whereon an oily substance was obtained, which solidified gradually. It was dissolved in chloroform, treated with sodium bicarbonate solution, washed with water, dried with anhydrous sodium sulphate, and the chloroform distilled off. The benzoyl acetyl glucose thus obtained, was purified in white crystals having a melting-point of 149°. It is soluble in chloroform, acetone, ether; slightly soluble in alcohol, petroleum ether; but insoluble in water.

$[\alpha]_D^5 = \frac{-0.20-0.12}{0.2031 \times 1} \times 100 = -15.7°$ (in chloroform)

Anal. Subst.=0.1069; CO_2=0.2364; H_2O=0.0509 gr. Found: C=60.31; H=5.27%.
Calc. for $C_{26}H_{26}O_{11}$: C=60.7; H=5.06%.

The molecular weight by Rast's method being 506, agrees with the calculated value, 514 for $C_{26}H_{26}O_{11}$

For the preparation of 1, 2-dibenzoyl 3, 4, 6-triacetyl glucose, 1, 2-anhydro 3, 4, 6-triacetyl glucose (m. p.=56°–57°, $[\alpha]_D^{29}=+106.8°$ in benzene) prepared by the method by Brigl⁽¹⁾ was used; 2 gr. of the substance dissolved in 100 c.c. of water at room temperature and dried in a vacuum desiccator to a syrup to form 3, 4, 6-triacetyl glucose,⁽²⁾ which dissolved in 3.0 gr. of pyridine, and 1.5 gr. of benzoyl chloride were added, and the mixture was left to stand for two days, then poured into ice water, whereon an oily substance was obtained, separated, and dissolved in chloroform, treated with sodium bicarbonate solution, washed with water and dried with anhydrous sodium sulphate. By distilling off the chloroform, there were

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(1) Loc. cit.

(2) P. Brigl., loc. cit.

obtained white crystals of a melting-point of 149°. The properties of the substance agree well with those of 1, 2-dibenzoyl 3, 4, 6-triacetyl glucose.

$$[\alpha]_D^8 = \frac{-0{\cdot}12-0{\cdot}13}{0{\cdot}1402\times 1}\times 100 = -17{\cdot}8^\circ \text{ (in chloroform)}$$

Anal. Subst.=0.1011; CO_2=0.2239; H_2O=0.0478 gr. Found: C=60.40; H=5.25%. Calc. for $C_{26}H_{26}O_{11}$: C=60.7; H=5.06%.

The molecular weight by Rast's method gave 507, ($C_{26}H_{26}O_{11}$=514).

1-Desoxy 3, 4, 6-Triacetyl Glucose. The filtrate separated from the crystals of 1-benzoyl 3, 4, 6-triacetyl glucose was poured drop by drop into ice water, whereon a white substance (A) was precipitated, weighing ca. 10 gr., on this being filtered, and the filtrate was concentrated to a syrup under reduced pressure at ordinary temperature, a white semi-solid substance (B) was yielded (ca. 0.6 gr.); this was filtered, and the final filtrate again concentrated to a slightly yellow-coloured syrup. This residue was changed to crystals on being left standing in a ice box, the yield being about 1.4 gr. By recrystallisation from hot 94% alcohol, it melted at 122°. It is soluble in hot ethyl alcohol, acetic acid and water, slightly soluble in benzene and ether, but it does not reduce Fehling's solution before and after treatment with dilute sulphuric acid, and does not oxidise Schiff's reagent. Nor does this substance give silver mirror with ammoniacal silver nitrate, nor change with dilute alkali solution.

Rotatory power in chloroform: $[\alpha]_D^7 = \frac{+0.30-0.12}{2.06\times 1}\times 100 = +8.7^\circ$

The dried substance gave the following analytical results:

Anal. Subst.=0.1158; CO_2=0.2112; H_2O=0.0686 gr. Found: C=49.74; H=6.58%. Calc. for $C_{12}H_{18}O_8$: C=49.7; H=6.2%.

Molecular weight by cryoscopic method in glacial acetic acid shows 283 ($C_{12}H_{18}O_8$=290).

Acetyl value was estimated and the results agreed with the triacetyl in the molecule.

The precipitate (A) was found to consist of a mixture of 0.7 gr. 1-benzoyl 3, 4, 6-triacetyl glucose and 0.3 gr. of 1-desoxy 3, 4, 6-triacetyl glucose.

The Isomer of 1-Benzoyl 3, 4, 6-Triacetyl Glucose. The semi-solid substance (B) was obtained in white crystals (ca. 0.15 gr.) m.p.=168° from an absolute alcohol solution. It reduces Fehling's solution when hot, and it's alcohol solution changes into yellow when heated with dilute alkali. The substance dried on a porcelain tile gave the following analytical results:

Anal. Subst.=0.1036; CO_2=0.2094; H_2O=0.0565 gr. Found: C=55.13; H=6.06%. Calc. for $C_{19}H_{22}O_{10}$: C=55.6; H=5.3%.

The molecular weight by Rast's method gave 401.

From the analytical results and also the chemical properties, it was ascertained to be an isomer of 1-benzoyl 3, 4, 6-triacetyl glucose.

Acetyl Sugar. From the filtrate separated from 1-desoxy 3, 4, 6-triacetyl glucose, 0.4 gr. of the syrup were obtained, which gradually changed to needle crystals. This substance is soluble in alcohol, ether and water, but insoluble in petroleum ether. It reduces Fehling's solution when hot.

$$[\alpha]_D^9 = \frac{+1.07-0.14}{0.2106\times1}\times100 = +44.15^\circ \text{ (in chloroform)}$$

IV. Action of Perbenzoic Acid on Diacetyl Pseudo-glucal. A cold solution of 7.5 gr. of diacetyl pseudo-glucal dissolved in 50 c.c. of chloroform were added to an ice-cooled solution of 220 c.c. of perbenzoic acid-chloroform (the amount of active oxygen in 1 c.c. of the solution corresponded to 3.80 c.c. of the N/10 $Na_2S_2O_3$ solution). The progress of reaction was very slow, as shown in the following Table 4, and almost all of the substance remained unchanged.

Table 4.

Reaction temp.	Reaction time	Number of c.c. of $\frac{N}{10}$ $Na_2S_2O_3$ solution required for 1 c.c. of the solution
0°	Soon after addition	3.14
0°	0.5 h ,, ,,	3.14
0°	3.5 h ,, ,,	3.06
8°	24.0 h ,, ,,	2.85
8°	48.0 h ,, ,,	2.85
9°	72.0 h ,, ,,	2.90

In conclusion, the present writer wishes to express his hearty thanks to Prof. S. Komatsu for his masterly guidance and also to Prof. Nodzu for his invaluable advice.

January, 1930. Laboratory of Organic- and Bio-Chemistry,
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SINOMENINE AND DISINOMENINE. XVII.

ON METHYL-SINOMENINONE.

By Kakuji GOTO, Taro NAMBO and Reikichi INABA.

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One of the authors (K.G.) has reported that the action of 2*n* hydrochloric acid on sinomenine⁽¹⁾ at 100°C. gives rise to the formation of sinomenine hydrate (II)⁽¹⁾ and the same treatment of 1-Bromo-sinomenine leads to the formation of 1-Bromo-sinomeninone (III)⁽²⁾ The difference in the behaviour of those two very similarly constituted bases might be due to the negativity of bromine atom in the latter. So, it was desirable to expose methyl-sinomenine to the same treatment in order to see whether it gives hydrate or diketone.

The experiment revealed that methyl-sinomenine was simply hydrolysed on its enol-ether group by the action of 2*n* hydrochloric acid at 100°C. and gave methyl-sinomeninone (III) in a yield about 70%. The hydrate was not isolated in this case, too, so it seems that the stage of hydrate was jumped over both in bromo- and methyl-sinomenine in the formation of the respective diketones.

By the action of concentrated ammonia, sinomenine hydrate was turned into a bimolecular bis-demethyl-sinomenyliden,⁽³⁾ and bromo-sinomeninone into a mono-molecular bromo-sinomeninone imine,⁽⁴⁾ but the methyl-sinomeninone was turned into an amorphous substance by the same reagent, and no base corresponding to one of the above substances could not be isolated.

By the reduction with Pd+H_2, methyl-sinomeninone absorbed two atoms of hydrogen and gave a new base $C_{19}H_{25}NO_4$, which formed a monoxime, showing that one of the two ketone groups was reduced to the alcohol group. This base should be called dihydro-methyl-sinomeninone (V).

It is interesting to examine which of the two ketone groups of the methyl-sinomeninone was reduced in this case. The clew may be obtained from the methylation of α- and β-demethoxy-sinomenine hydrate. But,

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(1) Goto and Sudzuki, this Bulletin, **4** (1929), 271.

(2) Goto and Nambo, this Bulletin, **5** (1930), 73.

(3) Loc. cit.

(4) Loc. cit.

unfortunately the reaction products of these two substances with diazomethane became syruppy and no conclusion could be obtained in this trial.

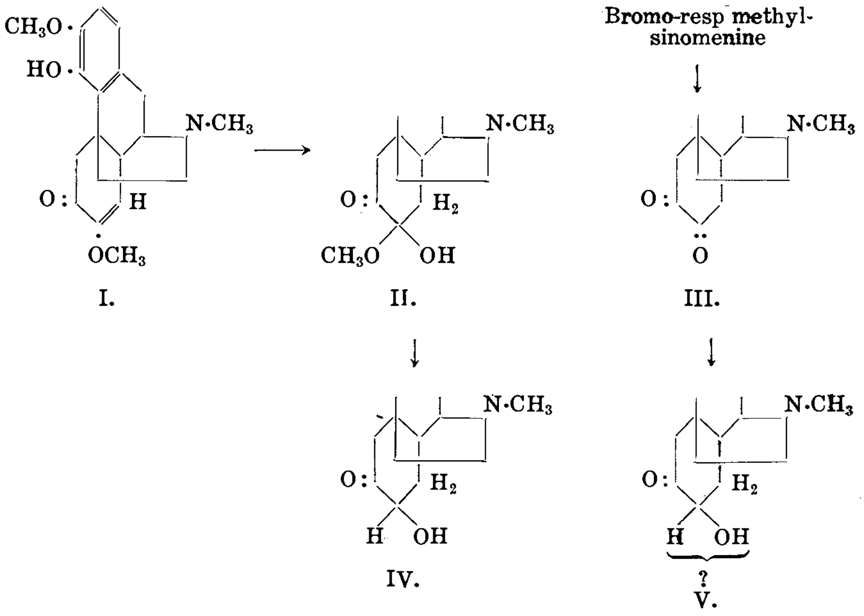
Then we tried to reduce catalytically bromo-sinomeninone and compared the reduced base with brominated α-demethoxy-sinomenine hydrate. From the mode of preparation, it is almost clear that α-demethoxy-sinomenine hydrate has its ketone group on C_6 and its secondary alcohol group on C_7 (IV). If, by the reduction of bromo-sinomeninone, the identical base was obtained as with the bromination of α-demethoxy-sinomenine hydrate, we may assume with some certainty that in the reduction of bromo-sinomeninone the ketone group situated in C_7 has been reduced. The result was affirmative. The substances prepared in these two different ways melted both at 231°C. as well as the admixture.

From these results, we should like to assume that in dihydromethylsinomeninone, the ketone group situated at C_7 is also reduced, though an exact proof is still lacking.

In these experiments, the methylation of sinomenine was again studied in a more detailed way and the yield was improved. Benzoylation of sinomenine was carried out with benzoyl chloride in pyridine solution with better yield. The detailed conditions are given in the experimental part.

Table 1.

	Methyl-sinomenine	Methyl-sinomeninone	Dihydromethyl-sinomeninone	Benzoyl-sinomenine
Yield	30–35%	70%	80%	40%
Solubility in methyl alcohol	12–52%	4.47%	—	—
M.p.	179°	188°	127° (dried) 108° (air dry)	225°
$[\alpha]_D$	−29.61°	+18.65°	+71.05°	+85.03°
Methoxyls	3	2	2	2
M.p. of oxim	139°	213°	117°	249°
M.p. of iodomethylate	157° (dec.)	225°~227°	248°	237°
$FeCl_3$-reaction	no	no	no	no
Diazo-reaction	20,000	10,000	almost no	appears slowly
$K_3Fe(CN)_6$-reaction	no	no	no	no
Formaline-sulphuric acid	yellow→green	green→bordeau	yellow	yellow



Experimental.

Note on Preparation of Methyl Sinomenine with Nascent Diazomethane. A better yield (30–35%) was attained in using methyl alcoholic solution of sodium hydroxide in an almost calculated quantity. Purification is easy, taking advantage of the facts that methyl-sinomenine is more easily soluble in ether than sinomenine itself and also that the hydrochloride of the former is less soluble in water (3.7%) than that of the latter (4.5%). Twice recrystallised from water, the methyl-sinomenine gives no ferric chloride reaction.

With diazomethane in ethereal solution, no better yield was obtained than in the above methcd.

The phenol-hydroxyl of sinomenine is, however, very easily methylated with dimethyl sulphate and caustic alkali, the fact being shown by the disappearance of the diazo-coupling faculty. But, the greater part of the sinomenine is splitted in its $N-C_9$ linking by this treatment.

The phenol-hydroxyl is also methylated by methyl-iodide and alkali in methyl alcoholic solution. But, the seperation of methyl-sinomenine iodomethylate from sinomenine iodomethylate gives some difficulties.

As for the properties, see the first column of the table in the theoretical part.

Anal. Found: C=70.03; H=7.49; N=4.03; methoxyl=26.51%. $C_{20}H_{25}NO_4$ requires C=69.97; H=7.29; N=4.08; Methoxyl=27.11%.

Optical rotatory power measured in chloroform:

$[\alpha]_D^{14}=(10\times0.52)\div(0.3515\times0.5)=-29.61°$

Oxim: Prepared in ordinary way. Amorphous precipitate formed with sodium carbonate becomes stout prisms, when left stand overnight under water added with ether. M.p. 139° (decomposes between 150–160°). Found: N=7.66%. Calc. for monoxime: N=7.82%.

Iodomethylate: Recrystallisable from water. Dired crystals decomposes at 151° (sintering from 141°C). Found: I=26.04% Calc. I=26.18%.

Metyl-sinomeninone. Methyl-sinomenine hydrochloride (10 gr.) is heated with 2*n* hydrochloric acid (50 c.c.) on a steam bath for an hour. Isolation was carried out in an usual way. Recrystallised from a large quantity of hot methyl alcohol, it forms large prisms. M.p. 188°. Yield ca. 70%.

See the table in the theoretical part for its properties.

Anal. Found: C=69·21; H=7.00; N=4.20; methoxyl=19.11%. $C_{19}H_{23}NO_4$ requires C=69.30; H=6.99: N=4·25; methoxyl=18.88%.

Sp. rotatory power, measured in chloroform: $[\alpha]_D^{14}=(10\times0.30)\div(0.5\times0.3216)=+18.65°$

Oxim: Prepared and crystallised in the same way as with methyl-sinomenine. M.p. is very unsharp, sintering above 100°, melting at 170° and decomposing completely at 213°. Found: N=11.74% Calc. for dioxime: N=11.70%.

Iodomethylate. Stout prisms, decomposing at 225~227° with yellow colour. Found: I=26.51% Calc. I=26.96%.

Dihydromethyl-sinomeninone. Methyl-sinomeninone (1.9 gr.) was reduced catalytically with palladinised charcoal and hydrogen gas in weakly acidic solution. Absorption of H_2 amounted to 50 c.c. (ca. 1 mol.) in 50 minutes. Isolation was carried out in an usual manner. It crystallises out in long prisms from the 33% methyl alcohol solution, saturated with ether. M.p. 108° (air-dry) or 128° (dried over P_2O_5 in vacuum). Yield ca. 1.5 gr. (80%).

Properties were given in the table in the theoretical part.

Anal. Found: C=68.61; H=7.62; N=4.41, 4.20; methoxyl=18.93%. $C_{19}H_{25}NO_4$ requires: C=68.84; H=7.60; N=4.25; methoxyl=18.73%.

Sp. rotatory power, measured in chloroform: $[\alpha]_D^{15}=(10\times0.81)\div(0.2280\times0.5)=+71.05°$

Oxim: Crystallised from methyl alcohol. M.p. 177°. Yield ca. 40%. Found: N=7.67%. Calc. for monoxime: N=8.09%.

Iodomethylate. Long needles from methyl alcohol. M.p. 248° (dec.). Yield good. Found: I=26.35%. Calc.: I=26.85%.

Benzoyl-sinomenine. Sinomenine (2.5 gr.) in a pyridine solution (12.5 gr.) was added with benzoyl chloride (3 c.c.) at 10°C. After half an hour, the pyridine solution was poured into the mixture of ice (100 gr.) and saturated ammonium carbonate solution. After standing two days, when the first appeared oil drops changed into fine solid, the latter was collected and recrystallised from the mixture of benzol and ether. M.p. 224°. Yield ca. 35%. This preparation is far more convenient than that formerly given.

Anal. Found: C=71.81; H=5.77; N=3.23; methoxyl=14.21%. Calc. for $C_{26}H_{27}NO_5$=433: C=72.05; H=6.23; N=3.23; methoxyl=14.31%.

Sp. rotatory power measured in chloroform: $[\alpha]^{4}_{D}=(10\times2.5)\div(0.294\times1)=-85.03°$

Iodomethylate: hairy crystalls from water. M.p. 237° (dec.). Found: I=22.14%. Calc.: I=22.08%.

Oxim: Prepared in ordinary way and extracted with chloroform. Prisms from methyl alcohol. M.p. 249° (dec.) Found: N=5.99%. Calc. for monoxime: N=6.25%.

Bromination of *α*-desmethoxyl-sinomenine hydrate.(1) The condition of bromination is the same as with sinomenine.(2) From a large quantity of alcohol, it forms long prisms, which melt at 231°. Yield about 50%.

Anal. Found: C=54.79; H=5.43; N=5.5. $C_{18}H_{22}BrNO_4$ requires: C=54.55; H=5.55; N=3.53; Br=20.20%.

Oxim: M.p. 147°. Found. N=6.54%. Calc.: N=6.81%.

Catalytic Reduction of Bromo-sinomeninone. Bromo-sinomeninone (2 gr.) was catalytically reduced with palladinised charcoal and molecular hydrogen. When the calculated quantity of hydrogen was absorbed the reduced base was isolated in the usual way. Yield good. It melted at 231° and the admixture with the above described specimen did not lower the melting point.

Errata.—To the constitution formula II of p. 94, this Volume, the following corrections must be given. The methoxyl on $C_{(7)}$ must be replaced by H. The—H on $C_{(8)}$ must be replaced by H and one free bond. Thus, the formula is brought in harmony with the facts and its name 1, 1′-dibromo-bis-[8, 8′]-demethoxy-dihydro-sinomenine.

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(1) Loc. cit., p. 275.

(2) Goto and Nambo, this Bulletin, **5** (1930), 167.

ON THE DISSOLUTION VOLOCITY OF OXYGEN INTO WATER. PART II.

By Susumu MIYAMOTO, Tetsuo KAYA and Akira NAKATA.

Received June 26, 1930. Published August 28, 1930.

Introduction. The oxidation velocity of sodium sulphite solution by means of air was found to be independent of the concentration of sodium sulphite under certain conditions.⁽¹⁾ This experimental fact can easily be explained if we consider that the observed reaction velocity is no other than the dissolution velocity of oxygen into water.

From this consideration, it was described in the previous paper,⁽²⁾ that the dissolution velocity of oxygen D and the velocity constant k, calculated as a zero-order reaction, can be expressed by the following equations.

$$D=\frac{1}{4}k\times 10^{-4} \quad \text{moles per minute.} \quad \cdots\cdots (1)$$

$$D=\frac{60\alpha p}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad \text{moles per minute.} \quad \cdots\cdots (2)$$

$$k=\frac{24\alpha p\times 10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+s_0\right) \quad \cdots\cdots (3)$$

where α =the ratio of the total number of the molecules of oxygen which enter into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time, the concentration of oxygen in the surface being kept to be zero.

p =the partial pressure of oxygen.
M=the molecular weight of oxygen.
R=gas constant.
T=absolute temperature.
V=the volume of the gas passed per minute.
l =the depth of the center of a bubble when it just leaves the exit.
r =the radius of a bubble.
u =the ascending velocity of the bubble.
s_0 =the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

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(1) S. Miyamoto, this Bulletin, **2** (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40.

(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 123.

If all the values in the equations 2 and 3 be kept constant except the value of p, the values of D and k can then be expressed by

$$D = A\alpha p \quad \dots\dots\dots\dots \quad (4)$$

$$k = B\alpha p \quad \dots\dots\dots\dots \quad (5)$$

If the value of α be independent of the partial pressure of oxygen,

$$D = A' p \quad \dots\dots\dots\dots \quad (6)$$

$$k = B' p \quad \dots\dots\dots\dots \quad (7)$$

where A' and B' are constants.

The present research was undertaken to ascertain if the present theoretical consideration be acceptable.

Experimental. The mixture of oxygen and air was passed through a narrow glass tube into the solution of sodium sulphite at uniform velocity and the oxidation velocity was observed.

The reacting vessel employed is shown in Fig. 1. The gas mixture, washed by acidified potassium bichromate solution and alkali, was passed at uniform velocity into the solution of sodium sulphite contained in A, the total volume of the reacting solution being made to 40 c.c. in each measurement. After t-minutes, the gas current was stopped and the stopcocks B and D were opened and the total quantity of the solution was poured into C, which contains a known quantity of iodine solution acidified with hydrochloric acid. After A was repeatedly washed by water, the vessel C was taken out, and the excess of iodine was titrated back by means of sodium thiosulphate solution, v in the following tables being the volume of sodium thiosulphate solution of 0.1000 normal, equivalent to the amount of sodium sulphite remained after the t-minutes passage of the gas mixture.

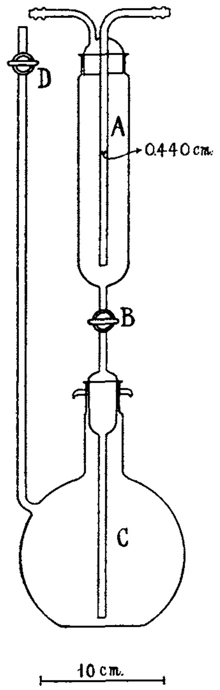

Fig. 1.

The experimental result shows that the oxidation velocity is independent of the concentration of sodium sulphite under the present conditions and the velocity constant k was calculated by

$$k = \frac{1}{t - t_0}(v_0 - v),$$

v_0 being the value of v at $t = t_0$. The values of $v_{calc.}$ were obtained by

$$v_{calc.} = v_0 - k(t - t_0)$$

using the mean value of k obtained experimentally.

The observed results are given in Tables 1 and 2, and graphically in Fig. 2. The partial pressure of oxygen, given in the first column of the Tables was calculated from the volumes of oxygen and air mixed.

Table 1.

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.21	3	18.18	—	—
	43	11.87	12.06	0.158
	3	18.48	—	—
	33	13.78	13.89	0.157
	3	27.70	—	—
	33	23.06	23.11	0.155
	3	32.10	—	—
	33	27.46	27.51	0.155
	3	39.23	—	—
	43	33.12	33.11	0.153
	3	39.33	—	—
	39	33.80	33.82	0.154
	3	46.27	—	—
	43	40.10	40.15	0.154
	3	50.97	—	—
	43	44.97	44.85	0.150
	3	57.95	—	—
	33	53.46	53.36	0.150
	3	59.49	—	—
	43	53.69	54.37	0.146
	3	62.18	—	—
	33	57.59	57.57	0.153
			Mean	0.153

Table 1.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.33	3	25.30	—	—
	33	17.95	18.04	0.245
	3	38.82	—	—
	33	31.26	31.56	0.252
	3	53.66	—	—
	33	46.20	46.40	0.249
	3	60.39	—	—
	33	53.70	53.13	0.223
			Mean	0.242
0.48	3	24.37	—	—
	33	13.79	14.41	0.353
	3	35.46	—	—
	33	25.55	25.50	0.330
	3	49.51	—	—
	33	39.68	39.55	0.328
	3	63.40	—	—
	33	53.87	53.44	0.317
			Mean	0.332
0.60	3	26.18	—	—
	33	13.88	14.09	0.410
	3	37.70	—	—
	33	25.26	25.61	0.415
	3	50.68	—	—
	35	37.74	37.78	0.404
	3	64.34	—	—
	33	52.86	52.25	0.383
			Mean	0.403

Table 1.—(*Continued*)

Temp. = 20°C. Velocity of Gas Passed = 60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.74	3	25.82	—	—
	33	10.74	11.06	0.503
	3	27.23	—	—
	33	12.37	12.47	0.495
	3	37.50	—	—
	33	22.46	22.74	0.501
	3	40.00	—	—
	33	25.60	25.24	0.480
	3	49.33	—	—
	34	33.74	34.08	0.503
	3	53.93	—	—
	33	39.17	39.17	0.492
	3	61.10	—	—
	33	46.85	46.34	0.475
	3	62.37	—	—
	33	47.85	47.61	0.484
			Mean	0.492
0.88	3	20.10	—	—
	23	8.60	8.74	0.575
	3	32.73	—	—
	33	16.43	15.69	0.543
	3	52.51	—	—
	33	35.25	35.47	0.575
	3	64.09	—	—
	33	46.77	46.05	0.577
			Mean	0.568

Table 1.—(*Concluded*)

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.97	3	22.88	—	—
	18	13.06	13.07	0.655
	3	23.58	—	—
	23	10.03	10.50	0.678
	3	29.75	—	—
	33	10.66	10.13	0.636
	3	32.32	—	—
	33	12.47	12.70	0.662
	3	33.22	—	—
	33	13.76	13.60	0.649
	3	37.79	—	—
	34	17.52	17.52	0.654
	3	39.28	—	—
	28	22.29	22.93	0.680
	3	43.73	—	—
	33	24.21	24.11	0.651
	3	44.01	—	—
	33	25.10	24.39	0.630
	3	49.09	—	—
	33	29.21	29.47	0.663
	3	52.36	—	—
	33	32.48	32.74	0.663
	3	55.51	—	—
	33	35.82	35.89	0.656
	3	60.90	—	—
	38	38.49	38.01	0.643
	3	63.46	—	—
	33	44.25	43.84	0.640
	3	65.72	—	—
	33	46.00	46.10	0.657
			Mean	0.654

Table 2.

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.21	3	18.62	—	—
	53	13.79	13.77	0.097
	3	26.59	—	—
	54	21.67	21.64	0.096
	3	32.95	—	—
	53	28.09	28.10	0.097
	3	38.04	—	—
	53	33.11	33.19	0.099
	3	46.04	—	—
	53	41.21	41.19	0.097
	3	52.36	—	—
	63	46.58	46.54	0.096
	3	59.12	—	—
	53	54.29	54.27	0.097
	3	64.60	—	—
	63	58.80	58.78	0.097
			Mean	0.097
0.34	3	18.21	—	—
	33	13.51	13.59	0.157
	3	25.70	—	—
	43	19.72	19.54	0.150
	3	32.09	—	—
	43	25.81	25.93	0.157
	3	39.05	—	—
	33	34.56	34.43	0.150
	3	46.37	—	—
	53	38.65	38.67	0.154
	3	52.97	—	—
	33	48.30	48.35	0.156
	3	59.71	—	—
	43	53.51	53.55	0.155
			Mean	0.154.

Table 2.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.46	3	18.72	—	—
	43	10.54	10.52	0.205
	3	23.68	—	—
	43	15.36	15.48	0.208
	3	39.43	—	—
	43	31.15	31.23	0.207
	3	45.42	—	—
	43	37.21	37.22	0.205
	3	52.88	—	—
	43	44.86	44.68	0.201
	3	65.96	—	—
	43	57.76	57.76	0.205
			Mean	0.205
0.59	3	18.56	—	—
	33	10.63	10.64	0.264
	3	23.64	—	—
	43	12.89	13.08	0.269
	3	32.29	—	—
	43	21.90	21.73	0.260
	3	45.69	—	—
	43	35.16	35.13	0.263
	3	51.81	—	—
	43	41.36	41.25	0.261
	3	58.74	—	—
	43	48.15	48.18	0.265
			Mean	0.264

Table 2.—(*Continued*)

Temp.=20°C. Velocity of Gas Passed=30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.72	3	18.57	—	—
	26	11.25	11.30	0.318
	3	26.90	—	—
	33	17.33	17.42	0.319
	3	32.81	—	—
	33	23.21	23.33	0.320
	3	41.49	—	—
	43	28.83	28.85	0.317
	3	45.70	—	—
	43	33.10	33.06	0.315
	3	57.61	—	—
	43	45.07	44.97	0.314
	3	61.25	—	—
	43	48.79	48.61	0.312
	3	66.40	—	—
	43	53.95	53.76	0.311
			Mean	0.316
0.84	3	19.67	—	—
	34	8.44	8.42	0.362
	3	26.43	—	—
	33	15.46	15.54	0.366
	3	31.47	—	—
	43	16.79	16.95	0.367
	3	37.86	—	—
	43	23.47	23.34	0.360
	3	52.73	—	—
	53	34.38	34.48	0.367
	3	61.07	—	—
	33	50.30	50.18	0.359
	3	64.02	—	—
	53	46.09	45.77	0.359
			Mean	0.363

Table 2.—(*Concluded*)

Temp. = 20°C. Velocity of Gas Passed = 30.5 c.c./min.

p_{O_2} atm.	t min.	v c.c.	$v_{calc.}$ c.c.	k
0.97	3	18.62	—	—
	23.5	9.98	10.05	0.424
	3	22.17	—	—
	35	8.92	8.79	0.414
	3	31.72	—	—
	43	14.98	15.00	0.419
	3	37.29	—	—
	44	19.99	20.15	0.422
	3	45.71	—	—
	43	28.98	28.99	0.418
	3	51.74	—	—
	53	31.11	30.84	0.413
	3	58.71	—	—
	43	41.92	41.99	0.420
	3	63.89	—	—
	53	43.07	42.99	0.416
			Mean	0.413

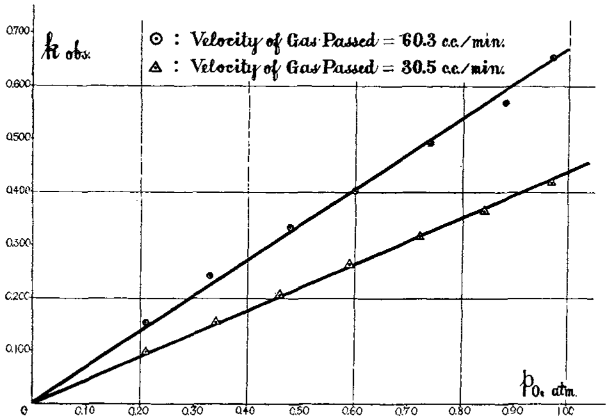

Fig. 2.

Table 3.

Temp.=20°C. Velocity of Gas Passed=60.3 c.c./min.

p_{O_2} atm.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles/min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles/min.
0.21	0.153	0.141	3.83×10^{-6}	3.51×10^{-6}
0.33	0.242	0.221	6.05 ,,	5.52 ,,
0.48	0.332	0.321	8.30 ,,	8.03 ,,
0.60	0.403	0.401	10.08 ,,	10.04 ,,
0.74	0.492	0.495	12.30 ,,	12.38 ,,
0.88	0.568	0.589	14.20 ,,	14.72 ,,
0.98	0.654	0.649	16.35 ,,	16.23 ,,

Table 4.

Temp.=20°C. Velocity of Gas Passed=30.5 c.c,/min.

p_{O_2} atm.	$k_{obs.}$	$k_{calc.}$	$D_{obs.}$ (Dissolution velocity of oxygen) moles/min.	$D_{calc.}$ (Dissolution velocity of oxygen) moles/min.
0.21	0.097	0.092	2.43×10^{-6}	2.29×10^{-6}
0.34	0.154	0.149	3.85 ,,	3.72 ,,
0.46	0.205	0.201	5.13 ,,	5.03 ,,
0.59	0.264	0.258	6.60 ,,	6.45 ,,
0.72	0.316	0.315	7.90 ,,	7.87 ,,
0.84	0.363	0.367	9.08 ,,	9.18 ,,
0.97	0.418	0.424	10.45 ,,	10.60 ,,

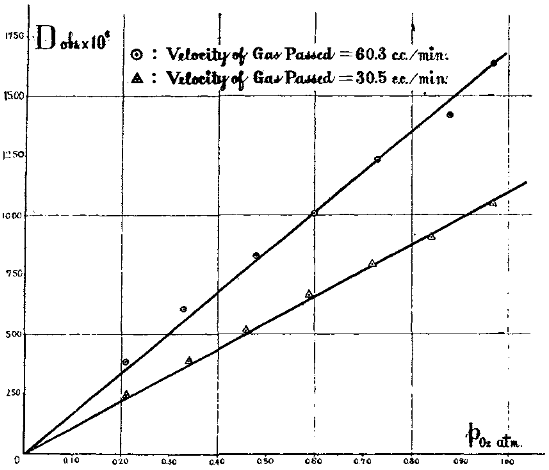

Fig. 3.

The values of $D_{obs.}$ in Tables 3 and 4 were calculated by the equation 1 using the observed values of k.

As will be seen in Tables 3 and 4 and in Figs. 2 and 3, the values of $k_{obs.}$ and $D_{obs.}$ can be expressed as a linear function of the partial pressure of oxygen of the gas passed. The values of $k_{calc.}$ and $D_{calc.}$ in the tables were calculated by the equations,

$$k_{calc.} = 0.669\,p$$
$$D_{calc.} = 16.73 \times 10^{-6}\,p$$

when the gas mixture was passed at the rate of 60.3 c.c. per minute, and

$$k_{calc.} = 0.437\,p$$
$$D_{calc.} = 10.93 \times 10^{-6}\,p$$

when the gas mixture was passed at the rate of 30.5 c.c. per minute.

The expectation was fullfiled; it was proved that the equations 6 and 7 can express the effect of the change of the partial pressure of oxygen on the velocity constant k or on the dissolution velocity D. The result confirms the author's consideration on the mechanism of this heterogeneous chemical reaction, described in the previous paper.

It was also verified that the value of a in the equations 2 and 3 can be regarded to be independent of the values of the partial pressure of oxygen of the gas mixture passed.

Summary.

(1) The oxidation velocity of sodium sulphite was observed when the mixture of oxygen and air was passed at uniform velocity under certain conditions.

(2) The observed oxidation velocities were independent of the concentration of sodium sulphite under the present conditions, and the velocity constant was found to be expressed as a linear function of the partial pressure of oxygen passed, as was expected.

(3) The theoretical interpretation on the observed result was given.

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STUDIES ON CATALYTIC ACTION AT HIGH PRESSURE AND TEMPERATURE.

CATALYTIC HYDROGENATION OF ETHERS.

By Shigeru KOMATSU and Masajiro MASUMOTO.

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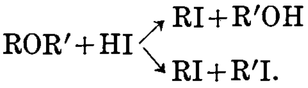
The erroneous view that ethers are stable against chemical reagents and heat, which has been held by numerous chemists has been partly modified by the investigation conducted by K. Kashima⁽¹⁾ into the thermal decomposition of aliphatic ethers which are decomposed by being passed over heated Japanese acid clay, into the corresponding olefines and alcohols at low temperature (200°C.) and at high temperatures into olefines and water.

Ethers, by hydrolysis with HI, yield alcohols and iodides, which differ according to the temperature at which the ether is treated.



$$ROR'+HI\begin{array}{l}\nearrow RI+R'OH\\ \searrow RI+R'I.\end{array}$$

According to P. Sabatier⁽²⁾, ethers of the aromatic series, are reduced in the presence of reduced nickel to alcohols and hydrocarbons. As he says in his book, "Les oxydes aromatiques subissent sur le nickel une scission analogue, qui à deja lieu a température peu élevée pour le oxydes mixtes phenol-alcooliques, et diminue beaucoup le rendement dans leur transformation en oxydes mixtes cycloformeniques."

The authors undertook the present research in order to get some idea concerning the affinity of alkyl or some atomic groups for oxygen, from which they might elucidate the chemical nature of ethers.

I. Catalytic Reduction of Diphenylether.

Diphenyl ether prepared⁽³⁾ from chlorobenzene and phenol shows m.p. 27.5°; b.p. 138° (21 mm.). $d_4^{25}=1.0712$; $n_D^{25}=1.5781$. In the experiment, a sample with reduced nickel which had been previously prepared from nickel oxide by reduction with hydrogen at 280° was placed in an autoclave of a capacity of 600 c.c. with compressed hydrogen. The autoclave, heated

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(1) This Bulletin, **5** (1930), 25.

(2) P. Sabatier, "La catalyse en chimie organique," (1920), 186.

(3) F. Ullmann & P. Sponagel, *Ber.*, **38** (1905), 2211.

externally by electric resistance, was mounted horizontally on a shaking machine.

In the following table, the weight of the sample, the conditions under which the reaction was performed, the yield of the product and its physical constants are shown.

No.	Sample gr.	Reaction conditions			H_2 absorb. in mols.	Reaction product		
		Max. temp.	Initial press.	Time hours		Yield gr.	d_4^{25}	n_D^{25}
I	53	250°	60 atmos.	8	7.4	51	0.863	1.447
II	17	170°	60 ,,	6	5.4	17	0.918	1.476
III	50	220°	60 ,,	7	1.9	—	1.004	1.536

No. I.

	Fraction b.p.	Yield gr.	d_4^{25}	n_D^{25}	Remarks
1	73°–108°	21	0.779	1.427	Hexahydrobenzene
2	156°–168°	27	0.940	1.463	Cyclohexanol
3	Residue	2	—	—	

When purified, fraction 1 showed the constants: $d_4^{25}=0.7687$; $n_D^{25}=1.4248$, which agree with those for pure cyclohexane, and the 2nd fraction shows the constants ($d_4^{25}=0.9469$; $n_D^{25}=1.4635$) of pure cyclohexanol.

No. II.

	Fraction b.p.	Yield gr.	d_4^{25}	n_D^{25}
1	60°–110°	4	0.7795	1.4313
2	73°–115° (17 mm.)	7	0.9546	1.4712
3	115°–120° ,,	1	1.0092	1.5210

Fraction 1 and 2, as their physical constants indicate, are composed of cyclohexane and cyclohexanol respectively.

The third fraction, a mixture of diphenylether and dicyclohexyl ether, was fractionated to isolate the latter, which showed b.p. 230°–240°;

$d_4^{25}=0.9947$; $n_D^{25}=1.5080$; M.R.$=54.51$ (54.86 for $C_{12}H_{22}O$); and analytical results: C$=79.1$; H$=12.1$, (theory C$=79.1$; H$=12.1$% for $C_{12}H_{22}O$).

No. III.

	Fraction b.p.	Yield	d_4^{25}	n_D^{25}	Remarks
1	72°-84°	3	0.8162	1.4625	48% benzene, cyclohexane
2	75°-86° (14 mm.)	9	0.9551	1.4727	5% phenol+cyclohexanol
3	134°-138° „	19	1.0617	1.5702	diphenylether-cyclohexanol

Although diphenyl oxide⁽¹⁾ is said to be hardly susceptible to the catalytic action of reduced nickel in the presence of hydrogen, the conversion of the compound into cyclohexane and cyclohexanol ought to place with quantitative yield on heating it to 250° under 60 atmospheric pressures at 15°, in the presence of reduced nickel and hydrogen, in which disruption of the linking between carbon and oxygen will happen first and then the hydrogenation of the benzene nucleus of the molecules decomposed. This assumption was realized in experiment III, in which the reaction temperature was 220°, and accordingly the consumption of hydrogen is very small compared with that in the first experiment. The isolation of benzene and phenol together with their reduced substances from the reaction product is in favour of the above view. The occurrence of benzene in abundance is due to difficulty of hydrogenation under the experimental conditions, while phenol is hydrogenated with facility.

The other explanation of the formation of cyclohexane and cyclohexanol from diphenylether is shown in the scheme, in which

$$(C_6H_5)_2O \rightarrow (C_6H_{11})_2O \rightarrow C_6H_{11}OH + C_6H_{12}$$

hydrogenation of the benzene nucleus of the oxide takes place under the conditions, (lower temperature and high pressure) shown in experiment II.

