A PINK KAOLIN, AND RUTHENIUM AS A MINOR CONSTITUENT OF THE TANOKAMI KAOLINS.

By Satoyasu IIMORI and Jun YOSHIMURA.

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A pink kaolin-like mineral has been found as one of the ingredients of somewhat weathered granite lying on the south side of the Tanokami Hill, Oomi Province (Shiga Prefecture), where the green kaolin and radioactive manganiferous deposits happen to occur.⑴ It usually associates with small grains of quartz, orthoclase and biotite, each measuring about one or two millimeters across, and the kaolin as irregularly shaped masses also measures one millimeter or so in diameter. It is essentially of an amorphous nature, but on being examined microscopically, sometimes reveals microcrystalline structure in part. Most of the kaolin granules are usually faintly pink in colour, but frequently of light brown or flesh colour. The hardness is 2.5 and streak white. It does not adhere to the tongue. The index of refraction at 12°C. was determined to be 1.515 ± 0.001 by Mr. T. Tomita of the Mineralogical Laboratory, Tokyo Imperial University. For analysis, pink coloured pieces were selected with care. The result obtained is given in the following table:

SiO_2	53.91‰	MgO	0.09
Al_2O_3	26.28	Rare earth oxides	0.67
Fe_2O_3	1.69	K_2O	0.62
FeO	0.26	Na_2O	1.03
MnO	0.39	F(less O-equiv.)	0.03
TiO_2	0.03	Loss on ignition	15.60
CaO	0.12		
		Total	100.72

The mineral contains, as given in the analysis shown above, a fairly marked quantity of rare earths. The spectrographical examination

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(1) This Bulletin, **1** (1926), 43; **2** (1927), 274.

showed that the latter consist chiefly of yttrium and contain insignificant quantities of La, Dy, Nd, Sc, Ce, Yb and Tm. Hence the mineral differs somewhat from the green kaolin(1) found in the same district, in its containing certain members of cerium group, such as lanthanum, neodymium and cerium and by far an inferior amount of scandium. Disregarding these minor constituents, the analysis is nearly in agreement with the formula 2 Al_2O_3.7 SiO_2.7 H_2O with alumina to silica as 1 to 3.5; it lies, therefore, just between the two well known pink clays, catlinite and montmorillonite in the ratio of alumina to silica, the former being Al_2O_3.3 SiO_2. H_2O(2) and the latter Al_2O_3. 4 SiO_2. n H_2O(3). The present mineral, therefore, seems to be considered as neither of these two, but as a new species of pink clay, and will be named *Takizolite* after the name of a villager, the late Takizo Ueno, of Tanokami who had first taken notice of this mineral and long been a collector of minerals occurring in this district. The pink colour of this mineral is, however, hardly explicable from the result of analysis, since the presence of the elements such as erbium, europium and terbium which gives rise usually to rose-coloured compounds could not be proved even spectroscopically, and it must be ascribed to some other causes which are at present unaccountable.

By the way, it seems rather striking, that this pink kaolin as well as the green kaolin from Tanokami give a distinct X-ray absorption corresponding to the element of atomic number 44 or 43, the minerals being directly subjected to examination, previously without letting them touch any platinum articles. The zinc-manganese fraction extracted from the green kaolin, being separated from iron and aluminium by the succinate method and subsequently precipitated by ammonium sulphide, displays pink-red colour after being ignited for the oxide, and gives more distinctly the same absorption limit. Dr. M. Nakaizumi of the Nishikawa Research Laboratory in the Institute was kind enough to carry out for us the absorption measurement in the X-ray spectra, the result being shown in the following figure. The measurement was made by the ionization method using Bragg's spectrometer. In the figure, θ denotes the glancing angle, the pyramidal face of quartz being used as the reflector, and the point marked with circlet in each curve the absorption edge respectively.

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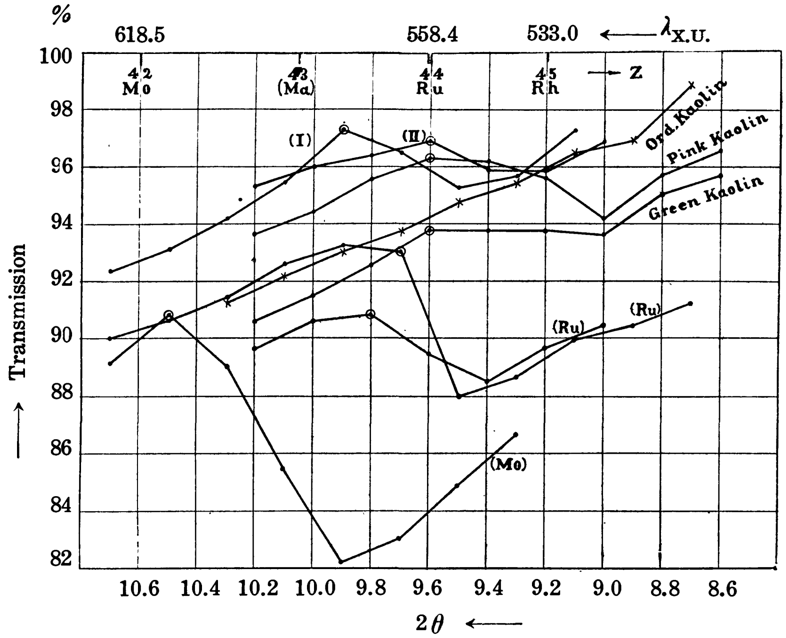
(1) Loc. cit.

(2) E. S. Dana, "The System of Mineralogy," (1914), p. 696; G. Catlin, *Am. J. Sci.*, **38** (1840), 138.

(3) E. S. Dana, "The System of Mineralogy," (1914), p. 690; C. Doelter, "Handbuch Min. Chem." Vol. II, (1917), p. 138.

The K-Absorption Edges for Kaolins.



As will be seen in the figure, whilst the ordinary white kaolin never shows the absorption in this region of wave-lengths, both of the kaolins from Tanokami and the zinc fraction (shown by the curve (II) in the figure) separated by the basic acetate method from the green kaolin exhibit the distinct K-absorption edge just corresponding to the ruthenium. The zinc fraction (shown by the curve (I) in the figure) obtained from the same green kaolin, being separated by the succinate method from the iron and aluminium, shows the edge more closely approaching to the element 43. The curves (Mo) and (Ru) are the results shown by the pure molybdic acid and metallic ruthenium (Kahlbaum's preparations) respectively and are depicted for comparison. In this case the K-absorption limit of the second order of praseodymium does not come to consideration, since the experimental condition of the arrangement was not suited to show this absorption, and the L-absorption limit of uranium which is also to appear in this region of wave length was also out of question, because the uranium as well as praseodymium were not detected chemically nor spectroscopically in the kaolins examined. The material of the pink kaolin was too scanty to allow the zinc-manganese fraction to be extracted for examination, so the measurement could not be made about the latter fraction of this kaolin.

The arc-spectrum of the zinc-manganese fraction, giving the X-ray absorption expressed by the curve (I) in the foregoing figure, gave a few lines which are to be ascribed to ruthenium and rhodium but to none of other elements. The lines were examined by a large Hilger spectrograph on Littrow mounting, the wave-lengths having been determined referring to the Exner and Haschek's scale(1) of the iron lines (the Rowland system) for the region of 2700 to 3700 Å which are given in the following table:

Lines observed, Å	A part of the lines of ruthenium, given by	
	H. Kayser(2)	F. Exner & E. Haschek
3696.81	3696.58	3696.74
3316.55	3316.38	3316.52
3297.14	—	3297.39
3296.15	3296.11	3296.25
3268.01	3268.20	3268.34
3238.90	3238.53	3238.65
3213.06	—	3213.10
3192.56	—	3192.20
3190.13	3189.96	3190.10
3177.16	3177.04	3177.16
3160.17	3159.91	3160.03
3045.72	3045.71	3045.83
3038.21	—	3038.29
2980.05	2979.94	2980.05
2976.62	2976.58	2976.70
2955.26	—	2955.48
2902.38	—	2902.20
2806.87	—	2806.86
2765.60	—	2765.54
2752.37	2752.76	2752.37
2745.22	—	2745.20
2743.90	—	2744.00

Lines observed, Å	A part of the lines of rhodium, given by	
	H. Kayser	F. Exner & E. Haschek
3268.93	—	3268.62
3155.90	3155.76	3155.90
2977.42	2977.69	2977.81
2819.49	2819.24	2819.35
2681.82	2680.62	2681.69

Lines observed, but not identified.

λ (Å)	Intensity
3383.06	6
2819.05	1
2804.47	2
2804.20	3

Further, on examining the fraction of heavy metals of the pink kaolin, precipitated by hydrogen sulphide from the acid solution, some of the chemical reactions, e.g. the rhodanate colour reaction, of ruthenium were perceived. The occurrence of ruthenium in such rock minerals has not been recorded hitherto, but from the foregoing evidence, it would seem that ruthenium or rhodium exists in the Tanokami kaolins

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(1) F. Exner u. E. Haschek, "Die Spektren der Elemente bei Normal Druck," (1911).

(2) H. Kayser, "Tabelle der Hauptlinien der Linienspektra aller Elemente," (1926).

as their minor constituent, though no hint was obtained as to its state of existence.

According to W. Noddack, I. Tacke and O. Berg.⑴ the zinc fraction extracted from tantalite, columbite, fergusonite, etc. is said to give always the distinct K-lines of *masurium*, as they called the element of the atomic number 43; hence the presence of the latter element in these kaolins may also be highly probable, and thus the unidentified lines of the optical spectrum pointed out in the above table might be attributed to this element.

Our best thanks are due to Professor S. Nishikawa and Dr. M. Nakaizumi for their kind advice as well as measurements of the X-ray absorption, and also to Professor S. Tsuboi and Mr. T. Tomita for giving us kind advices on the mineralogical side of this subject.

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(1) *Naturwissenschaften*, **13** (1925), 567; *Z. angew. Chem.*, **38** (1925), 1157.

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

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There have been proposed many viscosity formulas for a physical mixture of two constituents:

I. $\log \eta = (1-z_v) \log \eta_1 + z_v \log \eta_2$ (logarithmic formula),

II. $\eta = (1-z_v)\, \eta_1 + z_v \eta_2$ (viscosity formula),

III. $\frac{1}{\eta} = (1-z_v)\frac{1}{\eta_1} + z_v \frac{1}{\eta_2}$ (mobility or fluidity formula),

in which η_1, η_2 and η are viscosity coefficients of components 1, 2 and their mixture respectively; z_v a volume fraction of component 2.

Lees(1) deduced them theoretically, but discarded them because he found a more suitable expression :

$$\text{IV.} \qquad \eta^{\frac{1}{n}}=(1-z_v)\eta_1^{\frac{1}{n}}+z_v\eta_2^{\frac{1}{n}},$$

where n is an empirically determinate constant, varying for the most part between 2 and 5.

Kendall,(2) taking a molar fraction z_m in place of volume fraction z_v, gave a modified formula of I :

$$\text{V.} \qquad \log\eta=(1-z_m)\log\eta_1+z_m\log\eta_2\,.$$

He abandoned it,(3) however, four years later and again proposed a well known formula :

$$\text{VI.} \qquad \eta^{\frac{1}{3}}=(1-z_m)\,\eta_1^{\frac{1}{3}}+z_m\eta_2^{\frac{1}{3}}\,.$$

Viscosity of a gas increases with rise of temperature, whilst that of a liquid decreases. This fact suggests that both depend alike on the molecular motion, but there must be some different points between them.

The kinetic theory of gases postulates that a molecular motion of gases is non-restrictive. Such consideration, however, may not be applicable to a molecule of liquids, whose molecular distance or a mean free path having been estimated by some investigators to be equivalent to or less than a diameter of a molecule. We consider, then, that a liquid molecule moves unfreely in an attraction field, i.e., its motion is restricted or bound by others.

Now we may allow the following two assumptions as to liquid molecules :

Assumption A. An associated molecule is a fast combined molecule, a single molecule in which is quite different in any property from a singly existing molecule and is regarded to be a constituent as if it were of a chemical compound molecule.

Assumption B. An associated molecule is a group of single molecules which have the self-same dimension with singly existing molecules and the difference between them is no other than the abrupt greatness of the cohesion force of the former in comparison with that of the latter.

Let us denote the association degrees and numbers of formal molecules of chemically indifferent two liquids by a_1, a_2, n_1 and n_2 respec-

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(1) Lees, *Phil. Mag.*, [VI] **1** (1901), 128.

(2) Kendall, *Meddelanden f. K. Velensk. Nobelinstitute*, **2** (1913), 23.

(3) Kendall, *J. Am. Chem. Soc.*, **39** (1917), 1790; ibid. **42** (1920), 1776.

tively. Then the numbers of molecules can be expressed by $\frac{n_1}{a_1}$ and $\frac{n_2}{a_2}$ according to assumption *A*; and n_1 and n_2 according to assumption *B*.

Since an associated molecule in the former case is counted only one just as a singly existing molecule, we are reduced to assume, in general, *n* kinds of molecular sizes in place of regarding no attraction field, in other words, for one component of a binary mixture we must consider a mixture of *n* kinds of ideal gases and the treatment becomes very complicate in consequence.

The suitability of assumption *B* has been justified in the writer's as yet unpublished paper "Refractivity of a binary mixture and its relations to the molecular size of components." In our present study we will also adopt it.

If we consider the viscosity of a binary liquid mixture to be composed of the constituent viscosities, the partition of each component may be assumed to be proportional to (i) the number of molecules and (ii) the mean intensity of attraction field, which, according to assumption *B*, is proportional to the association degree. In short, the viscosity shares of components are, respectively, expressed by $k_1\, a_1\, n_1$ and $k_2\, a_2\, n_2$, in which k_1 and k_2 are the characteristic "field-constants" of components 1 and 2—the constants which depend probably on the kind, form and size of constituent molecules.

Let us call such viscosity share "effective number of molecules" and denote by z'_m "effective molar fraction" of component 2, then we have

$$z'_m=\frac{k_2a_2n_2}{k_1a_1n_1+k_2a_2n_2}=\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z_m}$$

where z_m is a formal molar fraction of component 2.

If a mixture is chemically non-reactive, it readily follows:

$$\eta=\eta_1(1-z'_m)+\eta_2 z'_m$$

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

or

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

Case I. $k_1 = k_2$

The assumption can only be allowed for homologous successive two liquids. In such cases,

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{a_2 z_m}{a_1(1-z_m)+a_2 z_m}.$$

Special case: If $a_1=a_2$,

$$\eta=\eta_1+(\eta_2-\eta_1)\,z_m,$$

or the viscosity of such a mixture is additive with respect to formal molar fraction.

Case II. $k_1 \neq k_2$

This contains all the cases where two liquids are chemically indifferent. For the verification of the formula, I have consulted as much published data as seen in the literature.

The association degrees are all quoted from the writer's recent paper, "A theory of binary mixtures and its application to calculating the association degrees of liquids," *Sexagint, Y. Osaka, Chem. Inst. Dept. Science, Kyoto Imp. Univ.* (1927), 103-41.

The validity of the formula will readily be understood from the constancy of $\frac{k_2a_2}{k_1a_1}$ in each table, which also shows the values calculated from Kendall's formula:

$$\eta^{\frac{1}{3}}=\eta_1^{\frac{1}{3}}(1-z_m)+\eta_2^{\frac{1}{3}}z_m.$$

The sufficient condition that any one of $\frac{k_B}{k_A}$, $\frac{k_C}{k_B}$ and $\frac{k_A}{k_C}$, which are obtained separately from three pairs *A-B*, *B-C* and *C-A*, must be quite equivalent to that calculated from the other two is also realized as seen from the notes of tables 5 and 9.

Table 1.

$CH_3COOCH_3-CH_3COOC_2H_5$, 25°C. (Chadwell).(1)

z_m-$CH_3COOC_2H_5$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.003594		—	—
0.0782	3638	(0.856)	0.003645	0.003645
0.1892	3713	0.960	3713	3709
0.3264	3801	0.965	3801	3804
0.4454	3876	0.954	3877	3877
0.5533	3943	0.936	3947	3944
0.7915	4098	0.909	4108	4104
0.8753	4158	0.935	4159	4158
1.0000	4244	0.943	—	—

$$\begin{cases} a_1=1.30 \\ a_2=1.25 \end{cases}, \quad \frac{k_2}{k_1}=0.943\times\frac{1.30}{1.25}=0.98$$

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(1) H.M. Chadwell, *J. Am. Chem. Soc.*, **48** (1926), 1918.

Table 2.

$C_2H_5OH-CH_3OH$, 25°C. (Herz).⁽¹⁾

z-CH_3OH	z_m-CH_3OH	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.01092		—	—
0.0437	0.0617	0.01047	1.41	0.01050	0.01052
0.104	0.143	0.009845	1.52	998	1002
0.4102	0.5000	7885	1.34	792	797
0.8069	0.8572	6175	1.18	623	623
0.8477	0.8892	6050	1.41	608	610
0.9125	0.9376	5862	1.40	587	588
1.0000	1.0000	5621	1.38	562	—

$$\begin{cases} a_1=1.37 \\ a_2=1.78 \end{cases}, \quad \frac{k_2}{k_1}=1.38\times\frac{1.37}{1.78}=1.06$$

Table 3.

$C_2H_5OH-n\text{-}C_3H_7OH$, 25°C. (Parks & Schwenck).⁽²⁾

z-C_3H_7OH	z_m-C_3H_7OH	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.01090		—	—
0.1250	0.0987	1169	(0.99)	0.01161	0.01157
0.2507	0.2041	1233	0.84	1238	1231
0.3760	0.3161	1319	0.86	1323	1314
0.4998	0.4337	1408	0.85	1414	1404
0.6251	0.5613	1522	0.90	1517	1506
0.7500	0.6971	1640	0.93	1630	1621
0.8746	0.8426	1759	0.90	1755	1750
1.0000	1.0000	1897	0.88	—	—

$$\begin{cases} a_1=1.37 \\ a_2=1.31 \end{cases}, \quad \frac{k_2}{k_1}=0.88\times\frac{1.37}{1.31}=0.92$$

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(1) W. Herz, *Z. anorg. allg. Chem.*, **104** (1918), 47.

(2) G.S. Parks & J.R. Schwenck, *J. Phys. Chem.*, **28** (1924), 720.

Table 4.

$CH_3OH-HCONH_2$, 25°C. (Merry & Turner).⁽¹⁾

z_m-$HCONH_2$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.00557		—	—
0.1000	746	(0.65)	0.00705	0.00705
0.2000	861	0.49	868	879
0.3000	1055	0.50	1052	1076
0.3966	1247	0.50	1250	1260
0.4978	1484	0.50	1484	1556
0.6000	1749	0.49	1756	1348
0.7000	2067	0.50	2067	2168
0.7988	2431	0.51	2421	2520
0.9020	2874	0.52	2867	2929
1.0000	3359	0.50	—	—

$$\begin{cases} a_1=1.78 \\ a_2=0.93 \end{cases}, \quad \frac{k_2}{k_1}=0.50\times\frac{1.78}{0.93}=0.96$$

Table 5.

$C_2H_5OH-HCONH_2$, 25°C. (Merry & Turner).⁽²⁾

z_m-$HCONH_2$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.01086		—	—
0.1005	1229	(0.60)	0.01248	0.01243
0.1991	1376	(0.59)	1419	1409
0.3014	1563	0.62	1607	1597
0.4017	1816	0.71	1806	1798
0.4991	2010	0.69	2010	2010
0.6093	2259	0.68	2264	2269
0.7024	2515	0.72	2494	2498
0.8108	2782	0.67	2784	2789
0.9000	3054	0.72	3043	3049
1.0000	3359	0.69	—	—

$$\begin{cases} a_1=1.37 \\ a_2=0.93 \end{cases}, \quad \frac{k_2}{k_1}=0.69\times\frac{1.37}{0.93}=1.02$$

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(1) E.W. Merry & W.E.S. Turner, *J. Chem. Soc.*, **105** (1914), 748.

(2) Loc. cit.

From tables 4 and 5, we have

$$\frac{(k)_{CH_3OH}}{(k)_{C_2H_2OH}}=\frac{(k)_{HCONH_2}}{(k)_{C_2H_5OH}}\times\frac{(k)_{CH_3OH}}{(k)_{HCONH_2}}=1.02\times\frac{1}{0.96}=1.06,$$

which is exactly coincident with the corresponding value $\frac{k_2}{k_1}=1.06$ in table 2.

Table 6.

$H_2O-HCONH_2$, 25°C. (Merry & Turner).⑴

z_m-$HCONH_2$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.00891		—	—
0.1001	1044	(0.59)	1016	1048
0.1998	1161	0.49	1155	1222
0.3003	1315	0.48	1313	1416
0.3989	1463	0.46	1487	1623
0.4997	1698	0.49	1691	1855
0.5997	1927	0.48	1923	2111
0.6920	2142	0.46	2171	2363
0.8004	2508	0.47	2515	2686
0.9013	2906	0.49	2901	3012
1.0000	3359	0.48	—	—

$$\begin{cases} a_1=3.18 \\ a_2=0.93 \end{cases}, \quad \frac{k_2}{k_1}=0.48\times\frac{3.18}{0.93}=1.64$$

Table 7.

$C_6H_5CH_3-C_6H_6$, 25°C. (Linebarger).⑵

z_m-C_6H_6	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.00000	0.00541		—	—
0.12719	555	(1.7)	0.00547	0.00549
0.34229	558	0.80	558	560
0.70240	579	0.81	579	581
0.92750	594	0.83	594	595
1.00000	599	0.81	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.00 \end{cases}, \quad \frac{k_2}{k_1}=0.81\times\frac{1.00}{1.00}=0.81$$

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(1) Loc. cit.

(2) C.E. Linebarger, *Am. J. Sci.*, **4** (1896), 331.

Table 8.

$C_6H_5Br-C_6H_5CH_3$, 20°C. (Yajnik & coworkers).(1)

z_v-$C_6H_5CH_3$	$\eta_{obs.}$	$\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)}$
0.00	0.00880	
0.10	831	1.15
0.20	776	1.26
0.30	734	1.19
0.40	698	1.09
0.50	652	1.11
0.60	609	1.12
0.70	561	1.20
0.80	528	1.09
0.90	487	1.09
1.00	447	1.14

$$\left\{\begin{array}{l} a_1=\text{unknown} \\ a_2=1.00 \end{array}\right. , \quad \frac{k_2a_2}{k_1a_1}=1.14\times\frac{1.495\times 92.06}{0.867\times 157.0}=1.15,$$

taking the densities of C_6H_5Br and $C_6H_5CH_3$ to be 1.495 and 0.867 respectively (from Landolt, "Tabellen").

Table 9.

$C_6H_5Br-C_6H_6$, 18.2°C. (Yajnik & coworkers).(2)

z_v-C_6H_6	$\eta_{obs.}$	$\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)}$
0.00	0.01129	
0.10	1086	0.90
0.20	1056	0.73
0.30	942	1.46
0.40	923	1.15
0.50	876	1.14
0.60	833	1.10
0.70	786	1.11
0.80	736	1.11
0.90	699	1.06
1.00	654	1.08

$$\left\{\begin{array}{l} a_1=\text{unknown} \\ a_2=1.00 \end{array}\right. , \quad \frac{k_2a_2}{k_1a_1}=1.08\times\frac{1.495\times 78.05}{0.879\times 157.0}=0.92.$$

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(1) N.A. Yajnik, M.D. Bhalla, R.C. Talwar, & M.A. Soofi, *Z. physik. Chem.*, **118** (1925), 305.

(2) Loc. cit.

The densities of C_6H_5Br and C_6H_6 are quoted from Landolt, "Tabellen." From tables 8 and 9, we get:

$$\frac{(k)_{C_6H_6}}{(k)_{C_6H_5CH_3}}=\frac{(k)_{C_6H_6}}{(ka)_{C_6H_5Br}}\times\frac{(ka)_{C_6H_5Br}}{(k)_{C_6H_5CH_3}}=0.92\times\frac{1}{1.15}=0.80.$$

This is concordant with the corresponding value $\frac{k_2}{k_1}=0.81$ in table 7.

Table 10.

$C_6H_6-CH_3COOC_2H_5$, 25°C. (Dunstan).(1)

z-$CH_3COOC_2H_5$	z_m-$CH_3COOC_2H_5$	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.005822		—	—
0.2704	0.2473	5181	1.94	0.005166	0.005388
0.3310	0.3049	4990	(2.38)	5022	5284
0.3584	0.3313	4990	2.11	5001	5241
0.4393	0.4099	4830	2.24	4865	5116
0.4830	0.4531	4803	2.01	4797	5046
0.4910	0.4610	4782	2.06	4785	5028
0.7595	0.7370	4446	1.94	4435	4590
1.0000	1.0000	4193	2.05	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.25 \end{cases},\quad \frac{k_2}{k_1}=2.05\times\frac{1.00}{1.25}=1.64$$

Table 11.

$C_2H_5OH-CS_2$, 25°C. (Dunstan).(2)

z-CS_2	z_m-CS_2	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.01113		0.01113	0.01113
0.1691	0.1096	0.009448	(2.30)	968	1003
0.1929	0.1263	9535	1.88	948	988
0.2564	0.1726	9065	1.83	896	945
0.3231	0.2241	8407	1.98	842	898
0.3950	0.2832	7621	2.24	787	845
0.5282	0.4040	6659	2.20	687	745
0.6995	0.5848	5669	1.93	564	611
0.7350	0.6266	5466	1.86	541	583
0.8193	0.7328	4926	1.78	483	514
1.0000	1.0000	3656	1.96	366	366

$$\begin{cases} a_1=1.37 \\ a_2=1.20 \end{cases},\quad \frac{k_2}{k_1}=1.96\times\frac{1.37}{1.20}=2.24$$

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(1) A.E. Dunstan, *J. Chem. Soc.*, **85** (1904), 817.

(2) Loc. cit.

Table 12.

$CS_2-C_6H_6$, 25°C. (Linebarger).⑴

z-C_6H_6	$\eta_{obs.}$	$\frac{(1-z)(\eta-\eta_1)}{z(\eta_2-\eta)}$
0.000	0.00358	
0.089	376	(0.83)
0.349	446	1.07
0.759	544	1.07
1.000	599	1.07

$$\begin{cases} a_1=1.20 \\ a_2=1.00 \end{cases}, \quad \frac{k_2}{k_1}=1.07\times\frac{78.05\times1.20}{76.12\times1.00}=1.32.$$

Table 13.

$C_6H_6-CCl_4$. 60°C. (Thorpe & Rodger).⑵

z-CCl_4	z_m-CCl_4	$\eta_{obs.}$	$\frac{k_2a_2}{k_1a_1}$	$\eta_{calc.}$	η_k
0.0000	0.0000	0.00391		—	—
0.3229	0.1949	422	0.79	422	425
0.5621	0.3944	456	0.78	456	461
0.7763	0.6377	503	0.79	503	508
1.0000	1.0000	584	0.79	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.24 \end{cases}, \quad \frac{k_2}{k_1}=0.79\times\frac{1.00}{1.24}=0.64$$

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(1) C.E. Linebarger, *Am. J. Sci.*, **4** (1896), 331.
(2) T.E. Thorpe & J.W. Rodger, *J. Chem. Soc.*, **71** (1897), 360.

Table 14.

$CHCl_3-CCl_4$, 25°C. (Linebarger).(1)

z_m-CCl_4	η_{obs}.	$\frac{k_2a_2}{k_1a_1}$	η_{calc}.	η_k
0.00000	0.00540		—	—
0.15663	569	0.50	570	586
0.50989	659	0.51	661	698
0.76985	761	0.54	758	794
1.00000	883	0.52	—	—

$$\begin{cases} a_1=1.00 \\ a_2=1.24 \end{cases}, \quad \frac{k_2}{k_1}=0.52\times\frac{1.00}{1.24}=0.42$$

Table 15.

$CH_3COOC_2H_5-CH_3COOH$, 25°C. (Kendall & Brakeley).(2)

z_m-CH_3COOH	η_{obs}.	$\frac{k_2a_2}{k_1a_1}$	η_{calc}.	η_k
0.0000	0.004236		0.004236	0.004236
0.1049	0.004590	(0.456)	0.004563	0.004769
0.2070	0.004949	(0.436)	0.004925	0.005323
0.3037	0.005331	0.427	0.005316	0.005888
0.3990	0.005762	0.422	0.005756	0.006486
0.4985	0.006289	0.420	0.006289	0.007154
0.5996	0.006890	0.411	0.006926	0.007880
0.6988	0.007668	0.418	0.007676	0.008627
0.8011	0.008590	0.413	0.008616	0.009460
0.8742	0.009430	0.420	0.009426	0.01008
1.0000	0.01121	0.42	0.01121	0.01121

$$\begin{cases} a_1=1.25 \\ a_2=1.51 \end{cases}, \quad \frac{k_2}{k_1}=0.42\times\frac{1.25}{1.51}=0.35$$

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(1) Loc. cit.

(2) J. Kendall & E. Brakeley, *J. Am. Chem. Soc.*, **43** (1921), 1826.

UEBER DIE KONSTITUTION DES NODAKENINS, EINES NEUEN GLUCOSIDS VON PEUCEDANUM DECURSIVUM MAXIM. I.(1)

Von Junzo ARIMA.

Eingegangen am 5. Dezember 1928. Ausgegeben am 28. Januar 1929.

Peucedanum decursivum Maxim. ist ein perennierendes Kraut aus den Umbelliferaeen, dessen Wurzel seit Alter her in Japan und China als Hustenmittel oder Stomachicum gebraucht war. In dieser Droge hat der Verfasser ein neues, kristallisierendes Glucosid, das die Formel $C_{20}H_{24}O_9$ und den Schmp. 215° hat, gefunden, und das wird „Nodakenin“(2) genannt.

Das Nodakenin wird durch Hydrolyse in eine *d*-Glucose und ein Aglykon gespalten. Das Aglykon hat die Formel $C_{14}H_{14}O_4$ und den Schmp. 185°, und wird „Nodakenetin“ bezeichnet.

$$\underset{\text{Nodakenin.}}{C_{20}H_{24}O_9} + H_2O = \underset{d\text{-Glucose.}}{C_6H_{12}O_6} + \underset{\text{Nodakenetin.}}{C_{14}H_{14}O_4}.$$

Das Nodakenetin ist eine neutrale Substanz und unlöslich in kaltem Alkalien. Das zeigt mit Eisenchlorid keine Färbung, und durch Azetylierung bildet es eine Monoazetylverbindung, während es sich in keiner Weise methylieren lässt. Daraus kann man schliessen, dass das Nodakenetin ein Alkoholhydroxyl enthält. Es enthält aber keine Methoxylgruppe und ferner zeigt keine Keton- oder Aldehydreaktionen. Es ist unlöslich in kalten Alkalien, doch ist es löslich in heissen oder alkoholischen Alkalien mit gelber Farbe, und aus diesen Lösungen wird es mit Säuren wieder unverändert bekommen. Aus diesen Verhalten gegen Alkalien und durch Bestimmung der Verseifungszahl des Nodakenetins kann man das Vorhandensein einer Lactongruppe nachweisen, aber die entsprechende Oxysäure ist beständig nur in alkalischer Lösung und kann in freiem Zustande nicht isoliert werden; jedoch wird es durch das längere Kochen mit alkoholischen, etwas konzentrierten Alkalien in eine Oxysäure umgewandert, die in Kristallen vom Schmp. 205–206° isoliert werden kann.

Diese Oxysäure, die der Verfasser „Isonodakenetinsäure“ benennen will, ist eine einbasische Säure und zeigt mit Eisenchlorid eine braune

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(1) Vorläufig mitgeteilt in *J. Chem. Soc. Japan*, **48** (1927), 88 u. 457.

(2) Nach “Nodake,” der japanischen Bezeichnung von dem Kraute.

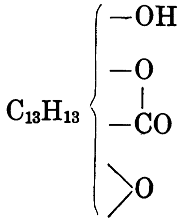
Färbung, und wird mit Diazomethan in Dimethylverbindung vom Schmp. 65–67° übergeführt.

Die oben erwähnten verschiedenen Verhalten des Nodakenetins gegen Alkalien sind den von Cumarin-reihen sehr ähnlich.

Durch Kalischmelze des Nodakenetins werden Resorzin, Essigsäure, und eine neue Verbindung, die die Formel $C_8H_8O_4$ und den Schmp. 258–260° hat, nachgewiesen. Diese Abspaltung des Resorzins zeigt, dass das Nodakenetin einen Resorzinkern enthält, und die zwei phenolischen Sauerstoffatome dieses Kernes in verbundenen Zuständen liegen, da das Nodakenetin, keine freie, phenolische Hydroxylgruppe besitzt.

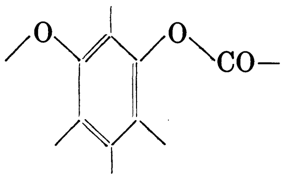
Aus diesen Resultaten ergibt es sich, dass eins von den vier Sauerstoffatomen von Nodakenetin in der Alkohol-hydroxylgruppe, zwei davon in der Lactongruppe liegen und ein anderes ein Bruckensauerstoff ist, und dass eins von zwei Sauerstoffen in Lactongruppe und das Bruckensauerstoff den zwei Sauerstoffen des Resorzinkernes in Nodakenetin entsprechen. Das Nodakenetin muss daher das Formelbild wie (I) besitzen und enthält in seinem Moleküle das Kern wie (II).

(I)



$$C_{13}H_{13}\left\{\begin{array}{l} -OH \\ -O \\ \quad\mid \\ -CO \\ \rangle O \end{array}\right.$$

(II)



Beschreibung der Versuche.

Isolierung des Nodakenins. 500 gr. zerkleinierte Wurzeln wurden einige Tage lang mit 2.5 Liter 1% iger Schwefelsäure extrahiert. Im Extrakt war so viel Phosphowolframsäurelösung zugesetzt, bis keine weitere Fällung erfolgte, und der Niederschlag wurde abfiltriert und auf den Tonplatten getrocknet. Die getrockneten Massen waren im Mörser mit 500 c.c. Wasser und überschüssigem Bariumhydroxyd behandelt, und der gebildete Niederschlag wurde abfiltriert. Das Filtrat war mit verd. Schwefelsäure neutralisiert, und abgeschiedenes Bariumsulphat wurde auch abfiltriert. Die Flüssigkeit war unter vermindertem Druck bis auf 20 c.c. eingeengt und dann einige Tage lang stehen bleiben gelassen. Es schied sich fast reines Glucosid in feinen Prismen aus. Die Ausbeute betrug ca, 2 gr., 0.4% der Droge. Zur Reinigung wurde es aus kochendem Wasser oder absolutem Alkohol umkristallisiert.

Eigenschaften des Nodakenins. Das Glucosid kristallisiert sich aus absolutem Alkohol in schneeweissen Blättchen vom Schmp. 215°. Aus Wasser erhält man glänzenden Prismen mit 1 Mol. Kristallwasser, die bei 216° schmelzen. Es ist leicht löslich in heissem Wasser, Phenol und Eisessig, und wenig in kaltem Wasser, Alkohol und Azeton, und sehr wenig in Aether und Benzol. Mit konz. Schwefelsäure gibt es eine gelbe Lösung, deren Farbe allmählich ins Rotviolette und schliesslich ins Violette umschlägt. Die wässerige Lösung reagiert sich neutral, zeigt violette Fluorescenz, und schmekt etwas bitter. Das Nodakenin ist rechtsdrehend und zeigt $[\alpha]_D^{30}=+56.6$ im Wasser.

Anal. Gef.: C=58.98, 59.08, 58.83; H=6.14, 5.98, 6.10%. Ber. für $C_{20}H_{24}O_9$: C=58.80, H=5.93%.

Mol. Gew. Gef. (in Phenol): 404, 386, 395. Ber. für $C_{20}H_{24}O_9$: 408.

Hydrolyse des Nodakenins. 1.94 gr. Nodakenin (wasserfreies) wurden mit 100 c.c. 2% iger Schwefelsäure versetzt und 4–5 Stunden auf dem Wasserbade erwärmt. Nach dem Erkalten wurden die ausgeschiedenen Kristalle vom Nodakenetin abfiltriert und mit kaltem Wasser gewaschen. Die Ausbeute betrug 1.10 gr. Das Filtrat wurde zum Nachweis von Zucker gebraucht.

Nachweis von *d*-Glucose. Das Filtrat vom Aglykon wurde unter Erwärmung mit Bariumkarbonat neutralisiert, und das ausgeschiedene Bariumsulphat abfiltriert. Dem Filtrat, das schon auf dem Wasserbade konzentriert war, war uberschussiges Essigsäure-phenylhydrazin zugesetzt und es war in siedendem Wasserbade erwärmt, und nach Erkalten wurde das auskristallisierte Phenylosazon filtriert. Durch einmaliges Umkristallisieren mit verd. Alkohol bekommt das Osazon den Schmp. 205–206°, der dem des *d*-Glucose-phenylosazons identisch ist.

Eigenschaften des Nodakenetins. Das Nodakenetin bildet farblose Nadeln vom Schmp. 185°. Es ist leicht löslich in Chloroform, Azeton und Eisessig, wenig in Alkohol, und fast unlöslich in Wasser, Aether und Benzol. In kalten Alkalien löst es sich nicht, doch ist es löslich in erwärmten oder alkoholischen Alkalien mit gelber Farbe, und es wird durch Zusetzen von verdünter Säure unverändert ausgeschieden. Wässerige oder alkoholische Lösung reagiert sich neutral und gibt mit Eisenchlorid keine Farbenreaktion. Es ist rinksdrehend: $[\alpha]_D^{30}=-22.4$ (in Chloroform).

Anal. Gef.: C=68.40, 68.43, 68.20; H=5.94, 5.93, 6.00%. Ber. für $C_{14}H_{14}O_4$: C=68.27; H=5.73%.

Mol. Gew. Gef. (Rast): 257, 261. Ber. für $C_{14}H_{14}O_4$: 246.

Verseifungszahl. Gef. (mit Phenolphtalein als Indikator): 226.6, 226.7. Ber. für $C_{14}H_{14}O_4+1$ Mol KOH: 228.1

Jodzahl. Gef. (Wijs): 0.960. Ber. für $C_{14}H_{14}O_4J_2$: 1.023.

Monoazetylnodakenetin. 0.4 gr. Nodakenetin wurden mit 4 gr. Essigsäure durch Zusetzen von 1 gr. Natriumazetat in üblicher Weise azetyliert. Farblose Nadeln beim Umkristallisieren aus verd. Alkohol. Schmp. 129–130°. Es ist leicht löslich in Aether und Alkohol, aber unlöslich in Wasser.

Anal. Gef.: C=66.90, 66.40; H=5.78, 5.76%. Ber. für $C_{14}H_{13}O_4$ $(CO \cdot CH_3)$: C=66.64; H=5.60%.

Verseifungszahl. Gef. (Phenolphtalein als Indikator): 394, 391. Ber. für $C_{14}H_{13}O_4$ $(CO \cdot CH_3)+2$ mol KOH: 390.

Nitronodakenetin. 0.1 gr. Nodakenetin wurden mit 1 c.c. konz. Salpetersäure (d=1.2) versetzt, und eine Minute lang auf der kleinen Flamme erwärmt. Nach Erkalten wurde das Reaktionsgemisch in 10 c.c. Wasser gegossen, so schieden sich gelbe Kristalle ab, die filtriert und aus Alkohol umkristallisiert wurden. Gelbe Nadeln vom Schmp. 206–207°. Es ist leicht löslich in Alkohol und Chloroform, und schwer in Wasser und Aether. In wässerigen Alkalien löst es sich mit roter Farbe.

Anal. Gef.: C=57.25; H=4.72; N=5.10%. Ber. für $C_{14}H_{13}O_4NO_2$: C=57.71; H=4.51; N=4.81%.

Mol. Gew. Gef. (Rast): 321. Ber. für $C_{14}H_{13}O_4NO_2$: 291.

Kalischmelze des Nodakenetins. 1 gr. Nodakenetin wurde mit 10 gr. Kaliumhydroxyd und etwas Wasser im Nickel-tieger 3 Stunden lang auf 190–200° erhitzt. Beim Erkalten wurde die Schmelze im Wasser gelöst und mit verd. Schwefelsäure neutralisiert, und nach Zusatz von etwas Natriumbicarbonat mehrmals mit Aether ausgeschüttelt. Der nach Verdampfen des Aethers bleibende Rückstand wurde mit kaltem Wasser extrahiert, und nach Filtrieren wurde die wässerige Flüssigkeit im Exsiccator stehen gelassen. Nach einiger Woche schiedet es sich farblose Kristalle ab, die bei 106–108° schmolz und die mehreren Farbenreaktionen des Resorzins zeigte.

Anal. Gef.: C=65.22; H=5.90%. Ber. für $C_6H_6O_2$: C=65.42; H=5.50%.

Die von der ätherischen Lösung getrennte, wasserige Flüssigkeit wurde mit Schwefelsäure angesäuert und mit Aether ausgeschüttert. Die ätherische Lösung wurde verdampft, und der Rückstand mit Wasserdampfen destilliert. Aus dem Destillate wurde das Silversalz der Essigsäure gefällt.

Anal. Gef.: Ag=65.41%. Ber. für $CH_3 \cdot COOAg$: Ag=64.64%.

Der Destillationsrückstand wurde filtriert, und aus dem Filtrate, das im Exsiccator stehen gelassen wurde, waren Kristalle von unbekannter phenolischer Substanz bekommen. Nach Reinigung mit Wasser und Aether schmolz die Substanz bei 258–260°. Es ist blass-gelbe Nadeln, und die wässerige Lösung reagiert stark sauer, und zeigt rotviolette Farbenreaktion mit Eisenchlorid.

Anal. Gef.: C=57.15; H=4.58%. Ber. für $C_8H_8O_4$: C=57.12; H=4.80%.
Mol. Gew. Gef. (Rast): 174. Ber. für $C_8H_8O_4$: 168.

Isonodakenetinsäure. 0.5 gr. Nodakenetin wurde in 8 c.c. Alkohol gelöst und mit 2 c.c. 10%iger Kaliumhydroxyd auf dem Wasserbade 3–4 Stunden lang erhitzt. Dann wurde das Alkohol unter vermindertem Druck abdestilliert, und der Rückstand mit 20 c.c. Wasser zugesetzt und durch Einleiten von Kohlendioxyd neutralisiert. Das unverändert ausgeschiedene Nodakenetin wurde abfiltriert und das Filtrat wurde mit verd. Schwefelsäure angesäuert, die abgeschiedenen Substanzen gesammelt. Aus Methylalkohol kristallisiert es in farblosen Nadeln vom Schmp. 205–206° (zersetzt.). Die wässerige Lösung reagiert sauer und zeigt mit Eisenchlorid eine dunkel-braune Farbenreaktion. Es ist leicht löslich in Alkohol, Methanol, Chloroform, und wässeriger Natriumbicarbonatlösung, schwer in Aether und Benzol. In Alkalien löst es sich mit blauer Fluorescenz.

Anal. Gef.: C=63.79; H=6.22%. Ber. für $C_{14}H_{16}O_5$: C=63.64; H=6.11%.

Silversalz der Isonodakenetinsäure ist graues, kristallinisches Pulver.

Anal. Gef.: Ag=28.54%. Ber. für $C_{13}H_{15}O_3 \cdot COOAg$: Ag=29.08%.

Dimethylisonodakenetinsäure. Isonodakenetinsäure wurde in üblicher Weise mit Diazomethan methyliert. Es bildet die gelblichen Prismen vom Schmp. 65–67°.

Best. des Methoxyls. Gef. (Zeisel): 20.68%. Ber. für $C_{14}H_{14}O_3\ (OCH_3)_2$: OCH_3=21.23%.

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ACETYLIEREN VON KOHLENHYDRAT MIT ESSIGSÄUREANHYDRID UND ALKALIRHODANID.

Von Yojiro TSUZUKI.

Eingegangen am 14. Dezember, 1928. Ausgegeben am 28. Januar 1929.

Es ist mir vor kurzem gelungen,(1) die Stärke mit Essigsäureanhydrid leicht zu acetylieren, indem ich sie vorher in die heissgesättigte $ZnCl_2$-lösung dispergierte. So interessiert es mich zu versuchen, ob sich die Stärke auch mit Hilfe anderer Dispergierungsmittel acetylieren lässt. Dank der zahlreichen Versuchen P.P. von Weimarns(2) wissen wir jetzt, dass die konzentrieten wässrigen Lösungen von verschiedenen, äusserst löslichen Salzen (LiSCN, LiI, NaSCN, NaI, $Ca(SCN)_2$ u.a.) und auch von einigen organischen, wasserlöslichen Verbindungen (wie mehrwertige Phenole und Thioharnstoff) zur Dispergierung von Cellulose, Seide, und andere, ähnlich hochmolekular-komplexe Substanzen wie Chitin, Casein, Fibrin und Keratin stark befähigt sind und, dass das Dispergierungsvermögen des Salzes sich auf seine Löslichkeit (oder auf die Hydratation der Ionen, aus denen das Salz zusammengesetzt ist) im allgemeinen parallel bezieht.(3) Bei der Stärke, zur Herbeiführung ihrer Kaltverkleisterung ist Natriumrhodanid (und auch andere Alkalirhodanide) von Wo. Ostwald und G. Frenkel(4) als besonders geeignet erwiesen worden (mit Lithiumsalzen aber kein Versuch).

Mit diesem Salze im gleichen Prinzip wie beim $ZnCl_2$ gearbeitet, hat sich die Stärke („starch soluble Merck") leicht acetylieren lassen. Das Produkt ist aber von dem früher gewonnenen etwas verschieden; es verteilt sich nur langsam in organischen Lösungsmitteln und gibt hochviskose Lösungen. Es gestattet uns ein der originalen Stärke ähnliches Verseifungsprodukt zurückzugewinnen, das sich mit Wasser verkleistert, sich mit Jod blau färbt, und die spezifische Drehung ca. 190° besitzt. Über diese Acetylstärke soll noch Eingehenderes später mitgeteilt werden.

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(1) Dieses Bulletin, **3** (1928), 276.

(2) Zusammenfassend dargestellt bei *Kolloid-Ztschr.*, **40** (1926), 120; **42** (1927), 134; *Japan. J. Chem.*, **3** (1928), 71.

(3) Diese letztere Tatsache ist aber zuerst von R.O. Herzog und F. Beck (*Z. physiol. Chem.*, **111** (1920), 287) an Cellulose beobachtet worden.

(4) *Kolloid-Ztschr.*, **43** (1927), 296.

Ich habe weiter versucht, andere einfachere Kohlenhydrate mit Essigsäureanhydrid und trocknem Natriumrhodanid (anstatt geschmolzenem Natriumacetat) zu acetylieren, da sich NaSCN nun bei der Acetylierung der Stärke als katalytisch wirksam erwiesen hat. Das Ergebnis ist ganz befriedigend. Aus Glucose und Galactose sind respektive, β-Pentaacetylglucose und β-Pentaacetylgalactose erhalten worden. Die Ausbeute am aus Alkohol einigemal umkrystallisierten, reinen Produkt betrug 40–60% der Theorie also nicht schlechter als die beim Natriumacetat.

Die Acetylierung: zum heissen Gemisch (etwa 70°) von Zucker und etwa 4 facher Menge Essigsäureanhydrids fügt man eine geringe Menge (ca. 1/10–1/5 des Zuckers genügen) von getrocknetem NaSCN hinzu und rührt das Gemisch andauernd um. Nach kurzer Zeit tritt eine lehbhafte Reaktion ein. Durch die Selbsterwärmung steigt die Temperatur bis auf 120°. Man tut gut, die Reaktion durch Abkühlen zu mässigen. Hält man die Temperatur auf 80–100°, so geht der Zucker in 5 Minuten zum grössten Teil in die Lösung und nach 15 Minuten entsteht eine klare Lösung. Man giesst die noch etwa eine Stunde auf derselben Temperatur erwärmte, schwachgelblich gefärbte Lösung in Wasser und krystallisiert das ausgeschiedene Acetylprodukt aus Alkohol um. Auf diese Weise ist erhalten worden, aus Glucose das Produkt von Schmp. 133° (korr.) und $[\alpha]_D^{12}$ +3.8° (14.5 gr. in 100 c.c. Chloroformlösung), $[\alpha]_D^{14}$ +4.4° (7.3 gr. in 100 c.c. Eisessiglösung) also identisch mit der β-Pentaacetylglucose,(1) und aus Galactose das Produkt von Schmp. 143° (korr.) und $[\alpha]_D^{13}$ + 7.5° (6.6 gr. in 100 c.c. Benzollösung); $[\alpha]_D^{13}$ + 25.5° (14.3 gr. in 100 c.c. Chloroformlösung) also identisch mit der β-Pentaacetylgalactose.(2) Die Identität des Acetylierungsproduktes mit dem aus dem Zucker mit Natriumacetat erhaltenen wurde auch durch die Mischprobe bestätigt.

Wie aus oben ersichtlich, steht NaSCN an der Wirkung nicht dem Natriumacetat nach, sondern hat es den Vorteil, dass selbst eine geringe

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(1) E. Erwig und W. Koenigs (*Ber.*, **22** (1889), 1466) gaben zu der aus Glucose mit Essigsäureanhydrid und $ZnCl_2$ erhaltenen β-Pentaacetylglucose den Schmp. 134° an. A.P.N. Franchimont (*Rec. trav. chim.*, **11** (1892), 110): Schmp. 134° (aus Clucose, mit Essigsäureanhydrid und Natriumacetat). W. Koenigs und E. Knorr (*Ber.* **34** (1901), 976): Schmp. 130–131° (aus Acetonitroglucose und Natriumacetat). C. Tanret (*Bull. soc-chim.*, [3] **13** (1895), 269); Schmp. 130°; $[\alpha]_D$ +3.66° (in $CHCl_3$); $[\alpha]_D$ +2.8° (in Benzol) (aus Glucose, mit Essigsäureanhydrid, $ZnCl_2$ und Natriumacetat). E. Gebauer-Füllnegg, W.H. Stevans und E. Krug (*Monatsh.*, **50** (1928), 326): Schmp. 132°; $[\alpha]_D$ +3.6° (in $CHCl_3$) (aus β-Acetochlorglucose und Silberacetat).