The reaction products obtained from diphenyl oxide at high pressure and temperature in the presence of reduced nickel and hydrogen, are not entirely the same as those obtained by W. Ipatiew,⁽²⁾ who conducted the experiment at 230° and under 100 atmospheric pressures in the presence of nickel oxide.

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(1) A. Mailhe & M. Murat, *Bull. soc. chim.*, [4] **11** (1912), 122.

(2) *Ber.*, **41** (1908), 1001; *Compt. rend.*, **181** (1925), 793; refer W. Schrauth and W. Wege, *Ber.*, **57** (1924), 858.

II. Catalytic Reduction of Furfurol.[1]

1. Partial Hydrogenation of Furfurol. Reduction of furfurol was tried to see the behaviour of oxygen in ring, since furane forms a closely allied family with benzene from the standpoint of methods of formation and chemical behavior; the chain of four CH groups in the benzene molecule is closed as a ring by O.

M. Padoa and U. Ponti[2] performed the catalytic hydrogenation of furfurol at 190° by Sabatier's method, obtaining furfuryl alcohol with some α-methylfurane, α-methyl tetrahydrofurane, sec-n-amyl-alcohol and methyl propyl ketone, while at 270°, furane and CO were formed and these results are similar to these obtained by H. Pringsheim and H. Noth.[3]

Furfurol from Merck was used in the experiment after being purified ($d_4^{25}=1.153$; $n_D^{25}=1.522$).

(A) *Furfuryl alcohol.* (1) 50 gr. of furfurol were heated in the autoclave to 160°, with hydrogen under a pressure of 100 atmospheres, the reaction was completed with the absorption of 1 mol hydrogen in 6 hours, and the product ($d_4^{25}=1.132$; $n_D^{25}=1.498$) was fractionated:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	70°–140°	3 gr.	0.984	1.504
2	70°–80° (28 mm.)	9	1.141	1.505
3	80°–97° ,, ,,	33 (80 %)	1.136	1.498
4	97°–183° ,, ,,	6	1.154	1.506
5	Residue	trace	—	—

The first fraction consisted of furane and methyl furane, and the second fraction of furfurol and furfuryl alcohol. The main component of the reaction product was assumed to be furfuryl alcohol and confirmed to be so by purifying with distillation under 17 mm. pressure; b.p. 74° (17 mm.): $d_4^{25}=1.1317$; $n_D^{25}=1.4928$; M.R.=25.15. Combustion: C=61.5; H=6.2%. Theory: C=61.3; H=6.1% for $C_5H_6O_2$. Phenyl urethane $C_{12}H_{11}O_3N$: m.p. 43°, N=6.4%.

(B) *Tetrahydro furfuryl alcohol.* In order to get the tetrahydro compound, 50 gr. of furfuryl alcohol were subjected for 7 hours to a partial

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(1) The catalytic reductions in this part were conducted in the same autoclave and with a nickel catalyst which was prepared in the same way, as those in the former.

(2) *Chem. Zentr.* 1907, II, 570.

(3) *Ber.*, **53** (1920), 114.

hydrogenation which was carried out at around 180° and under an initial pressure of hydrogen of 85 atmospheres.

51 gr. of the product ($d_4^{25}=1.062$; $n_D^{25}=1.455$) were fractionated as usual and the physical constants of each fraction studied:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	60°–140°	2.4 gr.	0.922	1.396
2	76°–90° (16 mm.)	21	1.052	1.450
3	90°–113° „	3.4	1.050	1.453
4	113°–200° „	11	1.101	1.463

The second and third fractions were assumed from their physical constants to be composed of the tetrahydro compound, which was isolated in the pure state by fractional distillation with a yield of 70%. B.p. 79° (17 mm.); $d_4^{25}=1.0506$; $n_D^{25}=1.4509$; M.R.=26.14. Combustion: C=58.8, 58.5; H=10.1, 10.1%. Theory: C=58.8; H=9.8% for $C_5H_{10}O_2$. Its phenyl urethane $C_{12}H_{15}O_3N$ (m.p. 56°(1)) gave N=6.3%, which agrees with theoretical value N=6.3 for $C_{12}H_{15}O_3N$.

(*C*) *Dihydro furfuryl alcohol.* Partial hydrogenation of 25 gr. of furfuryl alcohol at 144°, with hydrogen under a pressure of 80 atmospheres, was tried, and the product formed by absorbing about 0.8 mol of hydrogen showed the constants: $d_4^{25}=1.084$; $n_D^{25}=1.470$.

The product was fractionated into the following 5 parts:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	50°–140°	0.5 gr.	—	—
2	77°–84° (18 mm.)	9	1.099	1.472
3	84°–90° „	5.7	1.098	1.472
4	90°–160° „	3.3	1.126	1.478
5	Residue	1.5	—	—

The second fraction seems to be a mixture of furfuryl alcohol and the tetrahydro-compound.

The third fraction was found to change its colour to yellow on exposure to air, with a characteristic odour; the physical constants of the purified

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(1) H. Wienhaus, *Ber.*, **53** (1920), 1663.

sample were determined: b.p. 79–81° (14.5 mm.); $d_4^{25}=1.0986$; $n_D^{25}=1.4727$. M.R.=25.52 quite agrees with the calculated value 25.80 for dihydro furfuryl alcohol and the analytical results shows: Found: C=59.9, 60.3; H=8.4, 8.2%. Calc. for $C_5H_8O_2$: C=60.0; H=8.0%.

2. **Complete Hydrogenation of Furfurol.** (*A*) *Complete hydrogenation of furfuryl alcohol* (*No. II*) *and tetrahydro furfuryl alcohol* (*No. I*). The furfuryl alcohol was subjected to complete hydrogenation under the conditions described in the table, and the behavior of tetrahydro furfuryl alcohol (No. I) in the presence of reduced nickel and hydrogen at high temperature and pressure was also studied for comparison.

No.	Sample	Reaction			H_2 absorb. in mols.	Product		
		Temp.	Initial press. at 60°	Time in hour.		Yield	d_4^{25}	n_D^{25}
I	22 gr.	300°	30 atmos.	8	0.94	18.5 gr.	0.955	1.417
II	25 „	300	90 „	13	3.72	22.0 „	0.948	1.410

No. I.

	Fraction	Yield	d_4^{25}	n_D^{25}
1	64°–105°	9.2 gr. 58%	0.8864	1.398
2	70°–74° (12 mm.)	3.4 21	1.053	1.447
3	75°–110° „	3.3 21	1.039	1.449

No. II.

	Fraction	Yield	d_4^{25}	n_D^{25}
1	64°–100°	10.5 gr. } 71%	0.827	1.398
2	100°–140°	2.4	0.874	1.402
3	67°– 82° (15 mm.)	4.3 24	1.023	1.446
4	82°–105° „	1.0 5	1.015	1.448

A compound which was supposed to occur in the third fraction in No. I, as will be seen in experiment No. II, diminished in yield when the reaction proceeded owing to transformation of the compound into substances of low boiling point. The molecular weight of the substance ($d_4^{25}=0.999$; $n_D^{25}=1.452$) isolated in a pretty pure state, in benzene solution by the cryoscopic method, was found to be 150, which corresponds approximately to the molecular weight of polymerized hydrofurfuryl alcohol or hydrofurfuryl ether $C_{10}H_{18}O_3$ (molecular weight 186).

Both the second fraction in No. I and the third fraction in No. II, were found to be composed of tetrahydrofurfuryl alcohol. The main portion of the reaction product, the first fraction in No. I and II, was again fractionated carefully into (I) b.p. 63–70°, (II) b.p. 76–82°, (III) b.p. 113°–130° and the following compounds were isolated:

(1) Tetrahydrofurane.—The fraction b.p. 63°–70°, which forms the main portion of the product, is a colourless liquid with a characteristic odour; $d_4^{25}=0.8669$; $n_D^{25}=1.4004$; M.R.=20.26. Combustion: Found, C=66.0, 66.4; H=11.5, 11.5%. Calc. for C_4H_8O, C=66.7; H=11.1%.

(2) Methyltetrahydrofurane.—The second fraction b.p. 76–82°, shows $d_4^{25}=0.9325$; $n_D^{25}=1.4027$, which indicates that the fraction consists mostly of methyl tetrahydrofurane with some tetrahydrofurane. For reference, the combustion was carried out: C=68.6, 68.9; H=12.5, 12.4%. (Theory C=69.8; H=11.6 for $C_5H_{10}O$ and C=66.7; H=11.1% for C_4H_8O).

(3) n-Butylalcohol.—The fraction b.p. 113–130° ($d_4^{25}=0.8184$; $n_D^{25}=1.402$; M.R.=22.02) was assumed to be butyl alcohol. Combustion: Found, C=64.7, 64.3; H=13.7, 13.4%. Calc. for $C_4H_{10}O$, C=64.9; H=13.5%.

Its phenyl urethane melts at 54°. The attempt to detect amyl alcohol and also amylene glycol in the reaction product failed.

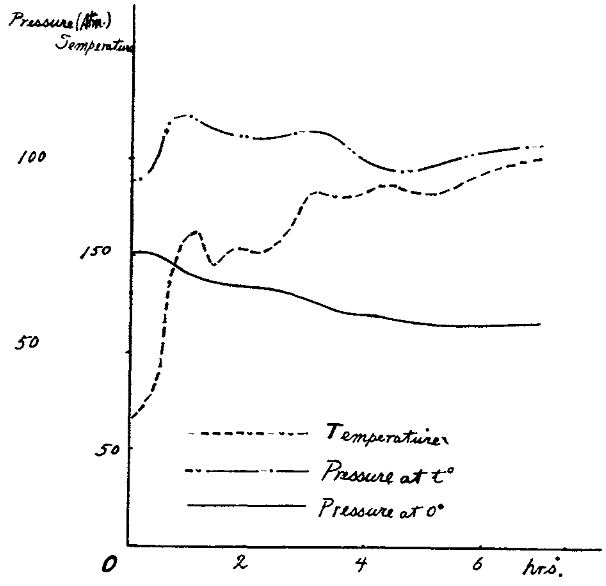
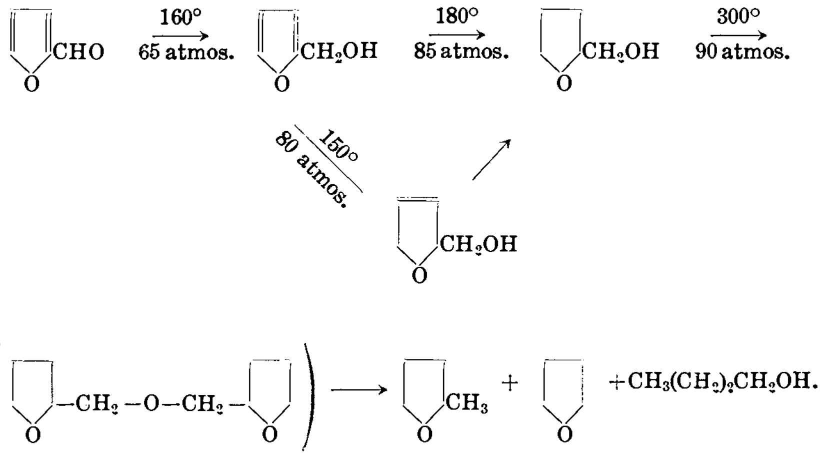


Fig. 1.

(*B*) *Complete hydrogenation of furfurol.* Furfurol was heated to 150° with hydrogen in the presence of the catalyst, under a pressure of 100 atmospheres; the pressure in the autoclave began to be depressed at 60°, and was kept constant after about one mol of hydrogen had been absorbed, the temperature being kept at 150°; it again showed the depression on the reaction temperature being raised, as is indicated in the figure.

Thus, the catalytic reduction of furfurol proceeds stepwise according to the temperature to which the reaction system is subjected.

The course of the chemical changes of furfurol on catalytic reduction in the presence of reduced nickel at high pressure and temperature is shown in the following scheme:



In the last phase of the reaction, tetrahydro furfuryl ether is assumed to occur as an intermediate reaction product which, owing to its instability towards heat or to the reducing agent, is immediately transformed by disruption of the carbon-oxygen linking into methyl furane, furane and butyl alcohol.

April, 1930.

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ON THE DECOMPOSITION OF METHANE, ETHANE AND ETHYLENE BY ELECTRIC SPARK.

By Chiko FUJIO.

Received July 12, 1930. Published August 28, 1930.

Berthelot(1) has already reported that methane decomposition by heat tends to form acetylene, ethane and hydrogen, in accordance with the following equations:

(1) $2CH_4=C_2H_2+3H_2$, (2) $2CH_4=C_2H_6+H_2$.

Ethane by heating yields ethylene, acetylene, methane, and hydrogen

(3) $C_2H_6=C_2H_4+H_2$, (4) $2C_2H_6=C_2H_2+2CH_4+H_2$

whilst ethylene tends to form ethane, acetylene and hydrogen,

(5) $C_2H_4=C_2H_2+H_2$, (6) $2C_2H_4=C_2H_6+C_2H_2$.

Acetylene was thus regarded by him as the ultimate decomposition product of hydrocarbons by heat.

The experiment for the decomposition of methane by the electric arc was carried out by W.A. Bone and D.S. Jerdan(2) and the gaseous products were noticed to be composed in the following proportion:

$$C_2H_2 : H_2 : CH_4=9.8 : 85.6 : 2.5.$$

and this ratio is maintained when acetylene is treated under the same conditions.

W.A. Bone and H.F. Coward(3) studied the decomposition of methane in the presence of porcelain at temperatures between 500° and 1200°, paying attention specially to the time factor for heating, and came to the following conclusions:—

(1) The rate of decomposition of methane in the presence of porcelain is appreciably below 700°, and for the most part it decomposed directly into carbon and hydrogen as postulated by M. Meyer and V. Altmeyer(4), and the process is probably reversible at all temperatures.

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(1) Compt. rend., **62** (1866), 905; **63**, 788.

(2) J. Chem. Soc., **71** (1897), 41.

(3) J. Chem. Soc., **93** (1908), 1197.

(4) Ber., **40** (1907), 2134.

(2) The formation of acetylene and olefines could be detected only so long as the methane concentration exceeded 60%.

Lately R.C. Cantelo(1) has conjectured the possibility of the production of the higher hydrocarbons thermodynamically, such as ethylene and acetylene from methane by heating, and this assumption was supported by the experimental results arrived at by H.V. Wartenberg.(2)

Recently R.V. Wheeler(3) and F. Fischer(4) have independently studied the acquisition of benzene from methane.

According to the investigation of S.C. Lind on the exposure of methane to α-radiation, ethane and ethylene are formed and ethane and propane behave similarly to methane in forming saturated and unsaturated hydrocarbons resulting from the elimination of hydrogen or lower hydrocarbons which subsequently build up the higher members by addition or condensa. tion as a result of valencies freed in the process.

On turning our attention to the molecular structure of methane, the infra-red absorption spectrum of methane have arrived at a tetrahedral structure of the methane molecule accepted already by chemists, but the experiments on the scattering of light, the absorption spectrum of the ultra-violet rays, and X-ray analyses are interpreted by numerous investigators in favor of the pyramidal structure which has been discussed by Weissenberg,(5) and the four valencies of carbon are not equivalent but consist of two different types, so that the six electrons of the carbon atom are distributed in three shells, two electrons in 1_1, 2_1, and 2_2 orbits, and accordingly the elimination of the hydrogen atom from the methane molecule should take place in succession, to form radicals of different reactivity.

$$CH_4 \longrightarrow -CH_3,\ =CH_2,\ \equiv CH,\ \equiv C.$$

Free radicals and hydrogen liberated from methane by heating or by radiating an α-particle, give a mixture of hydrocarbons still interacting since the reactions continue under further heating or radiation unless the products should be shifted from the sphere of the reaction system. As a matter of fact, the products so far studied in the thermal decomposition of methane, are so complicated by simultaneous and successive reactions to such a degree that only their broader aspects have been worked out.

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(1) *J. Phys. Chem.*, **28** (1924), 1036.

(2) *Z. physik. Chem.*, **61** (1908), 366.

(3) *Fuel*, **7** (1928), 535.

(4) *Brennstoff-Chem.*, **9** (1928), 309.

(5) *Naturwiss.*, **15** (1927), 662; v. Henri, *Chem. Rev.*, **3** (1927), 189; J.K. Morse, *Proc. Nat. Acad. Sci.*, **14** (1928), 166.

Owing to the difficulty of interpreting the mechanism of reactions from these data, even with the accurate analysis of the products separated from the reaction product from time to time, the writer has undertaken the present investigation to study the chemical mechanism of the decomposition of methane by the electric spark, in which comparatively unstable products would be produced retarding the complex side reactions.

The apparatus employed in the experiment is shown in the accompanying figure (Fig. 1).

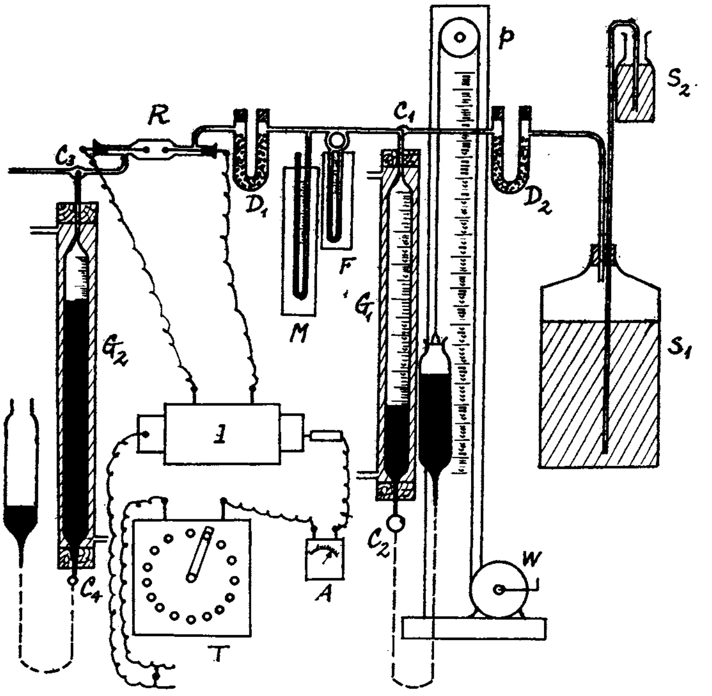

Fig. 1.

In the experiment, 100 c.c. of methane dried by passing into the dryers D_1 and D_2 containing calcium chloride, were passed into a reaction tube R the velocity being regulated with a flowmeter F and a manometer M ; each reaction tube consists of a bulb of 1.5–3.5 cm. diameter and 2.0–7.0 cm. length, provided with spherical brass electrodes of 0.5–0.2 cm. diameter, and the sparks were produced between these electrodes by applying 110 volts D.C. with the aid of the induction coil I, to which the rheostat T and the ammeter A are connected. A receiver G of 150 c.c. capacity for the gaseous products is also connected to the reaction tube, which contained mercury and was cooled with a water jacket to maintain a constant temperature.

As the gaseous products contain acetylene, ethylene, and hydrogen, as well as small quantities of heavy unsaturated hydrocarbons, special methods were adopted for their analysis. Acetylene was estimated with an absorbent in which 20 gr. of mercuric cyanide were dissolved in 100 c.c. of 2-N sodium hydroxide solution and saturated with ethylene and benzene, and for the estimation of ethylene another absorbent was used, composed of 20 gr. mercuric nitrate, 100 c.c. 2-N nitric acid saturated with sodium nitrate and benzene. The heavy hydrocarbons were estimated by fuming sulphuric acid. Ethane, if present, the sample being completely freed from acetylene, ethylene and the heavy hydrocarbons were subjected to oxidation with a palladium sponge at 100° to eliminate any hydrogen, the residual gas was subsequently exploded completely with an excess of oxygen, and the amount of ethane calculated by the ratio C/A(1) determined in the usual manner. The carbon deposited on the wall of the reaction tube was composed of carbon and some unsaturated hydrocarbon which can easily be dissolved by fuming sulphuric acid.

The percentage of the reaction products were calculated on nitrogen free bases.

Table 1.

Electrode dia. 1.0 cm. Spark gap 2.0 cm. Spark voltage 33,000 volts.

Gas velocity c.c./hour.	Percentage of decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4					Ratio of products
		Volume	H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
510	74.7	187.6	150.3	32.7	2.7	1.2	4.60
513	79.0	203.2	163.3	34.9	3.0	1.3	4.68
926	65.5	193.2	157.9	33.2	2.0	—	4.79
963	57.4	195.4	160.7	31.7	2.3	—	5.07
1005	74.7	204.2	163.6	35.3	3.0	2.2	4.64
1360	57.7	196.9	163.7	34.9	2.9	—	4.69
1360	44.0	209.4	171.2	35.9	2.5	—	4.77
1578	58.6	194.9	160.1	32.9	2.3	—	4.87
1989	57.7	192.6	157.0	31.5	3.6	—	5.01
2070	48.6	192.7	157.2	30.7	1.8	—	5.12
Mean		196.5	160.2	33.4	2.6	—	4.81

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(1) C : contraction after explosion; A : absorbed volume.

The spark voltages in the experiments were calculated referring to those measured by Heydweiller(1) for various lengths of sparks between electrodes of various diameters at normal atmospheric pressure and temperature.

Table 2.

Electrode dia. 2.0 cm. Spark gap 2.0 cm. Spark voltage 47,000 volts.

Gas velocity c.c./hour.	Percentage of decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4					Ratio of products
		Volume	H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
552	75.0	203.2	164.6	32.6	2.6	1.5	5.00
616	76.3	195.3	160.6	29.5	1.8	2.1	5.44
806	71.7	206.3	167.1	33.6	2.3	1.9	5.01
902	74.1	202.3	162.8	33.1	2.4	1.5	4.92
1181	77.4	204.2	168.4	33.0	2.0	—	5.10
1233	66.2	187.2	163.3	32.9	2.4	—	5.07
1396	63.8	201.7	166.1	33.5	2.4	—	4.97
1787	60.1	195.6	159.4	32.9	2.3	—	4.99
1916	62.1	200.4	164.7	33.0	2.0	—	4.99
	Mean	199.6	164.1	32.7	2.3	—	5.04

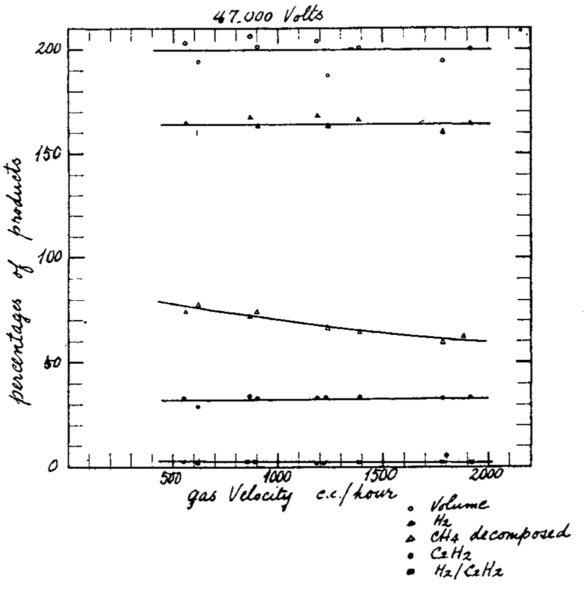

Fig. 2.

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(1) J.A. Fleming, " The Wireless Telegraphist's Pocket Book," p. 109.

In Fig. 2, yields of acetylene and hydrogen, volume of the products, and ratio H_2/C_2H_2 are plotted against gas velocity. From these experimental results shown in Fig. 2, the decomposition of methane seems to occur at an uniform rate.

The following series of experiments were carried out at various spark voltages and results as mean value for each product are shown in Table 3.

Table 3.

Spark voltage (volts)	Spark gap (cm.)	Volume change of reaction gas calculated for decomposed CH_4	Percentage of gaseous products calculated for decomposed CH_4				Ratio of products
			H_2	C_2H_2	C_2H_4	C_2H_6	H_2/C_2H_2
8,000	—	178.3	138.2	30.0	0.9–5.8	0–6.7	4.78
20,000	1	185.0	150.0	33.5	7.0–8.0	—	4.80
23,000	2	183.0	145.0	30.0	3.2–9.8	0–17.1	5.03
23,700	3	188.2	150.0	33.8	3.0–5.6	0–2.5	4.46
24,000	4	192.1	155.4	31.8	2.7–4.4	0–1.3	4.73
33,000	2	196.5	160.2	33.4	1.8–3.6	0–2.2	4.81
47,000	2	199.6	164.1	32.7	1.8–2.8	0–2.1	5.04

The decomposition rate of methane was decreased inversely to gas velocity, while the production of acetylene remained constant, and the production of ethylene and ethane was decreased at high voltages. The yield of acetylene, consisting of about 30 % of the product, is immensely great in our case when compared with the result of the thermal decomposition of methane.

'As regards the mechanism of the formation of acetylene from methane, the theory which seems to fit the fact, is to assume a temporary formation of the radical $-CH_3$ from methane by a collision of electrons in the process of the ionisation of the molecule, which will then be converted by destroying the electrical tension among the electrons of the radical, into radicals $\equiv CH$ and $\equiv C$ which will polymerise with one another to produce an electrical neutral molecule of acetylene and carbon, and also form methane by hydrogenation. The radicals $-CH_3$, $=CH_2$, in the same manner, would form, on the one hand, ethane and ethylene, and on the other, methane by hydrogenation.

Formation of radicals	Polymerisation	Hydrogenation
$CH_4 \rightarrow -CH_3+H$	$\rightarrow C_2H_6$	$\rightarrow CH_4$
$\rightarrow =CH_2+2H$	$\rightarrow C_2H_4$	$\rightarrow CH_4$
$\rightarrow \equiv CH+3H$	$\rightarrow C_2H_2$	$\rightarrow CH_4$
$\rightarrow$ ≣C $+4H$	$\rightarrow C_x$	$\rightarrow CH_4$

The decomposition of methane under a spark with considerably high voltage, will be shown by the equation,

$$3CH_4=C_2H_2+5H_2+C$$

in which two reactions were supposed to occur simultaneously.

$$CH_4 \rightleftarrows C+2H_2 \text{ .... (a)}$$
$$2CH_4 \rightleftarrows C_2H_2+3H_2 \text{ .... (b)}$$

When the electric spark voltage is very high or the gas velocity is very small, the reaction (a) is increased at the expense of ethane and ethylene.

The Decomposition of Ethylene and Ethane.

As will be understand in the foregoing theory for the formation of acetylene from methane, the radicals such as $-CH_3$ and $=CH_2$ were assumed to occur in the course of the transformation, which will result from the collision of electrons to produce $\equiv CH$, and for verification of this hypothesis which evidently demands production of the radical $\equiv CH$ by the action of an electric spark from $=CH_2$ and $-CH_3$ generated from a molecule of ethylene and of ethane, these gases were subjected to the action of an electric spark.

The ethylene used in the experiment was prepared by decomposition of ethylene-bromide (b. p. 130°–131.5°) with zinc powder, and washed by an alkali solution of pyrogallol to remove the oxygen in the gas. Ethane was also prepared by Grignard's method, that is, by the decomposition of ethyl magnesium iodide with water, and the generated gas was washed with fuming sulphuric acid, and the oxygen removed by contact with yellow phosphorus.

The results of the decomposition of ethylene are summarized in the following table.

Table 4.

Electrode dia. 1.0 cm. Spark gap 2.0 cm. Spark voltage 33,000 volts.

Gas velocity c.c./hour	Percentage of decomposed ethylene	Percentage of products calculated for decomposed ethylene				Ratios of products		
		Volume	C_2H_2	H_2	CH_4	C_2H_2/H_2	CH_4/H_2	CH_4/C_2H_2
754	85.2	196.7	56.2	132.4	6.7	0.43	0.05	0.12
798	81.0	200.0	58.4	133.4	6.6	0.44	0.05	0.11
1262	75.4	197.0	64.8	124.5	6.4	0.52	0.05	0.10
1609	74.3	198.9	64.4	127.2	5.5	0.51	0.04	0.09
1823	74.0	198.6	64.1	127.4	5.6	0.50	0.04	0.11
2170	71.0	196.5	61.0	124.6	4.3	0.49	0.04	0.08
2198	70.0	190.7	62.7	128.4	4.5	0.49	0.04	0.07
2651	60.4	190.0	67.8	124.1	5.3	0.55	0.04	0.08
2823	58.0	199.8	68.4	125.1	4.8	0.54	0.04	0.07
3115	58.0	188.8	63.1	122.4	3.4	0.52	0.03	0.05

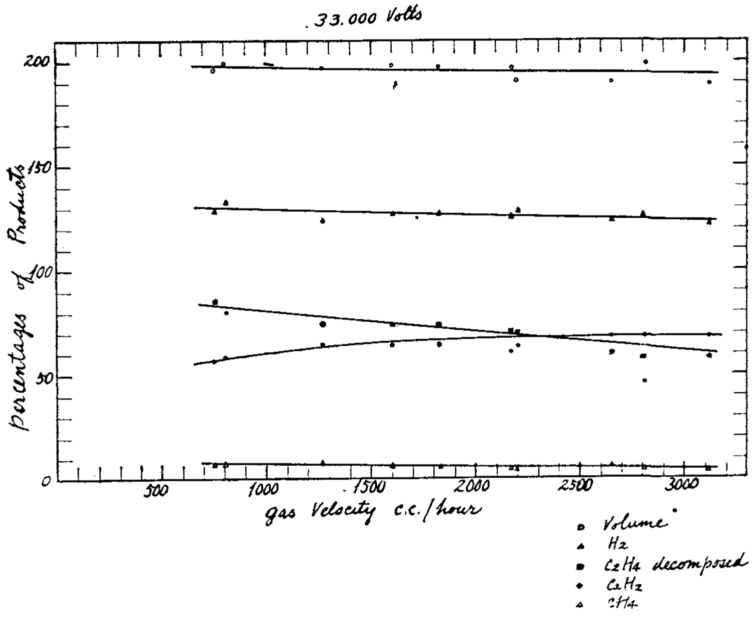

Fig. 3.

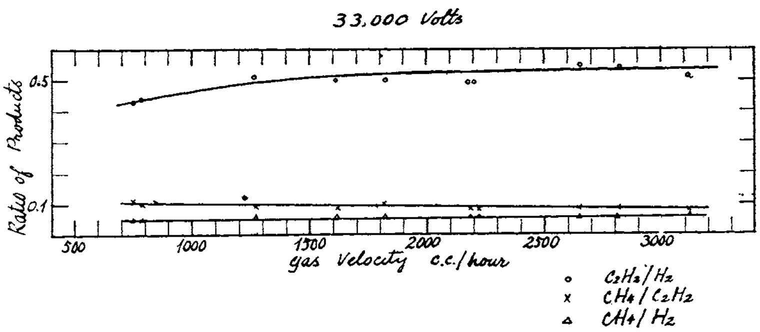

Fig. 4.

The production of hydrogen and methane is increased at a lower gas velocity, the ratio of acetylene to hydrogen in a reaction product increases almost proportionally to the gas velocity but the production of methane to acetylene, and of methane to hydrogen decreases, as indicated in Fig. 4.

The formation of acetylene and methane from ethylene can be explained by assuming that the ethylene molecule produced a radical $=CH_2$ temporarily by the collision of an electron, which was successively converted into radicals $\equiv CH$, $\equiv C$, and they tend to produce acetylene and carbon by polymerisation or methane by hydrogenation.

The fact that the production of acetylene increases with the gas velocity and the absence of ethane in the product certified the theory for the formation of $\equiv CH$ from $=CH_2$, but its hydrogenation is in a minimum degree.

Experimental results for the decomposition of ethane by an electric spark are shown in Table 5 and Fig. 5.

Acetylene, ethylene and hydrogen are the main reaction products and the deposited carbon is similar in nature to that produced by methane.

The production of acetylene and ethylene is almost constant with a gas velocity greater than 1000 c.c. per hour, but that of methane and hydrogen decreases slightly, that is, the ratio of acetylene to hydrogen is constant, but that of methane to ethylene, of methane to acetylene, and of methane to hydrogen, decrease and that of ethylene to acetylene and of ethylene to hydrogen, increase pari passu with the gas velocity, as shown in Fig. 6.

These experimental results indorse the opinion that the radicals $=CH_2$ and $\equiv CH$ are formed from $-CH_3$ dissociated from the ethane molecule, which then proceeds to produce the electric neutral molecules C_2H_4 and C_2H_2.

Table 5.*

Electrode dia. 2.0 cm. Spark gap 2.0 cm. Spark voltage 47,000 volts.

Gas velocity c.c./hour	Percentage of decomposed ethane	Percentage of gaseous products calculated for decomposed ethane				Ratios of products					
		C_2H_2	C_2H_4	H_2	CH_4	$\frac{C_2H_2}{H_2}$	$\frac{C_2H_4}{H_2}$	$\frac{CH_4}{H_2}$	$\frac{C_2H_4}{C_2H_2}$	$\frac{CH_4}{C_2H_2}$	$\frac{CH_4}{C_2H_4}$
519	64.1	70.7	14.3	226.4	19.2	0.31	0.06	0.09	0.20	0.27	1.34
546	61.1	69.1	15.5	211.2	17.2	0.33	0.07	0.08	0.22	0.25	1.10
750	56.7	66.4	17.4	217.6	16.2	0.31	0.07	0.07	0.26	0.24	0.93
834	48.2	66.7	24.7	209.2	17.9	0.32	0.12	0.09	0.37	0.27	0.73
843	52.9	64.6	23.7	217.0	17.6	0.30	0.11	0.08	0.37	0.27	0.74
1022	52.5	65.8	19.5	208.8	17.8	0.32	0.09	0.09	0.30	0.27	0.91
1290	49.7	62.2	24.9	198.9	17.2	0.31	0.13	0.09	0.40	0.28	0.69
1434	50.4	61.5	20.2	201.2	16.8	0.31	0.10	0.08	0.33	0.27	0.83
1505	47.4	66.5	26.5	217.5	17.2	0.31	0.12	0.08	0.41	0.26	0.65
1688	48.5	63.1	26.7	197.7	16.7	0.32	0.14	0.08	0.42	0.26	0.63
1693	44.2	66.7	25.7	221.5	18.1	0.30	0.12	0.08	0.39	0.27	0.70
1966	45.6	59.4	24.5	184.9	16.2	0.32	0.13	0.09	0.41	0.27	0.66
2228	39.1	61.7	30.3	192.8	15.7	0.32	0.16	0.08	0.49	0.25	0.52
2662	37.8	64.4	28.1	206.5	16.9	0.31	0.14	0.08	0.44	0.26	0.60
3247	39.8	62.3	26.8	194.5	15.3	0.32	0.14	0.08	0.43	0.26	0.57

* The total percentage of all the gaseous products become greater than 300%, indicating that, among the products, many higher hydrocarbons, such as propane and butane, are formed during the decomposition of the methane. For this reason we understand that the percentages of decomposed ethane must be really more abundant than the represented value for its behavior contrast with methane.

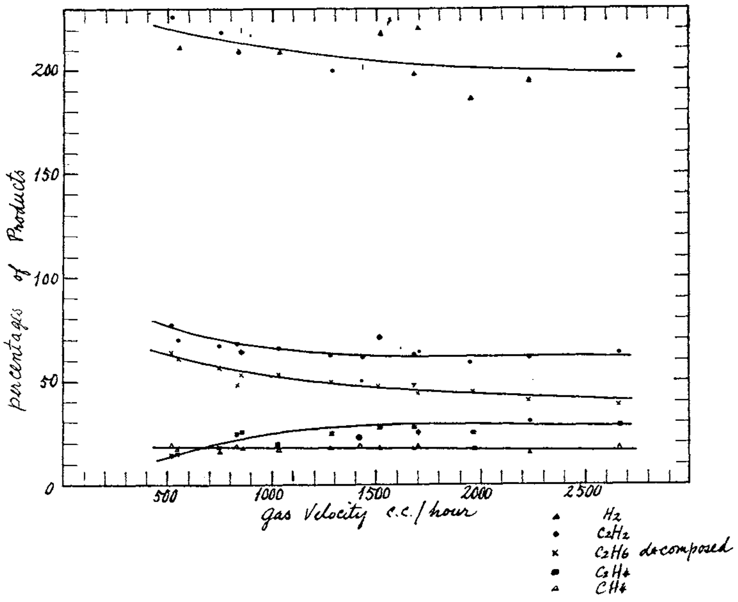

Fig. 5.

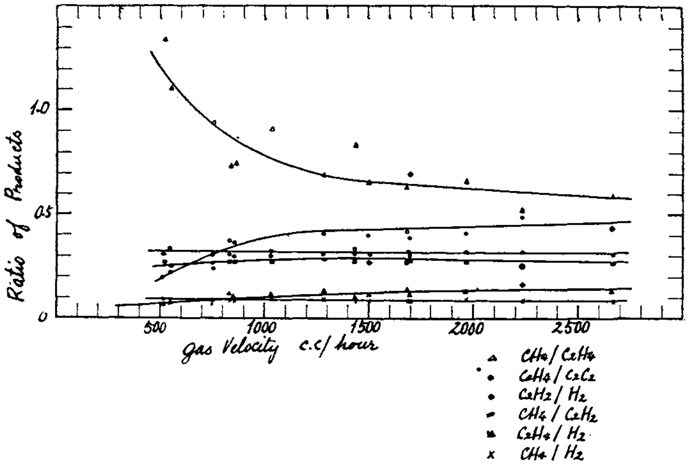

Fig. 6.

When reference is made to the investigation by Lind⁽¹⁾ for the decomposition of propane and butane by the action of α-radiation, the production of the higher hydrocarbons such as benzene in the writer's case is suspected with a great possibility, and further investigation into this interesting subject will surely be fruitful of results.

Conclusions.

Several stream experiments were carried out with methane, ethylene and ethane at varying spark voltages and at different gas velocity.

Considering the experimental results, the radicals ($-CH_3$), ($=CH_2$), ($\equiv CH$) and ($\equiv C$), are supposed to be formed temporarily from methane differing in the yield according to the strength of the electric current, and the rate of the gas velocity, and these radicals, polymerising with one another or combining with activated hydrogen, would produce ethane, ethylene, acetylene, methane and carbon. The polymerisation of the radical ($\equiv CH$), into acetylene is favorable under the experimental conditions, and the formation of benzene or higher hydrocarbons is in full force or promising.

In conclusion, the writer's thanks are due to Director Vice-Admiral S. Kishimoto, for permission to publish these results, and also he is desirous

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(1) *J. Am. Chem. Soc.*, **48** (1926), 2335.

of making grateful acknowledgement to Vice-Admiral G. Yamashita, former Director of the Imperial Naval Fuel Depot, and Engineer-Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch for promoting this investigation, and also to Professor S. Komatsu of the Kyoto Imperial University for his invaluable advice and neverfailing encouragement in the prosecution of this research.

The Scientific Research and Experimental Branch,
Imperial Naval Fuel Depot, Tokuyama.

ON THE FREEZING OF GEL.

By Kyoji KINOSHITA.

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The structure of gels which are formed by setting of the hydrophilic colloids such as gelatine, agar or starch etc. have been studied by numerous authors, and several opinions⑴ were given on this subject. Formerly it was considered to be a homogeneous or one phase system. But now, generally, two phases theory is adopted for, in some cases, even optical resolution into two phases are possible. The two phases theory are subdivided into two, namely liquid-liquid system and solid-liquid system. Whichever we may take, it will be interesting to study the nature of water in the gel. The present experiment have been undertaken to study this problem by freezing of gels.

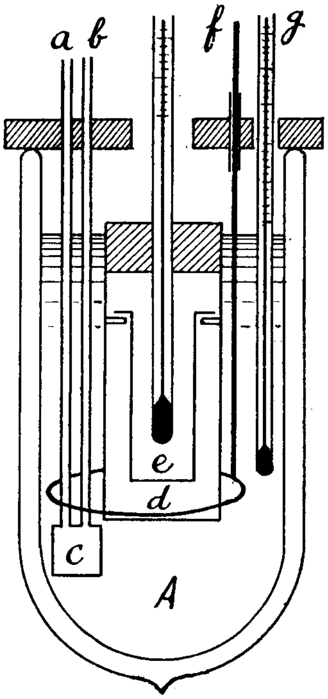

Fig. 1.