(2) E. Erwig und W. Koenigs (*Ber.*, **22** (1889), 2207): Schmp. 142° (aus Galactose, mit Essigsäureanhydrid und Natriumacetat). E. Fischer und E.F. Armstrong (*Ber.*, **35** (1902), 838): $[\alpha]_D^{20}$ +7.48° (in Benzol).

Menge davon (geringer als 1/5 von Natriumacetat) zur Vollziehung der Reaktion ganz genug ist. Trocknen von NaSCN ist nicht unbedingt nötig: der nicht getrocknete Krystall (von E. Merck, der nur 70% NaSCN enthält) wirkt auch ebenso gut. Getrocknetes sowie feuchtes KSCN beschleunigen das Acetylieren von Zuckern ja auch ziemlich stark; unter ähnlichen Bedingungen wie beim NaSCN wurden die gleichen Produkte durch KSCN in guter Ausbeute erhalten. LiSCN wurde nicht untersucht, aber da dieses Salz der kräftigste Dispergierungsmittel ist, könnte es beim Acetylieren vielleicht auch die Reaktion energisch befördern.

Herrn Prof. T. Soda bin ich für seine gütige Leitung zu grossem Dank verpflichtet.

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

By Tetsuya ISHIKAWA.

Received December 1, 1928. Published February 28, 1929.

In the former paper,[1] the writer proposed a viscosity formula for physical binary mixtures of the form:

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

where η, a, k with suffixes 1 and 2 signify the viscosities, the association degrees and the field-constants of components 1 and 2 respectively; z_m a formal molar fraction of component 2. The present paper is a continuation of it.

The relation between *k* and molecular structure. The application of the formula to the hitherto published data in the literature having been

Table 1.

Substance	k	$D\ (\lambda=\infty)$	Observers	$\sigma\times10^8$	Observers
C_6H_6	1	2.25 (20°) 2.28 (25°)	Linebarger Krchma & Williams	4.10	Rappenecker
$C_6H_5CH_3$	1.23	2.36 (20°) 2.38 (25°)	Linebarger Krchma & Williams	——	
CH_3COOCH_3	1.67	6.68 (25°)	,, ,,	3.91	,,
$CH_3COOC_2H_5$	1.64	6.03 (25°)	,, ,,	4.27	,,
$CHCl_3$	1.50	5.13 (20°) 4.77 (25°)	Linebarger Krchma & Williams	——	
CCl_4	0.63	2.24 (20°) 2.23 (25°)	Linebarger Krchma & Williams	4.60	Ishikawa
CS_2	0.76	2.58 (20°) 2.63 (25°)	Linebarger Williams & Ogg	3.91	,,
CH_3OH	0.36	31.2 (20°)	Abegg & Seitz	3.04	,,
C_2H_5OH	0.34	25.8 (20°)	,, ,,	3.43	,,
n-C_3H_7OH	0.31	22.2 (20°)	,, ,,	3.72	,,
H_2O	0.21	81.1 (18°)	Turner	2.61	Rappenecker
$HCONH_2$	0.35			——	
CH_3COOH	0.57	9.7 (18°)	Francke	1.95	Ishikawa

Linebarger, *Z. physik. Chem.*, **20** (1896), 131.
Krchma & Williams, *J. Am. Chem. Soc.*, **49** (1927), 2408.
Williams & Ogg, *J. Am. Chem. Soc.*, **50** (1928), 94.
Rappenecker, "Landolt-Tabellen," recalculated by taking $N=2.705\times10^{19}$.
Ishikawa, As yet unpublished paper "Refractivity of binary mixture and its relation to molecular size of components."

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[1] This Bulletin, **4** (1929), 5.

made with satisfactory results, the field constant k proves to be, as is expected, a particular constant for a particular liquid.

Now, in order to find whether or no there exists any relation between k and molecular structure, we calculate the relative values of k by putting that of C_6H_6 as unity. The values thus obtained are collected in the following table. It also shows the molecular diameter σ and dielectric constant $D\,(\lambda=\infty)$. Comparing k with these two values we find an interesting relation: *k of homologous liquids is proportional to the product $D\cdot\sigma$* as recognized from Table 2.

Table 2.

Substance	k.	$D\cdot\sigma\cdot10^8$	$\frac{D\cdot\sigma}{k}\cdot10^8$	
CH_3OH	0.36	$31.2 \times 3.04 = 94.9$	264	263
C_2H_5OH	0.34	$25.8 \times 3.43 = 88.5$	260	
n-C_3H_7OH	0.31	$22.2 \times 3.72 = 82.6$	266	
CH_3COOCH_3	1.67	$6.68 \times 3.91 = 26.1$	15.6	15.6
$CH_3COOC_2H_5$	1.64	$6.03 \times 4.27 = 25.7$	15.7	

Extension to gaseous mixtures. The author's formula is transformed into

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

As we have $a_1=a_2=1$ for a gaseous mixture,

$$\eta=\frac{\eta_1}{1+\frac{k_2}{k_1}\frac{z_m}{1-z_m}}+\frac{\eta_2}{1+\frac{k_1}{k_2}\frac{1-z_m}{z_m}}$$

Putting $\frac{k_2}{k_1}=K$, it becomes,

$$\eta=\frac{\eta_1}{1+K\frac{z_m}{1-z_m}}+\frac{\eta_2}{1+\frac{1}{K}\frac{1-z_m}{z_m}}\quad\cdots\cdots\cdots\cdots\cdots\cdots\text{(I)}$$

Thiesen(1) proposed the following viscosity formula for a gaseous mixture:

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(1) Thiesen, *Verh. d.D. phys. Ges.*, **4** (1902), 357.

$$\eta=\frac{\eta_1}{1+A\frac{z_v}{1-z_v}}+\frac{\eta_2}{1+B\frac{1-z_v}{z_v}},\quad A=\frac{a_{12}}{a_{11}},\quad B=\frac{a_{21}}{a_{22}}.$$

In which a_{11}, a_{12}, a_{22}, a_{21} are empirical constants as defined by him "Diffusions-konstante," and z_v a volume fraction of component 2.

Now that the equality of molecular volumes of all the gases is univesally acceptable, the above formula can be rewritten as follows:

$$\eta=\frac{\eta_1}{1+A\frac{z_m}{1-z_m}}+\frac{\eta_2}{1+B\frac{1-z_m}{z_m}} \quad\text{..................}\quad \text{(II)}$$

Comparing (I) and (II) we see that if $B=\frac{1}{A}$ holds good in (II) they are quite equivalent.

That Thiesen's formula gives more concordant values with experiments than those of Puluj's and of Sutherland's has been verified successively by Kleint,(1) Tänzler(2) and Gille,(3) from whose results we can examine in what pairs the equality of A to $\frac{1}{B}$ holds.

Table 3.

Pairs	$t°c.$	A	B	$B:\frac{1}{A}$	Observers
O_2 —— H_2	15	0.373	1.362	0.508	Kleint
	100	0.353	1.662	0.587	
	183	0.388	1.331	0.516	
O_2 —— N_2	15	0.456	2.443	1.11	Kleint
	100	0.93	1.10	1.02	
	183	0.48	2.32	1.11	
N_2 —— H_2	15	0.23	3.57	0.82	Kleint
	100	0.20	4.988	1.00	
	183	0.215	4.297	0.924	
A —— He	15	0.343	2.032	0.697	Tänzler
	100	0.375	1.957	0.734	
	183	0.446	1.692	0.747	
He —— H_2	10	0.847	1.170	0.991	Gille
	15	0.875	1.167	1.021	
	100	0.9203	1.110	1.021	

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(1) Kleint, *Verh. d. D. phys. Ges.*, **7** (1905), 145.
(2) Tänzler, *Verh. d. D. phys. Ges.*, **8** (1906), 222.
(3) Gille, *Ann. Phys.*, **48** (1915), 836.

As seen from the above table, that equality $B=\frac{1}{A}$, i.e.,

$$a_{12}=a_{22}, \qquad a_{21}=a_{11}$$

is not satisfied except in the cases O_2——N_2 and He——H_2.
The value $B:\frac{1}{A}$ seems to be apparently independent of temperature; its deviation from unity is the more distinct, the more difference there is in the molecular velocities of the components.

From this and the foregoing results we conclude that the diffusion effect of molecules which makes a great rôle in a gaseous mixture can be left out of consideration in a liquid mixture.

Application of the formula to any binary mixture accompanied with a chemical change. As stated before, the viscosity of a chemically indifferent (or physical) binary mixture can completely be expressible by

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{\left(\frac{k_2a_2}{k_1a_1}\right)z_m}{(1-z_m)+\left(\frac{k_2a_2}{ka_1}\right)z_m}.$$

But when a chemical reaction takes place in admixture, the viscosity η is no more identical to that calculated by the above formula. The deviation $\delta=\eta-\eta_0$ which we call hereafter "solvation viscosity," here η_0 being the calculated value assuming there no chemical change on mixing, may depend entirely upon the mutual molecular reaction between the two constituents.

If a part of component 1 and a part of component 2, at z_m— concentration of component 2, enter into a reaction, which occurs among ν_1 molecules of the former and ν_2 molecules of the latter to form a molecular compound or aggregate, then the solvation viscosity may be assumed to be

$$\delta=\eta-\eta_0 \infty (1-z_m)^{\nu_1}\cdot z_m^{\nu_2}=C\cdot z_m^{\nu_2}\cdot(1-z_m)^{\nu_1},$$

in which C is a proportional constant.

For test of the postulation, three cases $CH_3COOH-H_2O$, CH_3OH-H_2O, and $C_2H_5OH-H_2O$ have been taken, the calculated results being recorded in the last column of each table of the following.

Table 4.

H_2O-CH_3COOH, 25°C (Noack).(1)

z-CH_3COOH	z_m-CH_3COOH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)}$
0.00	0.0000	0.00895	———		
0.10	0.0323	1076	0.00905	0.00171	0.055
0.20	0.0698	1282	917	365	0.057
0.25	0.0910	1359	923	436	0.053
0.30	0.1140	1497	930	567	0.056
0.40	0.1677	1701	946	755	0.054
0.50	0.2417	1905	967	938	0.051
0.60	0.3104	2092	986	1106	0.052
0.70	0.4120	2326	1013	1313	0.054
0.75	0.4737	2370	1028	1342	0.054
0.80	0.5455	2404	1046	1358	0.055
0.90	0.7300	2128	1088	1040	0.053
0.95	0.8510	1698	1113	585	(0.046)
1.00	1.0000	1143			0.054

$$\frac{k_2a_2}{k_1a_2}=\frac{0.57\times1.51}{0.21\times3.18}=1.29,\quad \eta_0=\eta_1+(\eta_2-\eta_1)\frac{1.29z_m}{(1-z_m)+1.29z_m}.$$

The constancy of $\frac{\delta}{z_m(1-z_m)}$ holds strictly at all concentrations, and hence a molecular compound or hydrate $CH_3COOH\cdot H_2O$ exists evidently in solution.

Table 5.

H_2O-CH_3OH, 25°C (Dunstan).(2)

z.CH_3OH	z_m-CH_3OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^2}$
0.0000	0.0000	0.00891	———		
0.0683	0.0396	0.01055	0.00878	0.00177	0.049
0.1007	0.0592	0.01157	872	285	0.054
0.1974	0.1216	0.01378	851	527	0.056
0.2147	0.1333	0.01403	847	556	0.055
0.3592	0.2398	0.01600	812	788	0.057
0.3782	0.2550	0.01567	807	760	0.054
0.3785	0.2553	0.01575	807	768	0.054
0.4071	0.2787	0.01570	799	771	0.053
0.4619	0.3257	0.01570	784	786	0.053

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(1) K. Noack, "Landolt-Tabellen."
(2) A. E. Dunstan, *J. Chem. Soc.*, **85** (1904), 817;

Table 5. (*Continued.*)

z-CH_3OH	z_m-CH_3OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^2}$
0.4956	0.3560	0.01532	774	758	0.051
0.5131	0.3724	0.01540	768	772	0.053
0.5282	0.3865	0.01490	763	727	0.050
0.5535	0.4109	0.01475	755	720	0.051
0.5855	0.4430	0.01427	745	682	0.050
0.5861	0.4440	0.01399	744	655	0.048
0.6106	0.4686	0.01370	736	634	0.048
0.6653	0.5280	0.01282	716	566	0.049
0.7319	0.6056	0.01167	690	477	0.051
0.7741	0.6585	0.01105	671	434	0.057
0.7964	0.6876	0.01003	661	342	0.051
1.0000	1.0000	0.005525			0.052

$$\frac{k_2a_2}{k_1a_1}=\frac{0.36\times1.78}{0.21\times3.18}\doteq0.96,\quad \eta_0=\eta_1+(\eta_2-\eta_1)\frac{0.96z_m}{(1-z_m)+0.96z_m}.$$

For the range studied $\frac{\delta}{z_m(1-z_m)^2}$ keeps to be constant. The fact shows that a hydrate $CH_3OH\cdot2H_2O$ exists in solution.

Table 6.

$H_2O-C_2H_5OH$, 25°C (Dunstan).⑴

z-C_2H_5OH	z_m-C_2H_5OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^3}$	$\frac{\delta}{z_m(1-z_m)^2}$
0.0000	0.0000	0.00891	———			
0.2071	0.0986	1829	0.00907	0.00922	0.126	
0.2466	0.1159	1851	910	941	0.148	
0.2963	0.1415	2129	914	1215	0.136	
0.3240	0.1580	2162	917	1245	0.135	
0.3739	0.1893	2290	922	1368	0.136	
0.3826	0.1952	2301	923	1378	0.136	
0.3965	0.2044	2343	925	1418	0.138	
0.4121	0.2153	2327	927	1400	0.135	
0.4557	0.2468	2351	933	1418	0.134	
0.4617	0.2513	2368	934	1434	0.136	
0.4772	0.2631	2354	936	1418	0.135	
0.5020	0.2830	2337	939	1398	0.134	
0.5558	0.3284	2273	948	1325	0.133	
0.5583	0.3309	2273	948	1324	0.134	
0.5751	0.3462	2247	952	1295	0.134	
0.6015	0.3714	2243	956	1287	0.139	
0.6017	0.3714	2240	957	1287	0.139	
0.6049	0.3745	2226	957	1269	0.138	
0.6106	0.3802	2212	958	1254	0.138	(0.086)

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(1) A. E. Dunstan, & F.B. Thole, *J. Chem. Soc.*, **95** (1909), 1556.

Table 6. (*Continued.*)

z-C_2H_5OH	z_m-C_2H_5OH	η	η_0	δ	$\frac{\delta}{z_m(1-z_m)^3}$	$\frac{\delta}{z_m(1-z_m)^2}$
0.6185	0.3883	2173	960	1213	0.137	(0.084)
0.6536	0.4244	2104	967	1137	(0.140)	0.081
0.6585	0.4299	2112	968	1144	(0.140)	0.082
0.7054	0.4839	1995	979	1016	(0.153)	0.079
0.7390	0.5254	1957	988	969	(0.173)	0.082
0.7809	0.5825	1804	1002	802		0.079
0.8020	0.6132	1744	1010	734		0.081
1.0000	1.0000	1115			0.136	0.081

$$\frac{k_2a_2}{k_1a_1}=\frac{0.34\times1.37}{0.21\times3.18}=0.70, \quad \eta_0=\eta_1+(\eta_2-\eta_1)\frac{0.70z_m}{(1-z_m)+0.70z_m}.$$

The constancy of $\frac{\delta}{z_m(1-z_m)^3}$ holds for the range $z_m=0.1\sim0.4$, and for higher concentrations $\frac{\delta}{z_m(1-z_m)^2}$ keeps to be constant.

This suggests that a hydrate $C_2H_5OH\cdot3H_2O$ exists in solution up to 40 mol. % of C_2H_5OH, and a hydrate $C_2H_5OH\cdot2H_2O$ exists at higher concentrations than 40 mol. % of C_2H_5OH.

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FURFUROLS IN THE FERMENTATION PRODUCTS.

By **Masakazu YAMADA.**

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It has long been regarded as furfurol that which shows a red color with aniline-acetic acid in several fermentation products and usually the pentoses have been appointed as its mother substances.(1) The aldehyde is not found in the ethereal extract of the saké, shōyu (soya-sauce) or other fermented liquids at the end of the fermentation, but occurs for the first time after pasteurization or distillation and, therefore, it is not a real product of microbes.

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(1) S.H. Hastie and W.D. Dick, *Journ. Inst. of Brewing*, **34** (1928), 477.

On the one hand, many investigations have shown that the sugars remaining after the fermentation are mainly consist of rather glucose etc. than pentoses. This fact makes us to recall Foerster's early observation.⑴ Nevertheless the furfurol-like substance coming from sugar solutions by heating is not always furfurol but has been verified to be mainly oxymethylfurfurol in the case of hexose like glucose or fructose and furfurol from arabinose according to Akabori's new test with barbituric acid—aniline reagent⑵ and phloroglucid method.⑶ The oxymethylfurfurol was said to convert gradually into furfurol by repeated distillations. The fact was again ascertained on the distillates of sugar solutions and the real fermentation products. So the origins of furanaldehydes may be shown in the following diagram.

$$\text{Starch} \rightarrow \text{maltose} \rightarrow \text{glucose} \begin{pmatrix}\text{in the aqueous or}\\ \text{weak acid solution}\\ \text{by lactic acid etc.}\end{pmatrix} \xrightarrow{\text{heating}} \text{oxymethyl-furfurol,} \xrightarrow{\text{heating}} \text{furfurol,}$$

$$\text{Pentosan} \longrightarrow \text{pentose} \quad (\ ,,\ ) \xrightarrow{\text{heating}} \text{furfurol,}$$

$$\text{Methyl-pentosan} \rightarrow \text{methyl-pentose} \ (\ ,,\ ) \xrightarrow{\text{heating}} \text{methyl-furfurol.}$$

Thus so-called furfurol of fermentation products is the mixture of furfurol, oxymethyl-furfurol and methyl-furfurol; in sakè, beer, shōyu and some distilled wine oxymethyl-furfurol, and in impure alcohol, fusel oil, etc. furfurol occupying the main part, because in the former heating is only once at the stage of pasteurization (at most 70°C.) or distillation, while in the latter repeated distillations are expected. As an exception, shōyu looks like containing somewhat superior quantity of methyl-furfurol.

Experimental.

The distillate of glucose solution. A solution consisting of 100 gr. of glucose and the same quantity of water was distilled on the paraffin bath of about 160—180°C. with frequent supplies of water. The *p*-nitrophenylhydrazone prepared from the direct extract with ether of the distillate was reddish leaflet, melting point 180–182°C. and decomposed at 183–185°C.⑷ The analytical results are as follows.

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(1) Foerster, *Ber.*, **15** (1882), 322.

(2) S. Akabori, *Proc. Imp. Acad. Tokyo*, **3** (1927), 672; *Chem. Zentr.*, **98** (1927) II, 1962.

(3) Tollens and Ellet, *Z. Deutsch. Zuckerind.*, **55** (1905), 19.

(4) W.A.V. Ekenstein u. J.J. Blanksma, *Chem. Weekblad*, **6** (1919), 217.

Anal. Subst. =0.0510 gr.; N_2=7.1 c.c. (19°, 761.8 mm.) Found: N=16.09%.
Calc. for $C_{12}H_{11}N_3O_4$: N=16.09%.

It is doubtlessly oxymethyl-furfurol-*p*-nitrophenylhydrazone.

Comparison of furfurols obtained from various substances. The furfurols obtained from sugars by heating in their aqueous or weak acid solutions were compared with those in the distillates of sakė, shōyu and in some distilled wine, etc. The distillation of sugar solutions has been conducted in the same manner as described above using the mixture of 2 gr. of sugar and 5 c.c. of water. The phloroglucid has been prepared according to the ordinary method in hydrochloric acid solution of specific gravity 1.06.

The results of the barbituric acid-aniline test and the phloroglucid test are shown in the following table. In this table "Fract. 9 S" denotes the furfurol-like substance of boiling point 160°C. obtained from the distillate of the extract of sakė. "Fract. 14 SH," and "Fract. 15 SH" denote respectively, the furfurol-like substance of boiling point 160–168°C. and that of boiling point above 168°C. obtained from the distillate of shōyu.(1)

	Aniline+ acetic acid	Barbituric acid + aniline	Barbituric acid + aniline + acetic acid	Phloroglucid		
				precipitate		filtrate
				color	solubility in 95% hot alc.	
Furfurol	red	indigo-blue	violet	dark green	0	dark yellowish green
Oxymethyl-furfurol	orange-red	violet	red	brownish violet	100%	pale brown
Methyl furfurol	orange	reddish violet	orange red	,,	,,	,,
Distillate of glucose sol.	red	violet	red	,,	ca. 90%	brownish yellow
Repeated dist.	,,	bluish violet	violet	brownish green	ca. 30%	,,
Twice repeated	,,	,,	,,	dark green	a little	dark yellowish green

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(1) M. Yamada, *Bulletin of the Agricultural Chemical Society of Japan*, **4** (1928), 18.

	Aniline+ acetic acid	Barbituric acid + aniline	Barbituric acid + aniline + acetic acid	Phloroglucid		
				precipitate		filtrate
				color	solubility in 95% hot alc.	
Glucose 2 gr. lactic acid 1 gr. water 5 c.c. dist.	red	violet	red	brownish violet	90%	brownish yellow
Distillate of fructose sol.	„	slightly bluish violet	red	„	90%	„
Distillate of arabinose sol.	„	bluish violet	violet	dark green	trace	„
Distillate of extract of saké	„	reddish violet	red	reddish brown	almost the whole	brownish yellow
Repeated dist.	„	bluish violet	violet	——	——	——
Twice repeated	„	„	bluish violet	——	——	——
Distillate of shōyu	„	reddish violet	red	orange red	almost the whole	yellow
Twice repeated	„	„	reddish violet	——	——	——
"Fract. 9 S"	„	bluish violet	violet	dark green	20%	pale greenish yellow
"Fract. 14 SH"	„	„	reddish violet	„	50%	pale dark yellow
"Fract. 15 SH"	„	violet	„	brownish violet	almost the whole	yellowish brown
Mixture of acet-and valer-aldehyde	yellow	——	——	orange	„	yellow
Shōchu (Japanese whisky)	red	reddish violet	red	——	——	——
Fusel oil (sweet potato)	„	indigo blue	violet	——	——	——
Fusel oil (molasses)	„	„	„	——	——	——

"Fract. 15 SH" shows a reddish violet color characteristic for methylfurfurol with vanillin and HCl (or H_2SO_4) reagent, and coincides on the whole with the aldehyde in other points.

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STUDIES ON THE DISPERSOIDAL SYNTHESIS OF GOLD BY MEANS OF ALKALINE FORMALDEHYDE SOLUTIONS. I.(1)

By P. P. von WEIMARN.(2)

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Preface. In 1922 I carried out a systematic and detailed investigation on obtaining of dispersoidal solutions of gold by means of alkaline (KOH and K_2CO_3) solutions of formaldehyde. I used, in this investigation, beakers made of *ordinary* laboratory glass, which are used in other Departments of our Institute for chemical work; the distilled water and the reagents were also of *ordinary* purity, and not of extra purity.

By applying also to gold, the chief principles of my theory of dispersoidal synthesis, the correctness of which was verified by me almost a quarter of a century ago on more than a hundred substances and by way of thousands of experiments, I arrived in 1922 at the following conclusion: *The dispersoidal synthesis of gold by means of alkaline formaldehyde solutions, carried out by using ordinary distilled water and reagents of ordinary purity (not of extra purity),—provided that it be carried out according to the general principles of my theory of dispersoidal synthesis, —is accomplished as easily, and is as simple and readily reproducible as is for instance the "tannin method" of Wo Ostwald.*(3)

It is evident to every dispersoidologist that these experimental results stand in an extremely sharp contradiction to the experiments of R. Zsigmondy and others.

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(1) Translated from Russian by Mrs. P. P. von Weimarn.

(2) Compare P.P. von Weimarn, "Contributions to the Dispersoidology of Gold," *Reports of the Imperial Industrial Research Institute of Osaka*, **9** (1928), No. 7, 64. For the sake of brevity, in future references to this paper, it will be designated as W_1.

(3) Wo. Ostwald, "Kleines Praktikum der Kolloidchemie," 6 ed. (1926). Theodor Steinkopff, Dresden.

Therefore, previously to repeating my experiments with extra pure distilled water and extra pure reagents, I confined myself in 1923⁽¹⁾ to the publication of some quantitative data of only those experiments in which the extremely high stability of red dispersoidal gold solutions was caused by dispersoidal parasitism at the expense of the products of the resinification of the formoses (Hoppe-Seyler classifies these substances with humous substances, "Humine"; I designated them by the term "H-Dispersoid."

My other experiments,⁽²⁾ in which the influence of H-Dispersoid cannot even be supposed to exist, are described very briefly thus:

> " Ebenso kann man *rote* dispersoide Lösungen erhalten, indem man sie bloss 5 bis 10 Minuten lang sieden lässt (aber auch bei Zimmertemperatur kann man *nicht weniger beständige rote* dispersoide Lösungen erhalten); nur wären dabei verschiedene Konzentrationen des Formaldehyds oder des KOH anzuwenden, als die in Tabelle 1 angegebenen."⁽³⁾

Since 1922⁽⁴⁾ I have repeated my experiments of that year with *extra pure* distilled water and *extra pure* reagents. I used in these experiments beakers made not only of different sorts of glass, but also those made of gold and of platinum⁽⁵⁾ (all beakers were cylindrical).

The results of my repeated experimenting have only confirmed those obtained in 1922; the influence of the "purity" of the distilled water and of the reagents, manifested itself only in the degree of concentration of the red dispersoidal gold solutions which is obtainable by way of evaporating the water. Other conditions being equal, the higher the degree of purity, the stronger is the concentration which, by the evaporation of the dispersoidal gold solutions, can be reached without any change in the colour of these solutions from the excellent red, noted before, to violet or blue.

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(1) P.P. von Weimarn, *Kolloid-Z.*, **33** (1923), 74 & 242; **36** (1925), 1.

(2) As is known, R. Zsigmondy in his book " Das kolloide Gold " submitted my work to a sharp criticism; for my reply see *Kolloid-Z.*, **39** (1926), 278.

(3) P.P. von Weimarn, *Kolloid-Z.*, **33** (1923), 79. Compare ibid., p. 242 (§ 2) in which are indicated in one series of experiments, the limits of the concentrations of the alkaline formaldehyde solutions, that I have used.

(4) P.P. von Weimarn, *Kolloid-Z.*, **39** (1926), 281 (conclusive sentence).

(5) In my experiments I used water distilled in four manners: 1. Ordinary distilled water. 2. Water 1, redistilled through a condenser made of resistance Jena glass. 3. Water 2, distilled once more through a condenser made of platinum or gold. 4. Water 3, distilled through a platinum condenser, was redistilled again through a gold condenser. KOH and K_2CO_3, $AuCl_3HCl\,4H_2O$ and formaldehyde used were of several Japanese firms as well as of the firms Merck and Kahlbaum, *extra pure*. Moreover, I used formaldehyde of Japanese firms and that of Kahlbaum, redistilling them once more. Beakers were employed of three kinds of Japanese glass, and also those of Jena glass and quartz.

I. Essential Points of Dispersoidal Synthesis.

§ 1. Precipitation of sparingly soluble substances by double decomposition reactions.[(1)] For example:

$$\begin{array}{ccccccc} Ba(CNS)_2 & + & MnSO_4 & \rightleftharpoons & BaSO_4 & + & Mn(CNS)_2, \\ 2\,C & & 2\,C & & C & & C \end{array}$$

with water as the dispersion medium.

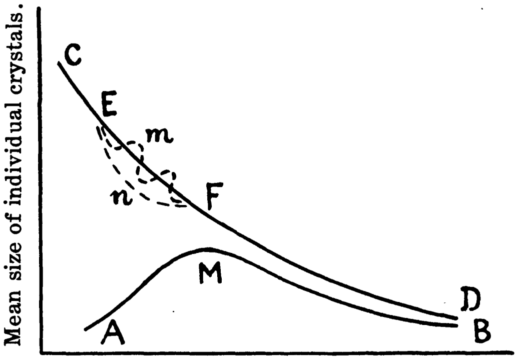

Fig. 1.

If we limit ourselves to knowing only the *qualitative* (or semi-quantitative) direction of precipitation processes, then the expression for the precipitation forms' coefficient is very simple: $N = N_e/J = (C\text{-}L)/L$; when L is extremely small—and this is usually the case in dispersoidal synthesis—then the *qualitative* determination of the change, taking place, in accordance with the concentration of the reacting solutions and solubilities, in the mean size of the *individual* crystals of the precipitating substance, may be expressed thus: $N = C/L$.[(2)]

When studying only one definite case of precipitation, L may be assumed as of constant value $1/k$, and then: $N = kC$. With the increase in N or in the value C, to which N is proportional, the mean size of the *individual* crystals of the precipitating substance passes at first through a maximum (curve AMB in Fig. 1); after the lapse of some time the maximum disappears[(3)] and the precipitation curve assumes the form CEFD (Fig. 1). For dispersoidal synthesis, it is of importance to take into con-

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(1) For more details, on the same subject, see my papers of previous years in *Kolloid-Z.*, my paper in *Chemical Reviews*, **2** (1925), 217, and a detailed paper in the book " Colloid Chemistry, Theoretical and Applied " edited by J. Alexander, (1926), 27. The translation of this paper into the Japanese language has been recently done by my Assistant, Dr. E. Iwase, and is edited as a separate volume by The Maruzen Co.

(2) It is clear that the expression C/L shows the *qualitative* direction of precipitation processes *only when* of all the variables, C and L are those predominating. See P. P. von Weimarn, " Grundzüge der Dispersoidchemie," (1911), 39. Therefore it is a grave mistake, when comparing two precipitation processes, to change C and L without preserving in both processes, equality or approximate equality with regard to other variables in their influence upon the precipitation. For a more exact expression of N and exact equations of precipitation curves for certain cases of precipitation, see my abovementioned paper in the book edited by J. Alexander.

(3) This appears from practical standpoints only; in theory the maximum does not disappear, but becomes strongly shifted to the left. See P.P. von Weimarn, " Die Allgemeinheit des Kolloidzustandes," (1925), 159, Theodor Steinkopff, Dresden.

sideration the fact that the precipitation curve possesses at first a maximum.

The branch AM of the precipitation curve AMB, under the influence of certain corresponding variables, may be forced to a very slow approach towards the branch CEF of the curve CEFD; in the region of concentration corresponding to the branch AM, the growth of the individual crystals proceeds not only at the expense of the truly dissolved substance, but also by means of "aggregation crystallisation" (Aggregation-Kristallisation) and "contact recrystallisation"(1) (Berührungsumkristallisation).

When the crystallisation is accompanied by processes of desolvation which go at a slower rate than the diffusion process, (for instance the dehydration of molecules of $SrSO_4xH_2O \rightarrow SrSO_4$, etc.) then the precipitation curve retains the maximum for a longer time.(2)

If the precipitation by a double decomposition reaction be accomplished not in pure water, but in an aqueous solution of any substance taken in a definite concentration, (e.g. agar-agar,(3) aniline dyes,(4) or of a truly soluble substance which is strongly adsorbed(5) by the surfaces of the precipitating crystals) then, owing to the contamination of the surfaces of the precipitating crystals, the course of the aggregation crystallisation and contact recrystallisation is hindered; as the result of this, the precipitation curve keeps its maximum. These influences, e.g. account for the successful dispersoidal synthesis of substances of small solubility, realised in water in presence of gelatin by C. A. Lobry de Bruyn,(6) and by others.

In the domain of semi-stable supersaturated solutions, very many variables (e.g. dust in water and from dissolved salts, shaking, sometimes even illumination, etc.) affect the *spontaneous* crystallisation, which becomes *forced*. If the influence of these variables is not removed (and it is sometimes very difficult to remove them) the part EF of the curve CEFD, corresponding to the semi-stable supersaturations, assumes the form either of the dotted line EnF or the dotted wavy line EmF; generally speaking, it assumes the form deviating from the smooth part EF of the curve CEFD.

After performing a great number of experiments, always trying to

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(1) P.P. von Weimarn, e.g. "Grundzüge der Dispersoidchemie," (1911), 27 & 60.

(2) P.P. von Weimarn, *Z. physik. Chem.*, **76** (1911), 215.

(3) P.P. von Weimarn, *J. Russ. Chem. Soc.*, **41** (1909), 322 & 728; *Kolloid-Z.*, **6** (1910), 179. When the concentration of agar-agar is kept constant for every concentration of the reacting solutions, then it is clear that the utmost influence of the agar-agar will manifest itself when the concentrations of the reacting solutions are weak.

(4) P.P. von Weimarn, "Grundzüge der Dispersoidchemie," (1911), 97.

(5) P.P. von Weimarn, "Die Allgemeinheit des Kolloidzustandes," 184–190. "Theory of the Colloid State of Matter" 62 (Fig. 8) in "Colloid Chemistry, Theoretical and Applied," edited by J. Alexander (1926). The Chemical Catalog Co., New York.

(6) C.A. Lobry de Bruyn, *Z. physik. Chem.*, **29** (1898), 562.

eliminate as much as possible the influence of these variables, one becomes convinced of their fortuitous character, and of the fact that after their complete elimination, the precipitation curve would possess the smooth contour CEFD.

When the precipitating substance forms a suspension or a dispersoidal solution, then the individual micro- or ultramicrocrystals at once, or after the lapse of some time, under the influence of variables which are not present in the expression $N_e=JC/L$ may form aggregates (aggregate particles). If such an aggregation does not go too far, the curves, which express the dependence upon concentration of the mean size of particles of a suspension or despersoidal solution, will possess the same form as the curve CEFD in Fig. 1.(1) In the cases of a considerable aggregation of the individual micro- and ultramicrocrystals, these curves (with as coordinates: the mean size of particles, concentration C) can have rather varied forms,(2) particularly when the intensity of the aggregative influences, with the progressive change in concentrations, decreases and increases alternately.

§ 2. **Precipitation of sparingly soluble substances, through the decomposition of a compound by a dispersion medium (solventolysis).**(3) For instance: $AlCl_3+xH_2O=Al(OH)_3+3HCl+(x-3)H_2O$;(4)
$AlO_2Na+xH_2O=Al(OH)_3+NaOH+(x-2)H_2O$.

I introduced the term "Precipitation forms' coefficient" as a substitute for the rate of formation(5) of a solid phase, which rate in many cases of dispersoidal synthesis is practically unmeasurable, and it is evident that in the case of the formation of a solid phase by hydrolysis, owing to the increase in the velocity of hydrolysis with dilution,(6) this coefficient, for the purposes of *qualitative* investigation of precipitation processes will have to be expressed thus: $N=(C_w-c_w)/L=C_{aw}/L$, where c_w stands for the dilution, beyond which the hydrolysis does not practically go; and C_w is the total dilution of the given solution; thus C_{aw} is the active dilution; when it is possible to assume L as constant, then $N=k_1C_{aw}$ · For solutions sufficiently diluted, N may be expressed thus: $N=k_2/CL=k_3/C$, where C is the

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(1) P.P. von Weimarn and S. Morishima, see figs. 10–13 (238–239), for the disperse systems of selenium, *Chem. Reviews*, **2** (1925).

(2) P. P. von Weimarn, *Kolloid-Z.*, **36** (1925), 8-9 (Fig. 2); *Chem. Reviews*, **2** (1925), 225 (Scheme C).

(3) Compare P.P. von Weimarn, *Kolloid-Z.*, **33** (1923), 230; *Chem. Reviews*, **2** (1925), 227.

(4) In reality the hydrolysis processes are more complicated and are accompanied by the formation of intermediate compounds, see e.g. J. Matula, "Allgemeine Chemie," (1923), 162.

(5) For the formulation of the precipitation law, see *J. Russ. Chem. Soc.*, **38** (1906), 267. This formulation appeared in German in *Kolloid-Z.*, **43** (1927), 26.

(6) H.M. Goodwin, *Z. physik. Chem.*, **21** (1896) 1–15, especially pp. 11 & 15.

concentration of the hydrolysed substance previous to the beginning of the hydrolysis (in the cases analogous to the hydrolysis of $AlCl_3$, concentration C represents also the concentration of the product after the termination of the hydrolysis).

Therefore, the experimentally established fact (W. Bilz),⑴ that in the formation of a solid phase by hydrolysis, the mean size of particles of the precipitating substance, decreases with the growing dilution, is not in contradiction to, but in full accord with, my theory of precipitation. That is, in the case of solventolysis also, after the lapse of some time from its commencement, with the increase of N, the mean size of the individual crystals decreases, i.e. the precipitation curve has the shape of the curve CEFD (Fig. 1).⑵

The producing of AgI or $BaSO_4$ dispersoidal solutions, in an alcohol-aqueous medium from their double compounds, AgIxKI or $BaSO_4xMnSO_4$, represents also an example of solventolysis. *And in general, cases of solventolysis are very often met with in dispersoidal synthesis.*⑶

II. Several Instances of the Obtaining of Red Dispersoidal Gold Solutions by means of Alkaline Solutions of Formaldehyde.⑷

§ 1. **General.** For acquiring a clear idea of the process of the reduction of gold by alkaline formaldehyde solutions, it is essential to remember the reactions:

$$\text{I.}\quad AuCl_3+3H_2O \rightleftarrows Au(OH)_3+3HCl;$$

$$\text{II.}\quad AuO_2K+2H_2O \rightleftarrows Au(OH)_3+KOH.^{(5)}$$

Further it is advisable to recall to mind the existence of aurous hydroxide, AuOH, producing in water a dispersoidal solution of an indigo-blue colour; the latter fact and Reaction II are most important for experimentation by the formaldehyde method.

When we experiment upon a stable, weak, but highly disperse AuOH solution, the reduction, in the case of an insufficient quantity of the

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(1) Quoted from Th. Svedberg's "The Formation of Colloids," (1921), 105, London.

(2) It is clear that in the case of complete solventolysis, when the concentration of the solutions approach the saturation concentration of the precipitating solid substance, the crystallisation goes on from the more or less stable supersaturated solutions, i.e. in this case, the expression $N=(C-L)/L$ must be assumed in which C is the concentration of the substance being precipitated. In substances which are actually sparingly soluble, the concentration corresponding to their solubility is so vanishingly weak, that in practice such infinitely diluted solutions are not used.

(3) Compare P.P. von Weimarn, *Chem. Reviews*, **2** (1925), 227.

(4) Compare P.P. von Weimarn, Paper W_1. A more detailed exposition is given in a paper which is in preparation, "Contributions to the Dispersoidology of Gold II." *Reports of the Imperial Industrial Research Institute of Osaka.* In future references this paper will be designated by W_2.

(5) What is said in Footnote (4) in page 39 is also applicable to these cases.

reducing agent, proceeds very protractedly, but in spite of this, a beautiful red dispersoidal gold solution is obtained. It is evident that in a dispersoidal AuOH solution, of coarser dispersity, but at the same time of greater concentration (possessing a greater number of particles in unit volume) the addition of larger quantities of reducing agent, proportionally to the increased concentration, will at first accelerate the reduction.

This happens because the molecules of the reducing agent meet a greater number of AuOH particles. But the particles being coarser, the resulting dispersoidal gold solution is of a coarser dispersity, and the transformation of AuOH particles totally into pure gold particles is more protracted than it is in weaker dispersoidal AuOH solutions with highly disperse particles. In general, the coarse dispersity of AuOH particles, acts in greatly hindering their transformation into pure gold, and AuOH can, for an extremely long time, remain embodied within the ultramicrocrystals (or their aggregates) of gold.

§ 2. **Several instances of the obtaining of red dispersoidal gold solutions, the stability of which is caused by the presence of small quantities of unreduced gold compounds.**⁽¹⁾ § **2a. Formaldehyde in a KOH-solution.** $A_1 \cdot 500\ H_2O\ (20°C.) \leftarrow 10\ AuCl_3HCl4H_2O\ (0.1\%) \leftarrow 0.7\text{–}1.4\ F^{10}_{0.2KOH}$⁽²⁾ The numbers preceding the formulae indicate the number of c. c.

The reagents (of room temperature) are poured rapidly, in succession, and the whole quantity of each, all at once,⁽³⁾ into water which meanwhile is being vigorously stirred with a thermometer.

When 0.7 c.c. $F^{10}_{0.2KOH}$ are added, although the reaction proceeds instantaneously i.e. on the surface of contact, the reduction is not complete, and an intensely indigo-blue liquid is obtained, which is perfectly transparent and has no opalescence. When allowed to remain at room tem-

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(1) On red dispersoidal gold solutions, the stability of which, over a period of six years, without change of the red colour into violet, is accounted for by the presence of a small quantity of „H-Dispersoid," see *Kolloid-Z.*, **33** (1923), 78. The repetition of these experiments with extra pure reagents has also fully confirmed the results obtained by me in 1922, with reagents of ordinary purity.

(2) The beakers of glass, gold and platinum used were of 1 litre capacity; the beaker of quartz was of 300 c.c. Reagents $F^{10}_{0.2\,KOH}$, $F^{10}_{0.1\,KOH}$, $F^{5}_{0.2\,KOH}$ etc. are concise designations for the following solutions. To 90 c.c. 0.2 norm. KOH solution, is added – to form 100 c.c. – a concentrated (about 35% by weight) formaldehyde solution; to 90 c.c. 0.1 norm. KOH-solution is added – to form 100 c.c. – the same formaldehyde solution; to 95 c.c. 0.2 norm. KOH-solution is added – to form 100 c.c. – the same formaldehyde solution, etc.

(3) I measured the reagent F in conical vessels of 5 c.c. capacity, graduated in half c.c. It must be pointed out that a part of the reagent (in my experiments amounting to about 0.2 c.c. for 3 c.c. of the reagent) adheres to the walls of the vessel. If in the producing of an intensely indigo-blue dispersoidal solution it is desirable to obtain always the same *quantitative* results, the quantity of the reagent $F^{10}_{0.2\,KOH}$ added, must be varied a little, in dependence upon the amount of water and upon the acidity of the commercial chloride of gold.

perature, the blue colour of this dispersoidal solution, passes through violet, to red (50–46–42–38–33–29); red 33 appears(1) after the lapse of 24 hours, and red between 33 and 29, after 48 hours. These red dispersoidal solutions are very stable. If the indigo-blue liquid, just after its being obtained, be heated over a powerful Teklu burner, the colour, after 10 minutes' heating, at the beginning of boiling, becomes red 25, and after 10 minutes' boiling, a beautiful red appears, with an orange nuance, 25–21, without any opalescence. By the addition of more than 0.7 c.c. of $F^{10}_{0.2KOH}$, at once a violet or reddish-violet dispersoidal solution is obtained. During the transition of colour of the dispersoidal solution into pure red, the intensity of colouring falls off sharply.

The experiments, carried out with ordinary distilled water, in beakers of every kind of ordinary laboratory glass, (made in Japan) and with reagents of different preparation, of ordinary purity, as well as of extra purity, have proved always successful.

By means of boiling off, this red dispersoidal solution may be concentrated to 1/3 of its original volume, without change in colour and without the appearance of opalescence. A further concentration is also practicable; but when reagents of only ordinary purity are used (this applies chiefly to all commercial solutions of formaldehyde)(2) the dispersoidal solutions which have so far preserved their beautiful red colouring, on cooling become blue (there is an increase in adsorption on cooling, owing to the decrease of solubility of the adsorbing coagulants); when after being sufficiently concentrated (e.g. to 120–100 c.c.) the hot solution with its beautiful red colour (possessing an orange nuance) is being poured in a thin stream into another beaker, the stream itself becomes at once bluish.

The concentration of the red dispersoidal gold solution, without any change in its red colour, by means of boiling off to 1/6 of the initial volume (80–85 c.c.) is accomplished always with success when redistilled formaldehyde solution is used; the use in this case of water redistilled through a condenser of Jena glass is only to be commended.

The red dispersoidal solutions, concentrated to 1/3 of their initial volume, may be mixed, without the colour's changing into blue, with concentrated (extra pure, freshly distilled) ammonia; under the ammonia test, the surface of separation remains red during e.g. two hours. However, these red dispersoidal solutions still contain traces of unre-

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(1) According to the standards established by W. Ostwald, "Die Farbenfibel." 10 ed. (1924), 19.

(2) The bottles in which the formaldehyde solution is kept are not of a high quality, therefore after a long preservation in such bottles, the formaldehyde solutions, whether of Japanese or of German preparation, take up considerable quantity of coagulants.

duced gold compounds which may be revealed by means of the ammonia test; in order to minimize these, more of the diluted KOH-solution (without formaldehyde) should be added (see below).

I should like to point out especially that the concentrations, indicated in Experiment A_1, should in no wise be regarded as *fixed;* quite the contrary, there exist variations of concentrations which are difficult to enumerate, with which red gold solutions are obtained and may be always reproduced. It is only necessary, that either the dispersoidal AuOH solution, *produced instantaneously,* should be stable, or that the reduction reaction of this solution into gold at first goes as rapidly as possible, whilst the AuOH is still in statu nascendi.(1)

For instance, by working with the following concentrations, there are obtained after 5–10 minutes' boiling, dispersoidal gold solutions which are also coloured a beautiful red with an orange tinge.

$$A_2 \cdot 500\ H_2O(20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.1\%) \leftarrow 1.4\ F^{5}_{0.2\,KOH};$$
$$A_3 \cdot 500\ H_2O(20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.1\%) \leftarrow 1.4\ F^{5}_{0.5\,KOH};$$
$$A_4 \cdot 500\ H_2O(20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.1\%) \leftarrow 1\text{-}1.4\ F^{10}_{0.1\,KOH}.$$

In the instance A_4 (with the presence of a larger quantity of unreduced gold compounds) by boiling, it is possible to concentrate the dispersoidal solution, without change in its red colour, to 1/10 (50 c.c.) of the initial volume. Instead of pure reagent F there may of course be added its mixture with KOH-solution, e.g. $(0.75\ F^{10}_{0.2\,KOH} + 0.75\ KOH,\ 0.2\ \text{norm.})$ etc.

All the above-mentioned solutions, after the dissolution of gold(2) by the addition of 1/10 norm. KCN solution, leave behind a liquid as perfectly transparent and colourless as water (even in a layer of 11 cm.); the influence on the stability of H-Dispersoid, cannot be even supposed to exist, because in the presence of even small quantity of H-Dispersoid, after the dissolution of gold by KCN solutions, the liquid left behind is coloured yellow.

The diminution of the amount of formaldehyde and the fall in the concentration of KOH-solutions below certain limits, make it either totally impossible to obtain red dispersoidal gold solutions, or else to produce them only by chance. For instance, if we add to 500 c.c. distilled water (20°C.) e.g. 1 c.c. $F^{10}_{0.05\,KOH}$ there is obtained a blue liquid, which under boiling does not change to red; even after the addition $3\ F^{10}_{0.05\,KOH}$, either strongly opalescent red dispersoidal solutions are obtained, or violet ones;

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(1) For more details see Paper W_2.

(2) Compare Paper W_1. In this case one fails to obtain a liquid coloured pure orange, by the incomplete dissolution of gold by KCN-solutions; however, there may be obtained an orange-red coloured liquid, with orange predominating.

provided only the concentration of the commercial preparation of formaldehyde is normal (35%).

In order to avoid the long procedure of eliminating formaldehyde by boiling it off from red dispersoidal gold solutions, and to decrease the quantity of coagulants introduced if the formaldehyde solution is employed without redistillation, it is advisable to take as small a quantity as possible of reagent F, diluting it with a pure (*without formaldehyde*) solution of KOH (i.e. $xF+yKOH$, where $y>x$). The temperature of water may be of course also varied; I worked with the water of 20°C. and also with that of temperatures from 2.5°C. At low temperatures (below 20°C.) the colour of the dispersoidal solution at first tends to blue-violet, but after boiling, it changes to the beautiful red with an orange nuance, possessing no opalescence.⁽¹⁾

The above-discussed dispersoidal solutions prove to be extremely stable; on the grounds of my experiments of 1922, I can say that dispersoidal solutions, obtained by the addition of 1 c. c. of $F^{10}_{0.2\,KOH}$ are stable for more than a year at least.

The obtaining at one time of large amounts of dispersoidal gold solutions with a beautiful red colour, of considerably higher concentration, may be carried out (see Footnote (3) in page 41), for instance, thus: $B_1 \cdot 500\ H_2O(20°C.) \leftarrow 60\ AuCl_3 \cdot HCl \cdot 4\ H_2O\ (0.1\%)$, or $10\ AuCl_3 \cdot HCl \cdot 4\ H_2O(0.6\%) \leftarrow 3.5\ F^{10}_{0.2KOH}$, or better thus: $B_2 \cdot 500\ H_2O\ (20°C.) \leftarrow 10\ AuCl_3 \cdot HCl \cdot 4\ H_2O\ (0.6\%) \leftarrow (1.5\ F^{10}_{0.2\,KOH} + 2\ KOH,\ 0.2\ norm.)$ or $(2\ F^{10}_{0.2\,KOH} + 2\ KOH,\ 0.2\ norm.)$ etc. If we keep the solution B_1, for instance, at room temperature, then after the lapse of approximately 1 hr. 40 min., its dark-red colouring (claret-red), very intense initially, changes as by leaps into the beautiful red with an orange tinge without perceptible opalescence; in this transition of colour, its intensity falls off sharply. Heating to boiling, accelerates the rate of this change of colour; and in the case when the quantity of $F^{10}_{0.2\,KOH}$ taken is somewhat less than that indicated, the intensity of colour on heating, at first increases very strongly and the liquid becomes quite opaque; but on further heating, the intensity of colour suddenly falls off sharply, and a beautifully coloured red dispersoidal solution results which is perfectly transparent (in a layer of 11 cm.) and possesses no perceptible opalescence in diffused day light.