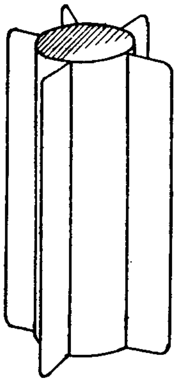

Fig. 2.

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(1) For example, Hardy, *Proc. Roy. Soc.*, A, **66** (1900), 95; Lloyd, *Biochem. J.*, **14** (1920), 147, 584; Bogue, *J. Am. Chem. Soc.*, **44** (1922), 1343.

Moran⁽¹⁾ and Hardy⁽²⁾ observed the microstructure of gels and the volume change by freezing. Most interesting result drawn from their experiments is an equilibrium relation between gel and ice.

According to Moran, when 12–40% gelatine gel was cooled at −3°C a part of water separated from the gel and solidified into ice and covered the unfrozen gel. Taking off the shell of ice the internal gel has a constant concentration depending on the freezing temperature. For example, the gel frozen at −3°C. always has 54.3% internal gel concentration and at −19°C. internal gel concentration reached 65.2%. He also reported that the frozen gel reabsorbs water if it was warmed and the gel comes back to its initial concentration. From these and other observations he concluded that there are two kinds of water in a gel, namely the water combined with gelatine particles and the water contained in a capillary formed by the aggromeration of these particles. In the case of gelatine gel 30% of water is said to combine with gelatine particles.

Experimental. Commercial food gelatine was used all through the experiments, ash content of which was found to be 0.5%.

Cooling apparatus used for the freezing of gel is shown in Fig. 1. *A* is a Dewar's vessel of about 1 litre capacity and is filled with petroleum ether. The liquid air was dropped into the copper vessel *c* through the tube *a*, which then vaporizes and escapes through another tube *b*. *d* is a vessel made of thin copper plate and contains a small copper vessel *e* of about 20 c.c. capacity. The vessel *e* contains gelatine gel, and a Beckmann's thermometer is inserted into the gel. *f* is a stirrer, and *g* a pentane normal thermometer for the measurement of the bath temperature.

Gelatine, stored in a desiccator, is weighed and some amount of distilled water is added. After the swelling of gelatine was completed it is heated on a water bath for a while to obtain a homogeneous solution. A part of the solution is transferred into the vessel *e* and let to set into a gel. Remaining portion is taken into a porcelain crucible and is heated to dryness at 100°C. in an air bath untill the weight constant is attained. The concentration of the gel is determined by this manner.

Beckmann's thermometer is inserted into the gel contained in *e* and the reading is taken every 30 seconds in order to construct a cooling curve of the gel. The Beckmann's thermometer, however, is not sufficiently sensitive to the small change of temperature, so the bulb of thermometer is dipped into mercury contained in a copper cylinder to which some copper

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(1) Moran, *Proc. Roy. Soc.*, A, **112** (1926), 30.

(2) Hardy, *Kolloid-Z.*, **46** (1928), 270.

wings are attached (Fig. 2). This small cylinder with wings is inserted into gel and the temperature of gel is measured indirectly. Gelatine gel increases its volume when it is frozen, and we have experienced that, if we insert a thermometer directly into a gel the mercury bulb is subjected to a high pressure, so that not only the thermometer indicates an incorrect reading but also it is liable to be broken by the pressure. Using the above described small cylinder we can get rid of these inconveniences.

Results of Measurement. Some of the cooling curves of gels, which we have obtained in the various concentrations of gelatine (from 5% to 60%) are shown in Fig. 3. As seen from the figure, the phenomena of supercooling is appeared very markedly. This may explain as a result of protective actions of gelatine on the formation of ice nucleus and on the growing of ice crystals.

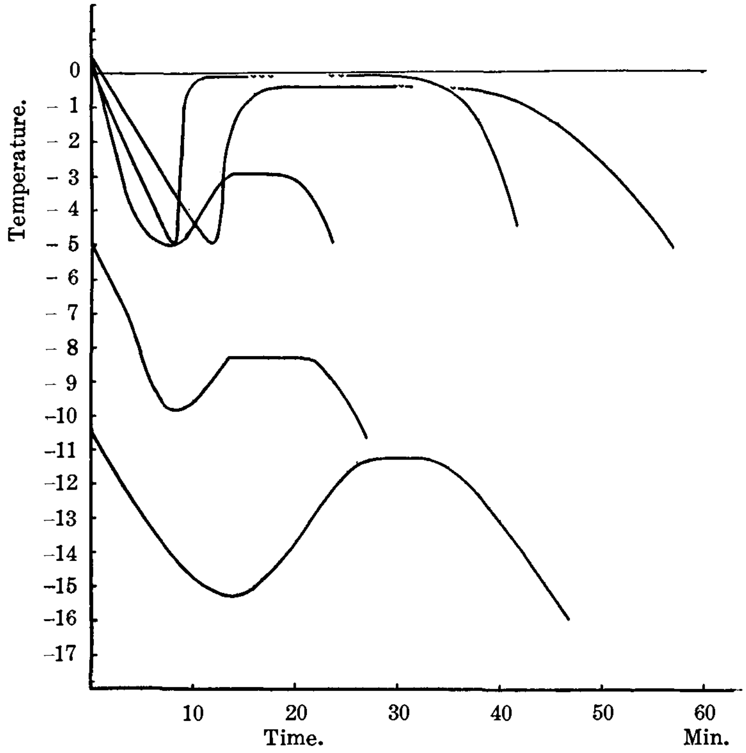

Fig. 3.

It is noteworthy, moreover, that the structure of the frozen gel thus produced differ from each other according to their concentrations. Namely, in the case of gel below 15% frozen in a cylindrical vessel, the concentric thin layers of ice and gel are seen. The layers come alternately and the thickness of which are about 0.5 mm. Of these alternating shells the first shell is always of ice. When it is left to thaw, then again it absorbs water from ice into the layer of gel. However, a little quantity of water can be squeezed out by pressing, immediately after it thawed. Therefore, it seems that the melted ice is reabsobed by the swelling of the gel if we do not press it.

Formation of these shells can be explained in the following manner. At first water which can be separated by cooling comes out of gel (dehydration of gel is caused) and forms shell of ice but the effect of this dehydration of gel does not go very deep into the gel owing to its poor heat conductivity. Thus the thin gel layer under the shell of ice is concentrated by dehydration, and this layer of gel does not freeze by cooling, for its freezing point is lowered by dehydration so that it remains unchanged. Then the cooling effect goes deeper and again a layer of ice is formed. This process is repeated and thus the alternate shells of ice and gel are produced.

Frozen gel of stronger than 20% shows somewhat different structure from that of weaker than 15%. In this case it is a very hard mass of pale brownish white colour and the separation of water as ice cannot be observed with eyes. By the use of a microscope small ice crystals can be seen here and there.

The gelatine gel increases its volume by freezing. Moran measured the change of volume by using a dilatometer, but I could not do any quantitative measurement on this point.

Similar cooling curve can be seen in a case of starch gel. The frozen starch gel is white in colour, and when it is left on the funnel to thaw it secredes water in drops. Agar gel slso becomes whitish and are found many cracks. The frozen agar gel, when left on a funnel to thaw, it separates water drop by drop, and we can press out considerable amount of water from it.

Conc. of gelatine gel by weight %.	Freezing temeprature °C.
5	- 0.10
10	- 0.42
15	- 2.96
20	- 5.66
25	- 8.33
30	- 9.74
40	-11.25
60	-12.65

It is almost a doubtless fact that the hydrophilic colloids are in hydrated states. Many authors have reported the investigations on the degree of hydration. Moran determined the quantity of water separated from a frozen gel as ice, and concluded that the degree of hydration in the case of gelatine is about 30%.

The freezing temperatures of various gels obtained by the present experiment are shown in the table above.

Plotting these values on a temperature concentration diagram we obtain a curve of inverse S type (Fig. 4). In the case of 5% and 10% gel we find that its freezing temperature is nearly equal to, or little lower than that of pure water. The form of cooling curve obtained in this case is similar to the curve which can be obtained when the pure ice is separated from the solution. In the case of 15–30% gel freezing temperature falls suddenly, and in the 40% up to 60% gel freezing temperature curve becomes asymptotical to the axis of concentration.

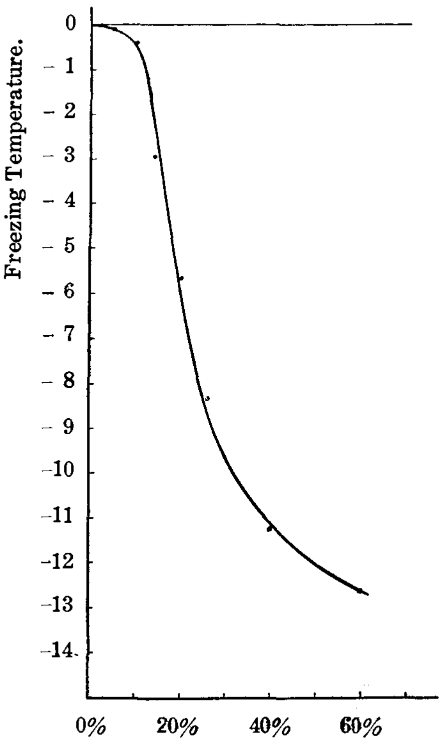

Fig. 4.

Now let us assume that the gelatine particle can take any degree of hydration according to its concentration. These hydrated water molecules have their own strength of hydration, some of them may cling to the particle very strongly and others may be very weakly attach to the particle, just as we can see in the case of ion-atmosphere around the ion of strong electrolyte. Weakly attached water must be separated when gel is subjected to dehydration, and the constitution of dehydrated gel must depend on the process and intensity of dehydration. In the above experiments 5–15% gel has a weakly combined water which can be separated out by freezing, so that there remains the mixture of gel and ice. In the gel more concentrated than 15% there is no water which can be separated by freezing, and hence it freezes in a hydrated state, and is turned into a pale brownish white mass. In the case of 40–60% gel, the freezing point curve runs asymptotically to the axis of concentration. From this fact it is probable that some water must be combined in gel rather strong, in the form of chemical compound or of solid solution. By these assumptions we can explain the above described formation of alternating shell of ice and gel.

In conclusion, I should like to express my hearty thanks to Prof. J. Sameshima for his kind guidance throughout my experiments.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

ACTION OF REDUCED NICKEL AND HYDROGEN ON AROMATIC HYDROCARBONS UNDER HIGH PRESSURE AND TEMPERATURE.

By Toru OGAWA and Toshio YOKOTA.

Received July 9, 1930. Published September 28, 1930.

The reduction of benzene was assumed to proceed by the following steps:

$$C_6H_6 + H_2 = C_6H_8 + 0.8 \text{ cal.}$$
$$C_6H_8 + H_2 = C_6H_{10} + 25 \text{ cal.}$$
$$C_6H_{10} + H_2 = C_6H_{12} + 27.8 \text{ cal.}$$
$$C_6H_{12} + H_2 = C_6H_{14} + 11 \text{ cal.}$$

which were investigated comprehensively by Stohmann(1) in the series of his thermochemical studies of organic compounds, and he concluded that the jump in heat-toning between the first and second terms of the series compared with the two following, as well as between the third and fourth, indicates a fundamental difference of structure between benzene and its di- and tetra-hydrobenzenes, and also between tetrahydro- and hexahydrobenzenes, viz., that the benzene molecule is in the most stable state by packing together by the bonds and the combination by them in di- and tetra-hydrocompounds more loosely, reaching again a high degree of stability in hexahydrobenzene, and such observation led him to reject the Kekulé formula for benzene.

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(1) *J. prakt. Chem.*, **48** (1893), 447; **49** (1894), 260.

The structural formula for naphthalene proposed by Graebe was also rejected by Bamberger⁽¹⁾, and lately by Willstätter⁽²⁾ from their studies of its reduction.

According to Professor Sabatier⁽³⁾ benzene begins the catalytic hydrogenation to cyclohexane in presence of reduced nickel at 70° and proceeds with increased velocity as the temperature is increased to about 300°, and above this temperature there is no formation of cyclohexane, but the conversion of the latter into benzene and decomposition into methane and carbon have started. Under similar conditions naphthalene yields tetralin and decalin which decompose at high temperature into methane and benzene homologues.

When benzene and naphthalene treated in presence of nickel oxide at high temperature and under pressure, the experimental results⁽⁴⁾ are on the whole very similar to those obtained by Sabatier's method.

The catalytic action of reduced nickel at high temperature and under pressure, apart from these theoretical considerations on the structure of aromatic hydrocarbons, would afford an idea for the cracking process in which permanent gas and volatile fuels for internal combustion engines are prepared from heavy hydrocarbons, and the formation of these compounds is regarded generally as depending on the temperature and pressure at which the process is carried out, with or without catalyst and hydrogen, and the present investigation was so carried out.

In the experiment, 100 gr. of pure benzene, b.p. 80°–80.5° (761 mm.), $n_D^{25}=1.498$, were introduced in an autoclave of 2 litres capacity, with 5 gr. of reduced nickel and hydrogen, and heated at 470° for 1 hour, under pressure of 80 atmospheres at 0°, after cooling the apparatus, the depression of pressure of hydrogen was 35 atm. at 0°, which corresponds to 2.7 mol %. (Fig. 1.) The gas in the autoclave was analysed with the following results:

CO_2	CO	C_nH_{2n}	C_nH_{2n+2}	H_2	n
0.1	—	—	1.4	98.5	1.2

The liquid reaction product was 92% in yield for theory, and on being fractionated:

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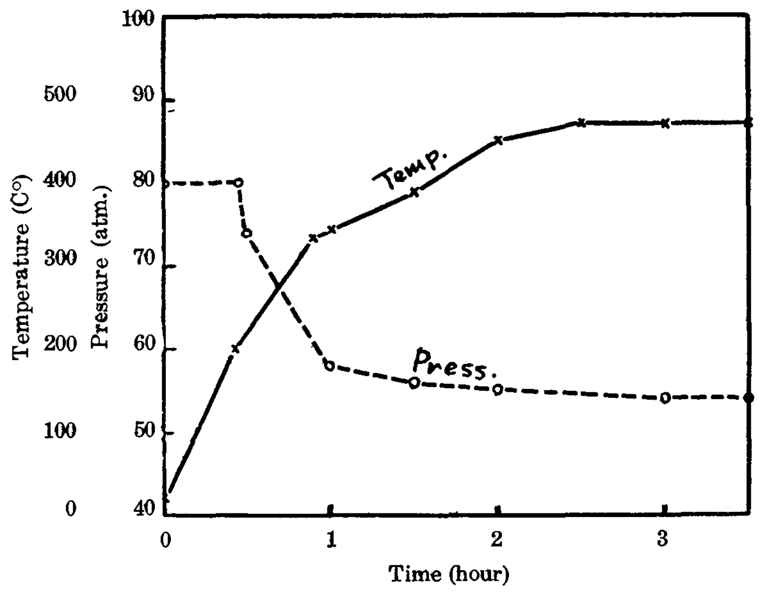
(1) *Ann.*, **257** (1890), 47.

(2) *Ber.*, **45** (1912), 1478.

(3) "La catalyse en chimie organique," (1920), p. 171, 221.

(4) W. N. Ipatiew "Aluminiumoxyd als Katalysator in der organischen Chemie," (1929), 78.


Temperature (C°)
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Pressure (atm.)
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Temp.
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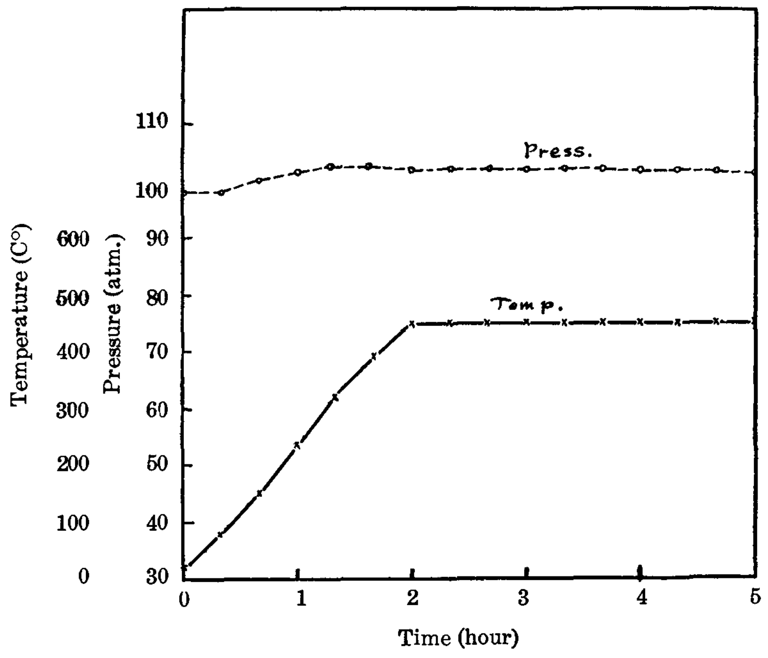
Time (hour)

Fig. 1.


Temperature (C°)
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Press.
Temp.
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1
2
3
4
5
Time (hour)

Fig. 2.

	Fraction	Yield	n_D^{25}	d_4^{25}
1	77°–79°	55%	1.433	0.7843
2	79°–80.7°	30%	1.433	0.7806

The two fractions showing no reaction with bromine, were treated with a mixture of nitric and sulphuric acids, and show b.p. 80°–82°, $n_D^{25}=1.423$, $d_4^{25}=0.777$ which agree with the constants for cyclohexane.

When 166 gr. of pure cyclohexane heated in presence of hydrogen and 20 gr. reduced nickel in the autoclave at 450° for 3 hours under 100 atmospheric pressures at 0°, no appreciable change on pressure was noticed as indicated in Fig. 2, and the liquid substance in the autoclave boils from 80° to 85°, and thus cyclohexane is confirmed to be a stable compound under the above conditions, and the same is also noticed of benzene treated with hydrogen at 460° for 1 hour, and 100 atmospheric pressures at 0°.

While, benzene heated for 5 hours with hydrogen in presence of reduced nickel at 500°, under pressure of 100 atmospheres at 0°, undergoes the hydrogenation which follows with decomposition of the hydrogenated compound into methane on the one hand, and on the other into aromatic hydrocarbons. (Fig. 3).

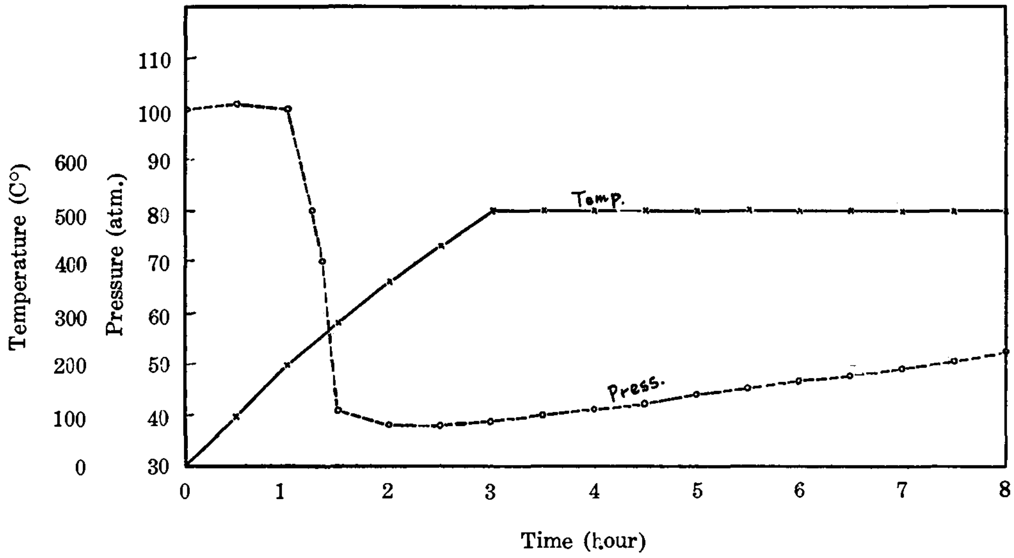

Fig. 3.

The reaction products are 28% gas, 41% liquid hydrocarbons and 14% coke. The gas was composed of 94.5% methane and 5.5% hydrogen. The liquid product was fractionated as follows:

Fraction	B.p.	%	n_D^{25}	d_4^{25}
1	48°– 65°	0.6	1.413	—
2	65°– 75°	1.4	1.446	0.789
3	75°– 85°	6.5	1.492	0.859
4	85°–120°	5.5	1.494	0.866
5	120°–180°	2.3	1.502	0.875
6	180°–250°	2.6	1.551	0.942
7	250°–300°	2.3	1.603	1.012
8	300°–320°	1.5	1.651	1.07
9	Residue	3.6	—	—

These results indicate that the fractions are composed of aromatic hydrocarbons, and benzene and toluene occur in fractions 3 and 4.

When benzene was first heated with hydrogen in presence of the catalyst under 200° and 100 atmospheric pressures at 0° for 2 hours, 3.9 mol % of hydrogen were absorbed, and the product was again heated at 500° for 3 hours with a new supply of hydrogen of 78 atmospheric pressures, and a depression of 17 atm. was noticed. (Fig. 4.) The reaction product was 5.4% methane and 95% of a liquid substance which was composed of cyclopentane, methyl cyclopentane and cyclohexane as will be seen in the following table:

Fraction	B.p.	Yield	d_4^{25}	n_D^{25}
1	48°–65°	2.9	0.744	1.409
2	65°–75°	28.7	0.753	1.415
3	75°–85°	31.7	0.772	1.424
4	85°–90°	0.4	—	1.423

The formation of cyclopentane, methyl cyclopentane with cyclohexane from benzene by catalytic reduction at high temperature and under pressure, is explained by assuming the formation of cyclohexene which is formed from cyclohexane by dehydrogenation and converted by isomerisation into methyl cyclopentane. The latter phase of the reactions has al-

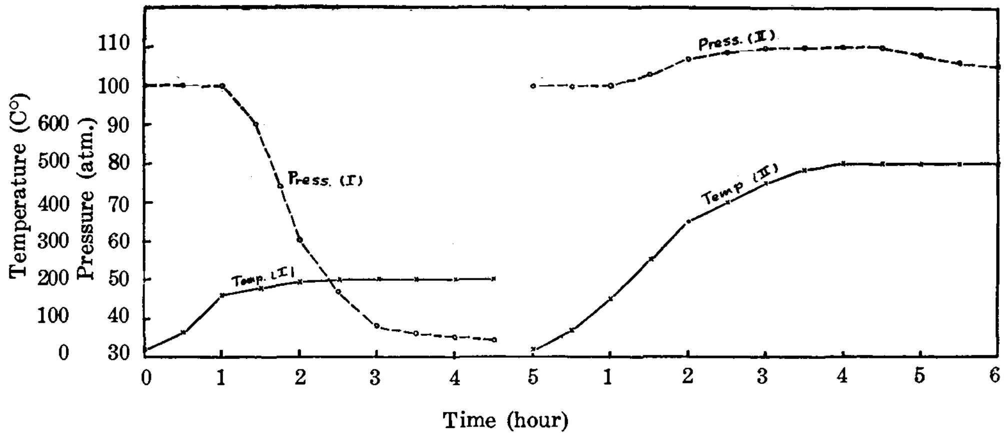

Fig. 4.

ready been noticed by Dr. H. Inoue(1) in his study on the catalytic action of Japanese acid earth on cyclohexanol and its drivatives, where cyclohexanol by passing on the catalyst heated at 200° was converted into cyclohexene, while at a high temperature, such as 330°, methyl cyclopentane occurred in the reaction product, which was actually derived from cyclohexene by the contact action of the catalyst at high temperature.

Such a view for the conversion of cyclohexane into cyclohexene was also accepted by D. T. Jones(2) in the transformation of cyclohexane, heated to 500° in contact with porous porcelain, into hydrogen, ethane, benzene and some olefine hydrocarbons.

According to Ipatiew cyclohexane at high temperatures such as 600° appears to be more stable than n-hexane, and the isomerization of cyclohexane into methyl cyclopentane takes place under high pressure and in presence of alumina, but with ordinary pressure, even at 760°, there is no such isomerization.(3) These facts are in harmony with the writers' case that cyclohexane and methyl cyclopentane occur in the product from benzene by catalytic reduction, but there is no formation of n-hexane.

Naphthalene. Although naphthalene(4) itself gives no benzene on pyrolysis, dihydronaphthalene, tetralin and decalin pyrolyse at about 400° in forming hydrogen and naphthalene as chief products with some methane,

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(1) This Bulletin, **1** (1926), 219.

(2) *J. Chem. Soc.*, **107** (1915), 1582.

(3) *Ber.*, **37** (1904), 2961; **44** (1911), 2987.

(4) Egloff, *J. Soc. Chem. Ind.*, **35** (1916), 920.

ethane, benzene and unsaturated hydrocarbons.⑴ In order to study the behavior of these hydrocarbons toward the catalyst and hydrogen at high temperature and under pressure, pure naphthalene b.p. 215°; m.p. 80°, was heated with hydrogen at 460°–500° under 80 atmospheric pressures at 0°, and no appreciable reaction was noticed to occur in the treatment. A similar situation is also noticeable even in presence of ferric oxide or copper oxide.

When, however, 100 gr. of naphalene in presence of 5 gr. of reduced nickel and hydrogen are heated at 470° and under 80 atmospheric pressures at 0° (Fig. 5.) yield 5% methane and 91% of a liquid substance which seems by fractional distillation to be composed of benzene homologue and tetralin as indicated in the table:

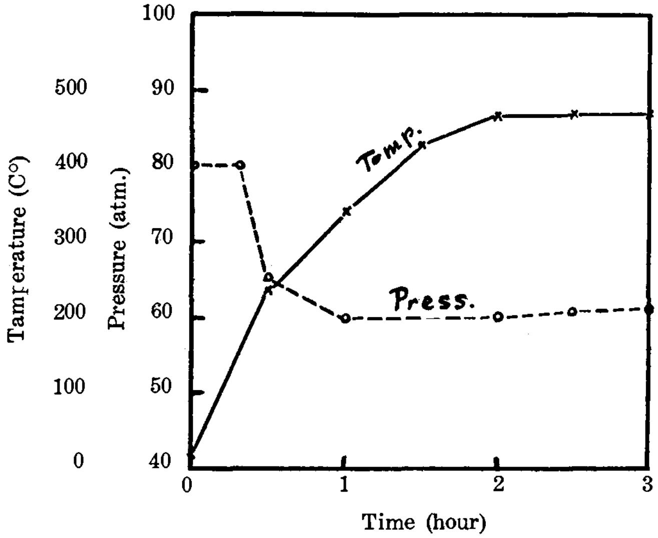

Fig. 5.

	Fraction	Yield	d_4^{25}	n_D^{25}	Remark
1	100°–150°	7%	0.825	1.487	Benzene homologue
2	150°–180°	8 ,,	0.895	1.498	
3	180°–190°	18 ,,	0.901	1.502	Tetralin
4	190°–200°	26 ,,	0.935	1.521	
5	200°–210°	26 ,,	0.962	1.542	
6	Residue	2 ,,	—	—	

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(1) Jones, loc. cit.

Tetralin. When 100 gr. of tetralin, b.p. 206° (760 mm.) treated in presence of hydrogen and the catalyst under the same conditions described in the case of naphthalene (Fig. 6.), 5.6% methane and 92% of a liquid substance are formed and the latter is composed of benzene homologue and decalin.

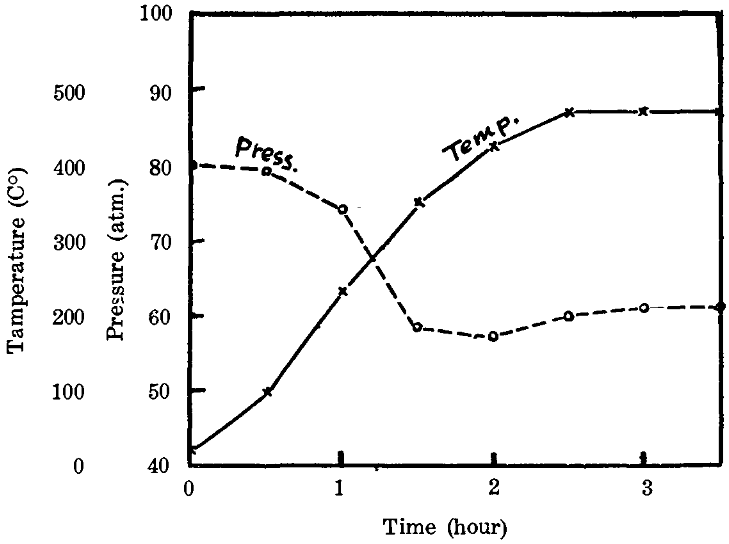

Fig. 6.

	Fraction	Yield	d_4^{25}	n_D^{25}	Remark
1	85°-180°	28 %	0.845	1.454	Benzene homologue
2	180°-185°	39 „	0.874	1.473	
3	185°-188°	18 „	0.879	1.477	Mostly decalin
4	188°-191°	5 „	0.889	1.483	
5	Residue	2 „	—	—	

Decalin. 200 gr. of pure decalin, b.p. 188° (760 mm.) heated with 20 gr. reduced nickel and hydrogen to 450° under 100 atmospheric pressures at 0° for 3 hours (Fig. 7), 3% methane and 97% of a liquid substance of the following compositions are formed.

When decalin is heated in presence of reduced nickel and hydrogen at 450° under 100 atmospheric pressures at 0°, only one part of the compound was decomposed into cyclohexane derivatives, while tetralin and naphthalene under similar conditions tend to be transformed into benzene homologues and decalin and benzene homologues and tetralin respectively.

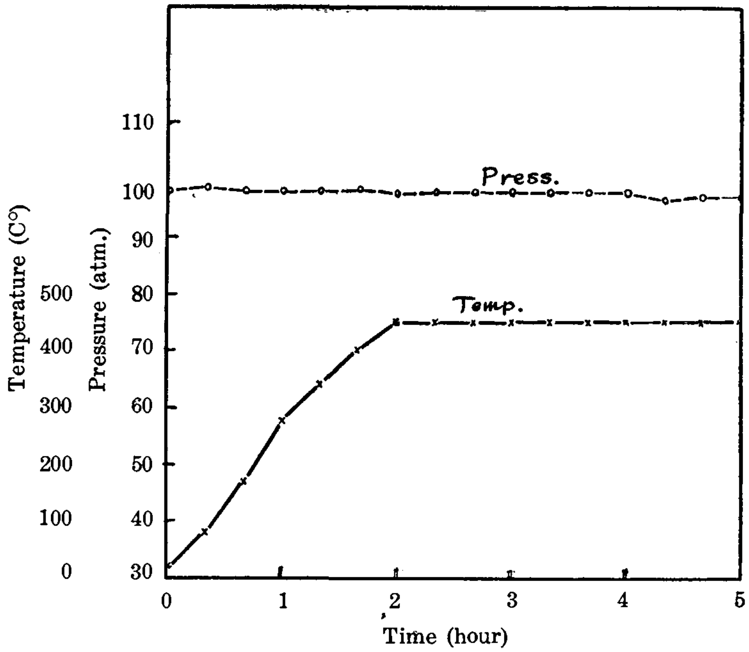

Fig. 7.

	Fraction	Yield	d_4^{15}	n_D^{20}	Remark
1	29°- 90°	3 %	0.777	—	Cyclohexane and its homologue
2	90°-130°	6 ,,	0.785	1.437	
3	130°-150°	7 ,,	0.826	1.451	
4	150°-188°	81 ,,	0.872	1.469	Mostly decalin
5	188°-192°	2 ,,	0.889	1.476	

The fact that tetralin decomposes into benzene homologues with fruitful yield is in favour of the view that the naphthalene molecule is in a more stable state than tetralin. The stability of hydronaphthalene again reaches a maximum in decahydronaphthalene. The relation in chemical behavior among naphthalene and its reduced compounds by the process of cracking in presence of reduced nickel and hydrogen is on the whole very similar to that among benzene and its hydrogenated compounds.

In conclusion, the writers wish to express their sincere thanks to Vice-Admiral S. Kishimoto, Director of the Imperial Naval Fuel Depot, who gave them permission to publish this paper; to Engineer-Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch, for their kindness in enabling them to take part in this work; and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

June 1930.

Naval Fuel Depot, Imperial Japanese Navy,
Tokuyama.

X-RAY INVESTIGATIONS ON COPPER-ARSENIC ALLOYS.

By Nobuyuki KATOH.

Received July 22, 1930. Published September 28, 1930.

Earlier Investigations. According to the thermal and microscopic investigations of Hiorns⁽¹⁾ there should exist no less than three intermediate phases in the copper-arsenic system within the range 0–44% As, corresponding to the formulas Cu_3As, Cu_5As_2 and Cu_2As. Friedrich⁽²⁾ using the same methods of investigation, claims to have found Cu_3As and Cu_5As_2, but he did not confirm the existence of Cu_2As.

The electrical properties of these alloys were first studied by Matthiessen and Holzmann.⁽³⁾ Friedrich⁽⁴⁾ observed an abrupt change of direction in the conductivity curve at the limit of the saturation, of arsenic in the copper phase. Puschin and Dischler⁽⁵⁾ measured the conductivity of a series of alloys containing up to 43% As. This investigation have only confirmed the existence of one intermediate phase, namely Cu_3As.

By passing arsenic vapour over hot copper Koenig⁽⁶⁾ succeeded in producing macroscopic crystals of Cu_3As which have been subjected to cryst-

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(1) A. Hiorns, "Electro-chemist and Metal," (1904).

(2) K. Friedrich, *Metallurgie*, **5** (1908), 529.

(3) A. Matthiessen and Holzmann, see *Metallurgie*, **5** (1908), 529.

(4) K, Friedrich, ibid.

(5) N. A. Puschin and E. Dischler, *Z. anorg. Chem.*, **80** (1913), 65.

(6) G. A. Koenig, *Z. Kryst.*, **38** (1903), 529.

allographic measurements. According to Stevanoic(1) they crystallize in orthorhomic system with axial ratios 0.5771 : 1 : 1.0206, while Wright(2) describes the symmetry as hexagonal with an axial ratio 1 : 1.539.

Quite recently Ramsdell(3) found that crystals of Cu_3As produced by Koenig's method and material produced by fusion give the same X-ray pattern, a result which has been confirmed by the present author. Although the crystals are quite well developed, the powder photograms show that their composition is not uniform. Ramsdell made no attempt to determine the structure.

By melting the theoretical quantities of the components in an evacuated quartz tube, Machatschki(4) prepared alloys of the compositions Cu_3As and Cu_5As_2, and subjected them to an X-ray investigation. All interferences of Cu_3As were accounted for by a quadratic form of the hexagonal type, and the lattice dimensions were found to be the following :

$$a=7.200\text{Å}, \qquad c=7.478\text{Å}.$$

The axial ratio is c : a=1.039.

Machatschki also made a goniometoric determination of the axial ratio of crystals obtained by Koenig's method, The following table shows the result obtained by him compared with those which he has calculated from the data of Stevanoic and of Wright.(5)

	c : a
Machatschki	1.023
Stevanoic	1.0206
Wright	1.0259

The alloy with the composition Cu_5As_2 was found by Machatschki to be inhomogeneous but to consist mainly of a phase with the same structure as Cu_3As but with slightly different lattice dimensions.

Preparation of Samples and their Chemical Analysis. The alloys with less than 30% As were prepared in a high frequency induction furnace in nitrogen atmosphere,(6) 20 grams of electrolytic copper were first melted in a magnesia crucible. The arsenic (Kahlbaum) was then dropped

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(1) S. Stevanoic, *Z. Kryst.*, **37** (1903), 246.

(2) F. E. Wrignt, *Z. Kryst.*, **38** (1903), 509.

(3) L. S. Ramsdell, *The American Mineralogist*, **14** (1929), 188.

(4) F. Machatschki, *Neues Jahrbuch für Mineral.*, **59**, Bl. Bd. (1929), 137; *Centralblatt für Mineralogie*, A, (1930), 13–19.

(5) Loc. cit.

(6) G. Hägg, *Nova Acta Regiæ Soc. Scient. Ups.*, Ser. IV, 7, No. 1 (1929).

into the melt. The alloys with higher content of arsenic were prepared by melting copper and arsenic together in an evacuated quartz tube, as described by Thomassen.(1) In order to obtain a uniform product, the tube was turned after fusion, allowing the melt to flow down along the wall of the tube. Samples of 6 to 7 grams were prepared in this way.

The composition of the samples could be estimated by weighing the product obtained and assuming that no copper was lost during the melting process.(2) The content of copper was, however, also determined analytically by one of the following methods.

All samples were dissolved in warm nitric acid and evaporated with sulphuric acid. When the arsenic content was low, a copper sulphate solution free from arsenic was obtained by evaporation with hydro-fluoric acid. Copper was then determined electrolytically in the presence of nitric acid.(3) The samples with higher content of arsenic were treated according to a method described by Jannasch and Biedermann.(4) The sulphate solution was made strongly alkaline and the copper was reduced by hydrazine sulphate. The copper was then dissolved in acid and determined iodometrically.

X-ray Analysis. The X-ray tube used was of the Hadding-Siegbahn type and was run at 45 kv. and 10 ma. Three cameras of the focussing type(5) covering together the whole diffraction range, were used. The time of exposure varied from 5 to 8 hours. The cameras were constructed by G. Phragmen and were calibrated with sodium chloride. The K-radiation of chromium was used throughout the work.

The α Phase. According to Friedrich,(6) copper dissolves about 4% As at room temperature. The dimensions of the face-centred cubic copper phase (α) increase with the arsenic content. While the edge of the elementary cube is for pure copper 3.608Å, it was found to be 3.629Å for an alloy with 2.0% As. At the limit of solubility at room temperature the edge was found to be 3.640Å.

The β Phase. Friedrich found the β phase to have a homogeneity range extending from 28.6 to 29.6 % As. This was confirmed by the present author. As already mentioned, Machatschki succeeded in finding the ele-

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(1) L. Thomassen, *Z. physik. Chem.*, **135** (1928), 385.

(2) Puschin, loc. cit.

(3) A. Classen, "Quantitative Analyse durch Elektrolyse," (1927).

(4) P. Jannasch and K. Biedermann, *Ber.*, **33** (1900), 631.

(5) H. Bohlin, *Ann. der Physik*, **61** (1920), 422; A. Westgren and G. Phragmen, *Phil. Mag.*, **50** (1925), 318.

(6) Loc. cit.

mentary dimensions of this phase. Before Machatschki's work was published, the present author had also found the quadratic form. The following dimensions were determined by the author.

	a	c	c : a
Cu-limit of homogeneity range	7.121 Å	7.293 Å	1.024
29.1 % As	7.118 Å	7.279 Å	1.023
As-limit of homogeneity range	7.095 Å	7.267 A	1.024

The density of Cu_3As was determined by several authors as follows:

Stevanoic	7.02–8.10
Weisbach	7.0–7.5
Machatschki	7.88
Calculated from Koeing	7.94

The most probable number of molecules in the unit cell is 6, which according to the X-ray data of the author would give the theoretical density 8.22.

Table 1 gives the X-ray data of an alloy within α–β two phase range. Table 2 shows the data of a slowly cooled alloy with 30.9% As, only faint lines appear besides those belonging to the β phase. When the same specimen was quenched from 630°C., however, a number of new lines appeared (Table 3). This might also expected from Friedrich's diagram. The lines of the β phase occupy exactly the same positions in both photograms, which shows that the limit of the homogeneity range is not appreciably influenced by the temperature.

Alloys with higher content of arsenic will be subjected to continued investigations. An alloy with the composition Cu_5As_2 was tempered at 700°C. for 7 days and quenched from 670°C. The photogram was not homogeneous but showed lines belonging to the β phase. A quenched alloy containing 38.7% As contains no more β phase. It was found to consist of primary crystals in an eutectic. The author confirmed Friedrich's observation that these primary crystals slowly decompose into two new phases.

Table 1.

Powder Photogram of a Cu-As Alloy with 19.6 % As.

Chromium-K-radiation.