The reduction process, carried out according to B_2, proceeds quite

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(1) By pouring even extra pure reagents into *boiling* water, distilled even thrice, in spite of experimenting in a gold beaker, there are obtained strongly opalescent and even turbid dispersoidal solutions, and their red colouring changes to violet-red. Compare K. Hiege, *Z. anorg. Chem.*, **91** (1915), 148. When working with water of 20°–2.5°C., it may with success be used distilled ordinarily, as well as redistilled thrice. If it is desirable to concentrate as much as possible, by way of evaporation, the dispersoidal solution obtained, it suffices to use water redistilled once.

similarly to that of B_1; when to a portion of dispersoidal solution, cooled to room temperature, be added, after the fall of intensity in the colour, concentrated (extra pure) ammonia, (dispersoidal solution 2/3+concentrated ammonia 1/3), the solution becomes at once blue; this is a proof, as it is also for the dispersoidal gold solutions obtained by the "phosphorus method," of the presence of certain quantities of unreduced gold compounds.(1) The quantity of these unreduced compounds may be minimized in various simple ways. If it is desirable to attain this rapidly, strongly diluted KOH-solutions, e.g. 0.02 norm., are poured as soon as the intensity of colouring has fallen, by small portions (in order not to stop boiling), into boiling mixture B_2; after the addition of only 50 c.c., the intensity of colour of the dispersoidal solution falls off somewhat, and a slight brown opalescence in reflected light appears; this solution may be mixed with concentrated ammonia and the mixture remains for a time red. The same is observed after the addition of 100–150 c.c. of a diluted KOH-solution. However, after the addition of 300 c.c. KOH-solution of 0.02 norm. (in certain experiments even of 200 c.c.) and after the reducing by boiling of the volume of the dispersoidal solution to 500 c.c., it becomes again extremely sensitive to ammonia; an immediate change of colour to violet and blue ensues, after the addition of ammonia to this solution.

Thus a minimum of sensitiveness to ammonia exists. It corresponds to the addition of about 150 c.c. of a diluted KOH-solution (more details are given in Paper W_2). The greater sensitiveness to ammonia, observed after the addition of 300 c.c. of a diluted KOH-solution, is accounted for by the increased activity, caused by the ammonia, of coagulants(2) which are present in the dispersoidal solution.

Previously to the addition of diluted KOH-solution, dispersoidal solutions B_1 and B_2 can be easily concentrated by way of boiling, to 1/5 of their original volume. Dispersoidal solutions of double concentration can be obtained at once by the addition to 500 c.c. water (20°C.) of 20 c.c. 0.6% $AuCl_3HCl4H_2O$, and by increasing correspondingly the quantities of mixture $F^{10}_{0.2KOH}$ and KOH solution of 0.2 norm.

Of course, beautiful red dispersoidal gold solutions may be also obtained by taking instead of 500 c.c., 1 litre of water and by doubling the quantities of the reagents. The use of a mechanical stirrer makes it possible to apply much larger volumes of water.

Thus, by my modification of the formaldehyde method, very large quantities of beautifully coloured red dispersoidal gold solutions may be obtained in a short time with ordinary distilled water and reagents of ordi-

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(1) See Paper W_1; more details will appear in Paper W_2.

(2) For more details see Paper W_2. In the presence of H-Dispersoid, when the eduction is complete, no coagulation is observed by the addition of ammonia, even when the content of KOH is great.

nary purity; these solutions, whether in the *minimal* contents of unreduced compounds of gold, or in other properties are not inferior to the dispersoidal gold solutions obtained by the prescript given by R. Zsigmondy; according to which they can be prepared only with extra pure distilled water and extra pure reagents; in spite of these precautions the obtaining of the dispersoidal gold solutions by this prescript is not always successful.⁽¹⁾

The less the unreduced compounds of gold, contained in a dispersoidal gold solution the more is this solution sensitive to coagulants; therefore the dispersoidal solution containing a minimum of unreduced compounds, when very long preservation is desired, must be kept in bottles of resistant glass of high quality.

§ 2b. Formaldehyde in K_2CO_3-solution. For the understanding of this case, the following reactions for salts of iron and especially for those of silver, must be remembered: $2\,FeCl_3 + 3\,K_2CO_3 + 3\,H_2O = 2\,Fe(OH)_3 + 6\,KCl + 3\,CO_2$; $FeCO_3 + CO_2 + H_2O = Fe(HCO_3)_2$; $4\,FeCO_3 + 6\,H_2O + O_2 = 4\,Fe(OH)_3 + 4\,CO_2 \cdot 2\,AgNO_3 + K_2CO_3 = Ag_2CO_3 + 2\,KNO_3$; $Ag_2CO_3 + K_2CO_3 = Ag_2CO_3 \cdot K_2CO_3$; $Ag_2CO_3 \cdot K_2CO_3 + aH_2O = Ag_2CO_3 + K_2CO_3 + aH_2O$; $Ag_2CO_3 + H_2O + CO_2 = 2\,AgHCO_3$; $Ag_2CO_3 + (b+2)H_2O = 2\,AgOH + CO_2 + (b+1)H_2O$.

Similar reactions take place under suitable conditions, for gold salts also, and the possibility of a temporary formation of gold carbonate, gold bicarbonate and of double carbonates of gold and potassium,⁽²⁾ must be kept in mind. It must also be especially emphasised that the rate of decomposition of "carbonates of gold" is influenced not only by the CO_2, which is in the water, but also by the oxygen from the air dissolved in water.

In order to obtain results, approaching those described in § 2a for formaldehyde solutions in KOH, the following is one of the ways recommended: $A'_1 \cdot 500\,H_2O\,(50°C.) \leftarrow 10\,AuCl_3HCl\,4\,H_2O\,(0.1\%) \rightarrow 1.5\,F^{10}_{0.2\,K_2CO_3}$; $B'_1 \cdot 500\,H_2O\,(50°C.) \leftarrow 10\,AuCl_3HCl\,4\,H_2O\,(0.6\%) \leftarrow 3.5\,F^{10}_{0.2K_2CO_3}$. On being heated to boiling and on further boiling, mixtures A'_1 and B'_1 behave very similarly to mixtures A_1 and B_1 in § 2a.

The completion of the reduction is achieved by the addition of a diluted K_2CO_3 solution (0.2 norm. is also possible), similarly to that described in § 2a. Reagent $F^{x}_{0.2\,K_2CO_3}$ is more sensitive than Reagent $F^{x}_{0.2\,KOH}$ to the decrease in the amount of formaldehyde. Under other conditions, equal to $F^{x}_{0.2\,KOH}$, turbid, red dispersoidal solutions are obtained, when only the quantity of formaldehyde in K_2CO_3 is somewhat decreased.

§ 3. On the degree of dispersity possessed by dispersoidal gold solutions, obtained by the author's modification of the formaldehyde method.⁽³⁾

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(1) With more details, in Paper W_2.

(2) I propose to devote a special paper to the transformation of "carbonates of gold" into gold.

(3) For more details see Paper W_2.

The mean size of particles of dispersoidal gold solutions, stands in direct dependence upon the mean size of particles of dispersoidal AuOH solutions, the transformation of which particles into gold, causes the appearance of dispersoidal gold solutions. If in the course of the reduction process, the aggregation of particles in a dispersoidal AuOH solution, has not proceeded too far, there exists between the mean size of particles of the dispersoidal gold solution and the dilution, the same dependence as this is in AuOH dispersoidal particles, i.e. with the increase in $N=k_1C_{aw}$ (see § 2, Chapter I) or in $N=k_3/C$ the mean size of particles decreases. Of course, a far-reaching aggregation of AuOH particles, alters completely this dependence.

By applying for the dispersoidal gold synthesis, the formaldehyde method modified by me, in the reduction carried out at low temperatures (approaching e.g. that of the room), amicroscopical dispersoidal gold solutions are very easily obtained; it is also possible to obtain dispersoidal gold solutions possessing any degree of dispersity, including of course those with the degree of dispersity obtained by Zsigmondy's prescript, which requires the use of extra pure water and extra pure reagents.

Conclusion.

In one of my papers(1) I have already directed attention to the fact that without a scrupulous mental analysis of the vast number of variables governing dispersoidal processes, one may easily go astray and approach the solution of the problem from a wrong angle.

When conditions are created according to my old theory of dispersoidal synthesis,—the observance of which conditions is necessary for its success,—then by using ordinary distilled water and reagents of ordinary purity, as the reader has already learned from the previous pages *it is possible, working by the formaldehyde method, to obtain easily dispersoidal gold solutions of a splendid red colour, which are always reproducible.*

I wish here also to thank once more Prof. Emer. Y. Osaka, for his kind hospitality which I enjoyed from 1922 to 1926, in his laboratory at the Kyoto Imperial University; in this laboratory were carried out the first ultramicroscopical investigations of the dispersoidal gold solutions, obtained by my modification of the formaldehyde method. The author takes it as his pleasant duty, to express here many cordial thanks to Mr. I. Shoji, President of the Imperial Industrial Research Institute of Osaka, for the opportunity kindly afforded him to repeat the experiments of 1922, with extra pure reagents and with very expensive distilling apparatus.

1922–1928 Dispersoidological Department of the
Imperial Industrial Research Institute of Osaka.

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(1) P.P. von Weimarn, *Journal of Chemical Education*, **3** (1926), 373.

ON THE OXIDATION OF STANNOUS CHLORIDE IN SULPHURIC ACID SOLUTION BY AIR AND THE DISSOLUTION VELOCITY OF OXYGEN INTO SULPHURIC ACID SOLUTION.

By Susumu MIYAMOTO.

Received December 30, 1928. Published February 28, 1929.

Introduction. The dissolution velocity of oxygen into sodium hydroxide, sodium carbonate and hydrochloric acid solutions of various concentrations when air is passed into the solution under certain conditions was obtained indirectly from the oxidation velocity of sodium sulphite, stannous chloride or ferrous hydroxide in the mentioned solutions.(1)

The present research was undertaken with an expectation that the oxidation velocity of stannous chloride in sulphuric acid solution will also give the dissolution velocity of oxygen into the solution under the same conditions.

Experimental. The experimental procedure was quite the same with that employed in the study of the oxidation of the same substance in hydrochloric acid solution by means of air.(2)

Air, washed by passing through acidic solution of potassium bichromate and sodium hydroxide solution, was passed into the reacting solution, contained in a large test tube (diameter $\fallingdotseq$ 3 cm.) through a glass tube (inside diameter $\fallingdotseq$ 4 mm., outside diameter $\fallingdotseq$ 6 mm.), at the rate of 7.78 litres per hour, the total volume of the reacting solution in the vessel being made to 40 c.c. in each measurement. After t-minutes the air current was stopped, and the total quantity of the substances contained in the vessel was poured into a known quantity of iodine solution, and the excess of iodine was titrated back by means of sodium thiosulphate solution. The value of v, given in the following tables, is the volume of sodium thiosulphate solution of 0.09962 normal, which is equivalent to the total quantity of stannous sulphate, remained after the t-minutes passage of air.

As will be shown later, the oxidation velocity was independent of the concentration of stannous sulphate, when the concentration of sulphuric acid is greater than about 0.8 normal under the conditions of the present experiment.

The observed results at 20°C. are given in Table 1, and illustrated in

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(1) S. Miyamoto, this Bulletin, **3** (1928), 100 & 139; *Scientific Papers of the Institute of Physical and Chemical Research,* **8** (1928), 243; **9** (1928), 203.

(2) S. Miyamoto, this Bulletin, **2** (1927), 259; *Scientific Papers of the Institute of Physical and Chemical Research,* **8** (1928), 93.

the accompanying figure. The velocity constant k, given in the last column of the table, was calculated by an equation, $k=\frac{1}{t}(v_0-v)$, v_0 being the value of v at $t=0$. The calculated value of v by an equation, $v_{calc.}=v_0-kt$, using the mean value of k, is given in the fourth column of the table.

Table 1.

Temp.=20°C. Velocity of Air=7.78 litres per hour.

$C_{H_2SO_4}$ normal	t min.	v c. c.	$v_{calc.}$ c. c.	k
0.837	0	28.27	—	—
	20	25.96	25.97	0.116
	40	23.80	23.67	0.112
	60	21.36	21.37	0.115
	0	22.64	—	—
	20	20.06	20.34	0.129
	40	18.17	18.04	0.112
	60	16.32	15.74	0.105
	0	21.37	—	—
	20	18.99	19.07	0.119
	40	17.07	16.77	0.108
			Mean:	0.115
0.3900	0	20.11	—	—
	20	17.48	17.57	0.132
	40	14.98	15.03	0.128
	60	12.64	12.43	0.125
	0	13.94	—	—
	20	11.46	11.40	0.124
	40	8.81	8.86	0.128
			Mean:	0.127
0.9720	0	24.39	—	—
	20	21.85	21.97	0.127
	40	19.49	19.55	0.123
	60	17.37	17.13	0.117
	0	19.71	—	—
	20	17.33	17.29	0.119
	40	14.51	14.87	0.130
	60	12.98	12.45	0.112
			Mean:	0.121

Table 1. (*Continued.*)

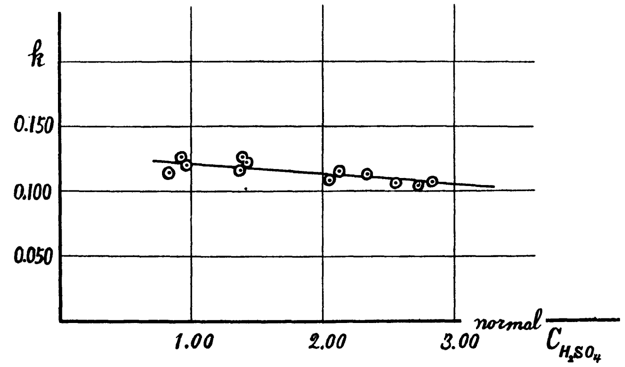
$C_{H_2SO_4}$ normal.	t min.	v c. c.	$v_{calc.}$ c.c.	k
1.377	0	18.53	—	—
	20	16.10	16.19	0.122
	40	13.91	13.85	0.116
	60	11.48	11.51	0.118
	0	16.94	—	—
	20	14.61	14.60	0.117
	40	12.18	12.26	0.119
	60	10.36	9.92	0.110
			Mean:	0.117
1.396	0	17.70	—	—
	20	15.08	15.16	0.131
	40	12.68	12.62	0.126
	60	10.06	10.08	0.127
	0	14.86	—	—
	20	12.29	12.32	0.129
	40	10.08	9.78	0.120
	60	7.12	7.24	0.129
			Mean:	0.127
1.423	0	16.56	—	—
	20	14.30	14.10	0.113
	40	11.57	11.64	0.125
	60	9.17	9.18	0.123
	0	24.32	—	—
	20	21.89	21.86	0.122
	40	19.44	19.40	0.122
	60	16.54	16.94	0.130
			Mean:	0.123
2.052	0	21.41	—	—
	20	19.18	19.23	0.112
	40	17.20	17.05	0.105
	60	14.80	14.87	0.110
	0	14.34	—	—
	20	12.13	12.16	0.111
	40	9.96	9.98	0.110
	60	8.09	7.80	0.104
			Mean:	0.109

Table 1. (*Continued.*)

$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
2.127	0	20.23	—	—
	20	18.11	17.91	0.106
	40	15.76	15.59	0.112
	60	13.29	13.27	0.116
	0	24.36	—	—
	20	21.88	22.04	0.124
	40	19.54	19.72	0.121
	60	17.34	17.40	0.117
			Mean:	0.116
2.335	0	21.40	—	—
	20	19.25	19.12	0.108
	40	16.84	16.84	0.114
	60	14.82	14.56	0.110
	0	12.99	—	—
	20	10.67	10.71	0.116
	40	8.22	8.43	0.119
	60	5.96	6.15	0.117
			Mean:	0.114
2.558	0	20.50	—	—
	20	18.45	18.36	0.103
	40	16.20	16.22	0.108
	60	13.99	14.08	0.109
	0	19.77	—	—
	20	17.67	17.63	0.105
	40	15.38	15.49	0.110
	60	13.53	13.35	0.104
			Mean:	0.107
2.727	0	19.66	—	—
	20	17.52	17.56	0.107
	40	15.36	15.46	0.108
	60	13.45	13.36	0.104
	0	18.04	—	—
	20	15.98	15.94	0.103
	40	13.93	13.84	0.103
			Mean:	0.105

Table 1. (*Continued.*)

$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
2.832	0	18.15	—	—
	20	15.93	15.99	0.111
	40	13.91	13.83	0.106
	60	11.38	11.67	0.113
	0	24.66	—	—
	20	22.58	22.50	0.104
	40	20.50	20.34	0.104
	60	18.17	18.18	0.108
			Mean:	0.108



When the concentration of sulphuric acid is less than about 0.8 normal, the oxidation velocity of stannous sulphate depends upon its initial concentration and decreases as the concentration of sulphuric acid decreases.

The experimental error was great, and no sufficient experimental results, a part of which being given in Table 2, for the quantitative discussion was obtained, but it can only qualitatively be described that the oxidation velocity increases slowly with the increase of the concentration of sulphuric acid until it reaches the dissolution velocity of oxygen when the concentration of the latter is about 0.8 normal. In the case of the oxidation of stannous chloride in hydrochloric acid solution, the oxidation velocity increases more rapidly with the increase of the concentration of hydrochloric acid and attains the dissolution velocity of oxygen into the solution when the concentration of hydrochloric acid is about 0.2 normal.(1)

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(1) Loc. cit.

Table 2.

Temp. = 20°C. Velocity of Air = 7.78 litres per hour.

$C_{H_2SO_4}$ normal	t min.	v c.c.	v_0-v c.c.
0.01410	0	14.12	—
	10	13.79	0.33
	50	12.54	1.58
	120	10.47	3.65
0.2959	0	13.69	—
	10	13.47	0.22
	50	11.94	1.75
	120	9.02	4.67
0.7185	0	13.85	—
	10	12.91	0.94
	50	10.46	3.39
	0	15.66	—
	10	14.41	1.25
	50	12.11	3.55

The effect of the concentration of sulphuric acid. The relation between the velocity constant k and the concentration of sulphuric acid can be expressed approximately as a linear function, when the concentration of sulphuric acid is greater than about 0.8 normal. The calculated values of k by an equation,

$$k=0.128-0.00718C_{H_2SO_4}$$

are given as $k_{calc.}$ in the third column of Table 3.

The effect of temperature. The values of the oxidation velocity, observed at 30°C. and 40°C., are given in Table 4. By comparing Table 1 with Table 4 it will be seen that the change of temperature has negligible effect on the oxidation velocity when the concentration of sulphuric acid is greater than about 0.8 normal. The result means only that the effect of temperature on the dissolution velocity of oxygen, not on the true reaction velocity, is negligible. The effect of temperature on the oxidation velocity, when the concentration of sulphuric acid is less than about 0.8 normal, can be expected to be more complex, but it was not the purpose of the present study.

Table 3.

Temp. = 20°C. Air = 7.78 litres per hour.

$C_{H_2SO_4}$ normal	$k_{obs.}$	$k_{calc.}$ ($=0.128-0.00718C_{H_2SO_4}$)	Dissolution velocity of oxygen. moles per minute.
(0)	—	—	(8.2×10^{-6})
0.837	0.115	0.122	2.9×10^{-6}
0.930	0.127	0.121	3.2 ,,
0.972	0.121	0.121	3.0 ,,
1.377	0.117	0.118	2.9 ,,
1.396	0.127	0.118	3.2 ,,
1.423	0.123	0.118	3.1 ,,
2.052	0.109	0.113	2.7 ,,
2.127	0.116	0.113	2.9 ,,
2.335	0.114	0.111	2.8 ,,
2.558	0.107	0.110	2.7 ,,
2.727	0.105	0.108	2.6 ,,
2.832	0.108	0.108	2.7 ,,

Table 4.

Velocity of Air = 7.78 litres per hour.

Temp.	$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
30°C.	1.423	0	23.37	—	—
		20	20.81	20.85	0.128
		40	18.48	18.33	0.122
		60	15.99	15.81	0.123
		0	24.58	—	—
		20	21.98	22.06	0.130
		40	19.47	19.54	0.128
		60	17.10	17.02	0.125
				Mean:	0.126
30°C.	2.127	0	17.14	—	—
		20	14.52	14.68	0.131
		40	12.31	12.22	0.121
		60	9.95	9.76	0.120
		0	26.73	—	—
		20	24.19	24.27	0.127
		40	22.01	21.81	0.118
		60	19.50	19.35	0.121
				Mean:	0.123

Table 4. (*Continued.*)

Temp.	$C_{H_2SO_4}$ normal	t min.	v c.c.	$v_{calc.}$ c.c.	k
40°C.	1.423	0	18.10	—	—
		20	15.73	15.46	0.119
		40	12.76	12.82	0.134
		0	24.31	—	—
		20	21.58	21.67	0.137
		40	18.83	19.03	0.137
				Mean:	0.132
40°C.	2.127	0	16.91	—	—
		20	14.31	14.35	0.130
		40	12.11	11.79	0.120
		60	9.71	9.23	0.120
		0	24.31	—	—
		20	21.59	21.75	0.136
		40	19.00	19.19	0.133
		60	16.72	16.63	0.127
				Mean:	0.128

The dissolution velocity of oxygen into sulphuric acid solution. It is quite probable to consider that the observed oxidation velocity, given in Table 1, is not the true reaction velocity, but the dissolution velocity of oxygen into the solution. According to this consideration it is able to calculate the approximate values of the dissolution velocity of oxygen into sulphuric acid solution of various concentrations under the conditions of this experiment from the observed values of the velocity constant k.

The calculated values are given in the last column of Table 3. The dissolution velocity of oxygen into pure water, given in the Table, is the value obtained from the oxidation velocity of sodium sulphite in water.(1)

From Table 3 it can be described that the dissolution velocity of oxygen into sulphuric acid solution decrease rapidly with the increase of the concentration of sulphuric acid as far as it attains a certain value which is nearly unaltered by the further increase of the concentration of sulphuric acid, quite the same way as in the case of the dissolution velocity into hydrochloric acid solution, which was given in the previous paper.(2)

We see also that the dissolution velocity has almost the same value for both of sulphuric acid and hydrochloric acid solutions, when their concentrations are not small. It can be explained by the consideration that the ratio

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(1) S. Miyamoto, this Bulletin, **3** (1928), 100; *Scientific Papers of the Institute of Physical and Chemical Research,* **8** (1928), 243.

(2) Loc. cit.

of the number of molecules of oxygen which enters into the surface film, and the total number of molecules which hit the liquid surface, has almost the same value for both of the liquids, neglecting the small difference of the total surface area of the air bubbles for both of the solutions.

Summary.

(1) The oxidation velocity of stannous chloride in sulphuric acid solution was observed under quite the same conditions as in the case of the oxidation of the same substance in hydrochloric acid solution, which was reported in the previous paper. The velocity increases slowly as the concentration of sulphuric acid increases as far as it reaches the dissolution velocity of oxygen into the solution, when the concentration of sulphuric acid attains about 0.8 normal, and the further increase of the concentration of sulphuric acid has almost no effect on the oxidation velocity, which was found to be almost independent of the initial concentration of stannous sulphate. The velocity constants, calculated as a zero-order reaction, were approximately expressed as a linear function of the concentration of sulphuric acid.

(2) The dissolution velocity of oxygen into sulphuric acid of various concentrations was calculated from the oxidation velocity observed. The dissolution velocity has nearly the same value as that into hydrochloric acid solution under the same conditions.

(3) The effect of temperature on the oxidation velocity, when the concentration of sulphuric acid is greater than about 0.8 normal, was ascertained to be negligible under the present conditions.

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ELECTRONIC CONCEPTION IN ORGANIC CHEMISTRY. II. AN INTERPRETATION OF THE REARRANGEMENTS OF TRISUBSTITUTED α-GLYCOLS.*

By Masao MIGITA.

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It has been brought to light that the trisubstituted α-glycols may be dehydrated by acids and undergo subsequent transposition in three ways: (I) by the *semihydrobenzoin rearrangement* it gives a trisubstituted aldehyde with the elimination of the tertiary OH-group; (II) by the *vinyl dehydration* the tertiary OH is removed, yielding a ketone without changing the skeletone of the carbon chain; and (III) by the *semipinacolin rearrangement* a ketone is formed with the removal of the secondary OH-group.

$$\mathrm{RR'C\,(\mathbf{OH})\cdot CHR''\,(O\,\mathbf{H})} \longrightarrow (\mathrm{RR'}\underset{\bullet}{\mathrm{C}}\cdot\mathrm{CHR''(O\cdot)}) \longrightarrow \mathrm{RR'R''C\cdot CHO} \;\ldots(\;\mathrm{I}\;)$$

$$\mathrm{RR'C\,(\mathbf{OH})\cdot CHR''\,(O\,\mathbf{H})} \longrightarrow (\mathrm{RR'C{=}CR''(OH)}) \longrightarrow \mathrm{RR'CH\cdot CO\cdot R''} \ldots(\mathrm{II})$$

$$\mathrm{RR'C\,(O\,\mathbf{H})\cdot CHR''\,(\mathbf{OH})} \longrightarrow (\mathrm{RR'C\,(\dot{O}\cdot)\cdot}\underset{\bullet}{\mathrm{C}}\mathrm{HR''}) \longrightarrow \mathrm{R\cdot CO\cdot CHR'R''} \ldots(\mathrm{III})$$

The first occurs almost exclusively by the action of boiling dilute sulphuric acid, and the other two either by the same reagent or by cold concentrated sulphuric acid, the nature of the substituents also influencing the direction of the rearrangements. These transpositions have been studied from various points chiefly by French chemists, above all, Orékhoff, Tiffeneau and Lévy, but they have not gone the length of interpreting these rearrangements from one and the same standpoint, for the rearrangement is so manifold as appears to be particular to each type of the glycols. It is attempted, in this paper, to throw a light on the mechanism of these rearrangements by applying the theory of alternate polarity and the relative electronegativity of organic radicals on the pile of experimental data given by the above mentioned and other chemists. According to Kharasch and his colaborators the electronegativity of some organic radicals are in the following order:

$$p\text{-}\mathrm{CH_3O\cdot C_6H_4}{-} > \alpha\text{-}\mathrm{C_{10}H_7}{-} > \text{Halogenophenyl} > \mathrm{C_6H_5}{-} > \mathrm{CH_3}{-} > \mathrm{C_2H_5}{-} > \text{n-}\mathrm{C_3H_7}{-} > \text{n-}\mathrm{C_4H_9}{-} > \mathrm{C_6H_5\cdot CH_2}{-}^{**}$$

In order to explain the influence exerted by the acids a presumable assumption is made that *the dilute acid dehydrates catalytically*, as in case

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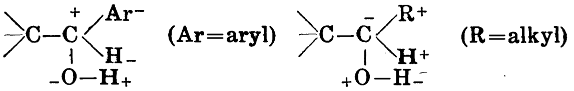
*In the previous paper, (this Bulletin, **3** (1928), 308–316), the rearrangements of pinacones and tertiary amino-alcohols are discussed.

of pinacones and tertiary amino-alcohols, whereas *the concentrated acid acts substitutionally.* In this way, (1) we can explain clearly complicated influences exercised by various substituents as well as dehydrating agents, and can look through the rearrangements of all the glycols in question from one point. (2) We can afford theoretical basis to many facts and laws which have been established experimentally, including the problems of the migratory tendency of organic radicals. Thus the interpretation based on the electronic theory of valence would appear to offer a good working hypothesis.