Intensity	$\mathrm{Sin}^2\theta/2_{\mathrm{obs.}}$	Radiation	h k l	$\mathrm{Sin}^2\theta/2$	h k l	$\frac{\mathrm{Sin}^2\theta/2}{\Sigma h^2}$
w	0.0995	α	002	0.0982		
w	0.1042	α	110	0.1029		
w	0.1289	α	111	0.1275		
w	0.2020	α	112	0.2011		
m	0.2361	α	202	0.2354		
St	0.2453	β			111	.0818
m	0.2555	β	300	0.2558		
w	0.2642	α	211	0.2647		
w	0.2686	β	113	0.2683		
v. St	0.2958	α			111	.0986
St	0.3088	α	300	0.3088		
St	0.3238	α	113	0.3239		
v.w	0.3380	α	212	0.3384		
v.w	0.3465					
St	0.3946	α			200	.0987
v.w	0.4070	α	302	0.4070		
m	0.6323	α	223,214	0.6328, 0.6331		
v.w	0.6540	β			200	.0818
St	0.7889	α_1			220	.09861
m	0.7919	α_2			220	.09899
w	0.9000	β			311	
w	0.9254	α_1	330	0.9254		
w	0.9285	α_2	330	0.9285		
w	0.9408	α_1	404	0.9408		
w	0.9436	α_2	404	0.9442		

Table 2.

Powder Photogram of a Slowly Cooled Cu-As Alloy Containing 30.86 % As. Chromiun K-radiation.

Intensity	Sin² $\theta/2_{\text{obs.}}$	h k l	Sin² $\theta/2_{\text{calc.}}$
m	0.0987	(002)	0.0998
w	0.1035	110	0.1037
w	0.1296	(111)	0.1284
w	0.1716		
w	0.1968	β 202	0.1966
w	0.2032	(112)	0.2025
St	0.2378	202	0.2371
m	0.2569	300	0.2579
w	0.2656	211	0.2667
v. St	0.3106	300	0.3111
v. w	0.3176		
v St	0.3253	113	0.3261
m	0.3399	212	0.3408
m	0.4089	(302)	0.4099
w	0.4290	104	0.4299
v. w	0.4385	(221)	0.4395
v. w	0.4735	311	0.4741
v. w	0.4990	(114)	0.4991
w	0.5279	β 214, β 223	0.5284, 0.5284
St	0.6371	α_1 214, α_1 223	0.6372, 0.6374
w	0.6386	α_2 214, α_2 223	0.6396, 0.6394
v. w	0.6822	321	0.6815
w	0.7506	(411)	0.7508
m	0.7557	205, 322	α_1 0.7560, α_1 0.7556
w	0.7583	205, 322	α_2 0.7587, α_2 0.7583
m	0.8449	314	0.8448
w	0.8481	314	0.8481
v. w	0.8594	215	0.8598
m	0.8897	501, 006	α_1 0.8889, α_1 0.8896
w	0.8938	501, 006	α_2 0.8921, α_2 0.8928
St	0.9334	330	α_1 0.9334
w	0.9363	330	α_2 0.9366
St	0.9485	404, 413	α_1 0.9485, α_1 0.9484
m	0.9522	404, 413	α_2 0.9518, α_2 0.9517
w	0.9635	502	0.9631

Table 3.

Powder Photogram of an Cu-As Alloy with 30.86 % As Quenched from 630°C. Chromium K-radiation.

Intensity	$\text{Sin}^2\,\theta/2_{\text{obs.}}$	Radiation	h k l	$\text{Sin}^2\,\theta/2_{\text{calc.}}$
w	0.0988	α	002	0.0988
w	0.1185	α		
w	0.1289	α	111	0.1284
w	0.1860	α		
w	0.2129	α		
m	0.2195	α		
m	0.2369	α	202	0.2371
m	0.2492	β		
v. w	0.2566	β	300	0.2579
w	0.2632	β		
m	0.2707	β	113	0.2705
m	0.2796	α		
St	0.3018	α		
w	0.3106	α	300	0.3111
St	0.3193	α		
St	0.3259—0.3302	α	113	0.3261
m	0.3391	α	212	0.3408
m	0.4115	α	302	0.4099
w	0.4302	α	104	0.4299
St	0.6365	α_1	214, 223	0.6373, 0.6372
w	0.6394	α_2	214, 223	0.6396, 0.6394
m	0.6933	α		
v. w	0.7232	α	115	0.7215
m	0.7464	α		
m	0.7572	α	205, 322	0.7560, 0.7556
m	0.7744	β	330	0.7738
w	0.7867	β	404	0.7864
w	0.8241	α	412	0.8248
w	0.8454	α	314	0.8448
v. w	0.8912	α	501, 006	0.8921, 0.8919
St	0.9133	α_1		
w	0.9158	α_2		
w	0.9340	α	330	0.9334
St	0.9436	α_1		
w	0.9456	α_2		
St	0.9488	α_1	404, 413	0.9485, 0.9484
w	0.9514	α_2	404, 413	0.9518, 0.9517

Finally, the author wishes to express his gratitude for all interest and encouragement showed by Professor A. Westgren, Ph. D., under whose guidance this work has been carried out. He also desires to thank Professor C. Benedicks, Ph. D., who allowed him to carry out much of the work at the Metallographic Institute in Stockholm. The author also indebted to Dr. G. Hägg for much valuable assistance and advice.

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SINOMENINE AND DISINOMENINE. XIX. ON REDUCTION OF SINOMENINE AND DIHYDROSINOMENINE WITH Na-AMALGAM.

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In the 11th report of this study,(1) one of the authors (K.G.), reported that he obtained by the reduction with Na-amalgam bis-[8, 8′]-demethoxy-dihydrosinomenine [VII] from sinomenine and demethoxy-dihydrosinomenine (III; d-dihydrothebainone of Speyer) from dihydrosinomenine and by Clemmensen's method demethoxy-desoxo-dihydrosinomenine (VIII; d-β-tetrahydrodesoxy-codeine) from the both starting alkaloids. Recently, Ochiai and Hakozaki(2) repeated this reduction in several different ways and could this time obtain the demethoxy-dihydrosinomeninol [VI] in well crystallised form, melting at 138°. Thus they could endorse their former view,(3) that the ketonic group of sinomenine could be reduced to the alcohol group by Na-amalgam.

Since in my first report on this problem, no mention was given in the latter point, I felt somewhat responsible to look for the alleged alcoholic base in the reduction products, and was fortunately enough to affirm the result, obtained by Kondo, Ochiai and Hakozaki.

As is shown in details in the experimental part, the chief product of the reduction of dihydrosinomenine with Na-amalgam corresponding to 4H, is the mixed crystals (m.p. 149°) of demethylated ketonic and alcoholic

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(1) This Bulletin, 4 (1929), 244.

(2) *J. Pharm. Soc. Japan*, (1930), 53-59.

(3) Ibid., (1926), 99-104.

bases. They are well defined, uniformly appearing crystalls, but could not be resolved into the components by repeated recrystallisation from organic solvents, or by repeated dissolving in alkali and precipitating with carbonic acid gas. About one half of the mixed crystalls could be transformed into the semicarbazone, and also into the iodomethylate of the demethoxy-dihydrosinomenine. Yet, the separation, as free bases, was perfectly impossible. Such cases are often met with as in aconitines, studied by Majima and co-workers⁽¹⁾ and in disinomenine and ψ-disinomenine of one of the authors.⁽²⁾

It is, therefore, better to reduce again these mixed crystalls with Na-amalgam in order to obtain demethoxy-dihydrosinomeninol in a pure state. When the mixed crystalls were treated with Na-amalgam corresponding to 3H or 6H in water, tne alcoholic base was obtained in beautiful four-sided rhombic crystalls from acetone. It sintered at 138°, melted at 142°, and decomposed at 143°. It formed no semicarbazone. Its rotatory power was $[d]_D^{30}=+46.8°$ and its iodomethylate decomposed at 280°. These properties well coincide with the description of Speyer and Siebert given to the dihydro-thebainone, of which our alcoholic base is regarded to be the optical antipode. The racemization was, however, not tried in this case, since Kondo and Ochiai reported four years ago that they could racemise successfully their iodomethlates.

The reason, why I did not obtain the above mentioned mixed crystalls in the former study seems entirely due to the condition of Na-amalgam used at that time. Now, it was clearly settled that the best condition to obtain the demethoxy-dihydrosinomenine [III] in a pure state is to use the fresh Na-amalgam in an amount corresponding to 3H. Less than that, the demethylated ketonic base is contaminated by much unchanged dihydrosinomenine, whose separation presents always some difficulties.

In the course of this study, we could isolate a new alcoholic base (m.p. 162°) from that part of the reduction products of dihydrosinomenine, which is more soluble in the sodium carbonate solution containg much CO_2. The new alcoholic base has the formula $C_{19}H_{27}NO_4$, is monomolecular, retains two methoxyls and does not form semicarbazone. Its properties are given in the second column of the Table 1. The yield was 1/5~1/10 of the above mentioned demethylated bases.

The formation of this new alcoholic base is quite intelligible from the constitutional formula of sinomenine [I] proposed by one of the authors (K.G.). According to it, sinomenine is an α, β-unsaturated ketonic base,

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(1) Majima and Morio, *Ann.*, **476** (1929), 194.

(2) Goto, this Bulletin, **4** (1929), 129.

having an enol-methylether in the α-position. And the easy reduction of the methoxyl group by Na-amalgam is undoubtedly caused by the loosening (auflockende) action of the vicinal ketonic group. Now, in the course of the reduction, those molecules of dihydrosinomenine, whose ketonic group was first attacked and transformed into the alcohol, will loose this action on the methoxyl group, so that the methoxyl on $C_{(7)}$ may be kept intact to the last. The new alcohol base will be called, therefore, dihydrosinomeninol.

Table 1.

	Demethoxy-dihydro-sinomeninol (VI)	Dihydrosinomeninol (V)	Sinomeninol (IV)
Yield	12-30%	> 50%	> 30%
Mol. formula	$C_{18}H_{23}NO_3$	$C_{19}H_{27}NO_4$	$C_{19}H_{25}NO_4$
Solvents for recrystallisation	Acetone or ethyl acetate	Metyl alc. or benzene	Mehtyl alc., but not benzene
M.p.	138° (sinters) 143° (dec.)	160° (sinters) 162° (dec.)	125° (sinter) 127° (dec.)
$[\alpha]_D$	+46.8°	+1.93°	−23.7°
No. of Methoxyls	1	2	2
Formation of semicarbazone	No	No	No
M.p. of iodomethylate	280° (dec.)	249° (dec.)	272° (dec.)
$FeCl_3$-reaction	Green	Green	Green
Diazo-reaction	2,000.000*	2,000,000	2,000,000
$FeK_3(CN)_6$-reaction	500,000	500,000	500,000
Formaline-sulphuric acid reaction	Yellow → green → violet	Yellow → green → blue	Yellow → green → blue

* The figures show the dilution, at which the colour of the reactions is still visible.

The ratio of the reduction velocity of the ketone and the methoxyl groups in hydro-sinomenine may be calculated as about 10:1, on the basis of the yield of demethylated ketonic base and that of dihydro-sinomeninol. It is, therefore, very difficult to obtain the new base in a better yield by the alkaline reduction. We tried, accordingly, to reduce the ketonic group in acidic medium by Na-amalgam. As was seen in the catalytic reduction and in the Zn-amalgam reduction in the cold, sinomenine retains mostly its methoxyl group and the yield of hydrosinomenine amounts to the quantitative in the former case, and more than 50% in the latter. If we carry out the reduction of hydrosinomenine quickly in an acidic medium, the yield of dihydrosinomeninol may be increased.

This is actually so. In reducing hydrosinomenine in a dilute acetic acid solution with Na-amalgam corresponding to 6 H (considering the enormous loss of hydrogen) in half an hour, the yield of dihydrosinomeninol amounted to more than 50%. It melted at 162°, without depression even when admixed with that obtained in an alkaline reduction. All the other properties of both substances, originated from these two sources, coincided perfectly.

If the above supposition regarding to the formation of dihydrosinomeninol is correct, then sinomenine itself might be reduced to sinomeninol [IV], without loosing its double linking as well as its enol-ether group. This is also actually the case. When sinomenine hydrochloride was reduced quickly in a dilute acetic acid solution as above described, a new base (m.p. 127°) was obtained in a yield about 30%. Its elemental analysis corresponds to $C_{19}H_{25}NO_4$ (thus isomeric with dihydrosinomenine), it has two methoxyls, is monomolecular and does not form semicarbazone. The other properties are given in the third column of the Table 1.

The most striking properties of the sinomeninol are two. First, it is laevorotatory as sinomenine itself is. When the double linking of sinomenine was transformed into the single linking, the base invariably changes its direction of the rotation, no matter how this transformation was effected. Thus, sinomenine hydrate is dextrorotatory as dihydrosinomenine is. This unchanged direction of the rotation of sinomeninol speaks most fluently for the fact that the double linking of sinomenine was not attacked in the above reduction. But the decisive proof was given by the fact that sinomeninol could be reduced into dihydro-sinomeninol (m.p. 162°) by $Pd+H_2$. For, it is a known fact that the double linking of the phenanthrene alkaloid can be reduced catalytically,(1) whilst the reduction of a ketonic group goes on with much difficulty.(2)

The second property of sinomeninol, worthy of mention, is that it dissolves in caustic alkali without taking yellow colour. As was noticed first by R. Robinson,(3) those substances, which have a ketone group and a double linking in conjugation, dissolves yellow in caustic alkali. In this point, sinomenine partakes the property of thebainone, only the difference being that sinomenine does not give the halochromy of thebainone against conc. mineral acids. This shows also that the position of the double linking

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(1) Freund, *J. prakt. Chem.*, **101** (1921), 12.

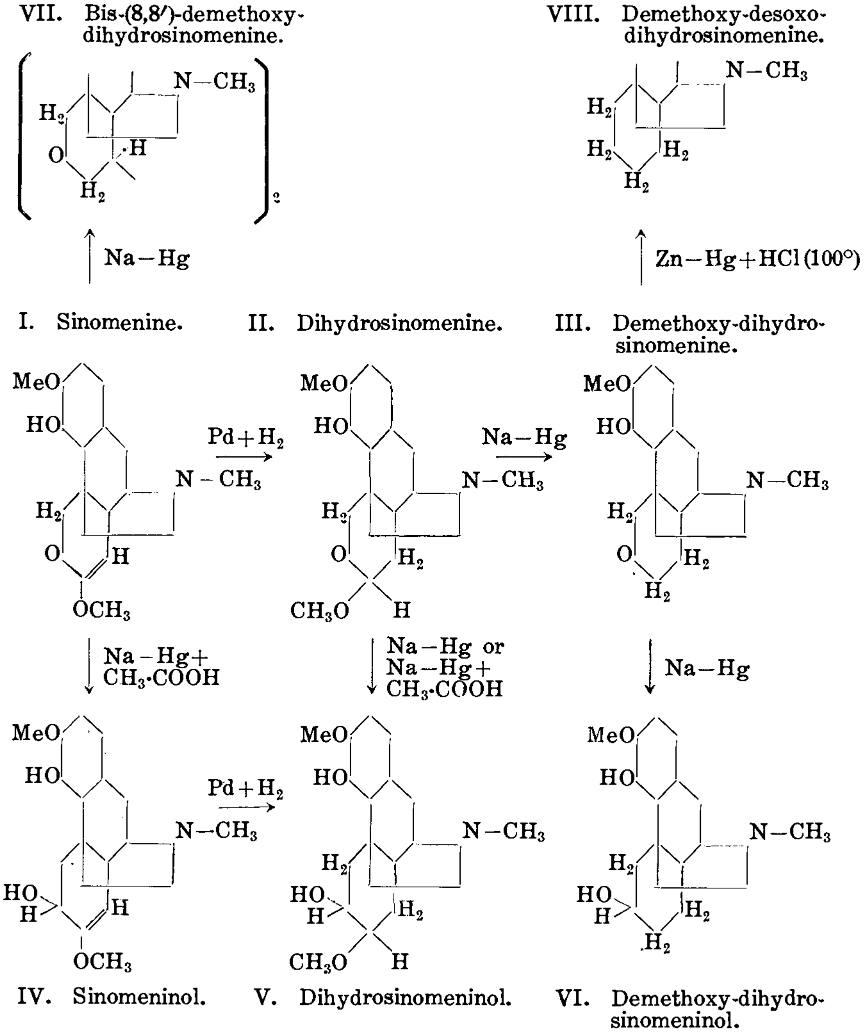
(2) Skita, *Ber.*, **54** (1921), 1562.

(3) Gulland and Robinson, *J. Chem. Soc.*, **123** (1923), 996.

may be reversed in thebainone and sinomenine. In this point, the recently proposed formula of thebainone by C. Schöpf⁽¹⁾ explains the property of thebainone as well as of sinomenine in some sense. Anyhow, the formation of sinomeninol and dihydro-sinomeninol gives one more proof that sinomenine must be an α, β-unsaturated, α-enolic ketone.

The relation of the bases, obtained hitherto by the reduction of sinomenine and dihydrosinomenine are given in the following Table 2.

Table 2.



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(1) Schöpf, *Ann.*, **468** (1927), 158.

Conclusions. 1.—The best condition to obtain demethoxy-dihydrosinomenine (III) from dihydrosinomenine is to reduce the latter with Na-amalgam corresponding to 3H.

2.—In using Na-amalgam corresponding to 4H in the above reduction, the chief product is the mixed crystalls of the demethylated ketonic and alcoholic bases (III+IV). As an accessory product, dihydrosinomeninol (V) is obtained.

3.—To prepare the demethoxy-dihydrosinomeninol in a pure state, it is better to reduce again the above mixed bases with much Na-amalgam.

4.—Dihydrosinomeninol is also produced by the Na-amalgam reduction of dihydrosinomenine in an acetic acid solution. The phenols C and D of Ochiai and Hakozaki, which they think to be two new isomerides of the demethoxy-dihydrosinomenine, are probably one and the same substance and are nothing but our dihydrosinomeninol.

5.—By reducing sinomenine in an acetic acid solution sinomeninol (IV) is produced. This is identical with the phenol F of Ochiai and Hakozaki. But they assigned to this base the dimeric formula $(C_{18}H_{24}NO_3)_2 \cdot H_2O$ and assumes it to be consisted of two molecules of an isomeric (?) demethoxy-dihydrosinomeninol.

Experimental.

Note on the Preparation of Dihydrosinomenine. Dihydrosinomenine can be prepared very easily from sinomenine by means of catalytic reduction with palladinised charcoal and hydrogen. The mixture, consisting of sinomenine hydrochloride (50 gr.) in 400 c.c. hot water, 0.3 gr. $PdCl_2$ in 40 c.c. dil. hydrochloric acid and charcoal (5 gr.), was shaken, while hot, vigorously with hand in a hydrogen atmosphere. The sorption of hydrogen amounts to 3600 c.c. (somewhat more than one molecule) in 15~30 minutes. Yield almost quantitative. M.p. 198° (from methyl alcohol).

The careful treatment of the methyl alcoholic mother liquor did not give other base than dihydrosinomenine.

Anal. Found: C=68.54; H=8.02; N=4.55. $C_{19}H_{25}NO_4$ requires: C=68.84; H=7.6; N=4.23%.

Sp. rotatory power, measured in chloroform: $[\alpha]_D^{25}=+193.58°$; measured in dilute hydrochloric acid: $[\alpha]_D^{24}=+33.06°$.

Oxim: m.p. 211° (dec.).

Semicarbazone: m.p. 209° (dec.) (Found: N=14.69%. Calculated for $C_{20}H_{28}O_5N_4$: N=14.43%.

Iodomethylate: m.p. 268° (dec.); solubility in water 0.34% (at room temperature).

Reduction of hydrosinomenine with Na-amalgam (corresponding to 4H). Hydrosinomenine (8 gr.) is suspended in 2% NaOH (80 c.c.) and is added with 5% Na-amalgam (50 gr.) After 24 hours, the aqueous part is diluted with water (80 c.c.) and supersaturated with CO_2. The pasty precipitate, first formed, changes gradually into rhombus plates, which are collected. The filtrate contains dihydrosinomeninol [IV].

The rhombus plates are again dissolved in 4% NaOH and precipitated with CO_2. This treatment is repeated once again. The united filtrate contains sometimes demethoxy-dihydrosinomenine [III].

The rhombus plates are finally recrystallised from acetone. When the substance crystallise out slowly, it forms stout prisms, but showing different faces more or less developed. M.p. 144° (dec. at 149°). These are the mixed crystalls of demethylated ketonic and alcoholic bases [III+VI], and can not be easily resolved by recrystallisation.

From 1 gr. each of these crystalls, 0.3 gr. and 0.4 gr. of semicarbazone was obtained.

From 1 gr. of these crystalls, 0.5 gr. of demethoxy-dehydrosinomenine iodomethylate (m.p. 120°) is obtainable. The rest of the iodomethylate, which is more soluble in water, melts at 278°.

From these results, the mixed crystalls must be consisted of almost equall parts of the two bases.

Methoxyls. Found: 10.68% (calc. for one: 10.23%)

Demethoxy-dihydrosinomeninol (VI). The above mentioned mixed crystalls are again reduced with 5% Na-amalgam, corresponding to 8H. The precipitate formed by CO_2 is not rhombus plates this time, but remaines pasty. This precipitate is purified through chloroform and recrystallised from acetone. It forms then nice rhombus plates, which softens at 138°, melts at 142° and decomposes at 143°. Yield about 50% (about 12.5% of dihydrosinomenine).

For the properties, see the first column of the Table 1.

Sp. rotatory power: 0.419 gr. subst. was dissolved into 10 c.c. methyl-alcohol. $\alpha = +0.98$; $d = 0.5$ dm. Therefore,

$$[\alpha]_D^{30} = (0.98 \div 0.419) \times (10 \div 0.5) = +46.8°$$

It does not form semicarbazone; the starting material was recovered almost quantitatively in this trial.

Iodomethylate; long prisms from methyl alcohol. M.p. 280°. Very soluble in water, but recrystallisable from it.

Dihydrosinomeninol (V). (A) This base was isolated from sodium carbonate solution, from which the precipitate of the above described mixed bases was removed. Twice recrystallised from methyl alcohol, it forms nice prisms and melts at 162° sharply, softening at 160°. Yield 4% and 6% each in two isolations.

(B) Hydrosinomenine (9.5 gr.) was dissolved in 6% acetic acid (50 c.c.) and added with 5% Na-amalgam (corresponding to 6H) in five portions, accompanied by the addition of glacial acetic acid to keep the solution always acidic (20 c.c. in total). The reduction finishes in 30 minutes. The base is isolated in the ordinary way, and recrystallised from methyl alcohol (60 c.c.). Yield 5 gr. (over 50% of the theoretical). M.p. 162°. The admixed m.p. with the preparate obtained in (A) shows no depression.

For the properties, see the second column of the Table 2.

Anal. Found: C=68.16; H=7.81; N=4.18; methoxyls=18.74%. $C_{19}H_{27}NO_4 = 333$ requires: C=68.46; H=8.11; N=4.21; methoxyls (2)=18.62%. The analysed substance was dried at 120°~130°.

Sp. rotatory power, measured in methyl alcohol: (A) the substance obtained by alkaline reduction.

$$[\alpha]_D^{30} = (0.07 \div 0.453) \times (25 \div 2 = +1.93°.$$

(B) the substance obtained by acidic reduction.

$$[\alpha]_D^{29} = (0.07 \div 0.499) \times (25 \div 2) = +1.75°$$

Mol. Weight, measured after Rast. $(179 \div 1525) \times (400 \div 16.15) \times 100 = 291$.

The substance does not give semicarbazone, but the starting substance was recovered in a good yield in this trial.

Iodomethylate: Both the iodomethylates from the sources (A) and (B) can be obtained by mixing the bases with methyliodide in methyl alcohol. They crystallise out in tetragonal or octagonal oblong plates, when the methyl alcohol is evaporated off. Recrystallised from water, it sinters at 218°, become waxy at 244° and decompose at 249°. (Found: J=26.88% Calc.: J=26.74%).

The specific rotatory power of the both iodomethylates are almost equal, when measured in aqueous solutions.

$$[\alpha]_D^{28} = -(0.35 \div 0.557) \times (10 \div 1) = -6.28 \quad \text{(from the source A)}$$

$$[\alpha]_D^{28} = -(0.40 \div 0.594) \times (10 \div 1) = -6.73 \quad \text{(from the source B)}$$

It is interesting to note, that both the iodomethylates are laevorotatory, in opposition to their free bases. Such inversion is often met with in amino-acids and in some of the alkaloids with carboxyl group.

In any way, the identity of the dihydrosinomeninols obtained by alkaline and acidic reductions seems to have been settled beyond doubt.

Sinomeninol (IV). 5% Na-amalgam (250 gr. corresponding to 10H) was put in a stout Erlenmeyer's flask, poured on with 100 c.c. of 20% sinomenine hydrochloride solution and added with glacial acetic acid in portions (50 c.c. in total), whilst the solution was cooled with ice-water from time to time. The reduction ends in 15 minutes. The isolated base is recrystallised twice from methyl alcohol. M. p. 127° (softening at 125°). Yield 5 gr. (over 30%).

For the properties, see the third column of the Table 1.

Anal. Found: C = 68.39, 68.73; H = 7.83, 7.81; N = 4 23; methoxyls = 18.59%.
$C_{19}H_{25}NO_4$=331 requires: C=68.88; H=7.56; N=4.23; methoxyls (2 =18.73%.

Mol. weight, measured after Rast: $(150 \div 1632) \times (400 \div 11.6) \times 100 = 328$.

Sp. rotatory power, measured in chloroform: $[\alpha]_D^{28} = -(0.92 \div 0.39) \times (10 \div 1) = -23.7°$

The base does not give semicarbazone, but the starting material is recovered in a good yield.

Iodomethylate: prepared in the methyl alcohol. Teragonal, oblong plates from methyl alcohol, but recrystallisable from water into long prisms. M.p. then 272° (dec.) (Found: I=26.88%. Calc.: I=26.74%).

Catalytic Reduction of Sinomeninol. Sinomeninol (1 gr.) was dissolved in dilute hydrochloric acid (110 c.c.), added with $PdCl_2$ (0.05 gr.) and charcoal (1 gr.) and shaken, while warm, in a hydrogen atmosphere. The sorption of hydrogen amounts to 97 c.c. (more than 2 H) in 40 minutes. The base, isolated in the ordinary way recrystallised from benzene, melted at 162°. Yield good. The admixture with the dihydrosinomeninol, obtained from dihydrosinomenine, does not lower the melting point.

Note. The constitution of sinactine (*l*-tetrahydro-epi-berberine(1)) is to be regarded the 18th report of this study.

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(1) *J. Chem. Soc.*, (1930), 1234.

ATOMIC HYDROGEN OCCLUDED IN IRON NITRIDE.

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Received September 19, 1930. Published October 28, 1930.

Introduction. Since Savart⁽¹⁾ first studied in 1828 the action of ammonia gas upon iron at elevated temperature, numerous investigations on iron nitride have been reported. In 1923, A. Fry⁽²⁾ invented the so-called nitriding process. By this process, or by treating the chrome aluminium steel with ammonia he obtained the hardest substance ever known in metallurgical products. This invention has stimulated the study of iron nitride. The equilibrium diagram of iron and nitrogen was partially determined by Fry,⁽²⁾ B. Sawyer⁽³⁾ and O. Eisenhut and E. Kaupp.⁽⁴⁾ As the results of X-ray studies conducted by G. Hägg,⁽⁵⁾ A. Osawa and S. Iwaizumi⁽⁶⁾ and Eisenhut and Kaupp,⁽⁴⁾ the existence of the compounds Fe_2N and Fe_4N was ascertained.

While investigating⁽⁷⁾ ⁽⁸⁾ iron nitride, the author discovered the existence of atomic hydrogen in nitrided iron and the formation of so-called porous iron by the action of ammonia on compact iron. The details of the investigation are shown in the following pages.

In 1880, A. H. Allen⁽⁹⁾ first reported the existence of hydrogen in iron nitride and in 1911 J. H. Andrew⁽¹⁰⁾ also admitted the existence of the occluded hydrogen in iron nitride. In 1913, W. Herwig⁽¹¹⁾ found that the nitrogen content in molten iron did not increase when it was treated with nitrogen but increased due to the action of the mixture of nitrogen and hydrogen. But in 1929, Hägg⁽¹²⁾ reported that he could find no traces of hydrogen in iron nitride.

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(1) Savart, *Ann. chim. phys.*, [2] **37** (1828), 326.
(2) A. Fry, *Stahl u. Eisen*, **43** (1923), 1271.
(3) B. Sawyer, *Am. Inst. Mining Met. Eng.*, **4** (1923), 356.
(4) O. Eisenhut und E. Kaupp, *Z. Elektrochem.*, **36** (1930) 392.
(5) G. Hägg, *Nova acta regiœ societates scientiarum Upsaliensis*, Ser. IV, Vol 7, No. 1.
(6) A. Osawa and S. Iwaizumi. *Z. Krist.*, **69** (1928), 26.
(7) S. Satoh, *Rev. métal.*, **26** (1929), 248.
(8) S. Satoh, *Tetsu to Hagane*, **16** (1930), 79.
(9) A. H. Allen, *J. Iron Steel Inst.*, **1** (1880), 181.
(10) J. H. Andrew, *Carnegie Schol. Memo.*, **3** (1911), 236.
(11) W. Herwig, *Stahl u. Eisen*, **33** (1913), 1721.
(12) Hägg, loc. cit.

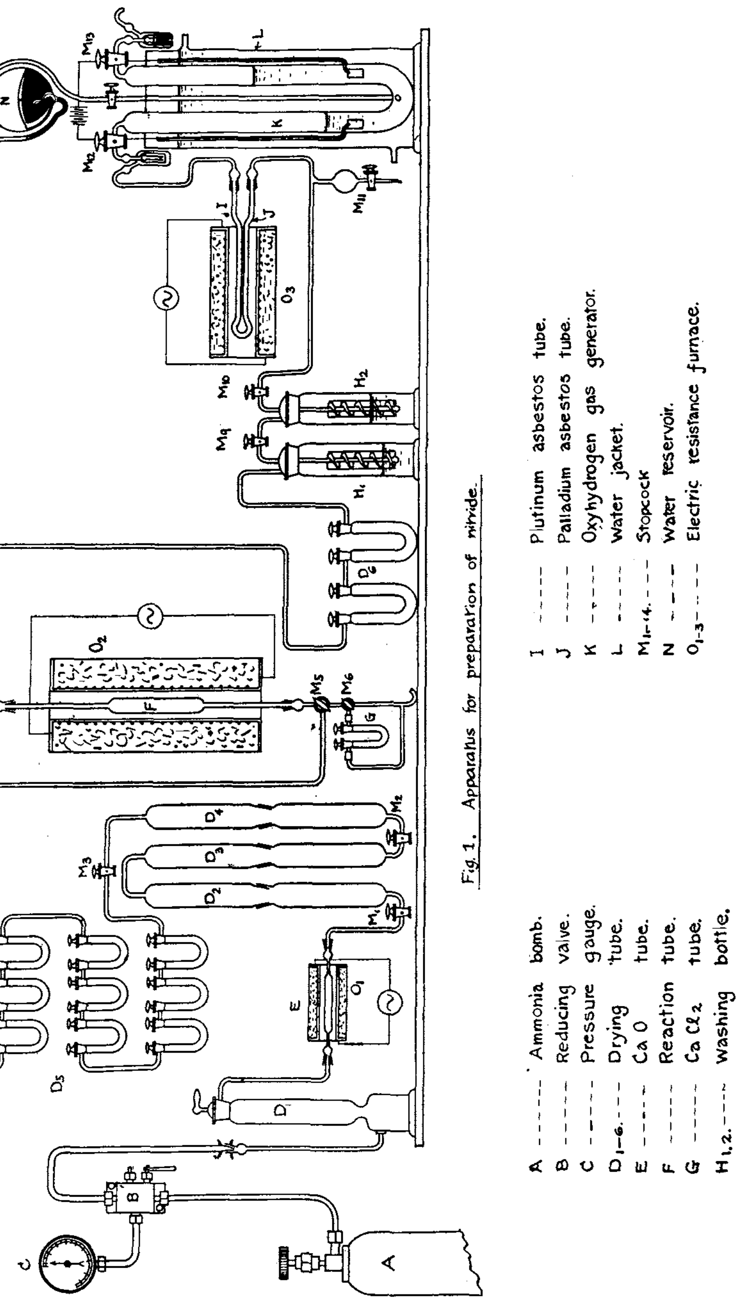
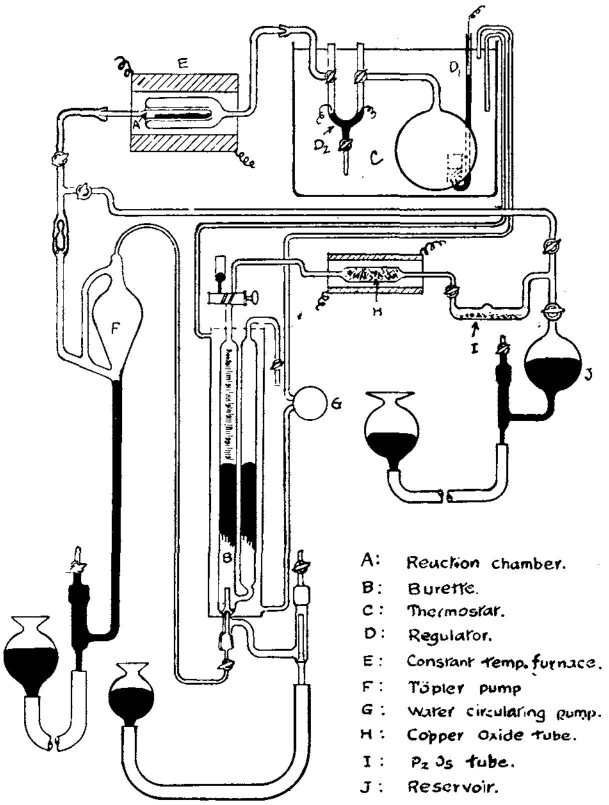


Fig. 1. Apparatus for preparation of nitride.

Fig. 1.

Hydrogen Occluded in Iron Nitride. With the object of ascertaining the existence of hydrogen in nitrided iron, the author prepared iron nitride by the use of the apparatus shown in Fig. 1. Iron oxide, which he obtained by igniting iron oxalate, was put in F and reduced with electrolytic hydrogen. Pure iron thus obtained was treated with ammonia gas at 450°C. for 250° hrs. Iron nitride which was formed in this way and which contains 9.796% nitrogen, was decomposed at 430°C. and 450°C. and analysed by means of the apparatus shown in Fig. 2. These two different degrees were chosen in order to ascertain the decomposition temperature of iron nitride and at the same time the existence of hydrogen, as Fry(1) re-



Apparatus for Hydrogen Determination.

Fig. 2.

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(1) Fry, loc. cit.

ported that the decomposition temperature of Fe_2N was 440°C. when he made his rapid decomposing experiment. 15.36 gr. of iron nitride was put in A and heated at 430°C. The evolved gas was analysed. Again the specimen was heated at 450°C. and the same process was repeated. The temperature was measured by means of the Pt-PtRh thermocouple standardized by the melting points of zinc and aluminium and kept constant within the range of $\pm 0.6°$ by the method used by J. H. Haughton and D. Hanson.⑴ The decomposed gas was collected by means of the Töpler pump into the burette B corrected with mercury at every 2 c.c. The collected gas passed backwards and forwards through the red heated copper oxide tube and phosphorus pentoxide tube by means of the mercury reservoir J. The gas thus treated was again collected into the burette B by the use of the Töpler pump and the amount of hydrogen was determined by the change of volume. The result is shown in Table 1.

Table 1.

Analysis of Gas Evolved by Heating Nitrided Iron.

Temp.	Heating time	Decomposed volume (N_2+H_2) (0°, 760 mm.)	Volume after combustion (N_2) (0°, 760 mm.)	Volume of hydrogen (0°, 760 mm.)	Volume of hydrogen per 1 gr. of sample
430°C.	97.5	23.76	22.63	1.08	0.0703
450°C.	49.0	27.10	27.03	0.02	0.0013

As may be seen from Table 1, iron nitride contains hydrogen and decomposes below 430°C.

Atomic Hydrogen Occluded in Iron Nitride. By the above experiment the author has confirmed the existence of hydrogen in iron nitride. But how hydrogen is occluded is unknown. According to Richards⑵ the iron may occlude atomic hydrogen by quenching it from 1000°C. into water or by depositing it electrolytically. But nobody has ever mentioned the existence of atomic hydrogen in iron nitride. The author has confirmed the existence of atomic hydrogen in iron nitride by the following experiments.

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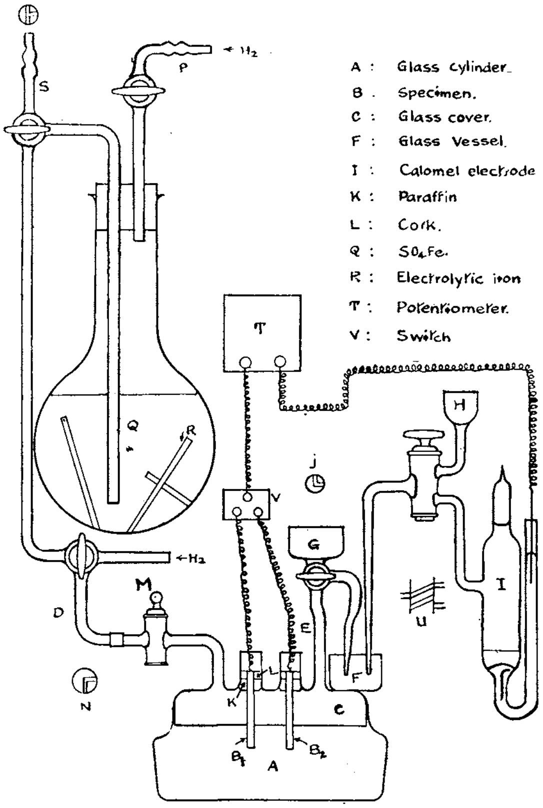
(1) J. H. Haughton and D. Hanson, *National Phys. Lab. Collected Res.*, **55** (1920), 51.

(2) T. W. Richards and G. E. Behr jr., *Z. physik. Chem.*, **58** (1907), 301.

(a) *Single Potential of Iron Nitride.* Reduced pure iron above mentioned is compressed in the form of a cylinder and nitrided at 500°C. for 4 hrs. The nitride thus formed is quickly immersed in 0.988 normal ferrous sulphate solution and the potential difference between the nitride and the deci-normal calomel electrode is measured with the Leeds and Northrup potentiometer. A deci-normalc alomel electrode was prepared by calomel, potassium chloride from Kahlbaum and mercury which has been distilled several times *in vacuo*.

The ferrous sulphate solution was prepared according to the method adopted by Richards.⁽¹⁾ Definite quantity of ferrous sulphate (Merck) was



Apparatus for Potential Determination in $FeSO_4$ Solution.

Fig. 3.

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(1) Loc. cit.

dissolved in distilled water which had been boiled *in vacuo* in the atmosphere of hydrogen. The solution, to which was added a definite quantity of sulphuric acid and pieces of electrolytic iron, was kept for about 100 days in the flask filled with hydrogen gas and covered with black paper to keep off light. The concentration of the solution was 0.988 normal which the author determined by titrating it with potassium permanganate standardized with sodium oxalate.

The measurement was carried out with the apparatus indicated in Fig. 3, which is an improved one of the apparatus reported by C. Benedicks and R. Sundberg(1): an enclosed glass cylinder A covered with black paper and containing the electrode, was filled with hydrogen gas through the tube M and then the solution of ferrous sulphate was poured in it through the tube D until it fills the vessel F. The deci-normal calomel electrode was dipped into the vessel F and the potential difference between the electrode and the deci-normal calomel electrode was measured, and as soon as the measurement was finished the deci-normal calomel electrode was taken out of the solution. As ferrous sulphate solution in the vessel F is oxidized by air, the fresh solution was poured into F through the funnel G at the beginning of each experiment. Between the vessel F and the cylinder A a glass cock was attached. By opening this cock the measurement was carried out and then the cock was closed to prevent the solution in A from being oxidized.