I. Rearrangements by Dilute Sulphuric Acid.

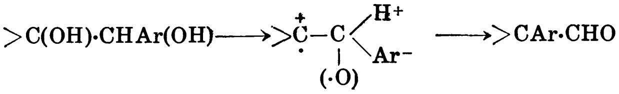
1. Glycols with negatively polarized tertiary OH-groups. Owing to the highly positive character of hydrogen, nearly all trisubstituted α-glycols have their tertiary hydroxyls negatively polarized. Therefore, if the dilute acid dehydrates catalytically according to the mechanism discussed in the previous paper, it must be the tertiary OH that attracts the H-ion of the acid, whereas we have two H-atoms which can combine with the anion of the acid, i.e. that of the secondary OH-group and that attached to the secondary carbon. This alternative will be influenced by the substituent in the secondary carbon in such a manner as to discriminate the polarity of the two H-atoms in question. The presence of a negative radical such as aryl, in the secondary carbon, produces a lessening effect on the negative polarity of this carbon, and this causes the adjoining hydrogen to be induced negative and that of hydroxyl positive, consequently it should be the latter hydrogen which will be brought with greater ease into ionic state (1a); on the other hand, the reverse holds in case of a glycol with an alkyl group in the secondary carbon (1b). Thus we have two different cases according to the negativity of the substituent in the secondary carbon.



$$\underset{{}_-O-H_+}{>C-\overset{+}{C}}\begin{smallmatrix}Ar^-\\ H_-\end{smallmatrix}\ (Ar=aryl)\qquad \underset{{}_+O-H_-}{>C-\overset{-}{C}}\begin{smallmatrix}R^+\\ H^+\end{smallmatrix}\ (R=alkyl)$$

(a) *Glycols with a grouping—CHAr(OH).* By the elimination of water it gives such a fraction of the molecule as RR′C·CHAr(O·), as can be seen from the reason just described, and subsequently one of the two substituents attached to the secondary carbon, either the hydrogen or the aryl, migrates to the tertiary carbon. But owing to the positive polarity of this carbon, it must be the aryl, the more negative group of the two, that wanders, giving a trisubstituted aldehyde (semihydrobenzoin rearrangement).

Kharasch and others, *J. Chem. Education,* **5 (1928), 408. This table contains some corrections and complements to the old one given in the previous paper.



$$>\text{C(OH)}\cdot\text{CHAr(OH)} \longrightarrow \, >\overset{+}{\underset{\cdot}{\text{C}}}-\underset{\underset{(\cdot\text{O})}{|}}{\text{C}}\begin{matrix}\diagup\text{H}^{+}\\ \diagdown\text{Ar}^{-}\end{matrix} \longrightarrow \, >\text{CAr}\cdot\text{CHO}$$

Ex.* 1. $\text{PhRC(OH)}\cdot\text{CHPh(OH)}\rightarrow\text{Ph}_2\text{RC}\cdot\text{CHO}$, where R=$\overset{**}{\text{Me}}$(6), Et,(6) Pr(13), iso-Bu(17), iso-Am.(17)

2. $\text{R}_2\text{C(OH)}\cdot\text{CHPh(OH)}\rightarrow\text{PhR}_2\text{C}\cdot\text{CHO}$, where R=Me(6), Et(18), Pr(18).

3. $\text{R}_2\text{C(OH)}\cdot\text{CHAnis(OH)}\rightarrow\text{AnisR}_2\text{C}\cdot\text{CHO}$, where R=Me(23), Et(18), Ph(14), Anis.(14)

4. $\text{RR}'\text{C(OH)}\cdot\text{CHAnis(OH)}\rightarrow\text{Anis RR}'\text{C}\cdot\text{CHO}$, where $\begin{matrix}\text{R}\ =\\ \text{R}'=\end{matrix}\left\{\begin{matrix}\text{Me}^{(26)},\\ \text{Et},\end{matrix}\right. \left\{\begin{matrix}\text{Anis}^{(8)},\\ \text{Bzl}.\end{matrix}\right. \left\{\begin{matrix}\text{Anis.}^{(9)}\\ \text{Ph}.\end{matrix}\right.$

In spite of the presence of the typical grouping —ArCH(OH), triaryl glycols $\text{Ar}_2\text{C(OH)}\cdot\text{CHPh(OH)}$, where $\text{Ar}_2=\text{Ph}_2$(5), (Ph, Anis)(14) and Anis_2(14), are not subject to semihydrobenzoin rearrangement but to vinyl dehydration, while the corresponding glycols with the grouping —CHAnis(OH), undergo semihydrobenzoin rearrangement, as is seen in the Ex. 3 and 4. These abnormal glycols have two characteristics in their structure; namely (i) both groups attached to the tertiary carbon are strongly negative, and (ii) the aryl radical bound to secondary carbon is phenyl and not anisyl. These characteristics account for the abnormal behaviour and prove that the state of polarity in these molecules is favourable to vinyl dehydration. Thus the accumulation of positivity on the part of the tertiary carbon due to the two aryl groups, will cause such a strongly negative polarity in the secondary carbon as being free from the influence exerted by the adjoining phenyl. Consequently the hydrogen bound to this carbon will be imparted with positive polarity; and this results in vinyl dehydration of the glycols in question. This unusual induced negativity on the part of the secondary carbon will be first reduced when the phenyl is replaced with anisyl, the most negative group, and semipinacolin rearrangement reappears. Thus it will be seen that these apparent contradictions make by no means an objection against the above electronic views, but on the contrary, afford a powerful support for them.

(b) *Glycols with grouping —CHR(OH).* These glycols, when dehydrated, should give derivatives of vinyl alcohol, $>\text{C}=\text{C(OH)R}$, as discussed above, which, being unstable, isomerize into their keto-form, $>\text{CH}\cdot\text{CO}\cdot\text{R}$, by the catalytic action of the acid present. This keto-enol isomerisation

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*Following symbols are adopted: Am=Amyl, Anis=*p*-Anisyl, Ar=Aryl, Bu=Butyl, Bzl=Benzyl, Et=Ethyl, Nap=Naphthyl, Ph=Phenyl, Pr=Propyl.

**For the convenience's sake, the literatures concerning to examples are collected in the end of this paper.

has already been interpreted as *prototropy* by Lowry* from the electronic standpoint.

$$R'_2C(OH)\cdot CHR(OH)\rightarrow R'_2C{=}C(OH)R\rightarrow R'_2CH\cdot CO\cdot R$$

Ex. 5. $R'{=}Ph$; $R{=}Me^{(4)}$, $Ph_2CH{-}^{(23)}$.

$$6.\quad \begin{matrix} R'= \\ R\ = \end{matrix}\left\{\begin{matrix} Me^{(1)}, \\ Me, \end{matrix}\right.\left\{\begin{matrix} Me^{(7)}, \\ iso\text{-}Pr, \end{matrix}\right.\left\{\begin{matrix} Me^{(20)}, \\ Bzl, \end{matrix}\right.\left\{\begin{matrix} Me_{(23)}, \\ Ph_2CH-, \end{matrix}\right.\left\{\begin{matrix} Et^{(3)}, \\ Me, \end{matrix}\right.\left\{\begin{matrix} Et,^{(3)} \\ Bzl, \end{matrix}\right.\left\{\begin{matrix} Et^{(20)}, \\ Bzl, \end{matrix}\right.\left\{\begin{matrix} Bzl^{(23)}. \\ Me. \end{matrix}\right.$$

2. Glycols with negatively polarized secondary OH-groups. Glycols of this type are very rare from the reason already mentioned; but if the tertiary carbon is combined to strongly electropositive radicals, and the secondary carbon to a highly negative group, it may be the case that the secondary hydroxyl is induced negative. Actually, glycols $Bzl_2C(OH)\cdot CHAr(OH)$, where $Ar{=}Ph^{(18)}$ or $Anis^{(24)}$, are subject to neither semihydrobenzoin rearrangement nor vinyl dehydration, but to semipinacolin transformation as follows:

$$Bzl_2C(OH)^+\cdot CHAr(OH)^-\rightarrow Bzl_2C(O\cdot)\cdot\underset{\bullet}{C}HAr\rightarrow Bzl\cdot CO\cdot CHBzlAr.$$

Summary. A delicate relation between the state of polarity in the molecule and the mode of dehydration by dilute sulphuric acid manifests itself in the rearrangements of the glycols $R_2C(OH)\cdot CHR'(OH)$, which are tabulated as under. This table serves also as a summary to the present chapter.

Typical reactions of $R_2C(OH)\cdot CHR'(OH)$ by dil. H_2SO_4.

R′ / R		− ←			+
		Anis	Ph	Me	Bzl
−	Anis	H	V		
↑	Ph	H+V	V	V	
|	Me	H	H	V	V
+	Bzl	P	P	V	No Reaction

H = Semihydrobenzoin-, P = Semipinacolin-rearrangement, V = Vinyl dehydration.

II. Rearrangements by Concentrated Sulphuric Acid.

It is a probable assumption that the dehydration by concentrated sulphuric acid takes place substitutionally, since we can prove it experimentally

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*Cf. *J. Chem. Soc.*, **127** (1925), 1371.

in case of primary alcohols. In a dihydric alcohol we may have selective substitution of the two OH-groups; and in case of a trisubstituted α-glycol, different from the case of a pinacone, the polarity difference of the two hydroxyls is not the only factor to affect this selection, for secondary and tertiary hydroxyls are not same in the ease for substitution. Namely, the former is substituted with greater ease as is seen, for example, in the Schotten and Baumann's reaction. It seems that this sterical influence is so strong that it overcomes some negative polarity on the part of the tertiary hydroxyl, so long as this is not marked, resulting in elimination of the secondary hydroxyl. Therefore, it is the degree of polarity developed in the molecule, and not its mere sence, that plays an important rôle in the rearrangements by concentrated sulphuric acid.

1. Glycols with marked polarity. (a) *Glycols with negatively polarized tertiary OH-groups.* In these commonest case, sulphuric acid attacks the tertiary hydroxyl substitutionally, inducing the secondary carbon strongly negative. As this causes the increase of the positive character of the hydrogen bound to this carbon, vinyl dehydration should result.

$$>\mathrm{C(OH)\cdot CHR(OH)} \rightarrow >\mathrm{C(SO_4H)\cdot CHR(OH)} \rightarrow >\mathrm{C{=}C(OH)R} \rightarrow >\mathrm{CH\cdot CO\cdot R}$$

Ex. 7. $\mathrm{Ph_2C(OH)\cdot CHR(OH)\rightarrow Ph_2CH\cdot CO\cdot R}$, where R=Me(4), iso-Bu(17), Bzl(20), Ph(9).

8. $\mathrm{PhRC(OH)\cdot CHPh(OH)\rightarrow PhRCH\cdot CO\cdot Ph}$, where R=Me(12), iso-Bu(17), Ph(9), Nap(21).

9. $\mathrm{PhRC(OH)\cdot CHR(OH)\rightarrow PhRCH\cdot CO\cdot R}$, where R=Et(18), Pr(18).

10. $\mathrm{R_2C(OH)\cdot CHR'(OH)\rightarrow R_2CH\cdot CO\cdot R'}$, where,

$$\begin{matrix}\mathrm{R} = \\ \mathrm{R'} = \end{matrix}\left\{\begin{matrix}\mathrm{Me}^{(1)}, \\ \mathrm{Me}, \end{matrix}\right. \left\{\begin{matrix}\mathrm{Me}^{(7)}, \\ \text{iso-Pr}, \end{matrix}\right. \left\{\begin{matrix}\mathrm{Me}^{(20)}, \\ \mathrm{Bzl}, \end{matrix}\right. \left\{\begin{matrix}\mathrm{Me}^{(23)}, \\ \mathrm{Ph_2CH}-, \end{matrix}\right. \left\{\begin{matrix}\mathrm{Et}^{(20)}, \\ \mathrm{Me}, \end{matrix}\right. \left\{\begin{matrix}\mathrm{Et}^{(20)}, \\ \mathrm{Bzl}, \end{matrix}\right. \left\{\begin{matrix}\mathrm{Bzl}^{(23)}. \\ \mathrm{Me}. \end{matrix}\right.$$

(b) *Glycols with negatively polarized secondary OH-groups.* It goes without saying that semipinacolin rearrangement takes place in these few cases.

Ex. 11. $\mathrm{Bzl_2C(OH)^+\cdot CHR(OH)^- \leftarrow Bzl_2C(O\cdot)\cdot CHR \rightarrow Bzl\cdot CO\cdot CHRBzl}$, where R=Ph(18), Anis(24).

2. Glycols without marked polarity. These glycols are generally subject to semipinacolin rearrangement as the result of predominance of the sterical influence over the effect due to polarity. In this rearrangement one of the two groups combined to the tertiary carbon undergoes either simple or selective migration according to the type of the glycols in question.

(a) *Case of simple migration.* When the substituents in the tertiary carbon are the same, the migration is simple.

Ex. 12. $R_2C(OH)\cdot CHPh(OH) \rightarrow R\cdot CO\cdot CHRPh$, where R=Me(15), Et(18), Pr(18), Bu(18), Bzl(18).

(b) *Case of selective migration.* When the tertiary carbon is substituted by two different groups, the migration takes place selectively. A close relation between polarity and selective migration has been often dealt with in the present and previous papers. But when dehydration is carried out substitutionally, it must be payed attention that the carbon which has been occupied by SO_4H-group becomes strongly positive regardless of the original polarity, because the SO_4H-radical deprives of the covalency electrons, when removed as ion. Therefore, if there exists sufficient difference of electro-negativity between the groups to be selected, the wandering group must be the one that is more negative.

Ex. 13.

$$PhR\overset{+}{C}(OH)\cdot\overset{-}{C}HPh(OH) \rightarrow PhRC(OH)\cdot CHPh(SO_4H) \rightarrow {}^{-Ph}_{+R}\!\!>\!C(O\cdot)\cdot\underset{\cdot}{\overset{+}{C}}HPh \rightarrow R\cdot CO\cdot$$

$CHPh_2$, where R=Et(10), Pr(13), iso-Pr(17), Bu(13), iso-Am(17). In these cases, ketones $PhRCH\cdot CO\cdot Ph$, are also formed, but only as by-products.); Bzl(17).

On the other hand, if the polarity difference between the two groups is small, as is the case between alkyls, it is conceivable that the migration of the radical does not necessarily comply with the above rule. It is not a great error to assume that the stability of the union between these radicals and the tertiary carbon might play an important rôle in this case. If so, it must be the more positive group that migrates, for "a low degree of affinity for electron (i.e. of electronegativity) on the part of a radical results in instability of the bond which that radical may form with another radical or atom."*

Ex. 14. $RR'C(OH)\cdot CHPh(OH) \rightarrow R\cdot CO\cdot CHPhR'$, where R′ is the more positive group, thus

$$\begin{matrix} R = \\ R' = \end{matrix}\left\{\begin{matrix} Me^{(19)}, \\ Et, \end{matrix}\right. \left\{\begin{matrix} Me^{(26)}, \\ Pr, \end{matrix}\right. \left\{\begin{matrix} Me^{(26)}, \\ \text{iso-Pr}, \end{matrix}\right. \left\{\begin{matrix} Me^{(26)}, \\ Bu, \end{matrix}\right. \left\{\begin{matrix} Et^{(26)}, \\ Bzl. \end{matrix}\right. \left\{\begin{matrix} Pr^{(26)}, \\ Bu, \end{matrix}\right. \left\{\begin{matrix} Pr^{(26)}, \\ Bzl, \end{matrix}\right. \left\{\begin{matrix} \text{iso-Pr}^{(26)}, \\ Bzl. \end{matrix}\right.$$

$$\left(\left\{\begin{matrix} Pr^{(26)}, \\ Et, \end{matrix}\right. \left\{\begin{matrix} \text{iso-Pr}^{(26)} \\ Et. \end{matrix}\right.\right)^{**}$$

Ex. 15. $MeEtC(OH)\cdot CHAnis(OH) \rightarrow Me\cdot CO\cdot CHAnisEt$(25).

Similarly we can explain the selective migration of such pinacones as $Me_2C(OH)\cdot CMeR(OH)$, where R=Et(2), Pr(22), iso-Pr(22); $Ph_2C(OH)\cdot CMeR(OH)$, where R=Et(11), Bzl(19); and $MeEtC(OH)\cdot CMeEt(OH)$(16), which have been dealt with as contradictions in the previous paper.

Conclusion.

Under the assumption that dilute sulphuric acid dehydrates catalytically, while the concentrated acid substitutionally, the mechanism of the

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* Kharasch and others, loc. cit.

**Exceptions.

rearrangements of all trisubstituted α-glycols can be interpreted causally from the stand point of the electronic conception of valence.

Semihydrobenzoin rearrangement occurs by the influence of dilute acid, when the tertiary hydroxyl has negative polarity and the hydrogen of the secondary hydroxyl is induced more positive than that bound to the secondary carbon.

Ex. $ArRC(OH)\cdot CHPh(OH)$, $R_2C(OH)\cdot CHPh(OH)$ and $Ar_2C(OH)\cdot CHAnis(OH)$.

Vinyl dehydration takes place either (i) by dilute acid when the tertiary hydroxyl has negative polarity and the hydrogen combined to the secondary carbon is induced more positive than that of the secondary hydroxyl group; or (ii) by the concentrated acid when the tertiary hydroxyl has markedly negative polarity. Ex. (i) $Ar_2C(OH)\cdot CHPh(OH)$, $R_2C(OH)\cdot CHR'(OH)$; (ii) $Ph_2C(OH)\cdot CHR(OH)$, $R_2C(OH)\cdot CHR'(OH)$.

Semipinacolin rearrangement results either (i) from the dehydration of glycols with negatively polarized secondary hydroxyls by dilute sulphuric acid as well as concentrated; or (ii) by the action of the latter upon glycols with tertiary hydroxyls induced feebly negative. Ex. (i) $Bzl_2C(OH)\cdot CHAr(OH)$; (ii) $RR'C(OH)\cdot CHPh(OH)$ where $R = \text{or} \neq R'$. Such a glycol as satisfies the condition of semipinacolin rearrangement should have a strongly negative group, such as phenyl, in the secondary carbon in order to diminish the influence due to the strong positivity of the adjoining hydrogen. This requirement is nothing but the experimental law given by Lévy.*

The rearrangements of the glycols of the type, $RR'C(OH)\cdot CHPh(OH)$, by concentrated sulphuric acid, are worthy of special mention, because they show plainly the close relation between the polarity and the mode of the rearrangements, making another maintenance to the electronic interpretation. Thus, if R′ is an alkyl, we have only semipinacolin rearrangement (Ex. 12 and 14); but if R′ is phenyl, the transformation is dependent on the electronegativity of the other radical R. Namely, the glycol, $RPhC(OH)\cdot CHPh(OH)$, undergoes vinyl dehydration, if R is a strongly negative group such as Nap, Ph, or Me (Ex. 8); and if R is Bzl, a strongly positive group, semipinacolin rearrangement occurs (Ex. 13); while the both reactions take place at the same time, in a case when R is a group with weak or intermediate negativity such as Et, Pr, Bu or iso-Am (Ex. 13). We can find a plausible explanation of this in the competitive influences of polarity and of sterical factor.

It shall be here added that iso-butyl radical appears to be more negative than it is usually supposed, and it seems to be at least as negative as

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Bull. soc. chim., [4] 33 (1923), 1655-66; ibid., [4] 39 (1926), 67-72.

methyl, since under the influence of concentrated sulphuric acid (iso-Bu) PhC(OH)·CHPh(OH), undergoes vinyl dehydration (Ex. 8), and (iso-Bu) RC(OH)·CHPh(OH), where R=Me⁽⁶⁾ or Et⁽²⁶⁾, yields (iso-Bu)·CO·CHPhR by the migration of Me or Et radical (compare Ex. 14 and 15).

Migratory tendency of organic radicals is not a definite property as it has been supposed, but a function of their electronegativity, and the relation between them seems to be conditioned by two factors, that is, the attraction between the migrating groups and the atom to which the group passes, and the stability of the bond between the wandering group and the atom to be quitted. The first or the second factor is predominant, according to whether there exists sufficient difference of electronegativity between the groups undergoing selective migration (i) or not (ii). In the former case, the sence of polarity of the atom to which the group migrates, exerts a directive influence; thus, if the atom is positively polarized, the wandering group must be the one that is more negative (ia), and vice versa (ib). This conception has a powerful support in the actual existence of these two cases, (ia) and (ib), as is exemplified below. On the other hand, in the case where the second factor predominates, the migrating group is the one which is held with less stable bond, i.e. is the more electropositive group. Ex. (ia) Semipinacolic deamination of tertiary amino-alcohols, semihydrobenzoin rearrangement, semipinacolin rearrangements of RArC(OH)·CHPh(OH), where R=alkyl, (ib) Stieglitz's rearrangements: RR′R″C·NHOH, RR′R″C·NHCl or $RR'R''C\cdot NH_2 \rightarrow RR'C=NR''$, where the more electronegative halogenophenyls have less mobility than phenyl,* since the migration of a group takes place toward a negative atom, nitrogen. (ii) Semipinacolin rearrangements of RR′C(OH)·CHPh(OH), pinacolin rearrangements of $R_2C(OH)\cdot CR'R''(OH)$, where R′ and R″ are alkyls.

I beg to tender my sincere thanks to Prof. K. Matsubara for his kind inspection of this paper.

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(2) Meerwein, *Ann.*, **396** (1896), 255.
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(6) Tiffeneau, *Ann. chim. Phys.*, [8] **16** (1909), 247.

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*Stieglitz and Stanger, *J. Am. Chem. Soc.*, **38** (1916), 2046; Stanger, ibid., 2069; Vosburgh, ibid., 2081; Morgan, ibid., 2095; Senior, ibid., 2718.

(7) Blaise and Hermann, ibid., [8] **20** (1910), 178.
(8) Orékhoff, *Bull. soc. chim.*, [4] **25** (1919), 4–9.
(9) Ibid., 111.
(10) Ibid., 179–82.
(11) Meerwein, *Ann.*, **419** (1919), 121.
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(15) Lévy, ibid., 820–9.
(16) Nybergh, *Ber.*, **55** (1922), 1960–6.
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(18) Tiffeneau and Lévy, ibid., 735–59.
(19) Ibid., 759–79.
(20) Lévy, ibid., 1655-66.
(21) Orékhoff and Tiffeneau, *Compt. rend.*, **178** (1924), 1619–21.
(22) Locquin and Leers, *Bull. soc. chim.*, [4] **39** (1926), 433-8.
(23) Tiffeneau and Lévy, ibid., 763–82.
(24) Tiffeneau and Lévy, *Compt. rend.*, **183** (1926), 1112.
(25) Lévy and Weill, ibid., **185** (1927), 135–7.
(26) Tiffeneau and Lévy, ibid., **186** (1928), 84-6.

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ON THE OXIDATION OF FERROUS HYDROXIDE BY AIR.—SUPPLEMENT.

By Susumu MIYAMOTO

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A study on the oxidation velocity of ferrous hydroxide in sodium hydroxide solution of various concentrations under certain conditions by means of air was reported in the previous papers.(1) Recently A. Krause carried out an excellent research(2) on the same subject under quite different conditions, and he refered the author's experimental results in his discussion on the inorganic chemistry of iron oxides.

The discussion, given by Krause, seems to be excellent except his consideration on the real meaning of the oxidation velocity, observed by the author. The observed oxidation velocity, given in the author's papers, were treated in his discussion, as if it means the real reaction velocity, but, as was described in the second paper of the author, it is no other than the dissolution velocity of oxygen into the solution.