The deci-normal potassium chloride solution was poured now and then into the vessel H to drive away the solution mixed with ferrous sulphate at the end of the calomel electrode. In this way, the change of voltage in relation to time was measured at room temperature (24–32.7°C.) until the constant voltage was obtained. The results obtained are shown in Table 2 and graphically in Figs. 4, 5 and 6.

The author calculated the single potential differences referring to one normal ferrous sulphate solution according to the equation :—

$$\epsilon_c = \epsilon_{c.0} + 2.3026\frac{RT}{nF}\log\frac{C}{C_0}$$

where $n=2$, $T=303$, $C_0=0.988$, $C=1$. But the correction was found negligible.

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(1) C. Benedicks and R. Sundberg, *J. Iron Steel Inst.*, **44** (1926), 177.

Table 2.

Potential Measurement of Iron, Nitrided or Not, in Ferrous Sulphate.

Time in ferrous sulphate hr. m.	Nitrided iron powder (curve 1) (29.8°∼32.3°C.) volt.	Nitrided iron powder dipped in O_2 free water (curve 4) (28.3°∼31.3°C.) volt.	Nitrided iron powder dipped in water (curve 3) (29.3°∼31.7°C.) volt.	Nitrided wrought iron (curve 5) (24.0°∼26.5°C.) volt.	Wrought iron (curve 6) (29.3°∼31.7°C.) volt.
0	—	-0.3 —	—	—	—
.01	—	—	—	—	-0.7510
.02	-0.7886	—	—	—	—
.03	—	—	-0.5071	-0.8079	-0.7540
.10	-0.8470	—	—	—	—
.25	—	-0.9370	—	—	—
.40	—	—	-0.6990	—	—
1.00	—	-0.9542	—	—	—
1.23	—	—	—	-0.8544	—
1.35	-0.9023	—	—	—	-0.7683
2.00	-0.9000	—	—	—	—
2.25	—	—	-0.8295	—	—
2.40	—	—	—	—	—
4.35	—	-0.9393	—	—	—
5.10	—	—	-0.8390	-0.8486	-0.7694
17.45	-0.8481	—	—	—	—
21.50	—	-0.9279	—	-0.8465	—
22.25	—	—	-0.8403	—	-0.7681
29.00	—	-0.9326	—	—	-0.7688
42.	-0.8353	—	—	—	—
46.	—	-0.9258	-0.8383	-0.8410	—
70.	—	-0.9324	-0.8361	-0.8344	-0.7634
76.	—	—	—	—	-0.7628
94.	—	-0.9311	-0.8297	—	-0.7646
100.	-0.8028			—	—
122.	—			-0.8201	-0.7665
141.	—			-0.8122	-0.7672
168.	—			-0.8005	-0.7675
191.	—			-0.7964	-0.7630
216.	—			-0.7926	—
236.	-0.7852			—	-0.7665
289.				-0.7882	-0.7663
460.				-0.7889	

In Fig. 4, the time voltage curves of nitrided iron powder (curve 1) and of iron powder quenched into water (curve 2 quoted from the paper of Richards(1)) show minima at their beginning. According to Richards this

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(1) Loc. cit.

minimum voltage was caused by atomic hydrogen occluded in iron, therefore it will be certain that nitrided iron powder is loaded with atomic hydrogen.

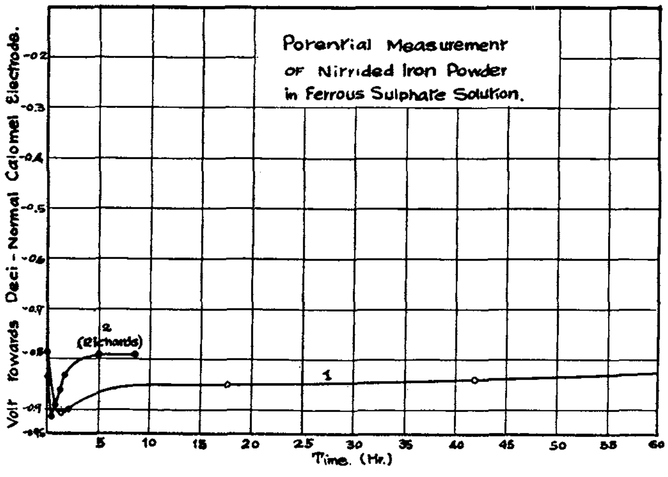

Fig. 4.

Richards⁽¹⁾ states that atomic hydrogen occluded in iron vanishes rapidly in ferrous sulphate solution and slowly in water. The author tested how atomic hydrogen occluded in iron nitride vanishes by the action of

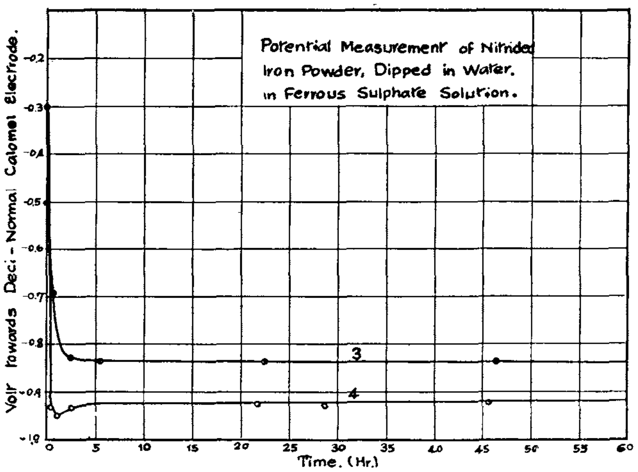

Fig. 5.

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(1) Loc. cit.

oxygen in water. For this purpose nitrided iron powder was on the one hand immersed in the oxygen free distilled water for 118 hrs. and the other in the distilled water for 90 hrs. Both of them were dried by absolute alcohol and quickly immersed in the ferrous sulphate solution and their single potentials were measured. The results obtained are indicated in Table 2 and Fig. 5. As may be seen from Fig. 5, the nitrided iron powder immersed in oxygen free distilled water (curve 4) shows minimum at the beginning, while that immersed in distilled water (curve 3) does not show it. From the above fact it may be confirmed that atomic hydrogen is oxidized by the oxygen contained in distilled water. The nitrided iron becomes black and never rusts to form red hydroxide of iron in distilled water and moreover it retains its silver white surface in oxygen free distilled water. L. Guillet and M. Ballay(1) reported that the nitrided special steel has great corrosion resistance in the water of the Seine.

(*b*) *Reducing Property towards Potassium Ferricyanide.* With the object of ascertaining the existence of atomic hydrogen in iron nitride, the author immersed nitrided iron in the 5% potassium ferricyanide solution after nitriding it, and after 48 hrs. he; by adding ferric chloride solution, noticed the formation of Prussian blue. This reaction takes place equally in the dark place. The reaction :

$$K_3Fe(CN)_6 \rightarrow K_4Fe(CN)_6$$

occurs due to atomic hydrogen occluded in nitrided iron. Iron loaded with atomic hydrogen by quenching it from a high temperature into water also reduces the potassium ferricyanide solution, but ordinary iron powder never reduces it. And it was observed that more Prussian blue is formed with the iron nitride immersed in the potassium ferricyanide solution directly after being nitrided than with the iron nitride which is dipped in distilled water before being immersed in the potassium ferricyanide solution.

Surface Change of Iron due to Nitriding. The results of the potential measurements of wrought iron (C=0.045%, Si=0.02%, Mn= trace, P= 0.047%, S=0.004%) and of that nitrided at 500°C. for 30 hrs. are shown in Table 2 and Fig. 6. As may be seen in Fig. 6, the time voltage curve of nitrided iron (curve 5) shows minimum due to atomic hydrogen at its beginning and remains constant finally (−0.7889 volt). This final potential difference is about 0.023 volt lower than that of iron not nitrided (curve 6). In 1913, F. Hanaman(2) measured the single potential difference of steel that had been treated with ammonia at above 650°C. and obtained the result :

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(1) L. Guillet and M. Ballay, *Compt. rend.*, **189** (1929), 957.

(2) F. Hanaman, Dissertation Berlin, 1913.

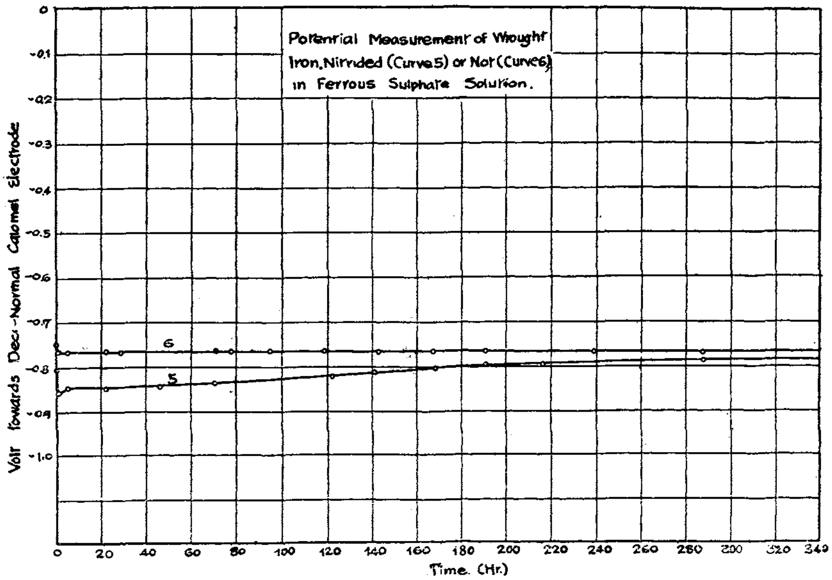


Fig. 6.

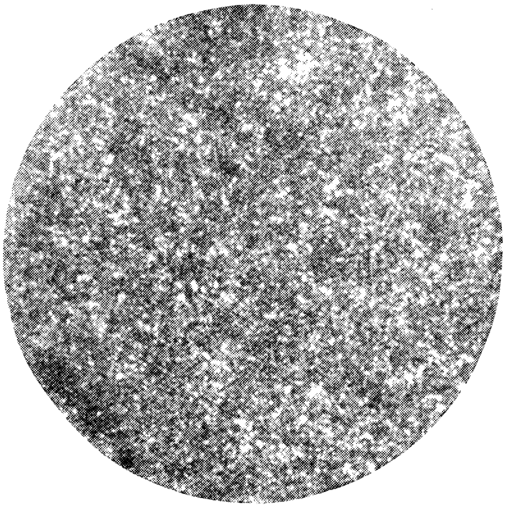
ϵ_h=0.51 volt for the iron nitride. For this reason the above mentioned potential of -0.7889 volt is not that of the iron nitride but that of the porous iron which contains nitrogen as a solid solution, and therefore the potential

Table 3.

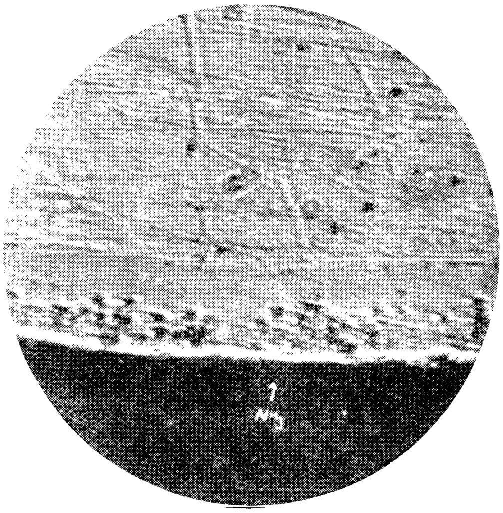
ϵ_h Values of Various States of Iron.

	T. W. Richards and G. E. Behr. (20°C.)	C. Benedicks and R. Sundberg (16°±2°C.)	Author (28°±2°C.)
Purest iron melted *in vacuo*.	-0.423	—	—
Technical pure iron.	-0.427	-0.422	-0.429
Purest porous iron containing hydrogen reduced at high temperature.	-0.442~-0.456	—	—
The same, reduced at low temperature.	-0.458~-0.462	—	—
Iron loaded with atomic hydrogen by quenching in water or by electrolysing.	-0.602~-0.562	—	—
Iron loaded with atomic hydrogen by nitriding.	—	—	-0.565
Technical pure iron nitrided.	—	—	-0.452
Iron powder nitrided.	—	—	-0.448

difference of 0.023 volt would correspond that between compact iron and porous iron reported by Richards,⁽¹⁾ i.e., the compact iron would trasfer into porous iron by the action of ammonia. This is clearly seen by the photomicrograph shown in Fig. 7.



Surface ×500



Section (unetched). ×500

Photomicrograph of Nitrided Wrought Iron.

Fig. 7.

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(1) Loc. cit.

The author calculated the single potential differences of nitrided iron, referring to hydrogen electrode according to the equation :

$$\epsilon_h=\epsilon_c+0.337.$$

The calculated values are shown in Table 3 together with ϵ_h values of the various states of iron reported by Richards.(1)

Influence of Light on the Single Potential of Iron Nitride. The photo-cells are known for silver, copper, tin and stainless steel(2) but, so far as is known, not for iron nitride. The author constructed a photo-cell by means of two plates of nitrided iron, immersed in a ferrous sulphate solution to determine whether it is light-sensitive or not. In Fig. 8, A and B are armco iron plates (C=0.011%, Mn=0.017%, P=0.008%, S=0.030%, Si= trace, Cu=0.025%) nitrided at 500°C. for 23 hrs. Illuminating a nitrided plates through the window C, the author observed the change of single potential of both plates but found that light produces no marked photochemical effect upon them.

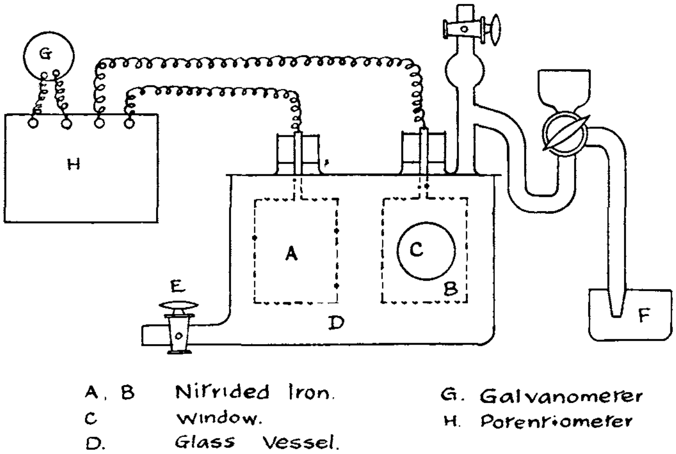

Photo-cell Made of Nitrided Iron.

Fig. 8.

Summary.

The author confirms the existence of atomic hydrogen in iron nitride :

(1) By the presence of hydrogen when heating iron nitride above 430°C. at which iron nitride is found to decompose slowly.

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(1) Loc. cit.

(2) Benedicks and Sundberg, loc. cit.

(2) By the measurement of the single potential of iron nitride in the normal ferrous sulphate solution.

(3) By the oxidation of atomic hydrogen due to oxygen in the water in which iron nitride is immersed.

(4) By the transformation of potassium ferricyanide into potassium ferrocyanide by atomic hydrogen occluded in iron nitride.

By measuring the single potential of nitrided iron, he observed the change of compact iron into porous iron by nitriding.

The influence of light on the single potential of iron nitride was tested and it was found that light produces no marked photo-chemical effect upon it.

In conclusion, the author expresses his cordial thanks to Professor M. Katayama for his valuable advice and suggestion. Thanks are also due to Mr. Hoshi and Mr. Shinozuka for their assistance in the experimental work.

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SORPTION OF GAS BY MINERAL. II. LAUMONTITE.

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Received September 20, 1930. Published October 28, 1930.

The results of observations on the sorption of gases by heulandite and chabazite were already reported.(1) In this paper, the sorption of gases by laumontite is described.

The composition of laumontite is $CaAl_2Si_4O_{12}.4H_2O$.(2) The mineral from Takashima, Hokkaido has been used in the present experiment. It is white crystal of silky lustre.

The method of observation is quite the same with that in the previous experiments. Before the measurement, the mineral is evacuated and heated to a certain temperature for certain length of time. Then, keeping the temperature of the dehydrated mineral to be constant by a thermostat, the gas is put in contact with the mineral and decrease of volume of the gas is measured. The gases tested are carbon dioxide and ammonia.

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(1) Sameshima, this Bulletin, **4** (1929), 96.

(2) Doelter, "Handbuch der Mineralchemie." Bd. II, 3 Teil, 43.

The result obtained on carbon dioxide is shown in Table 1.

Table 1.

Sorption of Carbon Dioxide by Laumontite at 25°C.

Time in min.	Vol. of CO_2 sorbed by 1 gr. of mineral in c.c.	Pressure of gas in mm. Hg.
0.5	0.52	751.4
45.	0.71	751.0
1355.	1.01	751.9

In the above experiment, the mineral is dehydrated at 300°C. for 30 minutes. Laumontite, thus, does not noticeably sorbs carbon dioxide. The same order of amount of this gas is sorbed by laumontite with heulandite.⁽¹⁾ Such a small amount of carbon dioxide will be sorbed by the lime or other substances which may be admixed as impurity. We can say, therefore, that laumontite sorbs practically no carbon dioxide.

A rather interesting result has been obtained on ammonia. At first the bulb containing laumontite is evacuated and heated to 300°C. until no evolution of gas (water vapour) is perceptible. By this treatment the decrease in weight of laumontite was 10.0%. Then the dehydrated mineral was kept to 25.0°C. and the sorption velocity and amount of ammonia was measured. The result is as follows:

Table 2. First Sorption.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	7.76	751.6
4.25	14 27	751.6
9.5	17.86	751.5
28.	23.36	751.3
90.	30.25	750.3
210.	33.48	749.8
1420.	38.69	751.3

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(1) This Bulletin, **4** (1929), 99.

In this table, the first column shows the time in minutes after the contact of mineral to ammonia, the second column the volume of ammonia sorbed by the material which is obtained by dehydrating 1 gram of air dry laumontite, and the third column the pressure of ammonia gas.

The material which has sorbed ammonia is now evacuated and heated to 300°C. and then second sorption is undertaken on this desorbed material. The result was as follows.

Table 3. Second Sorption.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	5.11	750.8
5.	7.37	750.8
9.5	8.04	750.8
26.	9.45	750.8
72.	11.21	750.6

The material was evacuated and heated to 300°C. and third sorption was observed.

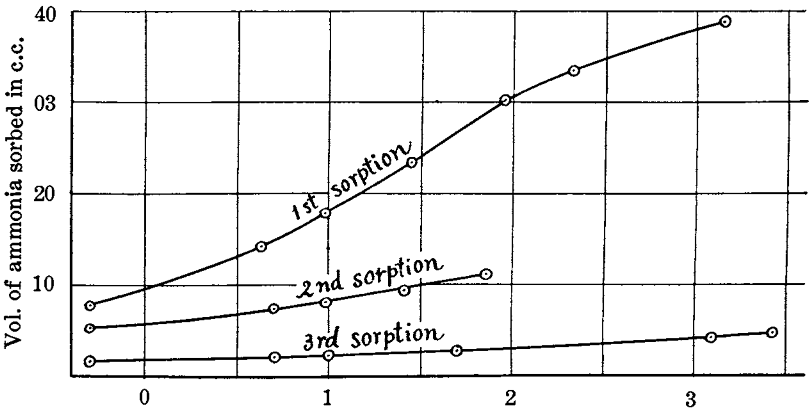
Table 4. Third Sorption.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	1.46	750.6
5.	1.94	750.6
10.	2.06	750.6
50.	2.62	750.6
1220.	4.00	754.6
2665.	4.47	751.8

These three series of observations are depicted in Fig. 1.

From these results, it is known that the sorption amount of ammonia by laumontite decreases rapidly by either repeating sorption or prolonged heating. Now the sorption amount was measured changing the heating time and the temperature of dehydration.

The glass bulb containing the mineral was evacuated and an electric furnace was put around the bulb. The temperature of bulb was now raised and after 5 minutes it reached 300°C. Then this temperature is maintained for 30, 20, 10 or 1 minute in the following four series of observations respectively (Tables 5, 6, 7 and 8). In Table 9 the results are shown in the case where the mineral was dehydrated at 150°C. for 15 minutes.



Logarithm of time in min.

Fig. 1.

Table 5.

The mineral was dehydrated by evacuating and heating to 300°C. for 30 minutes.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	2.14	751.8
5.	3.00	751.8
13.	3.52	751.8
68.	4.70	751.8
159.	5.55	751.2
1415.	8.08	752.6
4265.	10.01	756.6

Table 6.

The mineral was dehydrated by evacuating and heating to 300°C. for 20 minutes.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	6.92	757.0
5.	10.46	757.0
10.	11.98	756.9
50.	15.98	756.6
120.	17.90	756.0
1350.	22.54	754.3
2815.	23.72	751.2

Table 7.

The mineral was dehydrated by evacuating and heating to 300°C. for 10 minutes.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	19.59	757.4
5.	33.94	757.4
10.	37.59	757.3
45.	46.91	757.0
155.	54.35	756.5
1335.	63.54	757.9
2810.	65.45	757.4

Table 8.

The mineral was dehydrated by evacuating and heating to 300°C. for 1 minute.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	21.76	750.9
5.	37.44	750.9
10.	40.82	750.9
30.	47.38	750.7
160.	57.58	750.3
2830.	68.46	756.5

Table 9.

The mineral was dehydrated by evacuating and heating to 150°C. for 15 minutes.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 25.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	5.46	759.4
1.5	9.08	759.4
5.	15.34	759.4
10.	20.68	759.3
20.	26.29	759.2
60.	34.87	759.1
125.	38.92	758.7
300.	41.62	758.1
2965.	45.16	754.2

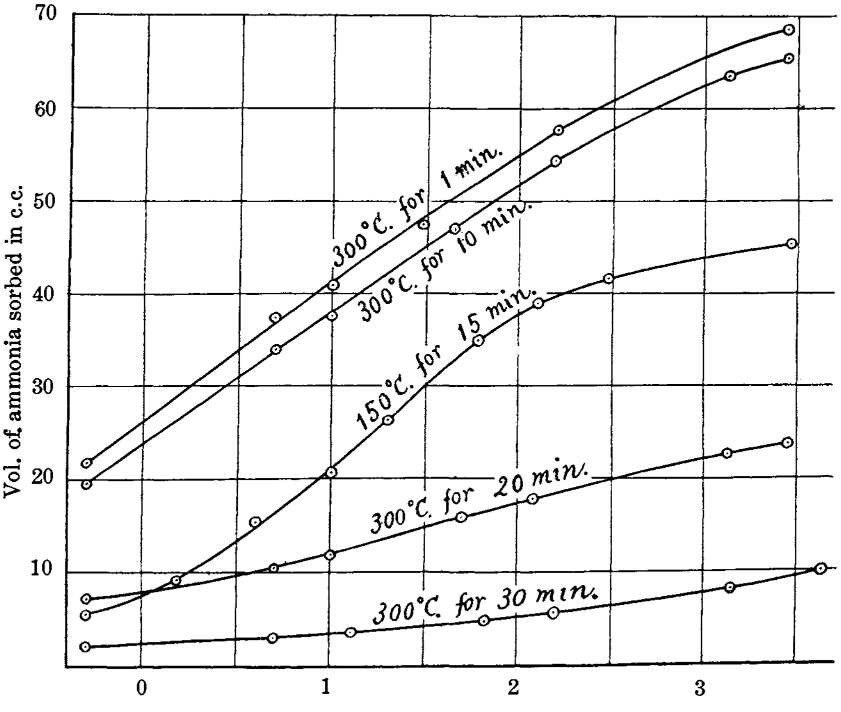


Fig. 2.

By evacuating and heating to 150°C. for 15 minutes the mineral decreases its weight 4.6%.

The data of Tables 5, 6, 7, 8 and 9 are plotted in Fig. 2.

The sorption amount by laumontite of ammonia is, thus, markedly effected by the heat treatment of the mineral at comparatively low temperature such as 300°C.

For the purpose of deciding whether ammonia combines chemically with dehydrated mineral or it is "sorbed" into the pores of the material,⁽¹⁾ an experiment was undertaken at 0°C. intead of 25°C. The material which had been dehydrated in the exactly same conditions as that in Table 9, was tested at 0.0°C. The material was kept at 0.0°C. by using a bath of melting ice during the whole observations, namely ca. 48 hours. The result is shown in Table 10.

Table 10.

The material was dehydrated by evacuating and heating to 150°C. for 15 minutes.

Time in min.	Vol. of NH_3 sorbed by 1 gr. of mineral at 0.0°C. in c.c.	Pressure of gas in mm. Hg.
0.5	4.65	757.3
1.	5.70	757.3
5.	8.62	757.3
15.	12.12	757.3
30.	15.57	757.3
60.	20.12	757.3
120.	25.65	757.1
320.	33.51	756.3
1270.	41.95	759.5
2830.	45.35	761.1

The data in Table 9 and Table 10 are plotted in Fig. 3.

From Fig. 3 it can be noticed that the amount of sorption of ammonia is nearly the same in both cases, while the velocity of sorption is considerably different.

In general, the sorption amount of gases by porous matters such as charcoal, dehydrated silica or chabazite increase by the lowering of temperature. Thus charcoal sorbs greater amount of ammonia at 0°C. than 25°C. In the case of a chemical combination between gas and solid, however, the sorption amount must remain constant at any temperature. Therefore, it is known that the ammonia sorbed by laumontite combines

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(1) Sameshima, this Bulletin, **4** (1929), 125; *Chem. News*, **139** (1929), 61.

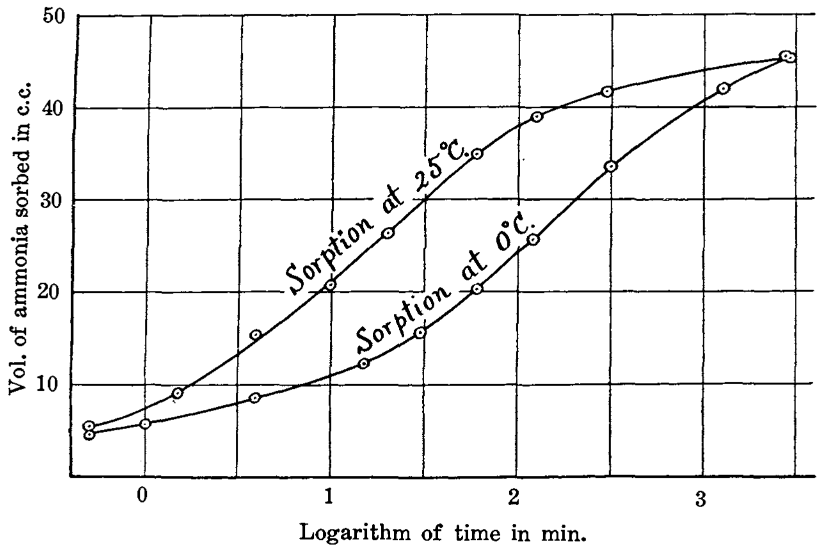

Fig. 3.

chemically with the dehydrated mineral. The retardation of the combination velocity by the lowering of temperature is the general rule in chemical kinetics.

The relation between the number of mols of ammonia sorbed and that of water evaporated is not exactly known by the present experiments, for the sorption amount varies by the heat treatment of the material. It is probable, however, that one molecule of ammonia enters in place of one molecule of water, just as the case of heulandite.(1)

The structures of zeolite minerals are considered to be rather complicated, and the constitution or crystal form of a mineral as laumontite is liable to change by a slight heat treatment. Accordingly, the sorption amount of ammonia will change also.

Summary.

Dehydrated laumontite sorbs ammonia but not carbon dioxide. The sorption amount of ammonia varies markedly by the conditions of the dehydration. Same amount of ammonia is sorbed at 25°C. and at 0°C. by a sample. The ammonia combines chemically with dehydrated mineral.

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(1) Sameshima, this Bulletin, **4** (1929), 96.

SINOMENINE AND DISINOMENINE. XX. ON BENZENE-AZO-SINOMENINE.

By **Kakuji GOTO** and **Hideo SHISHIDO**.

Received September 25, 1930. Published October 28, 1930.

The diazo-coupling reaction of sinomenine [I] and the bases derived therefrom is as strong as the red colour produced by it is still visible in the 2,000,000th dilution of the bases.(1) This property is shared by almost all the alkaloids of phenanthrene group, in which a free phenol group situates in (4) with the unsubstituted para-position (1). Thus, thebainone, dihydro-thebainone, desoxy-codeine, β- tetrahydro-desoxy-codeine, morphothebaine and apomorphine give the same reaction in the same strength.(2) On the contrary, those derivatives of sinomenine and thebainone, in which the para-position (1) to the phenol group (4), may be assumed, from the nature of reaction, to be substituted, namely, bromo-sinomenine both disinomenines and α- and β- dithebainones give this reaction in an exceedingly diminished degree (in the 20,000th dilution or thereabout) or not.

The diazo-coupling reaction is thus very conveniently to be taken use of in judging whether the para-position (1) is substituted or the phenol group (4) is perfectly etherified or esterified in these bases.

Now, the authors could, as is described in the experimental part, prepare the benzene-azo-compounds of sinomenine, hydrosinomenine and thebainone in nice crystalline form. M.p. of these coupled bases are the following.

	Benzene-azo-sinomenine	Benzene-azo-hydrosinomenine	Benzene-azo-thebainone
Solvent for recryst.	nitrobenzene	dil. methyl alc.	dil. methyl alc.
Cryst. form	hexagonal plates	prisms.	prisms.
Colour	dark red	dark red	yellowish brown
M.p.	253° (dec.)	231° (dec.)	152°

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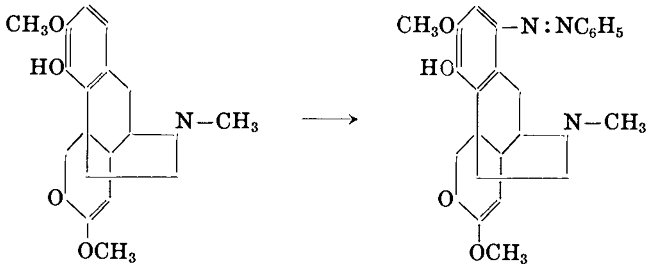
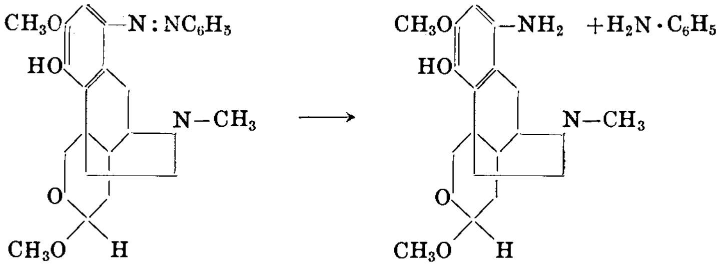
(1) *J. of Agr. Chem. Soc. Japan,* **1** (1924), 5.

(2) This Bulletin, **4** (1929), 103.


[I] [II]


[III] [IV]

By reducing benzene-azo-dihydrosinomenine [III] by sodium hydrosulphite, we could obtain 1-amino-dihydro-sinomenine [IV]. The free base was rather unstable and the analysis was made with its hydrochloride, crystallised from the mixture of alcohol and chloroform.

It contained tenaciously one molecule of water and chloroform. The analytical results were, however, satisfactory as such.

The same reduction of benzene-azo-sinomenine would give rise to the mixture of 1-amino-sinomenine and 1-amino-dihydro-sinomenine, as the preliminary experiment with sinomenine has shown. Therefore, the reduction of benzene-azo-sinomenine was not undertaken.

Recently, G. Charrier and A. Neri reported that by dissolving benzene-azo-morphine in conc. sulphuric acid, they could transform it into benzene-azo-apomorphine.(1) The same treatment of benzene-azo-sinomenine did not give the expected results. The base did not change the shade of the colour, but became water-soluble, indicating perhaps the sulphonation of the coupled benzene-nucleus.

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(1) Cited after *Chem. Zentr.*, **101** (1930), 1309; *Gazz. chim. ital.*, **59** (1929), 804.

Experimental Part.

Diazo Coupling Reaction. Five drops of N/25 sulphanilic acid solution are diazotised with two drops of 10% caustic soda solution, and 1 drop of N/5 sodium nitrite solution. To this alkaline solution of diazo-benzene sulphonic acid is added about 1 c.c. of the solution of the hydrochloride of the base in different concentration. When 1% hydrochloric acid is added to this mixture drop by drop, a beautiful red colour is produced at certain stage. Five to seven drops of the acid is enough to produce the maximum shade. Reaction still alkaline. Too much acid will decolourise the solution again.

Sinomenine and the bases of allied constitution give the red colour up to the 2,000,000th dilution.

Benzene-azo-sinomenine [II]. Anilin (1 gr.) was diazotised in acidic medium (8 c.c. of 10% HCl+92 c.c. Water) with the calculated quantity of $NaNO_2$ (0.7 gr. in 20 c.c. water) at 5–10°C. To this solution was added the aqueous solution (50 c.c.) of sinomenine hydrochloride (4 gr.). Since this mixture is still acidic, neither the red colour nor red precipitate is produced in this stage. When this solution is, however, added with sodium hydroxide solution, the red precipitate is richly formed. The latter, being redissolved in the excess of caustic soda solution, is precipitated again by CO_2 gas. The precipitates are collected, dried and recrystallised from boiling nitrobenzene. Dark red tetragonal or hexagonal plates, decomposing at 253°. Yield almost quantitative.

Anal. Found: C=69.08; H=6.05; N=9.18, 9.16; methoxyls=14.01%. $C_{25}H_{27}N_3O_4$ requires: C=69.28; H=6.23; N=9.70; methoxyls=14.31%.

Benzene-azo-dihydrosinomenine [III]. Mode of preparation is the same with the foregoing. Recrystallised from dilute methyl alcohol, it forms long, dark red prisms of m.p. 231° (dec.).

Found: N=9.41%. $C_{25}H_{29}N_3O_4$ requires: N=9.65%.

Benzene-azo-thebainone. Prepared in the same way as above. Yellowish brown prisms from dilute methyl alcohol. M.p. 152°.

Found: N=10.23%. $C_{24}H_{25}N_3O_3$ requires: N=10.42%.

Reduction of Sinomenine with Sodium Hydrosulphite. Sinomenine (10 gr.) was boiled with $Na_2S_2O_4$ (20 gr.) in aqueous solution (60 c.c.) for two hours, when a clear solution was produced. When the bases were separated in the ordinary way, the part, which was first extracted, consisted principally of hydrosinomenine (2 gr.; 20%). Next came the unchanged sinomenine (2.5 gr.). The rest was difficultly crystallisable.

l-Amino-dihydrosinomenine Hydrochloride [IV]. When a mixture of benzene-azo-dihydrosinomenine (5 gr.), sodium hydrosulphite (12 gr.), water (50 c.c.) and methyl alcohol (20 c.c.) was boiled, the mixture was decolourised in twenty minutes. After boiling for one hour, aniline was removed by steam-distillation (until the bleaching powder reaction was disappeared in the distillate). The base was, then, set free with sodium carbonate and extracted with chloroform.

The chloroform was dried with sodium sulphate, filtered and saturated with HCl gas, by which the hydrochloride of the amino-dihydro-sinomenine was thrown down in a pale yellow mass. Ethyl alcohol was added to this chloroform in a quantity which is just enough to dissolve the precipitate away. After standing some time, the hydrochloride appears in stout prisms, collected in rosettes. This was collected, and washed with chloroform and ether.

For recrystallisation, the hydrochloride is redissolved in alcohol and precipitated with much chloroform. Yield 2 gr., m.p. $>300°$.

The free base is unstable, and accordingly, the hydrochloride was analysed, after it was left in a desiccator over H_2SO_4 for twenty days, until the weight became constant. The hydrochloride seems to contain one molecule each of chloroform and water, the former appearing as a drop when the hydrochloride is dissolved in water.

Anal. Found: C = 43.33, 43.28; H = 5.82, 6.45; N = 5.25; Cl = 31.51; Methoxyls = 11.56%. $C_{19}H_{26}N_2O_4 \cdot 2HCl \cdot CCl_3H \cdot H_2O$ requires: C = 43.12; H = 5.57; N = 5.03; Cl = 31.89; methoxyls = 11.14%.

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SINOMENINE AND DISINOMENINE. XXI.

ON THE REACTION BETWEEN SINOMENINE AND FORMALDEHYDE.

By **Kakuji GOTO**, **Hideo SHISHIDO** and **Reikichi INABA**.

Received September 25, 1930. Published November 28, 1930.

When sinomenine (III) is boiled for two hours with ten times its weight of formaline (40%), two new bases can be isolated from the reaction mixture. As the base A is difficultly soluble in methyl alcohol and water and the base B is very soluble in these two solvents, they can be easily separated each other. The properties of these two bases are given in the following table.

Table 1.

	The base A (5-oxymethyl-sinomenine, I)	Dihydro-5-oxymethyl-sinomenine	The base B (1, 5-dioxymethyl-sinomenine, IV)
Mol. formula.	$C_{20}H_{25}NO_5$	$C_{20}H_{27}NO_5$	$C_{21}H_{27}NO_6$
Yield	30%	55%	10%
Solvent for recryst	Methyl alc.	Methyl alc.	Chloroform or methyl alc.
M.p.	260° (dec.)	244°	242° (fr. Me-A) 252° (fr. Chloroform)
$[\alpha]_D$	−40.71°	+73.03°	−74.39°
No. of methoxyls	2	2	2
Mol. weight	Monomolecular	—	Monomolecular
M.p. of oxime (all amorphous)	240–245°	215–225°	200–215°
M.p. of iodomethylate	223° (fr. Me-A)	205–220° (dec.)	210° (280 dec.)
$FeCl_3$ reaction	Green	Green	Brown
Diazo-reaction	2,000,000 th*	2,000,000 th	20,000 th
$FeK_3(CN)_6$ reaction	Faint	Faint	Almost no.
$HCOH$-H_2SO_4 reaction	Green → Brown	Blue violet	Green

* The figures show the dilution, at which the reaction is still visible.

The constitution of the base A, which is called to be 5-oxymethyl-sinomenine, is deduced from the following considerations.

1. The base A gives the diazo coupling reaction and ferric chloride reaction in the same strength as with sinomenine. The phehol group (4) and its para-position (1) must, therefore, be intact.

2. The base A is laevo-rotatory and its reduction product, dihydro-5-oxymethyl-sinomenine, is dextro-rotatory. This relation is the same with that of sinomenine (−) to dihydro-sinomenine (+) or to sinomenine hydrate (+). This shows that in the base A the original double linking of sinomenine must be kept intact.

3. By the acetolysis at 180°, the base A gives a nitrogen free product $C_{23}H_{22}O_5$ and methyl-ethyl amine. This shows that the reaction with formaldehyde did not occur on the methyl-amino-ethyl side chain.

In these state of affairs, there remain only four carbon atoms, which can be suspected to be able to enter the reaction with formaldehyde, namely, C(5), C(9), C(10) and C(14). Among these C(14) must be excluded, since the hydrogen atom on it must be lost in the course of acetolysis. The choice must be then made on C(5) C(9) and C(10). Of these three, C(5) is naturally the most susceptible point, where formaldehyde can react.

The reactivity of a methylene group, vicinal to a ketonic group, against aldehyde is well-known and is of two kinds. First, it is the linking together of the two methylene groups by means of the carbon atom of the aldehyde, that is the formation of the substance of the type of methylene bis-aceto-acetic ester. In the present case, this supposition is quite excluded, since the base A as well as its decomposition product are monomolecular.

Secondly, it is the formation of the substance of the type of piperonylidene thebainone. Yet, this supposition does not reconcile with the results of the elemental analysis of the base A and of its decomposition product. Mereover, this type of reaction is known thitherto only with aromatic aldehydes, and not with the aliphatic.

The elemental analysis of the base A and of its decomposition product shows that the formaldehyde must have been introduced, in our case, as oxymethyl group. We have not many examples of this type of reaction in the literature, yet we can cite the case of methylol chinaldine(1) from chinaldine and formaldehyde in favor of our reasoning, although in the latter case, the reactivity of the methyl group is enhanced by the neighbouring −C=N− group of the chinoline nucleus. The base A is called, accordingly, 5-oxymethyl-sinomenine.