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(1) This Bulletin, 2 (1927); 40; 3 (1928), 137; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 35; 9 (1928), 203.

(2) Alfons Krause, *Z. anorg. allgem. Chem.*, **174** (1928), 145.

The difference of the experimental conditions will sometimes give quite a different meaning on the observed reaction velocity of a heterogeneous chemical reaction, and the author considers that it may be necessary to give the following interpretations on the author's experimental results to prevent further misunderstanding.

C. C. Palit and N. R. Dhar have found that the oxidation velocity of some carbohydrates, induced by the oxidation of ferrous hydroxide, increases as the concentrations of sodium hydroxide increases.(1) A study, the results of which being published in the author's first paper, was undertaken to ascertain the expectation that the oxidation velocity of ferrous hydroxide will also increase with the increase of the concentration of sodium hydroxide under almost the same conditions, as those adopted by Palit and Dhar in their study, above cited. Quite unexpected result was obtained; the observed oxidation velocity of ferrous hydroxide decreases as the concentration of sodium hydroxide increases under the experimental conditions.

It was thus ascertained in the author's first paper that the increase of the velocity of the induced reaction with the increase of the concentration of sodium hydroxide, found by Palit and Dhar, is not due to the increase of the reaction velocity of the primary reaction. It will be difficult to explain the phenomenon by an usual consideration that only the increase of the velocity of the primary reaction causes the increase of the velocity of the induced reaction.

The author proposed to interprete the phenomenon by a new theory of induced reaction.(2) The theory means that a chemical reaction, whose velocity is extremely small, may be induced, when the molecules of the reacting substances are suitably activated by the direct transference of the active states of the molecules of the reaction products of some independent chemical reaction.

If we consider, according to this theory, that the induced reaction does not only depend upon the velocity of the primary reaction, but also upon the process of the transference of active states, the effect of sodium hydroxide on the induced reaction above described can easily be explained.

For the derivation of this conclusion, it is quite unnecessary to ascertain whether the observed oxidation velocity of ferrous hydroxide is the true reaction velocity or not.

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(1) *J. Phys. Chem.*, 29 (1925), 799.

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

By comparing the oxidation velocity of sodium sulphite(1) and stannous hydroxide,(2) observed under the same conditions, with that of ferrous hydroxide, it was found that it is quite probable to consider the observed oxidation velocity to be the dissolution velocity of oxygen into the solution. The author's second study on the same subject was carried out to confirm this consideration by a little modified method.

As was shown in the author's papers,(3) the observed oxidation velocity of ferrous hydroxide decreases as the concentration of sodium hydroxide increases under the conditions of the author's experiments. It only means that the dissolution velocity of oxygen into the solution decreases with the increase of the concentration of sodium hydroxide. Whether the true reaction velocity will also decrease with the increase of the concentration of sodium hydroxide, or, not, is a problem to be solved by the further studies.

A. Krause found the effect of temperature on the oxidation velocity, which was negligible in the author's measurements, to be very great.(4) It is not curious: it is only due to the great difference between his experimental conditions and mine, which will give quite a different meaning to the observed velocity of this heterogeneous chemical reaction. The effect of temperature on the oxidation velocity, observed under the conditions of the author's experiments, is no other than that on the dissolution velocity of oxygen into the solution, while the result, observed by A. Krause, will have quite a different meaning.

The effect of temperature or the effect of the increase of the concentration of sodium hydroxide on the true reaction velocity, the study of which was not the purpose of the author's papers, above cited, may perhaps be obtained by a similar method under some suitable conditions, but it was left for the later studies.

The fact, that the real meaning of the observed reaction velocity of a heterogeneous chemical reaction may sometimes be quite different, if the experimental conditions be not the same, causes the necessity to adopt nearly the same experimental conditions, under which the measurements of Palit and Dhar were carried out, for the purpose of the discussion on the mechanism of the induced reaction, found by Palit and Dhar. It is the reason why such experimental conditions, under which the results do not give the real reaction velocity but the dissolution velocity of air, were adopted by the author.

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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, this Bulletin, 2 (1927), 158; *Scientific Papers of the Institute of Physical and Chemical Research*, 7 (1927), 192.

(3) Loc. cit.

(4) Loc. cit.

According to the considerations above described, it will be clear that it is quite meaningless to compare the results of the author's experiments with those observed under quite different conditions, if the latter do not mean the dissolution velocity of oxygen into the solution.

Summary.

(1) An interpretation on the real meaning of the observed oxidation velocity of ferrous hydroxide under the conditions of the author's experiments was given to prevent misunderstanding of the author's papers.

(2) The reason, why the experimental conditions, under which the author's measurements were carried out, were adopted, was described.

(3) It was discussed that the oxidation velocity of ferrous hydroxide, observed by A. Krause under quite different conditions, will have quite a different meaning as that, observed by the author. The difference of the real meaning of the observed reaction velocity, caused by the difference of the experimental conditions, will explain why the effect of temperature, which was negligible under the author's conditions, was found by A. Krause to be very great.

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THE VISCOSITY OF LIQUIDS ABOVE THEIR BOILING POINTS. PART V.

By Toshizo TITANI.

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In the preceding papers(1) it has been shown that the relation between the molecular fluidity Φ defined as the reciprocal of the product of viscosity η and molecular distance $V^{\frac{1}{3}}$, and molecular volume V or temperature T can be expressed by the following simple equations;

$$\Phi=K(V^{\frac{2}{3}}-B^{\frac{2}{3}}) \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\Phi_K-\Phi=C\,(T_K-T)^{\frac{1}{5}} \ldots\ldots\ldots\ldots\ldots (2)$$

where K, B and C are arbitrary constants, and Φ_K the value of Φ at the critical temperature T_K.

Eliminating Φ from equations (1) and (2) the relation:

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(1) Part I, this Bulletin, **2** (1927), 95; II, ibid, 161; III, ibid, 196; IV, ibid, 225.

$$V_K^{\frac{2}{3}}-V^{\frac{2}{3}}=A\,(T_K-T)^{\frac{1}{5}}\;\ldots\ldots\ldots\ldots\ (3)$$

is obtained, where V_K is the critical molecular volume and A is a constant related with the constants K and C by the equation:

$$A=\frac{C}{K}\;\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

These relations were tested by comparing calculated values with known standard data and the agreement was good for many substances over a wide range of temperatures extending from 0°C. to far above their boiling points.

Recently several reliable data⁽¹⁾ have been added as regards the viscosities and densities of ethyl ether and acetone at low temperatures. The writer is highly indebted to the observers for enabling us to test the above relations also at remarkably low temperatures from 0°C. down to the freezing points.

As will be seen from Figs. 1 and 2, the molecular fluidity Φ of ethyl ether and acetone, calculated from the experimental data and plotted against the molecular surface $V^{\frac{2}{3}}$ or the quantity $(T_K-T)^{\frac{1}{5}}$, gives straight lines except very near the freezing points.

In the case of acetone, the curve of $(\Phi\sim V^{\frac{2}{3}})$ in Fig. 1 falls in two straight lines, respectively referred to the data of Mitsukuri and Tonomura⁽²⁾ below 0°C. and those of Thorpe and Rodger above it. This is not the case for the temperature relation in Fig. 2, where only one straight line has been obtained. The data of Archibald and Ure deviate from those of the other authors and give slightly curved lines. Such discrepancies may presumably due to the difference of the specimen employed, as is to be seen from the following comparison of density and viscosity of acetone at 0°C. observed by respective author.

Density and viscosity of acetone at 0°C.

Observer	Density	Viscosity
Mitsukuri and Tonomura	0.81392	0.00390
Archibald and Ure	0.81400	0.00389
Thorpe and Rodger	0.81858	0.00394

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(1) Mitsukuri and Tonomura, *J. Chem. Soc. Japan*, **48** (1927), 334; *Proc. Imp. Acad. Japan*, **3** (1927) 155. Archibald and Ure, *J. Chem. Soc.*, **125** (1924), 726; ibid, **128** (1927), 610. Taylor and Smith, *J. Am. Chem. Soc.*, **44** (1922), 2456. Felsing and Durban, ibid, **48** (1926), 2885.

(2) Mitsukuri and Tonomura have also determined the viscosity of methyl alcohol at low temperatures. For this substance the relations (1) and (2) fail as in the case of ethyl alcohol already pointed out in part II. (loc. cit.)

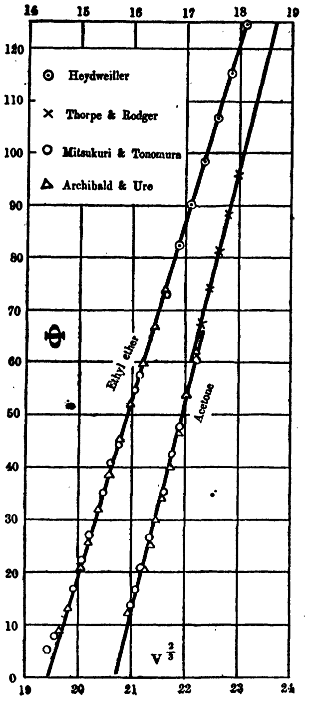

Fig. 1.

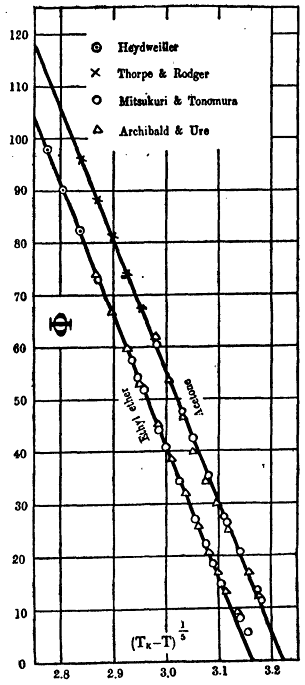

Fig. 2.

In tables 1 and 2, Φ_V gives the molecular fluidity calculated by equation (1) and Φ_T those obtained by equation (2). These values are compared with the experimental data Φ_{obs}.

Table 1.

Ethyl ether.

$$\Phi_V=33.8\ (V^{\frac{2}{3}}-85.69^{\frac{2}{3}}).^{**}$$

$$\Phi_T=791.0-250\ (193.8-t)^{\frac{1}{5}}.$$

$t°C.$	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−119.2	5.37	0.2	−52	2.1	−33
−111.7	8.10	3.6	−45	6.0	−21
−109.8	8.98*	6.6	−24	6.9	−21
− 99.8	13.16*	12.1	−11	12.1	−11
− 95.5	14.67	12.7	−20	14.4	− 3
− 92.2	16.81*	15.8	−10	16.1	− 7
− 88.2	18.47	16.9	−16	18.5	0

**These numerical equations have already been obtained from Heydweiller's data between 0° and 100°C. in part II. (loc. cit.)

Table 1. (*Continued.*)

t°*C.*	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−87.7	18.85	17.2	−17	18.7	−2
−84.4	20.78*	20.5	−3	20.5	−3
−80.9	22.25	20.8	−15	22.4	+1
−75.4	25.69*	25.5	−2	25.6	−1
−72.2	27.05	25.5	−16	27.3	+2
−64.5	31.98*	31.8	−2	31.9	−1
−58.9	34.23	33.7	−5	35.2	+10
−58.4	34.95	34.0	−4	35.6	+6
−53.9	38.41*	38.5	+1	38.2	−2
−49.0	40.69	40.1	−6	41.2	+5
−43.0	45.25*	45.3	0	44.9	−4
−42.6	44.25	44.2	−1	45.3	+10
−32.1	52.00*	52.0	0	51.9	−1
−30.1	53.10*	53.4	+3	53.3	+2
−27.5	54.05	54.4	+3	55.0	+9
−26.8	54.87	54.4	−5	55.5	+6
−23.5	57.41	57.4	0	57.7	+3
−20.2	59.71*	60.2	+5	59.9	+2
−10.2	66.71*	67.3	+6	66.9	+2
0.0	73.24	74.6	+14	74.2	+10
0.0	74.08*	74.3	+2	74.2	+1
0	74.40	74.3	−1	74.2	−2
10	82.24	82.4	+2	81.8	−4
20	90.16	89.9	−3	89.7	−5
30	98.42	98.3	−1	97.9	−5
40	106.8	107.3	+5	106.6	−2
50	115.4	116.0	+6	115.9	+5
60	124.6	125.1	+5	125.4	+8
70	135.0	135.3	+3	135.8	+8
80	146.6	145.9	−7	146.9	+3
90	159.1	158.8	−3	158.5	−6
100	172.6	171.8	−8	171.2	−14

Φ_{obs}: 0°—100°C., Heydweiller; * Archibald and Ure; the others, Mitsukuri and Tonomura.

Table 2. Acetone.

$\Phi_V=41.0\,(V^{\frac{2}{3}}-62.34^{\frac{2}{3}})$ . . . . Below 0°C.

$\Phi_V=41.0\,(V^{\frac{2}{3}}-61.91^{\frac{2}{3}})$ . . . . Above 0°C.

$\Phi_T=805.3-250\,(\overset{**}{234.4}-t)^{\frac{1}{5}}$.

t°*C.*	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−92.0	11.68	8.5	−32	9.9	−18
−89.7	12.20*	9.6	−26	11.0	−12
−88.2	13.36	10.2	−32	11.7	−17
−86.7	13.72	11.2	−25	12.4	−13
−79.7	16.57*	14.9	−17	15.9	−7
−79.5	16.78	14.9	−19	15.9	−9

**Galitzine (1890), Landolt-Börnstein-Roth Tabellen, 5 Aufl.

Table 2. (*Continued.*)

$t°C.$	$\Phi_{obs.}$	Φ_V	Δ	Φ_T	Δ
−71.1	20.67	19.3	−14	20.3	− 4
−69.7	20.68*	20.7	0	21.0	+ 3
−59.7	25.21*	26.1	+ 9	26.2	+10
−59.0	26.55	25.8	− 8	26.6	0
−57.4	27.42	27.0	− 4	27.5	+ 1
−56.9	27.58	27.0	− 6	27.7	+ 1
−49.9	30.11*	31.0	+ 9	31.4	+13
−42.6	35.29	34.9	− 4	35.5	+ 2
−40.0	34.42*	36.4	+20	36.8	+24
−30.2	39.87*	41.8	+19	42.5	+26
−29.7	42.46	42.3	− 2	42.7	+ 2
−29.4	42.42	42.5	+ 1	42.8	+ 4
−20.4	47.08*	47.4	+ 3	48.3	+12
−20.6	47.69	47.7	0	48.2	+ 5
−10.6	53.73*	53.4	+ 3	54.2	+ 5
0.0	62.00*	60.6	−14	60.7	−13
0.0	60.43	60.6	+ 2	60.7	+ 3
0	61.31	61.2	− 1	60.7	− 6
10	67.54	67.6	+ 1	67.2	− 3
20	74.22	73.9	− 3	74.0	− 2
30	81.30	80.8	− 5	80.9	− 4
40	88.43	88.6	+ 2	88.2	− 2
50	96.03	95.9	− 1	95.7	− 3

Φ_{obs}: 0°−50°C., Thorpe and Rodger; * Archibald and Ure; the others, Mitsukuri and Tonomura.

In both cases calculated and observed values stand generally very close to each other except near the freezing points, where calculated values become too small compared with those observed. In this region of tem-

Table 3.

$$\Delta V^{\frac{2}{3}}\% = \frac{V^{\frac{2}{3}} - B^{\frac{2}{3}}}{V^{\frac{2}{3}}} \times 100, \quad \Delta\Phi\% = \frac{\Phi_{obs.} - \Phi_{calc.}}{\Phi_{obs.}} \times 100.$$

$t°C.$	Ethyl ether		Acetone	
	$\Delta V^{\frac{2}{3}}\%$	$\Delta\Phi\%$	$\Delta V^{\frac{2}{3}}\%$	$\Delta\Phi\%$
−120	0	—	—	—
−110	1	−27	—	—
−100	2	− 9	—	—
− 90	3	− 6	1	−23
− 80	3	− 1	2	−11
− 70	4	− 1	3	− 7
− 60	5	− 1	4	− 2
− 50	6	0	5	—
− 40	7	0	5	− 1
− 30	8	0	6	0
− 20	8	+ 1	7	0
− 10	9	+ 1	8	—
± 0	10	0	9	0

peratures the ratio of the molecular free area $(V^{\frac{2}{3}}-B^{\frac{2}{3}})$ to the total surface $V^{\frac{2}{3}}$ becomes very small, as is shown in table 3, so that a slight change in the values of B has a great effect on the magnitude of molecular fluidity. As B is an effective volume of molecules and can hardly be absolutely constant under such a condensed state, it seems rather natural that the deviations from equations (1) and (2) are almost parallel to each other, if it be regarded to have been caused·by the change of B.

Table 4. Ethyl ether.

$$V^{\frac{2}{3}}=280.5^{\frac{2}{3}}-7.40\,(193.4-t)^{\frac{1}{5}}.$$

$$\left(A=\frac{C}{K}=\frac{250}{33.8}=7.40\right)$$

$t°C.$	$V^{\frac{2}{3}}$			V		
	Obs.	Calc.	Δ	Obs.	Calc.	Δ
−120	19.47	19.49	+ 2	85.94	86.04	(+ 10)
−110	19.63	19.64	+ 1	86.96	87.06	(+ 10)
−100	19.79	19.80	+ 1	87.98	88.12	(+ 14)
− 90	19.95	19.95	0	89.02	89.13	(+ 11)
− 80	20.10	20.11	+ 1	90.10	90.18	(+ 8)
− 70	20.28	20.28	0	91.31	91.33	(+ 2)
− 60	20.46	20.45	− 1	92.51	92.49	(− 2)
− 50	20.64	20.64	0	93.69	93.78	(+ 9)
− 40	20.83	20.82	− 1	95.01	95.01	(0)
− 30	21.01	21.01	0	96.34	96.29	(− 5)
− 20	21.21	21.21	0	97.70	97.68	(− 2)
− 10	21.42	21.42	0	99.13	99.06	(− 7)
0	21.63	21.64	+ 1	100.6	100.7	+ 1
+ 10	21.87	21.86	− 1	102.2	102.3	+ 1
20	22.09	22.09	0	103.9	103.8	− 1
30	22.34	22.34	0	105.5	105.6	+ 1
40	22.60	22.59	− 1	107.5	107.4	− 1
50	22.86	22.87	+ 1	109.5	109.4	− 1
60	23.13	23.15	+ 2	111.3	111.4	+ 1
70	23.43	23.46	+ 3	113.4	113.4	0
80	23.74	23.78	+ 4	115.7	116.0	+ 3
90	24.13	24.12	− 1	118.5	118.5	0
100	24.51	24.50	− 1	121.3	121.3	0
110	24.97	24.91	− 6	124.7	124.4	− 3
120	25.47	25.36	− 11	128.5	127.7	− 8
130	26.02	25.86	− 16	132.7	131.5	− 12
140	26.65	26.42	− 23	137.6	135.8	− 18
150	27.35	27.09	− 26	143.1	141.0	− 21
160	28.19	27.89	− 30	149.7	147.2	− 25
170	29.35	28.90	− 45	159.1	155.3	− 38
180	31.12	30.34	− 78	173.6	167.1	− 65
185	32.41	31.42	− 99	184.4	176.1	− 83
190	34.45	33.18	−127	202.2	191.1	−111
192	35.88	34.53	−135	214.8	202.9	−119
193	36.93	35.77	−116	224.5	214.0	−105
193.8	43.03	42.85	− 18	282.2	280.5	− 17

Densities above 0°C. refer to S. Young and below it Taylor and Smith.

This suggests that equation (3), obtained by eliminating the term Φ from equations (1) and (2), would accurately hold even at very low temperatures, and this is really the case as is seen in tables 4 and 5.

At first, the proportionality constant A has been computed from K and C by equation (4) and the constant V_K was then chosen so as to obtain the best agreement with experimental data.

Table 5. Acetone.

$$V^{\frac{2}{3}}=210.2^{\frac{2}{3}}-6.10\,(234.4-t)^{\frac{1}{5}}.$$

$$\left(A=\frac{C}{K}=\frac{250}{41.0}=6.10\right)$$

$t°C.$	$V^{\frac{2}{3}}$		Δ	V		Δ
	Obs.	Calc.		Obs.	Calc.	
−90	15.94	15.98	+ 4	63.75	63.89	+14
−80	16.08	16.09	+ 1	64.49	64.54	+ 5
−70	16.18	16.21	+ 3	65.25	65.27	+ 2
−60	16.34	16.34	0	66.04	66.07	+ 3
−50	16.47	16.47	0	66.85	66.82	− 3
−40	16.61	16.61	0	67.69	67.70	+ 1
−30	16.75	16.74	− 1	68.55	68.50	− 5
−20	16.90	16.89	− 1	69.44	69.44	0
−10	17.05	17.04	− 1	70.39	70.33	− 6
0	17.20	17.19	− 1	71.32	71.25	− 7
+10	17.36	17.35	− 1	72.30	72.24	− 6
20	17.52	17.52	0	73.31	73.33	+ 2
30	17.68	17.68	0	74.37	74.35	− 2
40	17.85	17.86	+ 1	75.46	75.50	+ 4
50	18.03	18.04	+ 1	76.60	76.61	+ 1

The agreement between calculated and observed values is very good even down to the freezing points, except that very near the critical temperatures a deviation of about 1 to 5% appears.

In part IV of this paper, it has been shown that B is an additive constant and K, B, C and Φ_K in equations (1) and (2) take universal values when they are expressed in reduced form. Since such calculations have been already given for ethyl ether, only the result for acetone is shown in the following:

$$\mathrm{B}_{obs.}=62.3\sim61.9 \qquad \mathrm{B}_{calc.}=61.8.$$

$$b_R=\frac{B}{V_K}=0.297\sim0.295\ (0.308).$$

$$k_R=\frac{KV_K^{\frac{2}{3}}}{\Phi_K}1.80\sim1.79\ (1.84).$$

$$k'_R=K.M.^{\frac{1}{2}}T_K^{\frac{1}{2}}V_K^{\frac{1}{3}}=4.18\times10^4\ (4.03\times10^4).$$

$$c_R=\frac{CT_K^{\frac{1}{5}}}{\Phi_K}=1.08\ (1.09).$$

$$c'_R=\frac{CM^{\frac{1}{2}}\ T_K^{\frac{7}{10}}}{V^{\frac{1}{3}}_K}=2.51\times10^4\ (2.40\times10^4).$$

$$\phi'_R=\frac{\Phi_K M^{\frac{1}{2}}T_K^{\frac{1}{2}}}{V_K^{\frac{1}{3}}}=2.32\times10^4\ (2.19\times10^4).$$

The mean values obtained as the average for many substances are shown in parentheses. From the above result it may be concluded that the reduced equations cited in Part IV would also hold fairly good for acetone without any change.

In conclusion, the author wishes to express his cordial thanks to Prof. M. Katayama for his kind guidance.

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Hongo, Tokyo.

March, 1929.

ON CURTIUS AND GOEBELS' GLYCINE ANHYDRIDE SILVER.(1)

By Tei-ichi ASAHINA

Received February 20, 1929. Published March 28, 1929.

In the preceeding report,(2) a molecular compound of glycine anhydride was described which was presumed to be an intermediate product in the formation of Curtius and Göbels' glycine anhydride silver.(3) The author, thereafter, examined whether other silver compound could behave like the nitrate.

When an excess of saturated aqueous solution of glycine anhydride was added to silver oxide newly precipitated, no appreciable change seemed

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(1) The III report of the "Studies on Amino-acid Anhydrides." I report, see this Bulletin, **3** (1928), 151; II report see *Hoppe-Seyler's Zeit. f. physiol. Chem.*, **179** (1928), 83.

(2) II report.

(3) *J. prakt. Chem.*, (2) **37** (1888), 178.

to occur, but on addition of a small quantity of ammonia solution under vigorous agitation the precipitate of silver oxide turned its colour from brown to gray white; the product is soluble either in excess of ammonia or nitric acid. The course of this reaction and the appearance and some properties of the product remind us of the Curtius and Göbels' silver compound, except that the compound now obtained by the present author was much more unstable, a colour change being observed within half an hour or so. In order to avoid this rapid change the author tried to prepare this substance in a dark chamber illuminated by a red light, but it was found that this precaution has been less effective. The black substance, dried in vacuo was proved to possess different properties from silver oxide: on heating it decomposes explosively just like the Curtius and Göbels' compound. The analytical results of the changed product were also proximate to those of the known silver compound of these authors. Thus the unchanged gray white substance, although it was not allowed to be isolated, would possibly be an identical or isomeric substance with the Curtius and Göbels' compound.

Experimental.

Silver nitrate (4.5 gr.) was dissolved in water, warmed on a water-bath and an excess of potassium hydroxide solution was then added under stirring. On standing for a few minutes, when silver oxide so formed flocculated and settled, the supernatant liquid was decanted. The oxide was several times washed and decanted with pure water and was suspended in 200 c.c. saturated solution of glycine anhydride, the content of anhydride being about 2 gr. When some five c.c. of 10% ammonia solution was poured into the liquid under constant agitation, the brown colour of silver oxide turned then gradually to grayish white. In this case the precipitate of silver oxide must necessarily be crushed, otherwise it seems that the change occurs only on the surface of silver oxide.