By heating 5-oxymethyl-sinomenine with acetic anhydride in a sealed tube at 180° for fifteen hours, we obtained a nitrogen free substance $C_{23}H_{22}$

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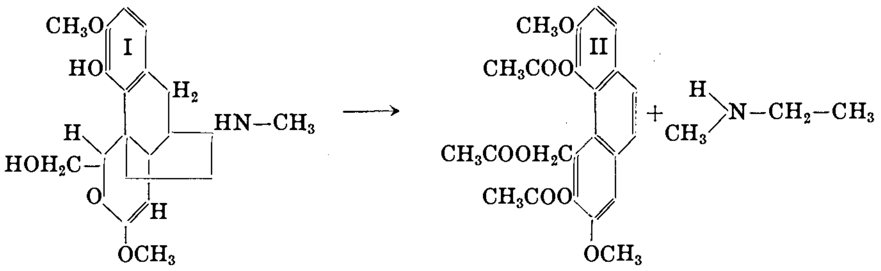
(1) Besthorn, *Ber.*, **39** (1906), 2329. Compare K. N. Welch, *J. Chem. Soc.*, **1930**, 257.

$O_8=C_{15}H_7(CH_3O)_2(CH_3COO)_3$ in 7% yield. The amine, splitted off, in this reaction, is also methyl-ethyl amine, as is the case with sinomenine⁽¹⁾.

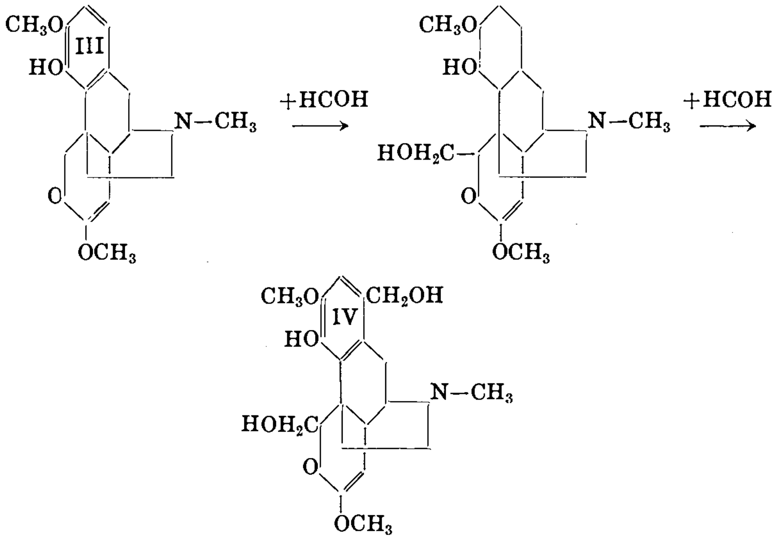


By reducing 5-oxymethyl-sinomenine with $Pd+H_2$, we obtained dihydro-5-oxymethyl-sinomenine, whose properties are given in the third column of the Table 1. Yet, in an attempt to prepare this substance from dihydrosinomenine and formaline, the reaction products became syrupy.

The constitution of the base B, 1, 5-dioxymethyl-sinomenine (III) can be deduced from the following three facts.

1. Its molecular formula is $C_{21}H_{27}NO_6$.
2. It gives diazo coupling reaction very faintly (1 : 20,000th or thereabout). A second oxymethyl group must, therefore, have been introduced in the para-position to the phenol group.
3. By boiling pure 5-oxymethyl-sinomenine with formaline for one hour, 1,5-dioxymethyl-sinomenine was produced in a tolerably good yield.

I.



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(1) Goto, *J. of Agr. Chem. Soc. Japan*, **1** (1925), 50, 89.

Neither the acetolysis nor the reduction of 1,-5-dioxymethyl-sinomenine gave crystalline products.

Such introduction of oxymethyl group to the para- and ortho position of the phenol, had been studied already in 1894 by Manasse(1), who isolated saligenin and *p*-oxymethyl-phenol from the reaction mixture. He stated also that by the action of formaline on β-naphtol a dioxy-dinaphtyl-methan was produced. The studies in this line have been recently much advanced in relation to Bakelite.

Experimental Part.

1-Oxymethyl-sinomenine (1) and 1,5-Dioxymethyl-sinomenine (IV). When sinomenine (10 gr.) is boiled with formaline (50 c.c.; with the precipitate of oxymethylene), the base dissolves away slowly, changing the colour of the liquid into purple. After one hour, when the colour of the liquid turns brown, the boiling is discontinued and the mixture is diluted with water (100 c.c.). The reaction of the liquid is strongly alkaline. The bases are isolated from this mixture in the ordinary way. The raw yield is about 6 gr., i.e. 55% of the theoretical.

The raw product is recrystallised from boiling methyl alcohol (500 c.c.). 5-Oxymethyl-sinomenine crystallises out in stout prisms. Three recrystallisation is enough to obtain the substance in a pure state. M.p. 260° (dec.) The substance takes a purple colour at about 230°. Yield 3 gr. (ca. 30%). It does not react with Schiff's reagent.

The methyl alcoholic mother liquor is evaporated down, and the 5-oxymethyl-sinomenine is removed as far as possible. When long, hairy crystals of 1,5-dioxymethyl-sinomenine appear richly, it is evaporated to dryness and extracted with a little hot water. When the latter was shaken with chloroform or ether, the solvent as well as the aqueous layer is sometimes filled with the crystals of the substance. These crystals sinter at 95°, but melt at 252° (dec.) sharply. But, those crystals obtained by the evaporation of the solvents melt generally at 242°. Yield about 1 gr. (10%).

5-Oxymethyl-sinomenine was also isolated in a pure state from the cold mixture of sinomenine (1 gr.) and formaline (5 c.c.), after it was left stand for two weeks.

For the properties of 5-oxymethyl-sinomenine, see the first column of the Table 1.

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(1) *Ber.*, **27** (1894), 2411.

Anal. Found: C=66.43, 66.55; H=6.87, 7.00; N=3.86, 3.88; methoxyls=16.62, 17.01, 16.58%. $C_{20}H_{25}NO_5$=359 requires: C=66.85; H=6.96; N=3.90; methoxyls=17.22%.

Mol. weight, measured cryoscopically in acetic acid: $(0.5692 \div 15.9052) \times (39 \times 0.379) \times 100 = 368$; after Rast: $(374 \div 4173) \times (400 \div 9.53) \times 100 = 376$.

Sp. rotatory power, in chloroform:

$$[\alpha]_D^{29} = -(0.78 \div 0.479) \times (50 \div 2) = -40.71^\circ$$

Oxime: amorph. decomposing between 240–245° (Found: N = 7.52%. Calc. for $C_{20}H_{21}N_2O_4$: N=7.48%).

Iodomethylate: long needles from methyl alcohol. M.P. 223° (dec.); m.p. 190–195° (from water). (Found: I=23.91%. Calc.: I=25.35%)

For the properties of 1,5-dioxymethyl-sinomenine, see the third column of the Table 1.

Anal: C=64.85; H=6.70; N=3.55; methoxyls=15.57, 16.01%. $C_{21}H_{27}NO_6$ = 389 requires: C=64.78; H=6.99; N=3.59; methoxyls=15.93%.

Mol. weight, measured after Rast:

$$(358 \div 3612) \times (400 \div 10.1) \times 100 = 392$$

Sp. rotatory power, measured in dilute methyl alcohol:

$$[\alpha]_D^{30} = -(2.77 \div 0.4654) \times (25 \div 2) = -74.39$$

Oxime: amorph. decomposing between 200–215°. Found: N=6.56%. Calc. for $C_{21}H_{28}N_2O_5$: N=6.93%.

Iodomethylate: crystallises out from methyl alcohol. M.p. 210°, but decomposes at 280–285°. Found: I=22.52%. Calc.: I=23.91%.

Decomposition of 5-Oxymethyl-sinomenine by Acetic Anhydride. 5-Oxymethyl-sinomenine is heated with 3–5 times its weight of acetic anhydride in a sealed tube for sixteen hours. The precipitate, formed by digesting the reaction mixture with much water, is dried and extracted with ether in a Soxleht's apparatus. The extracted substance is recrystallised first from methyl alcohol and then from glacial acetic acid. Long needles of pale yellow colour. M.p. 192–193°. Yield ca. 7%.

The above raw precipitate can be treated in the following away, also. It is dissolved in a small quantity of benzene and is added with petroleum ether in portions, until no precipitate is formed immediately after the addition. Then the mixture is filtered quickly and left stand. The needle crystals of the decomposition product appear after some time, and by its free evaporation some more is obtained.

This substance, presumably 5-acetoxy-methyl-diacetyl-sinomenol shows a green colour, when it is hydrolysed with alkali, but the hydrolysed solution does not give the sinomenol reaction⁽¹⁾. This might be due to the intervention of oxymethyl group in C (5).

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(1) This Bulletin, 4 (1929), 103.

Anal. Found: C=64.85; 64.66; H=5.09, 5.18; methoxyls=14.33%. $C_{23}H_{22}O_8$=426 requires: C=64.8, H=5.2; methoxyls=14.55%.

Mol. weight, measured after Rast:
(201÷3536)×(400÷5.48)×100=417.

Nitrogenous Substance. The aqueous part, from which the above precipitate was removed, was evaporated down and distilled with much caustic soda. The overdistilled amine was caught in dilute hydrochloric acid. The hydrochloride of amine, thus obtained, was once purified through absolute alcohol. Very hygroscopic. Yield about 0.3 gr. from 10 gr. of 5-oxymethyl-sinomenine. The chloroaurate of this amine crystallises well from water and melts at 179–180°. The chloroplatinate crystallises from alcohol and decomposes at 224°. We have, here, clearly, methyl-ethyl-amine.

Dihydro-5-oxymethyl-sinomenine. 5-Oxymethyl-sinomenine (2 gr.) was shaken in dilute hydrochloric acid solution with $PdCl_2$ (0.1 gr.) and charcoal (1 gr.) in a hydrogen atmosphere. The sorption of hydrogen amounted to 175 c.c. in two hours (a little more than 1 mol.). Dihydro-5-oxymethyl-sinomenine crystallises out in short prisms from methyl alcohol and melts at 244°. Yield 1.1 gr. (55% of the theoretical.).

Anal. Found: C=66.80; H=7.76; N=3.91%. $C_{20}H_{27}NO_5$=361 requires: C=66.48; H=7.48; N=3.88%.

Sp. rotatory power, measured in methyl alcohol+chloroform.

$$[\alpha]^{29}_{D} = +(1.92 \div 0.3286) \times (25 \div 2) = +73.03$$

Oxime: amorph. decomposing at 215–225°. (Found: N = 7.34, 7.29%. Calc.: N=7.44%)

Iodomethylates: crystallisable from methyl alcohol. M.p. 205–220° (dec. from water). (Found: I=24.99%. Calc.: I=25.23%).

Transformation of 5-Oxymethyl-sinomenine into 1,5-Dioxymethyl-sinomenine. 5-Oxymethyl-sinomenine (1 gr.) was boiled with formaline (40%; 5 c.c.) for two hours. From the mixture of the bases, isolated in the way given above, we could isolate 1,5-dioxymethyl-sinomenine in ca. 10% yield. M.p. 242°. It gave only a brown colouration with ferric chloride in alcohol. Diazo-reaction was also strongly diminished (1 : 20,000th).

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ON THE DISSOLUTION VELOCITY OF OXYGEN INTO WATER. PART III.

By Susumu MIYAMOTO and Tetsuo KAYA.

Received October 6, 1930. Published November 28, 1930.

Introduction. Sodium sulphite oxidizes at a definite velocity, quite independent of its concentration, when air is passed into the solution at uniform velocity under certain conditions(1). Following equations(2) were proposed to interprete the observed results from theoretical considerations.

$$k=\frac{v_0-v}{t-t_0} \qquad \text{(1)}$$

$$D=\frac{1}{4}k\times10^{-4}\text{ moles/min.} \qquad \text{(2)}$$

$$D=\frac{60ap}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+S_0\right)\text{ moles/min.} \qquad \text{(3)}$$

$$k=\frac{24ap\times10^5}{\sqrt{2\pi MRT}}\left(\frac{Vl}{20ru}+S_0\right) \qquad \text{(4)}$$

where k = the velocity constant calculated as a zero order reaction, v_0-v being the volume of sodium thiosulphate solution of 0.1000 normal equivalent to the amount of sodium sulphite oxidized during $t-t_0$ minutes,

D = the dissolution velocity of oxygen into water when the concentration of oxygen in the surface layer is kept to be zero,

a = the ratio of the total number of the molecules of oxygen which penetrate into water and the total number of the molecules of oxygen which collide with the unit boundary surface per unit of time, the concentration of oxygen in the surface layer being kept to be zero,

p = the partial pressure of oxygen,

M = the molecular weight of oxygen,

R = the gas constant,

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(1) S. Miyamoto, this Bulletin, **2** (1927), 74; *Scientific Papers of the Institute of Physical and Chemical Research*, **7** (1927), 40.

(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 123; S. Miyamoto, T. Kaya and A. Nakata, ibid., **5** (1930), 229.

T =absolute temperature,
V=the volume of the gas passed per minute,
l =the depth of the center of a bubble when it just leaves the exit,
r =the radius of a bubble,
u =the ascending velocity of the bubble,
s_0=the surface area of the liquid which is in contact with the gas outside of the boundary surface of the bubbles.

If all the values in the equations 3 and 4 be kept constant except the value of the radius of the bubble, the equations can be simplified.

$$D=\frac{A}{ru}+B \qquad \text{(5)}$$

$$k=\frac{A'}{ru}+B' \qquad \text{(6)}$$

where A, B, A' and B' are constants.

The present research was carried out to ascertain if the equations 5 and 6 be acceptable.

Experimental. The apparatus and the method of the observation are quite the same as those described in the previous paper(1). The bubbles of various magnitude were obtained by substituting the tube through which air is passed into the solution. The radius of the bubble and the corresponding ascending velocity given in the tables were obtained in quite the same manner as in the previous case(2).

The observed result is given in Table 1.

Table 1.

Temp.=25°C. Velocity of Air Passed=86.7 c.c./min.

Radius of a bubble r cm.	Time min.	v c.c.	$v_{\text{calc.}}$ $[=v_0-k(t-t_0)]$ c.c.	$k\left[=\frac{v_0-v}{t-t_0}\right]$
0.23	3	16.16	—	0.249
	33	8.70	8.63	
	3	16.71	—	0.255
	43	6.52	6.67	
	3	44.63	—	0.253
	53	31.96	32.08	
	3	56.32	—	0.248
	53	43.90	43.77	
			Mean:	0.251

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(1) S. Miyamoto, T. Kaya and A. Nakata, this Bulletin, **5** (1930), 230.
(2) S. Miyamoto and T. Kaya, this Bulletin, **5** (1930), 134.

Table 1.– (*Continued*)

Radius of a bubble r cm.	Time min.	v c.c.	$v_{calc.}$ $[=v_0-k(t-t_0)]$ c.c.	$k\left[=\frac{v_0-v}{t-t_0}\right]$
0.29	3 43	18.92 9.86	— 9.92	0.227
	3 52	23.88 12.83	— 12.85	0.226
	3 53	37.60 26.28	— 26.35	0.226
	3 53	50.86 39.74	— 39.61	0.222
	3 53	65.54 54.39	— 54.29	0.223
			Mean:	0.225
0.36	3 43	17.25 9.10	— 9.01	0.204
	3 53	23.25 12.78	— 12.95	0.209
	3 58	37.61 26.36	— 26.28	0.205
	3 53	50.51 40.12	— 40.21	0.208
	3 53	60.97 50.89	— 50.67	0.202
			Mean:	0.206
0.41	3 43	18.04 10.61	— 10.24	0.186
	3 43	18.02 10.19	— 10.22	0.196
	3 54	23.33 13.13	— 13.38	0.200
	3 53	38.01 28.24	— 28.26	0.195
	3 55	62.13 51.75	— 51.99	0.200
			Mean:	0.195

Table 1.—(*Concluded*).

Radius of a bubble r cm.	Time min.	v c.c.	$v_{\text{calc.}}$ $[=v_0-k(t-t_0)]$ c.c.	$k\left[=\frac{v_0-v}{t-t_0}\right]$
0.49	3	16.41	—	0.175
	43	9.42	9.33	
	3	23.02	—	0.175
	53	14.27	14.17	
	3	34.54	—	0.181
	53	25.49	25.72	
	3	46.55	—	0.181
	53	37.51	37.70	
	3	64.11	—	0.175
	53	55.34	55.26	
			Mean:	0.177

Table 2.

Temp. =25°C. Velocity of Air Passed=86.7 c.c./min.

r cm.	u cm./sec.	ru	$k_{\text{obs.}}$	$k_{\text{calc.}}$	$D_{\text{obs.}}$ $[=\frac{1}{4}k_{\text{obs.}}\times 10^{-4}]$ moles./min.	$D_{\text{calc.}}$ moles./min.
0.23	23.7	5.451	0.251	0.252	6.28×10^{-6}	6.29×10^{-6}
0.29	23.1	6.699	0.225	0.226	5.63 ,,	5.64 ,,
0.36	23.1	8.316	0.206	0.204	5.15 ,,	5.10 ,,
0.41	23.1	9.471	0.195	0.193	4.88 ,,	4.82 ,,
0.49	23.1	11.319	0.177	0.180	4.43 ,,	4.50 ,,

The values of k and D calculated by the following equations are given in Table 2.

$$D_{\text{calc.}} = \frac{1.886 \times 10^{-5}}{ru} + 2.83 \times 10^{-6}$$

$$k_{\text{calc.}} = \frac{0.7543}{ru} + 0.1132$$

where the constants were obtained by the least square method. The observed values are plotted in Figs. 1 and 2.

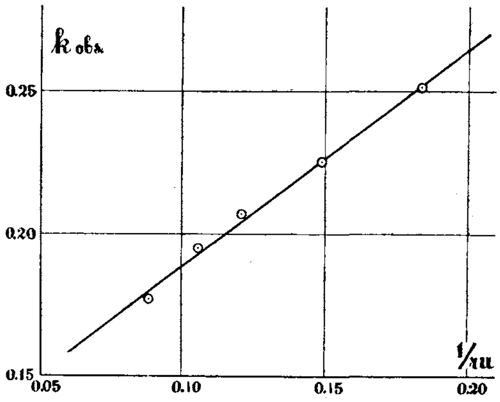

Fig. 1.

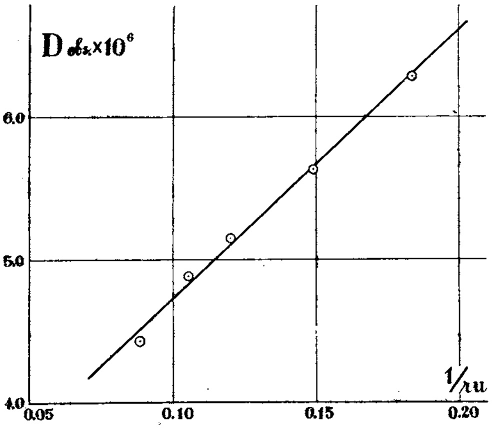

Fig. 2.

The result is thus quite favourable for the authors' considerations, as was expected.

Summary.

(1) The influence of the magnitude of the radius of the tube, through which air is passed, upon the oxidation velocity of sodium sulphite was observed.

(2) The theoretical considerations on the result was described.

The authors wish to express their appreciation for a grant from the Department of Education for the expenses of this research.

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UEBER DIE EINWIRKUNG DER KALILAUGE AUF DIE TETRACARBONSÄUREESTER VON DIMALONSÄURE-REIHE. (DARSTELLUNG VON AETHYL-PHENYLPROPIONSÄUREN).

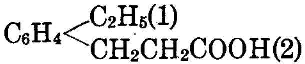
Von Hsiung Tsai LO.

Eingegangen am 9. Oktober 1930. Ausgegeben am 28. November 1930.

Es wurde schon in früher Zeit von W.H. Perkin gezeigt,(1) dass sich *o*-Phenylendipropionsäure leicht durch Verseifung der *o*-Xylylendimalonsäureester mit konzentrierter alkoholischer Kalilauge erhalten lässt. In der ähnlichen Weise stellte Kipping *m*- und *p*-Phenylendipropionsäuren aus *m*- und *p*-Xylylendimalonsäureestern dar.(2) Mit einer bestimmten Absicht(3) habe ich mich damit beschäftigt, nach Perkin und Kipping Phenylendipropionsäuren in grösserer Menge herzustellen.

Im Verlaufe einer Anzahl von Versuchen wurde aber es gefunden, dass bei ortho-, sowie bei para-Verbindung die Phenylendipropionsäuren nur mit sehr geringer Ausbeute entstehen und die grösste Teile von sich dabei gebildeten Substanzen von anderen Eigenschaften sind. Aus diesen Tatsachen wurde es mir von Interesse, die Reaktionen noch eingehender und die neu entstandenen Substanzen näher zu untersuchen.

o- Xylylendimalonsäureester wurde mit einer 25% alkoholischer Kalilauge verseift und die Flüssigkeit mit verdünnter Schwefelsäure angesäuert. Durch Extraktion mit Aether, Abdestillation des Lösungsmittel und Erhitzung des zurückbleibenden Syrups auf 150–155° bis zur Aufhörung der Kohlensäureentwicklung erhält man eine kristallinische Masse (A), ein Teil davon beim Behandeln mit Chloroform in Lösung geht, woraus sich eine Substanz vom Schmelzpunkt 103° scheidet. Auf Grund ihrer Zusammensetzung ($C_{11}H_{14}O_2$), Silbersalzbildung und Molekulargewichtsbestimmung ist sie mit grosser Wahrscheinlichkeit als *o*-Aethyl-phenylpropionsäure,


$C_6H_4\begin{array}{l}\diagup C_2H_5(1)\\ \diagdown CH_2CH_2COOH(2)\end{array}$, anzusehen, die um ein Mol. Kohlensäure ärmer als *o*-Phenylendipropionsäure ist. Genau wie bei *o*-Verbindung liess sich

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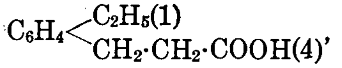
(1) Bayer, Perkin, *Ber.*, **17** (1885), 452; Perkin, *J. Chem. Soc.*, **53** (1888), 18; Titley, *J. Chem. Soc.*, **1928**, 2578.

(2) Kipping, *J. Chem. Soc.*, **53** (1888), 21.

(3) In unserem Kubota-Laboratorium in "Institute of Physical and Chemical Research" sind seit einiger Zeit mehrere Versuche über die Bildungsfähigkeit der Ringe, welche am Benzolkern angebunden sind, im Gange. Einige Resultate darüber werden in kurzem veröffentlicht werden.

p–Aethyl-phenylpropionsäure,  $C_6H_4{<}^{C_2H_5(1)}_{CH_2{\cdot}CH_2{\cdot}COOH(4)}$, aus *p*–Xylylendimalonsäureester gewinnen. Diese beiden Säuren sind meines Wissens noch nicht in der Literatur beschrieben und erscheinen zum erstenmale auf diesem einfachen Wege synthetisch dargestellt.

Beim Verseifen des *m*–Xylylendimalonsäureester unter den gleichen Bedingungen entstand dagegen keine Monocarbonsäure und das der Masse (A) entsprechende Produkt erwiess sich als fast reines *m*-Phenylendipropionsäure vom Schmp. 143–146°. Es ist nun vorzustellen, dass sich *m*–Verbindung verschieden von *o*– und *p*–Verbindungen verhalten müssen.

Nach Kipping⁽¹⁾ sind *m*– und *p*–Phenylendipropionsäuren destillierbar, ohne zersetzt zu werden. Ich habe auch beobachtet, dass *o*–Phenylendipropionsäure ebenso beständig gegen Hitze wie *m*– und *p*–Verbindungen ist. Daher ist es klar, dass Aethyl-phenylpropionsäuren nicht beim Erhitzen der Dikarbonsäuren gebildet werden. Dies wird auch dadurch gestützt, dass partielle Kohlensäure-Abspaltung von Dikarbonsäuren durch Erhitzen nicht mit Leichtigkeit, sondern in der Regel unter den Einwirkungen der Katalysatoren stattfindet.⁽²⁾ Hierzu ist es auch beobachtet, dass *o*–Phenylendipropionsäure und ihr Diäthylester auch durch zwei stündiges Kochen mit konz. Kalilauge nicht Aethyl-phenylpropionsäure bilden. Aus diesen Tatsachen kann man mit Recht die Entstehung der Aethylphenylpropionsäuren durch die Annahme erklären, dass Xylylendimalonsäureester durch die Einwirkung von Kalilauge beim Verseifen gleichzeitig drei Mol. Kohlensäure abspalten. Eine solche Entziehung von Carboxylgruppe durch Kalilauge ist als von der gewöhnlichen Esterverseifung verschiedener Vorgang anzusehen. Eine ähnliche Erscheinung findet man bei 3-Phenyl-5-methyl-pyrrol-4-carbonsäureester, die sich durch Kochen mit alkoholischer Kalilauge in geringer Menge in 3-Phenyl-5-methyl-pyrrol überführen lässt.⁽³⁾

Es sei noch erwähnt, dass die Konzentration der Kalilauge scheint in der Bildung der Aethyl-phenylpropionsäuren eine wichtige Rolle zu spielen. Zur Untersuchung über den Zusammenhang zwischen der Bildungsleichtigkeit der Aethyl-phenylpropionsäuren und der Konzentration der Kalilauge wurde die Verseifung unter verschiedenen Bedingungen versucht. Die bei *o*–Xylylendimalonsäureester erzielten Ergebnisse sind aus folgenden Tabelle zu ersehen :

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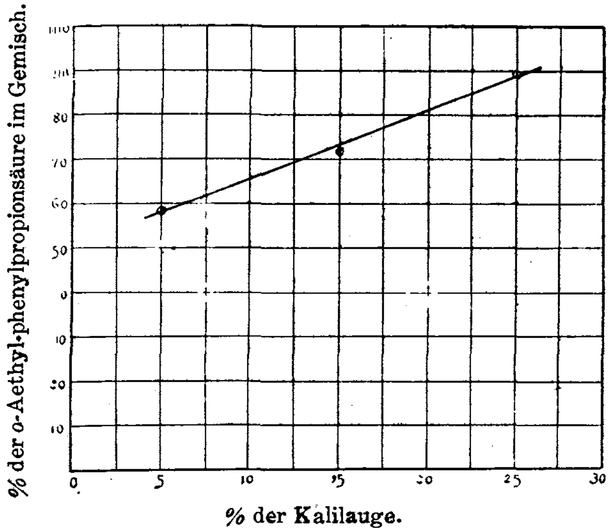
(1) Loc. cit.

(2) Seekamp, *Ann.*, **133** (1866), 253; Wisbar, *Ann.*, **262** (1891), 232; Mai, *Ber.*, **22** (1888), 2136; Farbenind, *A. G. Brit.*, **291** (1926), 326.

(3) Knorr, Lange, *Ber.*, **35** (1902), 3003.

% d. Kalilauge	% d. Monocarbonsäure im Gemische
5	58.52
15	72.16
25	89.70



Wie die obigen Zahlen zeigen, bildet die Monocarbonsäure leichter mit der Zunahme der Konzentration von Kalilauge. Daraus scheint es nun mir, dass Kalilauge von hocher Konzentration der Bildung von Phenylendipropionsäure ziemlich schädlich ist. Daher, wenn man die Phenylendipropionsäuren aus Xylylendimalonsäureestern mit besserer Ausbeute gewinnen will, hätte man besser getan, die Verseifung nicht mit konzentrierter, wie Perkin gezeigt hatte,⁽¹⁾ sondern mit verdünnterer Lauge auszuführen. Auch scheint es notwendig zu sein, die Verseifungsflüssigkeit nicht bis zum Trocknen zu verdampfen, sondern sogleich sie mit Wasser zu verdünnen, anzusäuern und dann mit Aether auszuschütteln. Durch Verdampfung der ätherischen Lösung und Erhitzung des Syrups auf 150–155° geht die Xylylendimalonsäure glätter in Phenylendipropionsäure über.

Verseift man Xylylendimalonsäureester mit konzentrierter alkoholischer Kali, verdünnt mit Wasser, säuert mit Schwefelsäure an und

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(1) *J. Chem. Soc.*, **53** (1888), 18.

extrahiert mit Aether, so ist es vorzustellen, dass in dem Aether extrakt Xylylendimalonsäure, Phenylendipropionsäure und Aethyl-phenylpropionsäure gemischt vorhanden sind. Beim Verjagen des Lösungsmittel und Erhitzen des zurückbleibenden Syrups auf 150–155° bis zur Aufhörung der Kohlensäureentwicklung würde nun alle Tetracarbonsäure in Phenylendipropionsäure übergehen, diese aber, wie oben beschrieben, wird nicht bei diesen Temperaturen zersetzt (Schmelzpunkt von Phenylendipropionsäure =168°). Daher muss die erstarrte Masse im wesentlichen aus Di- und Monocarbonsäuren bestehen. Die Menge von beiden Säuren in dem Gemische lässt sich also aus Silbersalz von Säuregemisch wie folgend abschätzen:

Setzt man

$M_1=C_6H_4(C_2H_5)\ (CH_2CH_2COOAg)=284.98$,

$M_2=C_6H_4(CH_2CH_2COOAg)_2=435.76$,

$A_1=Ag=107.88$,

$A_2=2Ag=215.76$,

s=Gewicht des Silbersalzgemisches,

a=Gewicht des zurückbleibeden Silbers,

x=Fraktion von Aethyl-phenylpropionsäure,

$1-x$=Fraktion von Phenylendipropionsäure,

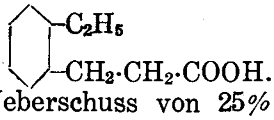
so erhält man

$$\frac{sx}{M_1}A_1+\frac{s(1-x)}{M_2}A_2=a,$$

$$x=\frac{A_1M_1}{A_2M_1-A_1M_2}-\frac{aM_1M_2}{s(A_2M_1-A_1M_2)}$$

$$=4.2515-8.5886.\ \frac{a}{s}.$$

Beschreibung der Versuche.

I. *o*-Aethyl-phenylpropionsäure, 

o-Xylylendimalonsäureester wurde mit einem Ueberschuss von 25% alkoholischer Kalilauge drei Stunden lang auf dem Sandbade gekocht. Die Flüssigkeit wurde mit Wasser verdünnt und dann mit Aether ausgeschüttelt, um den unverseiften Ester zu entfernen. Die alkalinische Lösung wurde mit verdünnter Schwefelsäure angesäuert und mit Aether ausgezogen. Durch

Trocknen des Auszugs über Calciumchlorid und Verdunsten des Lösungsmittel erhält man einen gelblichen Syrup, der beim Erhitzen auf 150–155° bis zur Aufhörung der Kohlensäureentwicklung in eine kristallinische Masse erstarrte. Beim Behandeln mit Chloroform geht *o*–Aethyl-phenylpropionsäure in Lösung. Die beim Verjagen des Lösungsmittel zurückbleibende Säure schmilzt nach Umkristallisieren aus Wasser bei 103°. Farblose Nadel. Schwer löslich in kaltem Wasser, leicht löslich in Aether, Chloroform, Alkohol, und Benzol. Sublimiert über Schmelzpunkt.

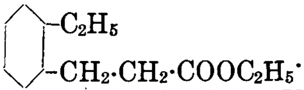
Anal. 3.996 mg. Subst. gaben 10.816 mg. CO_2 und 2.912mg, H_2O. (Gefunden: C=73.82; H=8.09. Berechnet: C=74.11; H=7.92%).

Molekulargewichtsbestimmung (nach Karl Rast). Subst. 0.309 mg., Kampher 7.677 mg., Depression 9.3°. (Gefunden: M=173.1. Berechnet: M=178.1).

Silbersalz der Aethyl-phenylpropionsäure. Versetzt man eine neutrale Lösung des *o*–äthyl-phenylpropionsauren Ammoniums mit einem Ueberschuss von 5% Silbernitrat-Lösung, so fällt das Silbersalz als weisser Niederschlag aus. Zur Analyse wurde das Salz über Schwefelsäure getrocknet. Amorpher Pulver.

Anal. 0.1387 gr. Subst. gaben 0.0527 gr. Ag. (Gefunden: Ag=38.00. Berechnet für $C_{11}H_{13}O_2Ag$: Ag=37.86%).

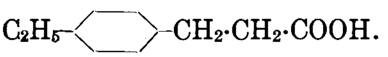
o–Aethyl-phenylpropionsäureester,



Das über Schwefelsäure gut getrocknete Silbersalz wurde mit einem Ueberschusse von Aethyljodid und Aether auf dem Wasserbade 4 Stunden lang erwärmt. Dann nach Zusatz von weiterem Aether filtriert und das Silberjodid mit Aether ausgewaschen. Zur Isolierung des Esters wurde die ätherische Lösung nach Trocknen über Calciumchlorid möglichst eingeengt und der Destillation im Vakuum unterworfen. Farblose Flüssigkeit, Siedepunkt 131°/10 mm.

Anal. 4.306 mg. Subst. gaben 11.835 mg. CO_2 und 3.548 mg. H_2O. (Gefunden: C=74.96; H=9.15. Berechnet: C=75.73; H=8.73%).

II. *p*–Aethyl-phenylpropionsäure,



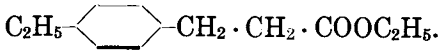
Verseift man *p*–Xylylendimalonsäureester mit 25% alkoholischer Kalilauge und behandelt die Reaktionsprodukte in genau gleicher Weise wie bei *o*–Verbindung, so erhält man *p*–Aethyl-phenylpropionsäure. Sie lässt sich aus Wasser als farblose Nadeln umkristallisieren. Schmelzpunkt 114–115°. Leicht löslich in Aether, Chloroform, Alkohol und Benzol, schwer löslich in kaltem Wasser.

Anal. 3.791 mg. Subst. gaben 10.227 mg. CO_2 und 2·835 mg. H_2O. (Gefunden: C=73.58; H=8.31. Berechnet: C=74.11; H=7.92%).

Molekulargewichtsbestimmung (nach Karl Rast). Subst. 0.368 mg., Kampher 2,720 mg., Depression 29.3°. (Gefunden: M=184.7. Berechnet: M=178.1).

Silbersalz der p–Aethyl-phenylpropionsäure. Das Silbersalz lässt sich aus der neutralen Ammoniumsalzlösung mit Silbernitrat ausfällen. Amorpher, weisser Pulver. Beim Erhitzen über 100° wird es braun gefärbt. Zur Analyse wurde das Salz über Schwefelsäure getrocknet.

Anal. 0.232 gr. Subst. gaben 0.0872 gr. Ag. (Gefunden: Ag=37.49. Berechnet für $C_{11}H_{13}O_2Ag$: Ag=37.76%).

p–Aethyl-phenylpropionsäureester, 

Dieser Ester lässt sich aus Silbersalz der *p*–Aethyl-phenylpropionsäure und Aethyljodid wie bei ortho-Verbindung erhalten. Farblose Flüssigkeit, Siedepunkt 141°/15 mm.

Anal. 3.837 mg. Subst. gaben 10.521 mg. CO_2 und 3.205 mg. H_2O. (Gefunden: C=74.78; H=9.28. Berechnet: C=75.73; H=8.73%).

III. Die Einwirkung der Kalilauge auf die Bildung von *o*–Aethylphenylpropionsäure. *o*–Xylylendimalonsäureester wurde mit (1) 5%, (2) 15%, (3) 25% alkoholischer Kalilauge verseift. Nach zwei stündigem Kochen, Verdünnen mit Wasser und Ausschütteln mit Aether wurde die Flüssigkeit mit verdünnter Schwefelsäure angesäuert und dann mit Aether extrahiert. Das Extrakt wurde über Calciumchlorid getrocknet. Die durch Abdestillation des Lösungsmittel und Erhitzen des zurückbleibenden Syrups erhaltene kristallinische Masse wurde in möglichst wenig verdünnter Natronlauge gelöst, filtriert und mit Schwefelsäure ausgefällt. Nach Umkristallisieren aus kleiner Menge Wasser wurden die Säuregemische in ihre Ammoniumsalze und dann mit Silbernitrat in die Silbersalzgemische übergeführt. Zur Analyse wurden die Salze über Schwefelsäure getrocknet.

(1) 5% KOH: 0.0752 gr. Silbersalzgemisch (*s*) gaben 0.0321 gr. Silber (*a*).
Fraktion von Aethyl-phenylpropionsäure im Gemische

$$=x=4.2515-\frac{0.0321}{0.0752}\times 8.5886=0.5852,\ \text{oder Monocarbonsäure}=58.52\%.$$

(2) 15% KOH: 0.0900 gr. Silbersalzgemisch gaben 0.0350 gr. Silber.
Monocarbonsäure=72.16%.

(3) 25% KOH: 0.0776 gr. Silbersalzgemisch gaben 0.0304 gr. Silber.
Monocarbonsäure=89.70%.

Aus diesen Zahlen geht es hervor, dass sich die Menge an Monocarbonsäure mit der Zunahme der Konzentration von Kalilauge vermehrt. Die Resultate sind schon oben graphisch wiedergegeben.

IV. Die Einwirkung der Kalilauge auf *o*-Phenylendipropionsäure und ihren Ester. Die zu unten beschriebenen Versuchen verwandete *o*–Phenylendipropionsäure enthält von vornherein etwas *o*–Aethyl-phenylpropionsäure. Nämlich:

0.2407 gr. aus dieser Probe hergestelltes Silbersalzes gaben 0.1166 gr. Silber. (Gefunden: Ag=48.44. Berechnet für $C_6H_4(CH_2CH_2COOAg)_2$: Ag=49.51%).

(1). Die Dipropionsäure wurde mit einer 20% alkoholischen Kalilauge zwei Stunden lang gekocht. Beim Ansäuern, Ausschütteln mit Aether und Verdunsten des Lösungsmittel wurde Säuresubstanz wieder erhalten. Sie wurde in bekannter Weise in das Silbersalz übergeführt.

0.2594 gr. Silbersalz gaben 0.1260 gr. Ag. (Gefunden: Ag=48.53%).

Aus diesem Resultat sieht man, dass die Phenylendipropionsäure nicht durch die Einwirkung von Kalilauge zersetzt wird.

(2). Das Silbersalz wurde mit Aethyljodid und Aether in den Aethylester umgewandelt. Der Ester wurde dann mit einer 20% igen alkoholischen Kalilauge während zwei Stunden gekocht. Behandelt man die Reaktionsprodukten in oben beschriebener Weise erhält man schliesslich wieder eine sauere Substanz, die sich nach Umkristallisieren aus Wasser als *o*–Phenylendipropionsäure ergab und dann in ihrès Silbersalz übergeführt wurde.

0.2347 gr. Silbersalz gaben 0.1145 gr. Ag. (Gefunden: Ag=48.79%).

Daraus wird es klar, dass auch der *o*–Phenylendipropionsäureester nicht durch Kali Kohlensäure abspaltet.

Zusammenfassung.

1. Es wurde beobachtet, dass *o*– und *p*–Xylylendimalonsäureester beim Verseifen mit konzentrierter alkoholischer Kalilauge leicht unter Abspaltung von drei Mol. Kohlensäure die Kaliumsalze von *o*– und *p*–Aethylphenylpropionsäuren bilden. Man muss deshalb Sorgfalt auf der Konzentration der Lauge verwenden, wenn man durch Verseifung dieser Dimalonsäureester *o*– und *p*–Phenylendipropionsäuren gewinnen.

2. Diese Versuche zeigen eine Darstellungsmethode von *o*– und *p*–Aethyl-phenylpropionsäuren, welche noch nicht nach anderen Verfahren dargestellt sind.

3. Aethyl-phenylpropionsäuren scheinen mit der Zunahme der Konzentration von Kalilauge leichter zu entstehen.

4. Im Gegensatz zu den *o*– und *p*–Verbindungen erhielt man keine Monocarbonsäure aus *m*–Xylylendimalonsäureester in diesen Versuchen.

Es sei mir gestattet, meinem hochverehrten Lehrer Herrn Prof. Dr. B. Kubota für seine wohlwollende Freundlichkeit, mit der er so eifrig mich leitete, meinen wärmsten Dank auszusprechen.

Aus der "Institute of Physical and
Chemical Research," Tokyo.

ON THE TRUE NATURE OF "PER-ACIDS" AND THE ALLEGED "ACID NUCLEUS THEORY."(1)

By Shin'ichirô HAKOMORI.

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Several years ago, the present author commenced the researches to make clear the true nature of the "Per-acid." The results obtained in the researches have already been reported time to time in three former papers.(2) In the present communication, the author proposes a new hypothesis concerning the structure of the "Per-acid," which explains the experimental results obtained by the author as well as those obtained by others.

"Per-acids" are "Acids" which are formed when "Oxy-acids" are treated with hydrogen peroxide or which turn into "Hydrogen peroxide" under suitable treatment. The "Permanganic" and "Perchloric" -acids, therefore, do not belong to this group although these are also prefixed with "Per-." When the "Oxy-acids" are "metallic," very sensitive and characteristic colorations are frequently produced. This is the reason why "Per-acids reactions are recommended for the detection of such metals in qualitative analysis. As for the other characteristics of "Per-acids," the unstability of these compounds may be mentioned. The literatures on this subject are so many and so divergent with each other that it is very difficult here to enumerate them briefly. The readers, however, may refer to the excellent book of T. Slater Price(3) on this subject.

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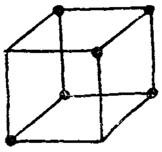
(1) Published in Japanese in the *Journal of the Chemical Society of Japan*, **50** (1929), 231.

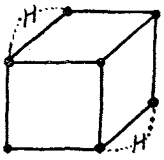
(2) Ibid., **48** (1927), 441; **49** (1928), 511; **50** (1929), 221.

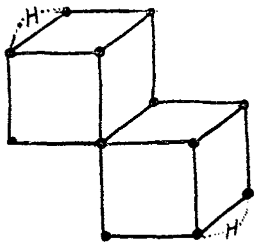
(3) "Per-acids and their salts", Longmans, Green & Co., London (1912).

The structure of the compounds should be considered very complicated but it can not be denied that it is related very closely in the fundamental aspects to that of the "Oxy-acids." Reflection upon the true nature of Oxy-acids," therefore, is required in order to make clear the true nature of "Per-acids." The present author here proposes a new hypothesis called "Acid nucleus theory" for these purposes. The theory starts from the following three postulates.

Postulate I. The natures of the elements which belong to the first, second and third short periods and the "Oxy-acid forming elements" are mainly determined by the arrangement of electrons of the outer shell as G. N. Lewis(1) suggested in his "Octet theory." Accordingly, for example, oxygen, water and hydrogen peroxide possess the following electronic configurations on the outer shells, the black dot showing an electron.







Postulate II. The valences are divided into the following three classes:

(1) Covalence, (2) Electrovalence, (3) Induction-valence.

Among these (1) and (2) have already been fully considered by G. N. Lewis(2) and are produced by the co-owning and locomotion of electrons respectively. Both of these are measurable with integral numbers. The combinations produced by (1) are stronger and firmer than those produced by (2), because, in the former cases, electrons are co-owned. The valence (3), is produced by the phenomenon of electric induction,(3) and is not measurable by integral numbers.

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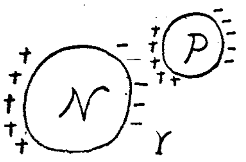
(1) G. N. Lewis, *J. Am. Chem, Soc.*, **38** (1916), 762.

(2) Loc. cit.

(3) Such conceptions as these may exist in everyman's thought implicitly. Cf. G.N. Lewis, *J. Am. Chem. Soc.*, **35** (1913), 1448. The author has attempted only to give a somewhat systematic external form to these conceptions with reference to the problem attempting the clearing up of the true nature of "Per-acid."

Assuming that N is a particle electrically neutral, P is a particle in a polarized state, and the latter approaches to the former, N is naturally polarized due to the electronic induction between the two, where P is called the "Inductor" and N, the "Acceptor."



The force F between them is given by

$$F=\frac{D_P \times D_N}{Kr^2}$$

where D_P denotes the electrical displacement in P, D_N the same in N, r the distance between the two, and K the dielectric constant of the medium.

The author's "Induction valence" is nothing but such a force as represented by F. Now, consider a case in which a molecule formed by such a combination is moved to the gaseous space from an aqueous solution. Then the dielectric constant of the medium will continuously change, so also the force F. The valence, therefore, can not be equal in the aqueous solution and in the gaseous state.

Next, any arbitrary inductor is not always capable of inducing any arbitrary acceptor. As to this relation, the following postulate is given. Every inductor radiates its own characteristic electromagnetic wave say an inducing wave. And the wave-length of the characteristic wave is determined by the electronic configuration and the mass of the inductor. When the acceptor receives the wave, there are two cases in which an electrical displacement is either produced or not. The former case is nothing but a phenomenon called "Electrical induction."

When the electronic configuration of an acceptor is of unsymmetrical arrangement, electrical displacement will readily be accomplished and therefore, it is easily induced.

And when the mass of the acceptor is large or the domain occupied in the medium is accordingly large, the specific effects exerted over the mass will be comparatively small as though the same amount of electrical displacement is produced as in the case in which the mass is small. In this case, therefore, the acceptor is not easily induced.

Potulate III. The atom of the "Acid forming element" has so many electrons at the corners of a surface octet as is equal to the valency of the element as an acid. The element has a remarkable tendency to combine with oxygen by a co-valence, namely, by co-owning the electrons to fill the vacancy in the octets and thus makes the whole mass stable.

Such a mass of octets is called "Acid nucleus." For example, the "Acid nucleus" of hexavalent sulphur is given by: Where $\mathrm{O}\!<$ shows an octet of oxygen combined with sulphur by co-owning two pairs of electrons. The "Acid nucleus" is not, however, to be hastily recognized at once as the same as the "Acid anhydride." The former is chiefly to be considered as a structural unit and the latter as a name of material.

Then, starting from the three postulates mentioned above, the "Acid nucleus theory" will be explained with reference to the data of a few "Oxy-acids" already existing.

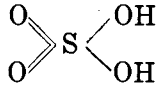
For the sake of convenience a part of the periodic table will be given below.

III	IV	V	VI
B	**C**	**N**	O
Al	Si	**P**	**S**
Sc	**Ti**	**V**	**Cr**
Ga	Ge	As	**Se**
Y	**Zr**	**Nb**	**Mo**
In	**Sn**	Sb	Te
La (?)	Ce	—	—
—	—	—	—
Yb	—	**Ta**	**W**
Tl	Pb	Bi	—
—	Th	—	**U**

In this table, those printed in Gothic type indicate the elements capable of forming "Per-acids." Glancing over the table, one will notice that all the elements capable of forming both "Oxy-acids" and "Per-acids" belong to the fourth, fifth and sixth groups in the table with a few exceptions.

For example, sulphur and phosphorus which form (A) sulphuric acid and (B) phosphoric acid, the most popular "Oxy-acid," belong to the sixth and fifth groups, respectively. They are explained here with the theory.

(A) *Sulphuric Acid.* The constitution of sulphuric acid is commonly represented as follows:



$$O_2S(OH)_2$$

.... (1)

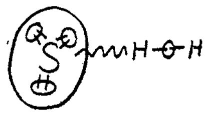
According to this formula, however, the two oxygen atoms out of four and the two hydrogen atoms must be of the same behavior. But in reality, the three oxygen atoms out of four are of the same behavior, e.g.

$$H_2SO_4 + PCl_5 = SO_3 + POCl_3 + 2HCl,^{(1)}$$

and one of the two hydrogen atoms dissociates more readily into an ion than the other.

The formula (1), therefore, is not pertinent to the real state of sulphuric acid molecule, regarding to even the above two points.

Now, according to "Acid nucleus theory," the "Acid nucleus" of sulphuric acid must be such that has been shown previously and be electrically neutral. In this case, a molecule of water, acting as an inductor, approaches to the "Acid nucleus," polarized the latter and combine with an "Induction valence." The above mechanism of the combination is shown schematically in the following figure, in which the wave line indicated the induction valence.



From the above view, the correct answers to the two facts above mentioned will be readily made: The three oxygen atoms out of four are of the same behavior because the combination within the "Acid nucleus" is accomplished by covalence and is, therefore, stronger and firmer than in the other part; and one of the two hydrogen atoms dissociates more readily into an ion than the other because the part ∿∿∿H⊖H is itself polarized and the two hydrogen atoms are not to be of the same behavior, and as is clear from postulate II the valency exerted between the "Acid nucleus" and water is not always to be measurable by a definite integral number. The large dehydrating power and the large heat of dilution of sulphuric acid mean a large Coulomb's force exerted between the "Acid nucleus" and water molecule, that is the valency force is large.

(B) *Phosphoric Acid.* The peculier property of phosphoric acid is that there are several kinds which are derived from the same pentavalent phosphorus; for example, there are: (a) orthophosphoric acid, (b) pyrophosphoric acid and (c) metaphosphoric acid.

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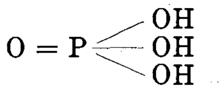
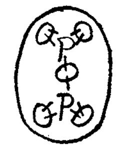
(1) Gerhardt and Chiozza, *Compt. rend.*, **36** (1853), 1050. In this case, SO_3 combines further with HCl and turns into SO_3HCl. Cf. Ostwald, "Grundlinien der anorg. Chemie", Leipzig (1922), 344.

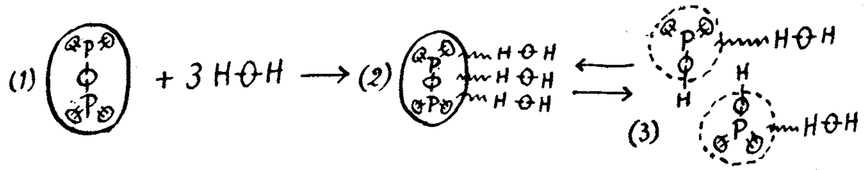
(b) is formed through dehydration of (a) by heating up to 213°C.; (c) is formed when (a) and (b) are thoroughly dehydrated by heating until no more water escapes or when phosphorus pentoxide is dissolved in cold water. These three substances are changeable with one another and the change is mainly controlled by the content of water. It is, therefore, most probable that, when the solution of any of them is boiled for a long time, it contains all three substances as the solutes. The constitutional formula for (a) is commonly represented as below:



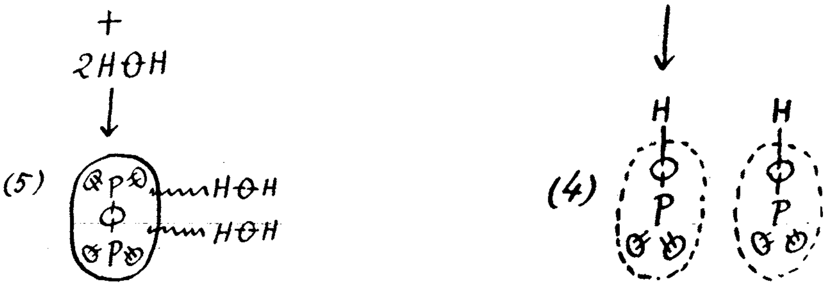
$$O = P \begin{cases} OH \\ OH \\ OH \end{cases} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The formula (2) is not also pertinent to the real state of phosphoric acid just as the formula (1) is not so to that of sulphuric acid. From the " Acid nuleus theory," the " Nucleus " of phosphoric acid is given as below: In this case, two atoms of pentavalent phosphorus gather together in order to render the " Nucleus " stable. But this " Nucleus " is not always the most stable, because it consists of octets of an odd number. It has, therefore, a tendency to separate itself further into two parts in order to form octets of an even number if possible and to combine with water by " Induction valence," as shown below:





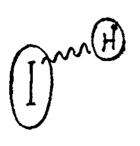
" Phosphoric acid nucleus " Water Orthophosphoric acid Orthophosphoric acid



Pyrophosphoric acid Metaphosphoric acid

As stated above, the "Acid nucleus theory" explains most conveniently the various properties of the "Oxy-acids." It must, therefore, be considered that, to explain the true nature of oxy-acid the present theory is more suitable than the commonly given formula.

The theory of indicator will also be explained easily by the theory as follows. A definite colour change is produced when the concentration of hydrogen ions has a definite value. All indicators are, in the widest sense, acid. The "Acid nucleus" (I) of such an acid can, therefore, be considered.



The above explanation is nothing but an electrical phenomenon produced by a hydrogen ion, an "Inductor" upon the "Acid nucleus" (I), an acceptor. From the standpoint of "Induction valence," the definite hydrogen ion concentration means a definite "inducing" force which produces a definite amount of electrical displacement in (I), or in other word the definite tautomeric change and colour change.

As mentioned above, it has become clear that the "Acid nucleus theory" is most conveniently applied not only to the problem of "Oxy-acids" but also to the theory of indicator. From this same standpoint, a consideration will be given to the true nature of "Per-acids."

As is readily known from Postulate 1, both water and hydrogen peroxide are typical polar compounds. For example, the dielectric constant of the former is 80, the latter is 92.8. Both of these are, therefore, capable of playing the rôle as inductors. This is the reason why there is formed, on the one hand, water of crystallization and hydrogen peroxide of crystallization on the other. In other words, both of these are no other than compounds of the same type being reviewed from a standpoint of "Induction valence." As already stated, if the substance which is formed by combination of "Acid nucleus" with water by "Induction valence" is "Oxy-acid," then "Per-acid" is nothing but a substance which is formed by combination of "Acid nucleus" with "Hydrogen peroxide" by the same valence. The meaning of the above statement will be explained more fully in the following.

Now, by the readiness of formation of "Per-acids" it is perceived that, in the periodic table already given, the elements whose atomic weights are small show a remarkable tendency to form "Oxy-acids" rather than "Per-acids." The latter are formed only under special suitable conditions, as in the case of "Persulphuric acid." But when the atomic weights become larger such as in the case of Ti and V, "Per-acids" are formed most readily by the simple addition of hydrogen peroxide to the acid solutions of the ,,Oxy-acids" and the readiness with which "Per-acids" are formed reaches a maximum in the case of Cr. In all these cases "Per-acids" possess deep characteristic colourations. This is the reason why the "Per-acids reaction" is most frequently recommended in qualitative analysis for the detection of these elements. And finally, as the atomic weights increase further, the readiness of formation and the depth of the colourations decrease, but the stability of "Per-acids" increases. In the case of uranium we find the most stable metallic "Per-acids." In other words, in the case of those elements which readily form "Per-acids" by simple addition of hydrogen peroxide to the solution, the colourations produced are deep but the stability is small. On the contrary, in the case of those elements which form "Per-acids" only under limited conditions, the colourations produced are light but the stability is large. This is the fundamental rule which governs the formation of "Per-acids." The experimental results cited below clearly indicate that the above rule is valid.

No. of exp.	Atomic weight of the acid forming element	Initial conc. of H_2O_2 (mol.)	The ratio of metallic acid present and hydrogen peroxide 1:1	The rise in potential (V.)	The conc. of H_2O_2 in the presence of metallic acids as calculated from the rise in potential (mol.)	The approxim. partial vapor press. of H_2O_2 in the presence of metallic acids estimated from the photographic action (atm.)	The colours of "Per-acids"
1	U =238	0.117	$UO_3 : H_2O_2$	0.0047	0.117×0.69	0.30×10^{-6}	yellow
2	Ti=48	,,	TiO_2: ,,	0.0195	,, $\times 0.22$	0.7×10^{-7}	orange
3	Mo=96	,,	MoO_3: ,,	0.1080	,, $\times 0.22 \times 10^{-3}$	no reducing aetion	yellow
4	V=51	,,	V_2O_5: ,,	0.3107	,, $\times 0.3 \times 10^{-10}$	do.	reddish browh
5	Cr=52	,,	CrO_3: ,,	0.4802	—	—	blue

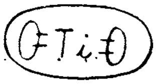
The above table shows that the concentrations of hydrogen peroxide in the "Per-acids" are gradually decreased in the order of U, Ti, Mo, V and Cr; the decreases of partial vapor pressure of the peroxide in these cases being also parallel to the quantity above mentioned. Considering from these points, it is clear that the degree of freedom of hydrogen peroxide in the "Per-acids" are restricted in the order above mentioned. In other words, the combinations of hydrogen peroxide with the "Acid nucleus" in the unstable "Per-acids" are firmer and stronger than those in the stable ones. And here exists, indeed, the key to the problem of clearing up the true nature of "Per-acids." The reason is that, from the above conjecture we know that the combining forces exerted between hydrogen peroxide and "Acid nucleus" are related very closely with the stability and colour of the "Per-acids."

G. N. Lewis⁽¹⁾ once published an opinion on the colour of the chemical substances that the compounds in which electrons are most firmly constrained have no colour; but when the constraints become gradually weaker, they begin to absorb the visible part of the spectrum, from longer wavelength to shorter and they show from yellow to orange or red; and finally, when the constrains reach its loosest condition, they absorb the red or ultra red part in the spectrum, and the colour of the compounds become blue. This theory also throws a light upon the true nature of "Per-acids."

As is clearly know from Postulate II, any arbitrary inductor is not capable of inducing any arbitrary acceptor. This is the reason why those elements situated in the early period of the periodic table show a more pronounced property as "Oxy-acids" than as "Per-acids." The "Acid nuclei" of C, N and S are readily induced by water as an inductor but not by hydrogen peroxide except under special conditions.

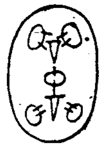
Next considerations will be given upon the case of Ti, V and Cr, whose atomic weights are larger than the preceding case. The "Acid nuclei" of these elements are as shown below:

(1)



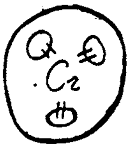
"Titanic acid nucleus"

(2)



"Vanadic acid nucleus"

(3)



"Chromic acid nucleus"

Glancing at the configurations of the "Nuclei" of the acids, one will perceive that they well explain the gradual alterations manifested in the properties of these acids. The "Nuclei" which possess as much mass as in these elements are induced both by hydrogen peroxide and water as inductors. Among them (2) and (3) are coloured; the fact means that some electrons whose constraints are loose in some parts, and the "Nuclei" are readily inducable by inductors. This is the reason why V and Cr have a marked tendency to form "Per-acids." In the case of Ti, the loose combining force of hydrogen peroxide with the "Acid nucleus" is due to its comparatively stable configuration. Next in acid solutions, "Per-vanadic" and "Per-chromic"-acids decompose very rapidly and evolve oxygen, the blue and greenish blue colourations of vanadyl ion and trivalent chromium

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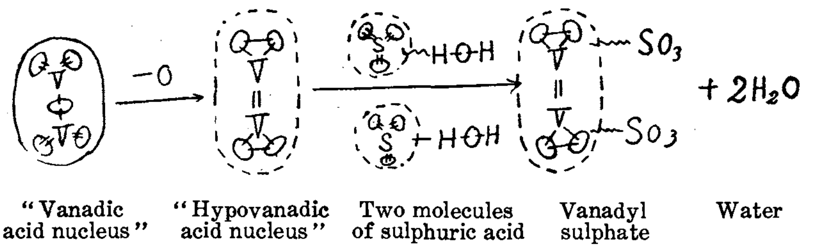
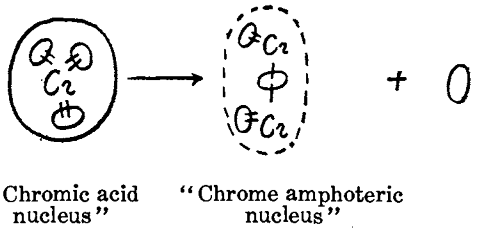
(1) Loc. cit.

respectively being finally produced. In these cases, the electrical displacement produced on the formation of "Per-acids" is so remarkable that the constraints upon some of the electrons are loosened over a definite range and the "Nuclei" suffer such fundamental alterations as mentioned above. The phenomena will most conveniently be represented by the following scheme.

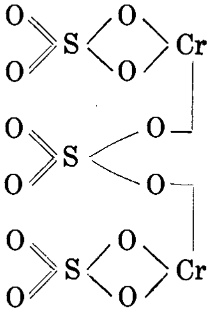


.. (3)



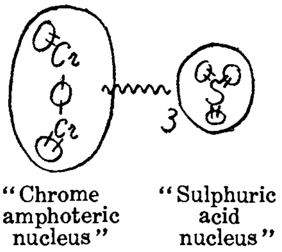
.... (4)

Such group as is shown in the right hand side of (4) is called "Amphoteric Nucleus." Reviewing from the standpoint of "Induction valence," such a salt as chromic sulphate which is readily hydrolized must be considered from a different point of view. The constitutional formula commonly given to chromic sulphate is represented as follows.



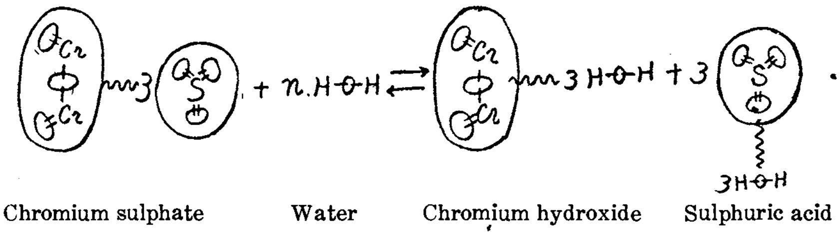
.... (5)

But by (5), the readiness with which this salt is hydrolized can hardly be explained. The "Induction valence theory," therefore, substitutes (6) for (5)



.... (6)

Then the phenomenon of hydrolysis will be represented by the following,



.. (7)

It is clear that (7) explains the phenomenon very easily. The fact that Al and Cr are not readily deposited from its salt solution by electrolysis will also be conveniently explained by considering the presence of such a "Nucleus."

Now, a consideration will be given upon the case of Mo whose atomic weight is larger than the preceding case. In this case, the constraints upon the electrons is firm and strong as is known from the fact that MoO_3 is colourless. The electrical displacement due to "Induction" is accordingly small and the resulting "Per-acid" is yellow in colour and more stable than those of V and Cr.

The case of U will next be considered. As the mass of the "Uranic acid nucleus" is large, it is easily understood that the "Nucleus" will not be readily induced by the inductor as has been already explained in Postulate II. This is the reason why the freedom of hydrogen peroxide is largest in the case of "Per-uranic acid." The inertia to "Electrical induction" in this case, however, must be considered large, and the resulted "Per-acid" stable.

Finally, an explanation will be given upon the diversity of the compositions of "Per-acids" isolated. As has been mentioned already, the combination of "Acid nucleus" with hydrogen peroxide is accomplished by "Induction valence." It is, therefore, partly dependent on the dielectric constant of the medium, and a different medium will give a different dielectric constant. The diversity of the compositions is, therefore, nothing but a natural consequence of the above reason. This is also the case that there exist various kinds of phosphoric acid.

By the descriptions given above the present author believes that the true aspects of his "Acid nucleus theory" which explains the true natures of "Oxy-acids" or "Per-acids" have been rendered clear. He is also eager to extend his theory to the other problems in chemistry in the near future.

Summary.

1. Starting from three postulates, the presence of "Acid nuleus" has been considered and a new idea "Induction valence" also introduced.

2. That "Oxy-acids" and "Per-acids" are nothing but "Acid nuclei" combined with water or hydrogen peroxide by means of "Induction valence" has been rendered clear.

In conclusion, the author wishes to acknowledge his obligations to Profs. M. Kobayashi, F. Ishikawa and S. Mitsukuri in the Institute of Chemistry, Faculty of Science for their useful suggestions and Prof. T. Murakami, in the Institute of Metallurgy, Faculty of Engineering for the encouragement given to him.

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THE SOLUBILITIES OF SILVER SALTS.

By Kosaku MASAKI.

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During the progress of work in the author's laboratory on the cyanide complex radical of metals, there arose a need for the data on the solubilities of cyanide and thiocyanate of metals. Numerous investigators have reported on the solubilities of cyanide, thiocyanate and other salts of metals in water. But the results reported by them are not in good agreement one another. The author measured, at first, the solubilities in water of thiocyanate, bromide, cyanide and carbonate of silver.

The data obtained by previous investigators are shown in the following table.

Table 1.

Solubilities of Silver Salts in Water (moles per liter).

Salts	Temp.	Solubility	Year	Observer
AgSCN	25°C.	1.08×10^{-6}	1903	Kuster and Thiel(1)
	25	1.25×10^{-6}	1903	Abegg and Cox(2)
	25	1.20×10^{-6}	1908	Hill(3)
	25	$1{\cdot}08\times10^{-6}$	1912	Kirschner(4)
	20	0.77×10^{-6}	1903	Böttger(5)
AgBr	25	8.8×10^{-7}	1908	Hill(3)
	25	6.6×10^{-7}	1894	Goodwin(6)
	25	8.1×10^{-7}	1900	Thiel(7)
	18	2.0×10^{-6}	1893	Kohlrausch and Rose(8)
	13	1.8×10^{-6}	1893	Holleman(9)
AgCN	25	2.22×10^{-6}	1904	Lucas(10)
	19.96	1.64×10^{-6}	1903	Böttger(5)
	17.5	3.17×10^{-7}	1903	Abegg and Cox(2)
Ag_2CO_3	25	1.16×10^{-4}	1909	Spencer and Le Pla(11)
	25	1.52×10^{-4}	1903	Abegg and Cox(2)

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(1) *Z. anorg. Chem.*, **33** (1903), 139.
(2) *Z. physik. Chem.*, **46** (1903), 11.
(3) *J. Am. Chem. Soc.*, **30** (1908), 74.
(4) *Z. physik. Chem.*, **79** (1912), 245.
(5) *Z. physik. Chem.*, **46** (1903), 603.
(6) *Z. physik. Chem.*, **13** (1894), 645.
(7) *Z. anorg. Chem.*, **24** (1900), 57.
(8) *Z. physik. Chem.*, **12** (1893), 139, 241.
(9) *Z. physik. Chem.*, **12** (1893), 139, 241.
(10) *Z. anorg. Chem.*, **41** (1904), 198.
(11) *Z. anorg. Chem.*, **65** (1909), 14.

Experimental. Silver thiocyanate, bromide, cyanide and carbonate were prepared from the dilute solutions of the corresponding potassium salts by precipitating with purified silver nitrate. The potassium salts were of Kahlbaum and purified by recrystallization before being used. The precipitated silver salts were further purified by washing with conductivity water. The conductivity water which was used in the experiment had a specific conductance of 1.2×10^{-6}. The works have been done in the dark room.

The solubilities have been measured by the potentiometric method. The cell used were of ordinary form composed of the electrodes of pure silver wires, 0.01 mol silver nitrate solution and the saturated solution of silver salts which is to be measured. The saturated solution of ammonium nitrate has been used as the junction liquid. Thus:

(1) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | AgSCN in 0.1N.KSCN | Ag
(2) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | AgBr in 0.1N.KBr | Ag
(3) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | AgCN in 0.01N.KCN | Ag
(4) Ag | 0.01N.$AgNO_3$ | NH_4NO_3 (sat.) | Ag_2CO_3 in 0.1N.Na_2CO_3 | Ag

All the electromotive force measurements were done after the cells had stood in a thermostat the temperature of which was kept constant within 0.1° for about one or two hours to attain equilibrium as indicated by a constancy of electromotive force. For the measurements a potentiometer and a D.L. type mirror galvanometer were used.

The electromotive force of the cells at 18°C. is given by the following equation, the transport number of anion being assumed to be 0.53.

$$e=0.53\times2\times0.058\ \log\frac{0.01a}{x}$$

The degree of ionization of silver nitrate in 0.01N. solution, a, is 0.93 at 18°C. x is the concentration of silver ion in the 0.1N. solution of potassium thiocyanate, bromide or carbonate and in the 0.01N. solution of potassium cyanide.

The concentrations of the thiocyanate, bromide and carbonate ions are assumed to be 0.01 normal, and that of the cyanide ion 0.1 normal.

The observed electromotive forces of the cells and the solubilities of silver salts calculated therefrom are shown in Tables 2, 3, 4 and 5. The concentrations, in these tables, are given in mol per litre.

Table 2.

Ag | 0.01N. $AgNO_3$ | NH_4NO_3 (sat.) | AgSCN in 0.1N. KSCN | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.1 N. KCNS solution	Solubilities of Ag SCN at 18°C.
1	1	0.545	1.2×10^{-11}	1.1×10^{-6}
2	1	0·550	1.0×10^{-11}	1.0×10^{-6}
3	1	0.552	0.9×10^{-11}	0.9×10^{-6}
4	1	0.549	1.1×10^{-11}	1.0×10^{-6}
5	1	0.551	1.0×10^{-11}	1.0×10^{-6}
mean	1	0.549	1.0×10^{-11}	1.0×10^{-6}

Table 3.

Ag | 0.01N. $AgNO_3$ | NH_4NO_3 (sat.) | AgBr in 0.1N. KBr | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.1 N. KBr solution	Solubilities of Ag Br at 18°C.
1	2	0.570	4.9×10^{-12}	7.0×10^{-7}
2	2	0.571	4.8×10^{-12}	6.9×10^{-7}
3	2	0.570	4.9×10^{-12}	7.0×10^{-7}
4	2	0.569	5.2×10^{-12}	7.2×10^{-7}
5	2	0.571	4.8×10^{-12}	6.9×10^{-7}
mean	2	0.570	4.9×10^{-12}	7.0×10^{-7}

Table 4.

Ag | 0.01N. $AgNO_3$ | NH_4NO_3 (sat.) | AgCN in 0.01N. KCN | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.01 N. KCN solution	Solubilities of Ag CN at 18°C.
1	2	0.572	4.5×10^{-12}	2.1×10^{-7}
2	2	0.571	4.8×10^{-12}	2.2×10^{-7}
3	2	0.572	4.5×10^{-12}	2.1×10^{-7}
4	2	0.573	4.4×10^{-12}	2.1×10^{-7}
5	2	0.571	4.8×10^{-12}	2.2×10^{-7}
mean	2	0.571	4.6×10^{-12}	2.1×10^{-7}

Table 5.

Ag | $0.01N\text{-}AgNO_3$ | NH_4NO_3 (sat) | Ag_2CO_3 in $0.1N\text{-}Na_2CO_3$ | Ag

No. of expt.	Elapsed time in hour	E. m. f. (volts)	Concentrations of silver ion in 0.1 N. Na_2CO_3 solution	Solubilities of Ag_2CO_3 at 18°C.
1	2	0.204	4.6×10^{-6}	1.2×10^{-4}
2	2	0.205	4.5×10^{-6}	1.2×10^{-4}
3	2	0.204	4.6×10^{-6}	1.2×10^{-4}
4	2	0.206	4.3×10^{-6}	0.9×10^{-4}
5	2	0.206	4.3×10^{-6}	0.9×10^{-4}
mean	2	0.205	4.5×10^{-6}	1.1×10^{-4}

Summary.

The solubilities of silver cyanide, thiocyanate, bromide and carbonate in water at 18°C. have been determined by the electromotive force measurements, and obtained the values:

Silver cyanide:	2.1×10^{-7}	mol per litre
Silver thiocyanate:	1.0×10^{-6}	,, ,, ,,
Silver bromide:	7.0×10^{-7}	,, ,, ,,
Silver carbonate:	1.1×10^{-4}	,, ,, ,,

The writer wishes to express his thanks to Professor J. Sameshima of the Tokyo Imperial University for the kind advice.

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SYNTHESE DES N-METHYLOXYNAPHTINDOLCHINONS UND N-METHYLNAPHTHOISATINCHINONS.

Von **Zenjiro KITASATO** und **Chuzaburo SONE**.
(Unter Beteiligung von Hideo SHISHIDO.)

Eingegangen am 10. November 1930. Ausgegeben am 28. Dezember 1930.

Im Jahre 1927 hat der Eine von uns (Kitasato) aus der Stammrinde von Nandina domestica, einem einheimischen Strauch von der Familie Berberidaceae, eine tief blaue krystalline Base Nandazurin (Schmp. über 350°)⁽¹⁾

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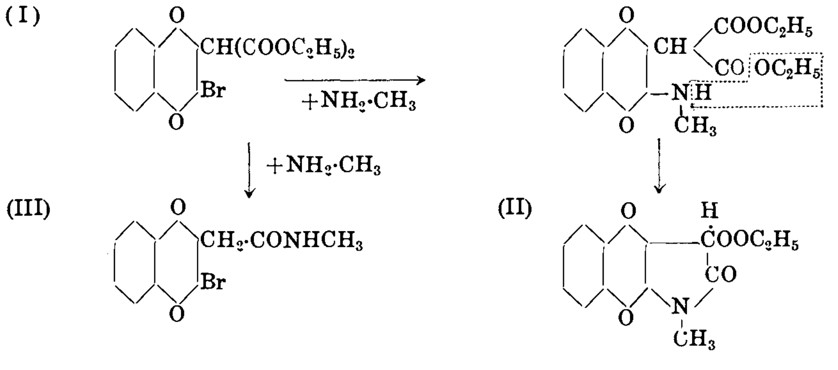
(1) *Acta Phytochimica*, **3** (1927), 180.

isoliert. Diese Substanz ist äusserst schwer löslich in organischen Lösungsmitteln und kann nur aus heissem Nitrobenzol, Anilin oder viel Aethylalkohol umkrystallisiert werden. Sie färbt sich durch konzentrierte Schwefelsäure schön violettrot und bildet mit Säuren rotbraun gefärbte Salze. Die Elementalanalyse zeigt, dass dem Nandazurin die Bruttoformel, $C_{28}H_{18}O_6N_2.H_2O$ oder $(C_{14}H_9O_3N)_2.H_2O$ zukommt. Wegen der Knappheit der uns zur Verfügung stehenden Menge der Substanz steht die Konstitutionsermittelung noch aus.

Um die Entstehungsbedingungen und Eigenschaften solcher indigoähnlichen Substanzen näher kennenzulernen, haben wir zunächst die vorliegenden Versuche unternommen. Im Jahre 1899 hat C. Liebermann Aethyloxynaphtindolchinon dargestellt⁽¹⁾. Wir haben jetzt nach seiner Methode N-Methyloxynaphtindolchinon synthetisiert. Zu diesem Zwecke wurde zunächst Brom-α-naphthochinon-malonsäure-äthylester (Schmp. 102°) (I) aus 2.3-Dibrom-α-naphthochinon und Malonsäureester dargestellt. Durch Einwirkung von Methylamin auf diesen Brom-α-naphthochinon-malonsäureester wurden zweierlei Substanzen erhalten; die eine ist citronengelber N-Methyl-α-naphtindolinon-carbonsäureäthylester (Schmp. ca. 220°) (II), und die andere, tiefrote Brom-α-naphthochinon-essigsäure-methylamid (Schmp. 165°) (III). Die Reaktion verläuft also in zwei Richtungen; einerseits reagiert Methylamin zuerst mit Brom und schliesst die so substituierte Methylaminogruppe den Ring unter Mitwirkung der einen der Estergruppen (II), und andererseits reagiert Methylamin nicht mit Brom selbst, sondern mit einer der Estergruppen, wobei der Ringschluss zwischen der so entstehenden Säureamidgruppe und dem Bromatom nicht mehr stattfindet (III).



Um den Mechanismus dieser auffallenden Reaktion zu erklären, dabei haben wir einige Experimente ausgeführt. Es hat sich gezeigt, dass der

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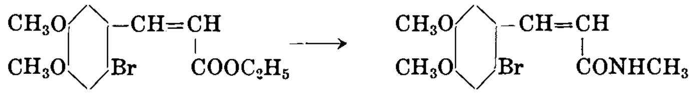
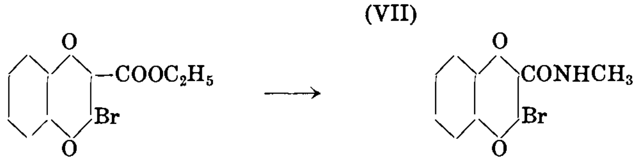
(1) *Ber.*, **32** (1899), 260, 919; **33** (1900), 569.

6-Brom-3.4-dimethoxyzimmtsäureäthylester (Schmp. 114–5°) (IV), dessen Bromatom nicht reaktionsfähig ist, leicht Methylamid (Schmp. 183°) (V) durch Einwirkung von Methylamin bildet, während der Brom-α-naphthochinon-ameisensäureäthylester (Schmp. 119°) (VI), welcher aus 2.3-Dibrom-α-naphthochinon und Ameisensäureester entsteht und ein Atom reaktionsfähigen Brom besitzt, er mit Methylamin das tiefrote Brom-α-naphthochinon-ameisensäure-methylamid (Schmp. 164–5°) (VII) in fast quantitativer Ausbeute gibt. Also in diesem Fall reagiert Methylamin auch gar nicht mit dem reaktionsfähigen Halogenatom, sondern nur mit Estergruppe.

(IV) (V)



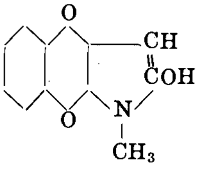
(VI) (VII)



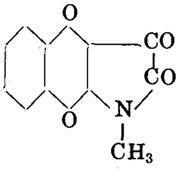
Daraus gehen folgende Tatsachen hervor: (1) wenn das Bromatom nicht reaktionsfähig ist, so reagiert Methylamin natürlich nur mit Ester, um ein Methylamid zu bilden (V); (2) auch wenn das Halogenatom reaktionsfähig ist, reagiert Methylamin viel leichter mit Estergruppe als mit dem Halogenatom und es entsteht ebenfalls nur Methylamid (VII). Nur in dem Falle, webei ein neuer fünf- oder sechsgleidriger Ring entstehen kann, reagiert Methylamin sehr leicht mit diesem reaktionsfähigen Halogenatom (vergl. II).

Wird der oben erwähnte N-Methyl-α-naphtindolinon-carbonsäureester (II) mit Alkali unter Einleiten von Luft gekocht, so entsteht eine tiefblaue Lösung und nach Ansäuerung mit Essigsäure erhält man schöne tiefblaue Krystalle von N-Methyloxynaphtindolchinon (Schmp. über 300°) (VIII), der durch Oxydation mit Salpetersäure N-Methylnaphtisatinchinon (IX) liefert. Dieses N-Methyloxynaphtindolchinon steht zwar in einigen Eigenschaften sehr nahe dem Nandazurin, obwohl es freilich keine Base wie das letztere ist.

(VIII)



(IX)



Beschreibung der Versuche.

1. **N-Methyl-α-naphtindolinon-carbonsäureäthylester** (II). Der in unseren Versuchen verwendete Brom-α-naphthochinon-malonsäureester (Schmp. 102°) (I) wurde nach der von C. Liebermann⁽¹⁾ angegebenen Methode aus 2.3-Dibrom-α-naphthochinon (Schmp. 218°)⁽²⁾ und Malonsäureäthylester hergestellt. 5 gr. dieses Brom-α-naphthochinon-malonester werden in 15 gr. absolutem Alkohol suspendiert, mit 5 gr. 33% alkoholischer Lösung von Methylamin versetzt und über Nacht stehen gelassen. Die abgeschiedenen Krystalle werden filtriert und mit Alkohol nachgewaschen. Dann werden sie auf dem Filter in Wasser aufgeschwemmt, wobei sie zum Teil allmählich in schön tiefblaue Lösung gehen und auf dem Filter hübsch rote Krystalle zurückbleiben. Auf Zusatz von Essigsäure zu dieser tiefblauen wässrigen Lösung fällen voluminöse, citronengelbe Krystalle aus. Sie werden aus viel heissem Alkohol umkrystallisiert, woraus sie in citronengelben Nadeln herauskommen, welche bei 190° sich violettblau zu verändern beginnen und bei ca. 220° zersetzt werden.

Anal. 4.454 mg. Subst. gaben 0.183 c.c. N_2 bei 27° und 766.3 mm. (Gefunden: N=4.55%. Berechnet für $C_{16}H_{13}NO_5$ (299): N=4.68%)

Es ist ziemlich leicht löslich in heissem Alkohol, unlöslich in Wasser und Säuren, dagegen löslich in Alkalien mit tiefblauer Farbe und wird durch Säuren wieder ausgefällt.

2. **Brom-α-naphthochinon-essigsäure-methylamid** (III). Die oben erwähnten hübsch roten Krystalle auf dem Filter werden aus kochendem Alkohol umkrystallisiert, wodurch sie in feuerroten Prismen vom Schmp. 165° erhalten werden.

Anal. 5.305 mg. Subst. gaben 3.244 mg. AgBr; 5.178 mg. Subst. gaben 0.22 c.c. N_2 bei 28° und 756 mm.; 4.127 mg. Subst. gaben 0.00 mg. AgJ. (Gefunden: Br=26.03; N = 4.61; OCH_3 = 0.00%. Berechnet für $C_{13}H_{10}NO_3Br$ (308): Br = 25.97; N = 4.55; OCH_3=0.00%).

Die Substanz ist unlöslich in Wasser, Alkalien und löslich in Alkohol. Ihre rote Farbe verändert sich durch Säure in gelb und kehrt durch Alkali wieder in Rot zurück.

3. **6-Brom-3.4-dimethoxyzimmtsäure-methylamid** (V). 6-Bromveratrumaldehyd wird mit Malonsäure in Pyridinlösung unter Zusatz von wenig

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(1) *Loc. cit.*

(2) Miller, *J. Russ. Phys. Chem. Ges.*, **16** (1884), 419.

Piperidin erhitzt. Dabei entsteht 6-Brom-3.4-dimethoxyzimmtsäure, welche aus Alkohol in Nadeln vom Schmp. 244° umkrystallisiert (Gef.: C=45.77; H=4.02. Ber. für $C_{11}H_{11}O_4Br$: C=45.9; H=3.8%). 20 gr. dieser Säure werden mit 100 gr. absolutem Alkohol und 10 gr. konzentrierter Schwefelsäure 4–5 Stunden auf dem Wasserbad unter Rückfluss gekocht, bis alles in die Lösung geht. Man filtriert die Lösung noch heiss, woraus nach dem Erkalten farblose glänzende Blättchen von 6-Brom-3.4-dimethoxyzimmtsäureäthylester (IV) vom Schmp. 114–5° sich ausscheiden. Dieser Ester ist sehr schwer löslich in Alkohol.

Anal. 6.197 mg. Subst. gaben 11.256 mg. CO_2 und 2.754 mg. H_2O. (Gefunden. C=49.46; H=4.95%. Berechnet für $C_{13}H_{15}O_4Br$ (315): C=49.52; H=4.76%).

Die Suspension von 10 gr. des Esters in 20 gr. 33% alkoholischer Lösung von Methylamin wird 2 Tage stehen gelassen, bis eine völlige Lösung stattfindet. Nach einem weiteren Tage beginnen Krystalle von 6-Brom-3.4-dimethoxyzimmtsäure-methylamid (V) sich abzuscheiden. Sie werden aus Alkohol umgelöst, woraus sie in farblosen kurzen Prismen vom Schmp. 183° auskrystallisieren.

Anal. 6.044 mg. Subst. gaben 9.333 mg. AgJ; 4.698 mg. Subst. gaben 0.206 c.c. N_2 bei 31° und 757 mm. (Gefunden: OCH_3=20.43; N=4.69%. Berechnet für $C_{12}H_{14}NO_3Br$ (300): OCH_3=20.66; N=4.67%).

4. **Brom-α-naphthochinon-ameisensäureäthylester** (VI). 2.5 gr. 2.3-Dibromnaphthochinons werden in 25 c.c. absolutem Alkohol suspendiert und mit einer Lösung von 2.7 gr. Ameisensäureäthylester in 15 c.c. Natriumalkoholat (0.88 gr. Natrium in 15 c.c. absolutem Alkohol) versetzt. Die Flüssigkeit wird mit 50 c.c. Wasser verdünnt, und die dabei abgeschiedenen Krystalle werden gesammelt und mit Wasser gewaschen. Die Substanz krystallisiert aus Alkohol in gelben Nadeln vom Schmp. 119°.

Anal. 3.686 mg. Subst. gaben 6.860 mg. CO_2 und 0.976 mg. H_2O; 3.206 mg. Subst. gaben 1.943 mg. AgBr. (Gefunden: C = 50.75; H = 2.94; Br = 25.79%. Berechnet für $C_{13}H_9O_4Br$ (309): C=50.48; H=2.91; Br=25.89%).

Die Substanz ist etwas löslich in heissem Alkohol und schwer löslich in kaltem Alkohol und Äther und unlöslich in Wasser. Sie gibt rote Farbenreaktion mit Schwefelsäure und mit Alkali eine tiefe rote Verbindung.

5. **Brom-α-naphthochinon-ameisensaure-methylamid** (VII). 2 gr. Brom-α-naphthochinon-ameisensäureester werden mit 5 gr. 33% alkoholischen Methylaminlösung über Nacht digeriert. Die abgeschiedenen tiefroten Krystalle werden mit Alkohol gewaschen und aus viel heissem Alkohol umkrystallisiert. Prachtvolle tiefrote Nadeln vom Schmp. 164–5°.

Anal. 4.050 mg. Subst. gaben 7.266 mg. CO_2 und 1.108 mg. H_2O; 4.427 mg. Subst. gaben 0.2 c.c. N_2 bei 30° und 759.5 mm. (Gefunden: C = 48.93; H = 3.04; N = 4.87%. Berechnet für $C_{12}H_8NO_3Br$ (294): C = 48.98; H = 2.72; N = 4.76%).

Die Substanz ist schwer löslich in kaltem Alkohol, leicht löslich in Alkalien und wird durch Säure wieder ausgefällt.

6. **N-Methyloxynaphtindolchinon** (VIII). 2 gr. des oben beschriebenen N-Methyl-α-naphtindolinon-carbonsäureester (II) werden in 100 c.c. 5% Natronlauge gelöst und mit 20 c.c. 20% Natronlauge unter Durchleiten von Luft-Strome 20 Minuten gekocht. Beim Ansäuren gibt die blaue Lösung reichliche Menge vom tiefblauen Niederschlag, welche durch Umfällen aus alkalischen Lösung mit Säure gereinigt werden. Tiefblaue kupferglänzende krystallinische Substanz vom Schmp. über 300°.

Anal. 2.908 mg. Subst. gaben 7.385 mg. CO_2 und 0.988 mg. H_2O; 3.845 mg. Subst. gaben 0.226 c.c. N_2 bei 31° und 756 mm. (Gefunden: C = 69.26; H = 3.77; N = 6.28%. Berechnet für $C_{13}H_9O_3N$ (227): C = 68.72; H = 3.96; N = 6.16. Berechnet für $(C_{13}H_8O_3N)_2$ (452): C = 69.02; H = 3.54; N = 6.19%).

Diese Substanz ist unlöslich in Wasser, verdünnten Säuren, Eisessig und organischen Lösungsmitteln, während sie in Chloroform mit violetter Farbe und in Alkalien mit tiefblauer Farbe löslich ist. Sie zeigt mit konzentrierter Schwefelsäure rotviolette Farbe und diese Farbe verändert sich durch Salpetersäure in gelbliches Rot.

7. **Oxydation der N-Methyloxynaphtindolchinon: Entstehung von N-Methylnaphtisatinchinon** (IX). 0.5 gr. des N-Methyloxynaphtindolchinon werden in 5 gr. konzentrierter Schwefelsäure gelöst und mit 3 c.c. verdünnter Salpetersäure (1 : 2) tropfenweise unter Eiskühlung und stetem Umrühren versetzt. Nun giesst man das Reaktionsgemisch auf 50 gr. Eisstücken und die dadurch abgeschiedenen Krystalle werden mit Wasser und Alkohol gewaschen. Durch Umkrystallisieren aus Eisessig stellt das N-Methylnaphtisatinchinon tiefrote (unterm Mikroskop orangerot) Blättchen vom Schmp. 268° dar. Ausbeute 70%. Die Analyse und Eigenschaften zeigen, dass es ohne Zweifel das N-Methylnaphtisatinchinon (IX) vorliegt.

Anal. 4.145 mg. Subst. gaben 9.844 mg. CO_2 und 1.039 mg. H_2O; 4.890 mg. Subst. gaben 0.262 c.c. N_2 bei 28° und 764 mm. (Gefunden: C = 64.77; H = 2.86; N = 5.88%. Berechnet für $C_{13}H_7O_4N$ (241): C = 64.73; H = 2.90; N = 5.81%).

Die Substanz ist unlöslich in Wasser, Alkohol und löslich in Chloroform, Eisessig. Ferner löst sie sich in Alkalien mit blauer Farbe und wird auf Zusatz von Säuren wieder ausgefällt.

8. In folgender Tabelle werden einige Eigenschaften des Nandazurins, N-Methyloxynaphtindolchinons und des Indigos vergleichshalber zusammengestellt.

	Nandazurin	N-Methyloxynaphtindolchinon	Indigo
Farbe der Krystalle	tiefblau, metallglänzend	tiefblau, metallglänzend	tiefblau, metallglänzend
Schmelzpunkt.	über 350°	über 350°	über 350°
In Chloroform.	etwas löslich	löslich	etwas löslich
In Eisessig.	löslich	unlöslich	löslich
In anderen organ. Lösungsmitteln.	äusserst schwer löslich	äusserst schwer löslich	äusserst schwer löslich
In Wasser.	unlöslich	unlöslich	unlöslich
In verd. Alkalien.	unlöslich	löslich	unlöslich
Mit verd. Säuren.	rotbraune Salze bildend	kein Salz bildend	kein Salz bildend
Mit konzentrierter Schwefelsäure.	violettrote Färbung	rotviolette Färbung	blaue-grüne Färbung
Mit Salpetersäure	gelbe Färbung	gelbrote Färbung	gelbe Färbung

Chem. Laboratorium des
Kitasato Institutes in Tokyo.

SPECTROCHEMICAL STUDY OF AMINO-ACID ANHYDRIDES.(1)

IV. LIGHT ABSORPTION OF DERIVATIVES OF AZLACTONE, DIKETOPIPERAZINE, HYDANTOIN AND THIOHYDANTOIN.

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In the foregoing reports,(2) the ultra-violet absorptions of derivatives of diketopiperazines, azlactones and hydantoins were described, and those experiments were discussed from the standpoint of chemical constitution. In this paper, the light absorption of some derivatives of benzal azlactone,

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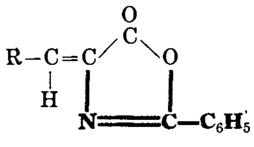
(1) Read before the Chemical Society of Japan, April 3rd, 1930.

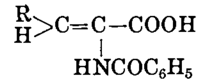
(2) For the 1st, 2nd and 3rd reports, see this Bulletin, **1** (1926), 71; **2** (1927), 324; and **4** (1929), 202.

diketopiperazine and hydantoin, and, further, those of thiohydantoin and the hydrolysis products of azlactones is described. The substances examined are as follows:

Azlactone of *o*-acetoxybenzal hippuric acid
Azlactone of *m*-acetoxybenzal hippuric acid
Azlactone of *p*-acetoxybenzal hippuric acid
Azlactone of *o*-methoxybenzal hippuric acid
Azlactone of *m*-methoxybenzal hippuric acid
Azlactone of *p*-methoxybenzal hippuric acid

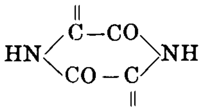


α-Benzoylamino-cinnamic acid
α-Benzoylamino-β-furyl-acrylic acid
α-Benzoylamino-*o*-oxycinnamic acid
α-Benzoylamino-*m*-oxycinnamic acid
α-Benzoylamino-*p*-oxycinnamic acid
α-Benzoylamino-*o*-methoxycinnamic acid
α-Benzoylamino-*m*-methoxycinnamic acid
α-Benzoylamino-*p*-methoxycinnamic acid

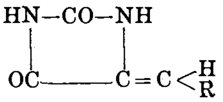


$$\genfrac{}{}{0pt}{}{R}{H}\!>\!C=\underset{\displaystyle HNCOC_6H_5}{\underset{|}{C}}-COOH$$

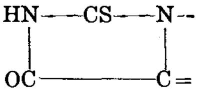
Dibenzal diketopiperazine
Difurfural diketopiperazine



4-Benzal hydantoin
4-Furfural hydantoin



2-Thio-hydantoin
2-Thio-3-acetyl-hydantoin
2-Thio-3-benzoyl-hydantoin
2-Thio-3-acetyl-4-benzyl-hydantoin
2-Thio-4-benzyl-hydantoin
2-Thio-4-(*p*-oxybenzyl)-hydantoin
2-Thio 4-benzal-hydantoin
2-Thio-4-furfural-hydantion



It was remarked in the preceeding report that the azlactone of furfural hippuric acid was more bathochromic and, at the same time, more hyperchromic than the benzal azlactone. Such relation had also been observed by Dr. I. Kasiwagi(1) in his study of furyl ketones. In the present studies, the furfural derivatives of diketopiperazine, hydantoin and thiohydantoin are found to be more bathochromic and hyperchromic than the correspond-

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(1) This Bulletin, **1** (1926), 150.

ing benzal derivatives (Figs. 1, 2 and 3). In the condensation products of hippuric acid and the three monoxybenzaldehydes, the absorption maxima

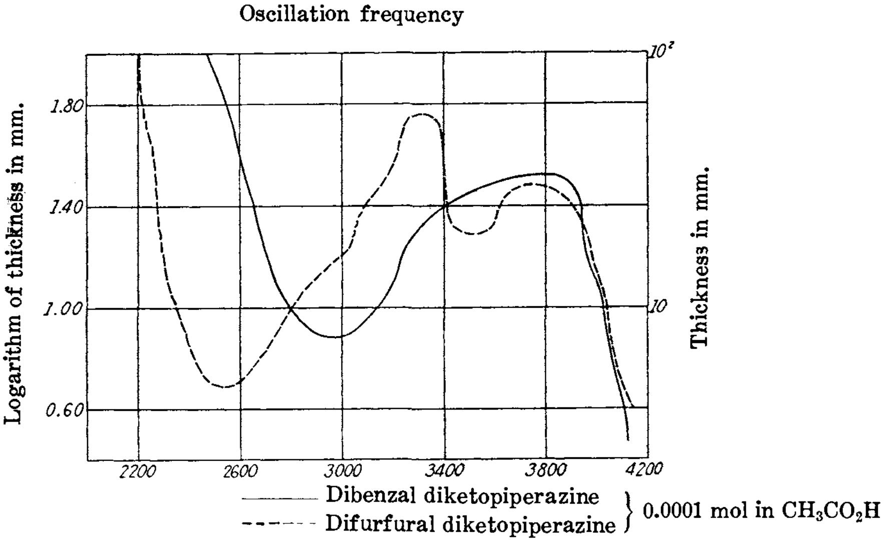


Fig. 1.

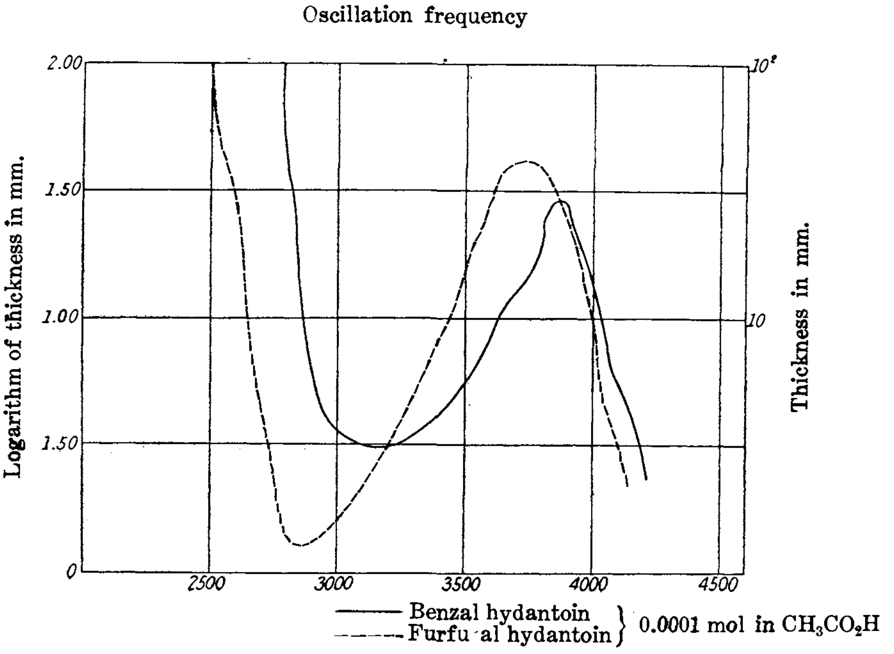


Fig. 2.

of azlactones of benzal, *o*-, *m*-, and *p*- acetoxybenzal hippuric acids are found nearly at the same wave-length of 3580 Å (Fig. 4).

Of the azlactones of three methoxybenzal hippuric acids, the *o*- and *p*- methoxy compounds show the identity in the absorption maxima, and the meta compound is less bathochromic than others (Fig. 5).

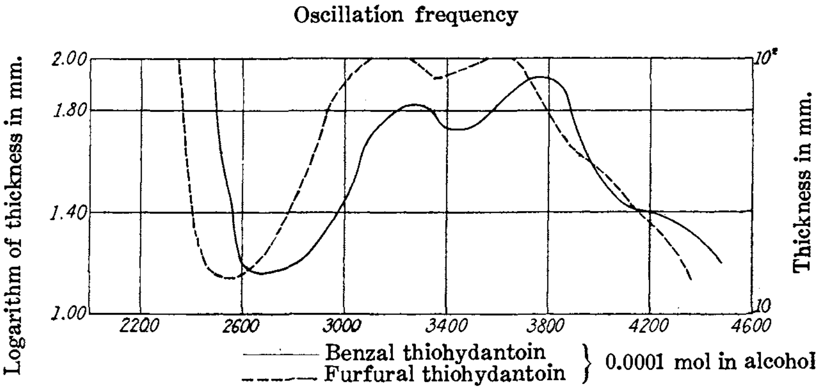


Fig. 3.

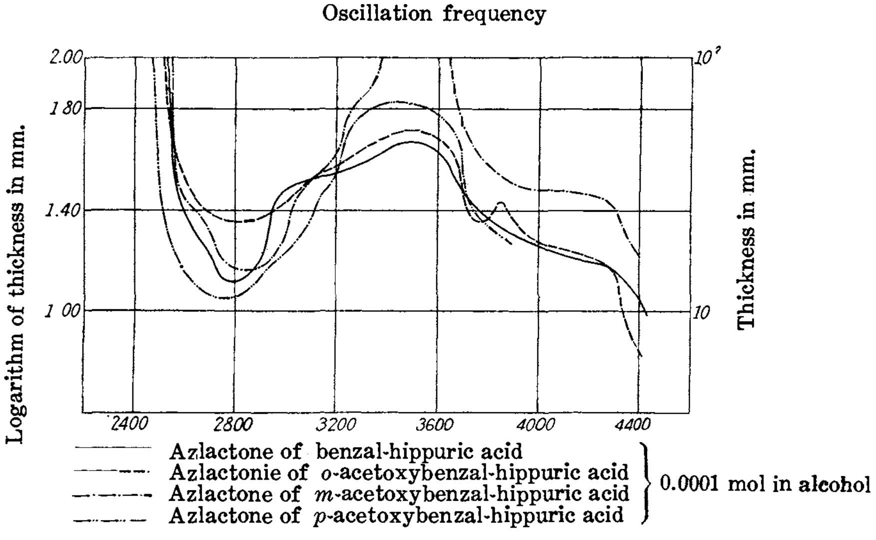


Fig. 4.

Azlactones are easily hydrolysed by dilute caustic soda to open the ring and form α-benzoylamino-β-aryl-acrylic acid, and the products are colourless and far less bathochromic than the corresponding azlactones (Figs. 6, 7, 8 and 9). It may be due to the rearrangement of the chromophore (substituted azomethine) group $-N=C=$ in the azlactones, to the non-absorbing benzoylamino group in the course of hydrolysis.

Of these α-benzoylamino-β-aryl-acrylic acids, the β-furyl acid is more bathochromic than the β-phenyl acid. Thus another example is added to the rule described above. For three hydroxy- and three methoxy-α-benzoylamino-cinnamic acids, the substitution of methyl group in the hydroxy group is not found essential to the light absorption (Figs. 7, 8 and 9).

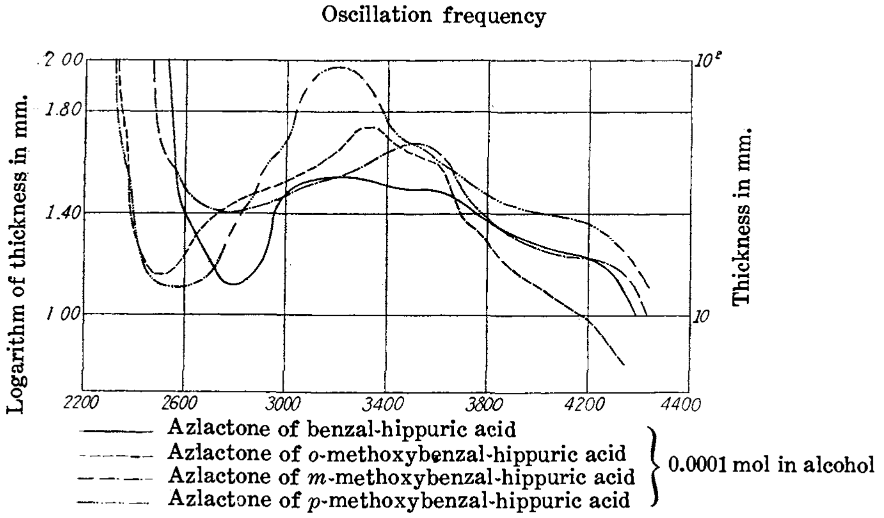


Fig. 5.

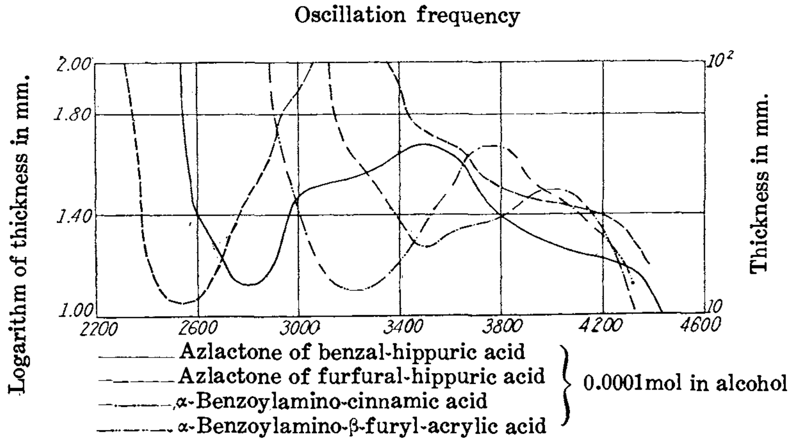


Fig. 6.

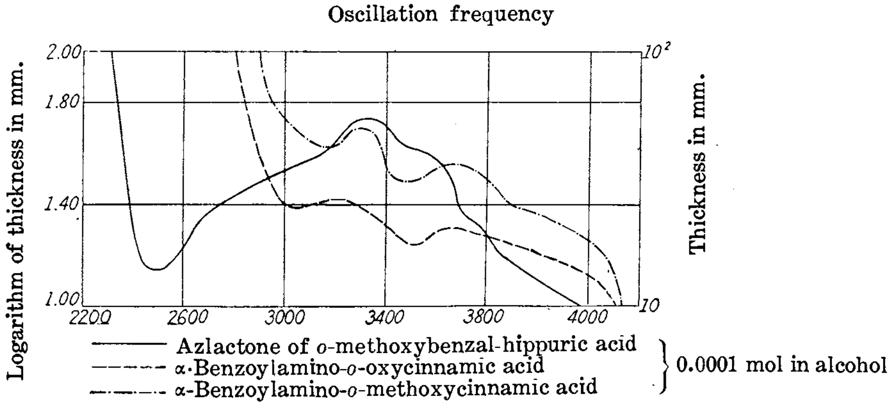


Fig. 7.

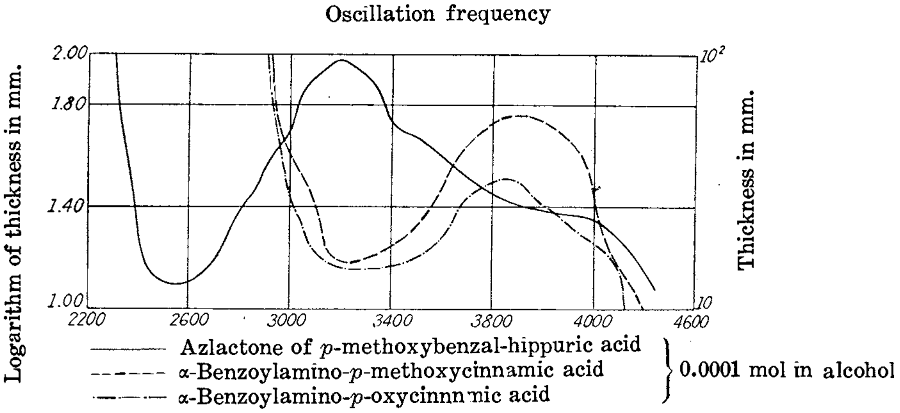


Fig. 8.

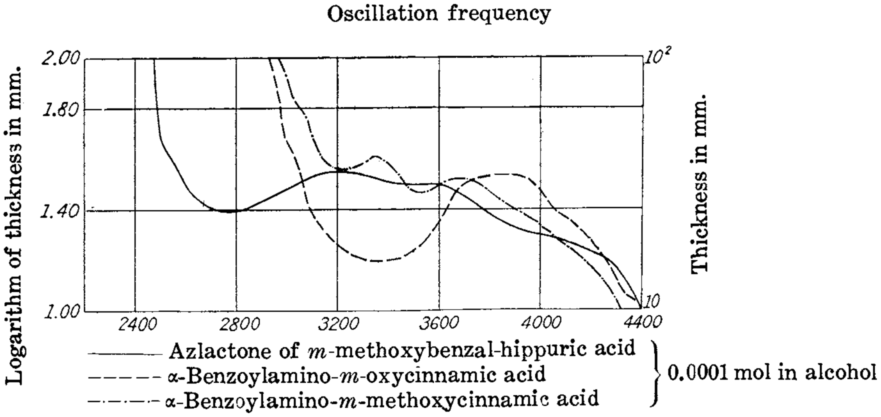
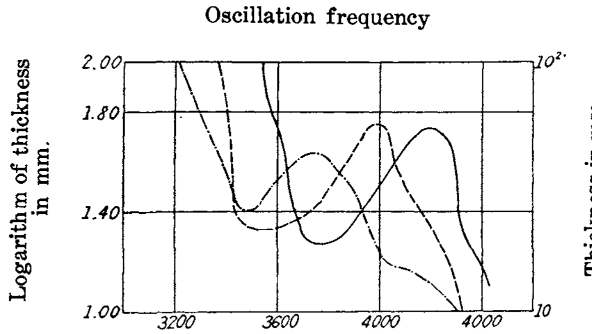
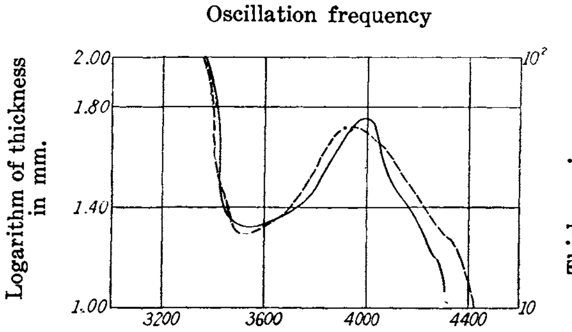


Fig. 9.



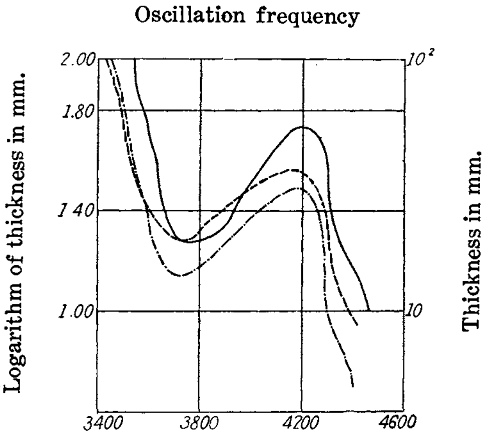
2-Thiohydantoin ——— }
2-Thio-3-acetyl-hydantoin – – – – } 0.0001 mol in alcohol
2-Thio-3-benzoyl-hydantoin —·—·— }

Fig. 10.



2-Thio-3-acetyl-hydantoin ——— }
2-Thio-3-acetyl-4-benzyl-hydantoin – – – – } 0.0001 mol in alcohol

Fig. 11.



2-Thio-hydantoin ——— }
2-Thio-4-(*p*-oxybenzyl)-hydantoin – – – – – } 0.0001 mol in alcohol
2-Thio-4-benzyl-hydantoin —·— —·— }

Fig. 12.

Thiohydantoins were first synthesized from amino acids by Prof. S. Komatsu.(1) In the present studies, the method is modified a little, and better results in the yield and the purity of the product is thereby obtained. The introduction of benzoyl or acetyl group in the position 3 gives a little bathochromic effect, and the interchange of these groups has only a slight influence on the absorption maxima (Fig. 10). 2-Thiohydantoin and its derivatives are more bathochromic owing to the existence of thiocarbonyl group =CS which is a more effective chromophore group than the carbonyl. The introduction of benzyl or oxybenzyl group in the position 4 of the hydantoin nucleus exerts almost no influence on the behaviour of light absorption (Figs. 11 and 12).

Experimentals.

The spectrograms were taken with the aid of Adam Hilger's quartz spectrograph; iron arc was used as the light source and the solutions were illuminated in the Baly tube provided with quartz plates. Alcohol was generally used as the solvent, but, in the case of the material insoluble in alcohol, glacial acetic acid was used instead. The concentrations are noted in the feet of the diagrams.

α-Benzoylamino-cinnamic acid. Benzal azlactone (2 gr.) was boiled in 200 c.c. of 0.5% caustic soda for 2 hours, filtered when cold and slightly acidified with hydrochloric acid.(2) The product was recrystallized from ten fold quantity of alcohol; m.p. 225–227° under decomposition (Erlenmeyer; 210–228° under decomposition).

α-Benzoylamino-β-furyl-acrylic acid.(3) Furfural azlactone was treated in the same manner as the preceeding; m.p. 211–212.5° under decomposition.

Azlactone of o-acetoxybenzal hippuric acid and α-Benzoylamino-o-oxycinnamic acid. The azlactone was prepared by the condensation of hippuric acid and salicyl aldehyde in the presence of sodium acetate and acetic anhydride(4). By this method, beside the azlactone, benzoylamido-coumaranone was produced. According to Erlenmeyer and Stadlin, these products were to be easily separated by the mere recrystallisation from ethyl alcohol. The procedure was literally followed, but on microscopical observation of the azlactone, this was found to contain not a small quantity of white needles of the coumaranone and on further recrystallisation from alcohol, the purification was accompanied by the loss of material and was

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(1) *J. Chem. Soc. Japan*, **31** (1910), 688.
(2) E. Erlenmeyer, jun., *Ann.*, **275** (1893), 10.
(3) E. Erlenmeyer, jun. and W. Stadlin, *Ann.*, **337** (1904), 284.
(4) E. Erlenmeyer, jun. and W. Stadlin, *Ann.*, **337** (1904), 290.

found rather difficult. Thus the method of separation was modified. The crude mixture was dissolved in benzene and to the solution, petroleum ether was added. The coumaranone first crystallized out and was separated by filtration; on addition of further quantity of petroleum ether to the filtrate, the azlactone was separated. This contained still a small quantity of coumaranone but the latter was easily removed by agitating the liquid and then decanting the supernatant suspension. The azlactone thus purified, on recrystallisation from alcohol, melted at 158.5° and showed no change of the melting point on further recrystallisation. (According to Erlenmeyer and Stadlin the melting point was 137–138°).

Anal. Found: C=70.1; H=4.40; N=4.58, 4.60%. Calc. for $C_{18}H_{13}O_4N$: C=70.4; H=4.27; N=4.56%.

On hydrolysis of the azlactone with dilute caustic soda, benzoylamino-coumaric acid was produced and after recrystallisation from alcohol, the melting point was 199.5° under decomposition (Erlenmeyer: 185.5)⁽¹⁾.

Anal. Found: N=5.13%. Calc. for $C_{16}H_{13}O_4N$: N=4.95%.

Azlactone of *o*-methoxybenzal hippuric acid and *α*-Benzoylamino-*o*-methoxycinnamic acid. One mol of *o*-methoxy-benzaldehyde (b.p. 236–240°, prepared from dimethyl sulphate and salicyl aldehyde⁽²⁾), 1 mol of hippuric acid and 1 mol of fused sodium acetate was intimately mixed with 3 mol of acetic anhydride; the mixture was heated for 30 minutes on a water bath. On cooling, the product was treated with large quantity of water, filtered and washed with dilute alcohol. The azlactone was recrystallized from alcohol. Light yellow needles of a little less intense colour than anisal azlactone, melted at 161°.

Anal. Found: N=5.17, 5.16%. Calc. for $C_{17}H_{13}O_3N$: N=5.02%.

The azlactone was hydrolysed with 100 times 1.5% caustic soda by heating for 5 hours on a water bath. The white crystals of benzoylamino-*o*-methoxycinnamic acid which separated on acidifying the hydrolysate, was recrystallized from alcohol; m.p. 208°.

Anal. Found: N=4.95%. Calc. for $C_{17}H_{15}O_4N$: N=4.71%.

Azlactone of *m*-acetoxybenzal hippuric acid and *α*-Benzoylamino-*m*-oxy-cinnamic acid. The azlactone was prepared by the condensation of *m*-oxy-benzaldehyde and hippuric acid; m.p. 148°⁽³⁾ (Erlenmeyer and

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(1) Plöchl and Wolfrum, *Ber.*, **18** (1885), 1183.
(2) Katschalowsky and St. v. Kostanecki, *Ber.*, **37** (1904), 2347, foot-note.
(3) Erlenmeyer, jun. and F. Wittenberg, *Ann.*, **337** (1904), 294.

Wittenberg: 145°); and the acid was obtained by the hydrolysis of the former; m.p. 213–214° (Erlenmeyer and Wittenberg: 204°).

Azlactone of *m*-methoxybenzal hippuric acid and *α*-Benzoylamino-*m*-methoxy-cinnamic acid. The azlactone was prepared according to the procedure of R. Pschorr;⁽¹⁾ the acid was obtained in the usual manner and was recrystallized from dilute alcohol; m.p. 164.5°.

Azlactone of *p*-acetoxybenzal hippuric acid and *α*-Benzoylamino-*p*-oxy-cinnamic acid. The materials were prepared according to the description of Erlenmeyer and Halsey;⁽²⁾ m.p. 177.5° and 231–232° (E. and H.; 172–173° and 228–229°).

Azlactone of *p*-methoxybenzal hippuric acid and *α*-Benzoylamino-*p*-methoxy-cinnamic acid. The materials were prepared according to the procedure of Erlenmeyer and Wittenberg; the melting points were coincident with their description.⁽³⁾

Dibenzal diketopiperazine and Difurfural diketopiperazine. The former was obtained from Dr. T. Sasaki⁽⁴⁾ and the latter was prepared after his method.⁽⁵⁾

4-Benzal hydantoin and 4-Furfural hydantoin. The both substances were prepared, according to the method of Wheeler and Hoffman, benzaldehyde, hydantoin, anhydrous sodium acetate, acetic acid and acetic anhydride being used for the former, and replacing the benzaldehyde with furfural and omitting acetic anhydride for the latter.⁽⁶⁾

2-Thio-3-acetyl-hydantoin and 2-Thio-hydantoin. The former substance was first obtained by Prof. S. Komatsu by the condensation of glycocoll and potassium rhodanate in the presence of acetic acid and acetic anhydride, and the latter also by him by the hydrolysis of the former.⁽⁷⁾ Here, instead of potassium rhodanate, ammonium salt was used and the procedure was a little revised. Ten gr. of glycocoll and 13 gr. of ammonium rhodanate were well pulverised and intimately mixed, to which 50 c.c. acetic anhydride and 5 c.c. acetic acid were added. The mixture was heated on a water bath

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(1) *Ann.*, **391** (1912), 44.

(2) Erlenmeyer, jun. and J. T. Halsey, *Ann.*, **307** (1899), 139.

(3) Erlenmeyer, jun. and Wittenberg, ibid. Dakin reports a little higher melting points, i.e. 158° and 230–232 (not sharp) instead of 156.5° and 225° (*J. Biol. Chem.*, **8** (1910), 11).

(4) T. Sasaki, *Ber.*, **54** (1921), 163.

(5) T. Sasaki, *Ber.*, **54** (1921), 2057.

(6) H.L. Wheeler and C. Hoffman, *Am. Chem. Journ.*, **45** (1911), 371 and 380.

(7) S. Komatsu, *J. Chem. Soc. Japan.*, **31** (1910), 688. T. B. Johnson and H.B. Nicolet, *J. Am. Chem. Soc.*, **33** (1911), 1937.

when content of the flask became clear light yellow liquid. The colour did not change further as when potassium rhodanate was used. In the course of five minutes, the liquid effervesced vigorously and the temperature rose spontaneously as high as 120°. The flask was taken off from the water bath, and when the violent reaction ceased, it was again heated for further ten minutes. The further treatment was the same as Komatsu's. The yield was 16 gr. (ca. 80% of the calculation); m.p. 174–175°. Komatsu, and also Johnson and Nicolet obtained thiohydantoin by evaporating the acetyl- (or benzoyl-) thiohydantoin with concentrated hydrochloric acid on the water bath. The procedure was followed, but always an intensely coloured product was obtained which was difficultly decolourised by recrystallisation from alcohol even with the aid of charcoal. If the acetyl- or benzoyl-thiohydantoin was boiled for 30 minutes with 15 times quantity of concentrated hydrochloric acid, colourless white needles of thiohydantoin was abundantly separated, on cooling; m.p. ca. 130° under decomposition.

2-Thio-3-benzoyl-hydantoin. The substance was prepared from hippuric acid and glycocoll and was recrystallized several times from alcohol; m.p. 163–164°.

2-Thio-3-acetyl-4-benzyl-hydantoin and 2-Thio-4-benzyl-hydantoin. The former substance was prepared by the condensation of phenylalanine and ammonium rhodanate and the latter by evaporating the former with hydrochloric acid; m.p. 167° and 183°.(1) (2)

2-Thio-4-(*p*-oxybenzyl)-hydantoin. The substance was prepared by the condensation of tyrosine with ammonium rhodanate, m.p. 211–212°; as the 3-acetyl derivative could not be easily isolated, it was not spectroscopically examined.

2-Thio-4-benzal hydantoin. The material was prepared by the condensation of benzaldehyde with 3-benzoyl- or 3-acetyl-hydantoin in the presence of anhydrous sodium acetate and glacial acetic acid.(3) The yellow substance, after purification, darkened on heating towards 258° and melted at 260° under decomposition.

2-Thio-4-furfural hydantoin. Two gr. of benzoyl-thio-hydantoin (or 1.5 gr. of acetyl-thio-hydantoin), 2.5 gr. of furfural, 4 gr. of anhydrous sodium

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(1) Johnson and W.B. O'brien, J. *Biol. Chem.*, **12** (1912), 205.

(2) Johnson and Nicolet, *Am. Chem. Journ.*, **49** (1915), 197.

(3) Ibid.

(4) Johnson and Nicolet, *J. Am. Chem. Soc.*, **33** (1911), 1973. Johnson and O'brien, *J. Biol. Chem.*, **12** (1912), 210.

acetate and 8 c.c. of glacial acetic acid were intimately mixed in a flask, and heated in an oil bath for 3 hours at 130°. On dilution the content of the flask with large volume of water, dark crystals were obtained; yield nearly theoretical. Recrystallisation from alcohol gave orange yellow crystals of m.p. 255° under decomposition.

Anal. Found: N=14.9%. Calc. for $C_{10}H_8ON_2S$: N=14.4%.

In conclusion, the author wishes to express his best gratefulness to Prof. K. Shibata and Prof. Y. Shibata for their kind guidances in this research and to Dr. T. Sasaki for supplying him with samples. He is also indebted to the Imperial Academy, a part of the research expenses being defrayed from its grant.

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