The product was quickly separated from liquid by a centrifugal machine, washed several times with water on the machine and quickly transferred into the desiccator of brown glass and dried under a reduced pressure. In the course of this operation the product changes gradually its colour. Before analysis it was brought into a brown glass tube and further dried at 50–60° in Abderhalden's desiccating apparatus.

Analysis. Silver: the substance was dissolved in nitric acid and the silver was precipitated with hydrochloric acid, as chloride. Subst. = 0.4106, 0.7798 gr.; AgCl = 0.3588, 0.6861 gr. Found: Ag = 65.79, 66.24%. Calc. for $C_4H_4N_2O_2Ag_2$: Ag = 65.88%.

Nitrogen: Micro-Kjeldahl. Subst. = 10.32, 17.65 mg.; HCl (1/70 N.) required = 4.16, 6.97 c.c. Found: N = 8.06, 7.90%. Calc. for $C_4H_4N_2O_2Ag_2$: N = 8.54%.

The rather low value of nitrogen is presumably attributed to the incomplete reaction in the formation of silver compound.

Appendix. It was recently reported by Ch. Gränacher, G. Wolff and A. Weidinger(1) that silver compound of Curtius and Göbel could only be formed with glycine anhydride and not with its homologues, i.e. other amino-acid—and dipeptide-anhydrides. According to the present author's experience, the molecular compound of silver nitrate was also obtained only with glycine anhydride and other anhydrides gave no such compounds under the same condition. This parallelity would perhaps be an indirect proof to the author's assumption stated in the preceeding report.

In conclusion the author's best thanks are due to Prof. K. Shibata and Prof. Y. Shibata for their kind guidance throughout the study.

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(1) *Helv.*, **11** (1928), 1229.

SPECIFIC HEATS OF ACETONE, METHYL—, ETHYL—, AND n-PROPYL-ALCOHOLS AT LOW TEMPERATURES.(2)

By Shinroku MITSUKURI and Kenji HARA.

Received February 21, 1929. Published March 28, 1929.

In the ordinary calorimetric works, the environment in which the calorimeter is placed has a constant temperature, but at low temperatures, it is very difficult to get such one which is so constant enough as to enable one to do the accurate thermal measurement. It is not difficult, however, to get an environment whose temperature is rising regularly. The present authors, therefore, used the latter as the environment of the calorimeter with which the specific heats of acetone, methyl-, ethyl-, and n-propyl-alcohols at low temperatures were measured.

The schematic diagram of the apparatus is shown in Fig. 1. M is the Dewar vessel containing petroleum ether in which the whole system of the calorimeter is imbedded. A is a brass cylinder, and B the calorimeter proper which is suspended in A. J is the platinum resistance thermometer for measuring the temperature of the calorimeter, and E the manganin wire wounded around B, through which the electric current for the heating of the latter is passed.

The liquid air contained in another Dewar vessel of flask-like shape is forced to go through the syphone H and the copper tube K, so that the

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(2) The abstract of this paper was published in *Proc. Imp. Acad. Japan*, vol. 4.

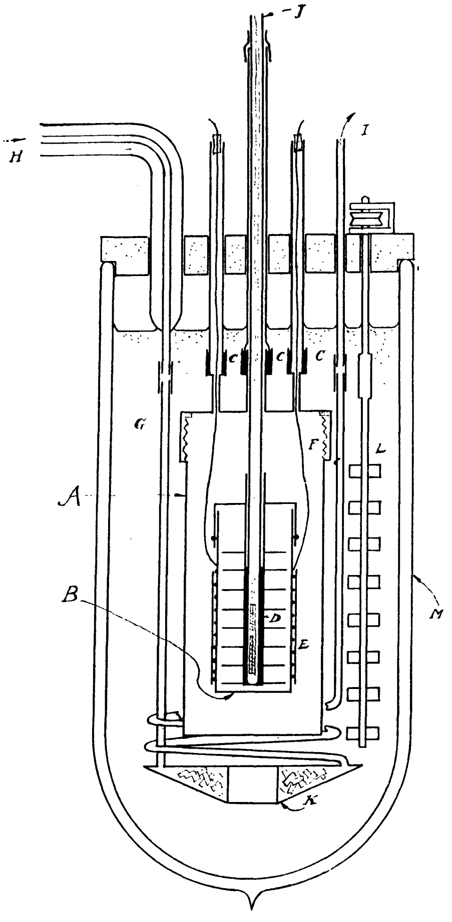

Fig. 1.

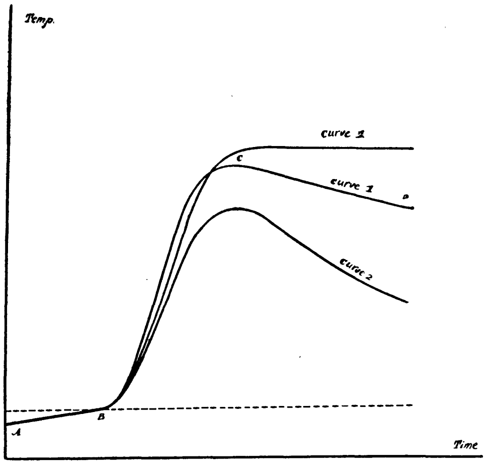

Fig. 2.

temperature in A goes down. When the temperature becomes low enough, the circulation of the liquid air is stopped, and then, being left in this state, the whole system in M finally takes the stationary state in which the temperature is rising regularly. At this time, electric current, which is measured with a potentiometer and a standard resistance, is supplied to the calorimeter for a proper interval of time, while the temperature of the calorimeter is measured at regular intervals.

The time-temperature curve thus obtained has the form shown by the curve 1 in Fig. 2, in which the part B C shows the region where electric current is passed in the calorimeter, while A B and C D show the regions before and after the passage of electric current.

Now, if the temperature of the environment is assumed to be constant throughout the measurement, the curve 1 must take the form shown by the curve 2 in the same figure. The curve 2 can be obtained from the curve 1, when, from each value of the temperature on the latter, the product of the time and the rate of rise of the temperature is substracted. From the curve 2, the curve 3 can be obtained, when the ordinary correction for the heat loss of the calorimeter is applied. With the value of the temperature rise obtained from the curve 3, the electric energy supplied to the calorimeter and the amount of the sample used, the specific heat of the sample can be calculated, if the heat capacity of the calorimeter is known. The last mentioned quantity is able to be measured in the same way as stated above, if the experiment is conducted with the empty calorimeter.

Table 1.

Specific Heats of Acetone

Absolute temp.	Specific heats
204.8	0.481
209.6	0.482
209.7	0.479
211.5	0.472
214.3	0.482
215.4	0.479
217.4	0.480
225.6	0.486
229.2	0.486
229.8	0.489
232.9	0.493
235.7	0.499
236.8	0.494
240.8	0.499
243.3	0.504
246.6	0.501
246.6	0.495
247.3	0.508
247.5	0.497
249.7	0.497
251.0	0.504
253.8	0.499
254.2	0.507
256.3	0.510

Table 2.

Specific Heats of Methyl-alcohol

Absolute temp.	Specific heats
190.5	0.524
192.0	0.537
198.3	0.536
198.7	0.535
204.6	0.541
208.9	0.539
211.5	0.557
214.0	0.540
220.5	0.544
225.9	0.559
238.7	0.566
242.0	0.571
246.6	0.580
249.9	0.582
254.7	0.570
258.4	0.584
262.4	0.582
264,8	0.577

Table 3.

Specific Heats of Ethyl-alcohol.

Absolute temp.	Specific heats	Absolute temp.	Specific heats
184.4	0.471	234.4	0.517
188.7	0.471	234.7	0.521
193.6	0.477	238.7	0.512
198.0	0.490	242.7	0.523
199.1	0.490	254.0	0.538
204.7	0.492	256.0	0.542
208.6	0.491	259.6	0.538
214.1	0.493	263.3	0.539
219.0	0.514	264.8	0.547
221.0	0.500	264.9	0.553
224.3	0.510	266.9	0.547
226.9	0.513	268.8	0.552
230.8	0.515		

Table 4.

Specific Heats of Normal-propyl-alcohol

Absolute temp.	Specific heats	Absolute temp.	Specific heats
162.8	0.422	233.6	0.497
168.0	0.433	234.3	0.504
170.7	0.423	236.9	0.491
176.0	0.444	237.1	0.500
182.0	0.445	243.3	0.510
192.3	0.464	244.7	0.504
192.3	0.466	246.4	0.510
196.8	0.468	248.3	0.507
202.5	0.471	250.7	0.506
207.6	0.473	254.5	0.517
209.6	0.475	257.3	0.520
215.5	0.480	259.2	0.523
222.5	0.495	266.0	0.533
222.9	0.493	268.3	0.551
226.5	0.486	269.8	0.550
228.6	4.495	270.5	0.540
230.7	0.489	274.4	0.545
231.1	0.500		

Table 5.

Abs. Temp.	Specific heats			
	Acetone	Methyl-al.	Ethyl-al.	n-Propyl-al.
170.	—	—	—	0.432
180.	—	—	—	0.449
190.	—	0.533	0.476	0.460
200.	0.470	0.539	0.488	0.469
210.	0.476	0.546	0.498	0.476
220.	0.482	0.551	0.505	0.484
230.	0.488	0.558	0.512	0.493
240.	0.496	0.564	0.519	0.502
250.	0.503	0.571	0.523	0.512
260.	0.511	0.577	0.539	0.525
270.	—	0.583	0.552	0.541

The results of the experiments were shown in Tables 1 to 4, and graphically represented in Fig. 3. The values of the specific heats shown in the Table 5 are those obtained from the curves in Fig. 3.

These values are not much different from those obtained by Parks and his co-workers(1) with the so-called Nernst method, but perhaps the former values have less errors.

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(1) G. S. Parks, *J. Am. Chem. Soc.*, **47** (1925), 338; **48** (1926), 2788 and K. K. Kelley, *J. Am. Chem. Soc.*, **47** (1925), 2089.

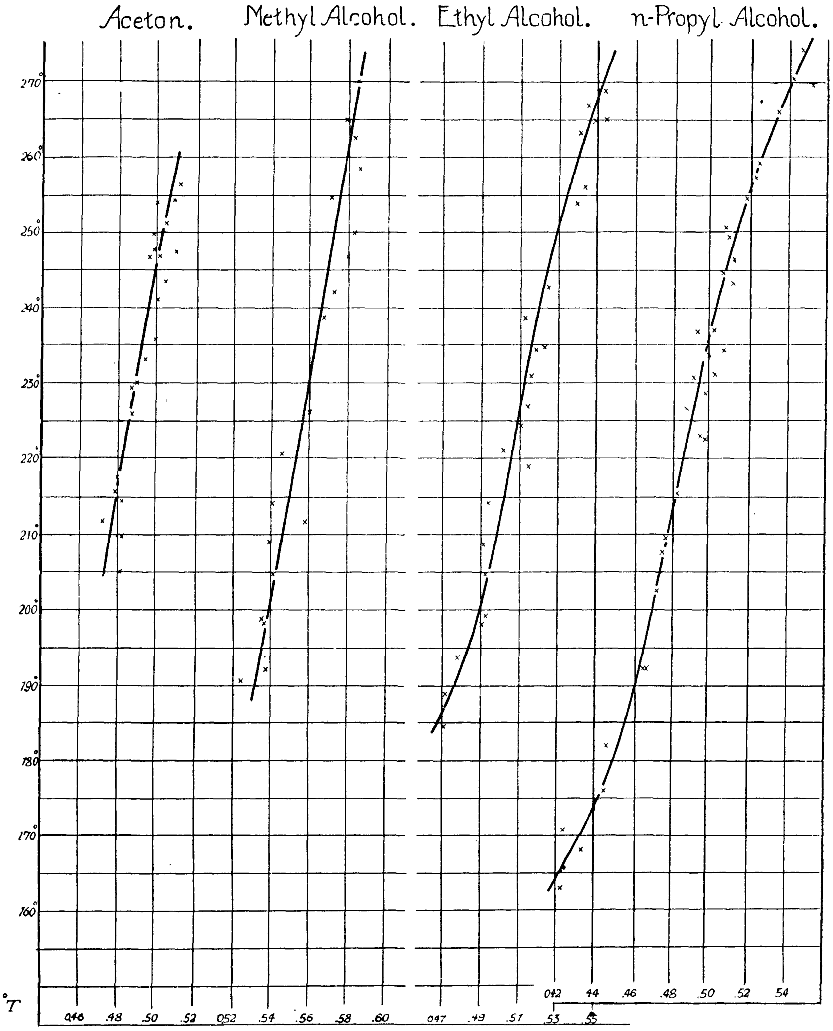

Fig. 3.

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UEBER DIE HOCHUNGESÄTTIGTEN SÄUREN DES SARDINENÖLS. I. MITTEILUNG: EINE NEUE SÄURE $C_{16}H_{26}O_2$ UND DIE HOCHUNGESÄTTIGTEN C_{18}–SÄUREN.

Von Yoshiyuki TOYAMA und Tomotaro TSUCHIYA.

Eingegangen am 14. März 1929. Ausgegeben am 28. April 1929.

Unter den japanischen Tranen nimmt das Sardinenöl die erste Stellung ein und die Jahresproduktion von Sardinenöl in Japan (ausschliesslich der Kolonie) liegt gegenwärtig in der Nähe von 11 Millionen kg. Das Sardinenöl stellt auch das beste Ausgangsmaterial für die Forschung der hochungesättigten Säuren dar, weil von den gewöhnlichen Tranen das Sardinenöl die höchste Menge dieser Säuren enthält.

Mit den hochungesättigten Säuren des Sardinenöls beschäftigte sich zuerst Fahrion.(1) Er glaubte im Sardinenöl eine Säure $C_{18}H_{30}O_2$ gefunden zu haben, die er Jecorinsäure nannte. Obwohl er(2) später die Existenz der Jecorinsäure wieder behauptet hat, ist es aber kaum zu zweifeln, dass die von ihm untersuchte Säure nicht einheitlich, sondern ein Gemisch war. H. Bull(3) zeigte schon im Jahre 1899 die Anwesenheit von Säuren der Reihen $C_nH_{2n-8}O_2$ und $C_nH_{2n-10}O_2$ im Sardinenöl und in verschiedenen anderen Tranen. M. Tsujimoto(4) analysierte die ätherunlöslichen Bromide, die aus den Fettsäuren des japanischen Sardinenöls gewonnen waren, und fand, dass das Analysenresultat annähernd mit der Formel $C_{18}H_{28}O_2Br_8$ übereinstimmt; somit gab er der zugehörigen Säure die Formel $C_{18}H_{28}O_2$ und den Namen Clupanodonsäure. Es wurde aber später von R. Majima und T. Okada(5) festgestellt, dass die hochungesättigten Säuren, die durch Entbromung der ätherunlöslichen Bromide von Sardinenölfettsäuren erhalten werden, nicht einheitlich sind, sondern in der Hauptsache aus C_{20}– und C_{22}–Säuren der Reihen $C_nH_{2n-8}O_2$ bzw. $C_nH_{2n-10}O_2$ bestehen. Sie schlossen ferner, dass der Hauptbestandteil vor allem eine Säure $C_{22}H_{34}O_2$ ist, während eine Säure $C_{18}H_{28}O_2$ höchstens in kleinen Mengen vorkommt, wenn sie überhaupt vorkommt. Auch J. D. Riedel(6) äusserte, dass die durch Entbromung der Polybromide von Sardinenölfettsäuren dargestellten Säuren nicht einheitlich sind. Später arbeitete Tsujimoto(7) erneut über die hochungesättigten

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(1) *Chem. Ztg.*, **17** (1893), 521.
(2) *Chem. Umschau*, **24** (1917), 4.
(3) *Chem. Ztg.*, **23** (1899), 966.
(4) *J. College of Eng. Tokyo Imp. Univ.*, **4** (1906), No. 1.
(5) *J. Tokyo Chem. Soc.*, **35** (1914), 13.
(6) *Chem. Zentralb.*, (1914), I, 1882.
(7) *Chem. Umschau*, **33** (1926), 285.

Säuren des Sardinenöls und es gelang ihm erstmals den Hauptbestandteil—die Säure $C_{22}H_{34}O_2$—zu isolieren. Er halte auch das Vorkommen der Säuren $C_{20}H_{32}O_2$, $C_{20}H_{30}O_2$ und $C_{18}H_{28}O_2$ in mehr oder weniger Mengen für wahrscheinlich. Durch diese Bestätigung trug er jetzt den Namen Clupanodonsäure auf die Säure $C_{22}H_{34}O_2$, weil die früher von ihm unter diesem Namen behandelte Säure hauptsächlich aus $C_{22}H_{34}O_2$ besteht. Die Säure $C_{18}H_{28}O_2$, für die zuerst der Name Clupanodonsäure eingeführt worden war, wollte er inzwischen als namenlos vorbehalten, bis diese tatsächlich isoliert und näher untersucht wird. Er(1) untersuchte neuerdings die Spaltungsprodukte der Clupanodonsäure $C_{22}H_{34}O_2$ mit Ozon. G. D. Beal und J. B. Brown(2) glaubte im Sardinenöl und in anderen Fischölen das Vorkommen von hochungesättigten Säuren der Formeln $C_{16}H_{26}O_2$, $C_{18}H_{28}O_2$, $C_{20}H_{32}O_2$, $C_{20}H_{30}O_2$, $C_{22}H_{34}O_2$ und $C_{22}H_{32}O_2$ nachgewiesen zu haben. A. Eibner und Ed. Semmelbauer(3) untersuchte die Eigenschaften der hochungesättigten Säuren, die durch Entbromung der Polybromide von Sardinenölfettsäuren dargestellt waren; es ist aber wohl nicht gerecht, dass diese Forscher die durch Entbromung erhaltenen Säuren als Clupanodonsäure beschrieben, weil diese ausser der Clupanodonsäure auch einige andere Säuren in mehr oder weniger Mengen enthalten.

Die obigen Literaturangaben sind die bisher veröffentlichten wichtigen Arbeiten über die hochungesättigten Säuren des Sardinenöls. Es soll hier noch einige Angaben über die hochungesättigten Säuren der anderen Trane angeführt werden. Nach den Untersuchungen von Beal und seinen Mitarbeitern(4) enthalten die hochungesättigten Säuren von Menhedenöl, Dorschleberöl, Herringsöl, Lachsöl und Sardinenöl im wesentlichen dieselben Verbindungen. Auch unsere früheren Forschungen(5) ergaben, dass die hochungesättigten Säuren von verschiedenen Waltranen, Dorschleberöl, Leberölen von Elasmobranch, und Spermöl im wesentlichen aus dieselben Verbindungen bestehen. Indessen sind andere Bestandteile als die Clupanodonsäure bisher noch nicht isoliert worden und ihre Identifizierung ist noch ungenugend begründet.

Wir haben nun die vorliegende Untersuchung unternommen mit der Absicht, die hochungesättigten Säuren des Sardinenöls in ihre einzelnen Bestandteile zu zerlegen und die letzteren vereinzelt nachzuweisen.(6)

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(1) Dieses Bulletin, **3** (1928), 299.

(2) *J. Am. Chem. Soc.*. **45** (1923), 1289.

(3) *Chem. Umschau,* **31** (1924), 196.

(4) Loc. cit., auch Beal u. R. R. McGregor, *J. Am. Chem. Soc.*, **48** (1926), 3150.

(5) *Chem. Umschau,* **31** (1924), 221, 238; **33** (1926), 293; **34** (1927), 19, 305, 342; **35** (1928), 21; auch *J. Soc. Chem. Ind., Japan,* **28** (1926), 95, 104; **29** (1927), 531, 538, 642; **30** (1928), 63, 116, 207, 519.

(6) Unter der Bezeichnung „hochungesättigte Säuren" versteht man gewöhnlich die Säuren, welche noch stärker ungesättigt sind als die Säuren der Linolensäurereihe; in dieser Mitteilung sind aber der Bequemlichkeit halber die Säuren der Linolensäurereihe darin eingeschlossen.

Zunächst beschäftigten wir uns mit der Isolierung der ätherunlösliche Bromide ergebenden C_{16}– und C_{18}–Säuren. Bei diesem Versuch konnten wir eine neue C_{16}–Säure von der Formel $C_{16}H_{26}O_2$ isolieren. Von den C_{18}–Säuren konnten wir die Säure $C_{18}H_{28}O_2$ sicherlich nachweisen, obwohl sie nicht in reinem Zustand isoliert wurde. Die Säure $C_{16}H_{26}O_2$ ist bereits von Beal und Brown⁽¹⁾ als ein Bestandteil von Tranfettsäuren angenommen worden; sie haben aber nur daraus auf das Vorkommen dieser Säure geschlossen, dass beim Fraktionieren der Methylester der hochungesättigten Säuren von Menhedenöl eine Fraktion gewonnen wurde, deren Mol.–Gewicht um einige Einheiten kleiner ist als dasjenige der Methylester der C_{18}–Säuren. Auch wir⁽²⁾ haben früher das Vorkommen der Säure $C_{16}H_{26}O_2$ in Finnwaltran und kalifornischem Grauwaltran vermutet, aber die sichere Identifizierung dieser Säure war damals nicht gelungen. Die Säure $C_{16}H_{26}O_2$ wurde also erstmals beim vorliegenden Versuch isoliert. Wir nennen diese Säure Hiragonsäure nach einer japanischen Bezeichnung der japanischen Sardine ,, Hirago.''⁽³⁾

Beschreibung der Versuche.

I. Abtrennung der hochungesättigten Säuren und Fraktionieren ihrer Methylester. 19 kg. einer Probe von japanischem Sardinenöl wurden durch die Natriumseife-Aceton Methode⁽⁴⁾ behandelt und es wurden aus den acetonlöslichen Natriumseifen 6550 gr. rohe hochungesättigte Säuren erhalten. Diese wurden in die Methylester übergeführt und die Ester unter vermindetem Druck destilliert, wobei die niedere Fraktion, Sdp. bis 215° (15 mm.), getrennt aufgefangen wurde. Während die beim Fraktionieren gewonnene höhere Fraktion fast ausschliesslich aus den Estern der hochungesättigten Säuren besteht, enthält die oben erhaltene niedere Fraktion beträchtliche Menge von Estern der schwach ungesättigten Säuren beigemischt und sie zeigte die Verseifungszahl 198.8, die Jodzahl (Rosenmund u. Kuhnhenn) 179.6 und n_D^{20} 1.4628.

II. Darstellung der ätherunlöslichen Bromide aus der niederen Esterfraktion und Behandlung der Bromide mit Benzol. Die niedere Fraktion, Sdp. bis 215° (15 mm.), wurden bromiert und die ätherunlöslichen Bromide abgetrennt. Sie sind weisse Pulver mit einem Bromgehalt von 67.34% und

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(1) Loc. cit.

(2) *Chem. Umschau,* **31** (1924), 238; **34** (1927), 19.

(3) In der Mitteilung von Beal u. Brown war die Säure $C_{16}H_{26}O_2$ als „Palmitolic acid" bezeichnet. Diese Bezeichnung ist aber unzuständig, weil sie bereits für eine Säure der Stearolsäurereihe von der Formel $C_{16}H_{28}O_2$ gegeben worden war. (Vergl. „Chemical Technology and Analysis of Oils, Fats and Waxes," 6 Aufl., I Bd., S. 240.)

(4) *Chem. Umschau,* **32** (1925), 204; **34** (1927), 51.

schmolzen gegen 220° zu einer teerartigen Substanz. Sie wurden mit Benzol behandelt und in drei Anteile getrennt. Die Bromierung und die Behandlung mit Benzol wurden folgendermassen ausgeführt.

Je 100 gr. der niederen Fraktion wurden in 1 Liter Aether gelöst. Die Lösung wurde in einem Kolben auf -5° abgekühlt und tropfenweise mit einer Bromlösung in Eisessig (1 Teil Brom und 1 Teil Eisessig) bis zur bleibenden Braunfärbung versetzt. Die Lösung wurde 15 Stunden bei 2 bis 3° stehen gelassen und hierauf von Niederschlag vorsichtig abdekantiert, der Niederschlag mit kaltem Aether aufgeschüttelt, wieder absitzen gelassen und dekantiert. Nach mehrmaliger Wiederholung des Dekantierens wurde der Niederschlag auf einem Filter gebracht und erneut mit kaltem Aether ausgewaschen. Zum Dekantieren und Auswaschen wurden insgesammt 2 Liter Aether verwendet. Nachdem die vereinigte ätherische Lösung durch Behandlung mit Natriumthiosulfat von überschüssigem Brom befreit und eingeengt wurde, erfolgte noch eine erhebliche Ausscheidung von Bromiden. Beim Auswaschen mit Aether gangen aber diese Bromide zum grossten Teil wieder in Lösung, bevor der Waschäther farblos wurde; der ungelöst gebliebene Anteil war sehr gering und nicht weiter verarbeitet.

Die oben erhaltenen ätherunlöslichen Bromide wurden luftgetrocknet, verrieben und dann mit Benzol behandelt. Je 20 gr. Bromide wurden mit 500 c. c. Benzol am Rückflusskühler 40 Min. auf dem Wasserbade gekocht und noch heiss schnell abfiltriert. Der Rückstand wurden noch zweimal nach gleicher Weise mit Benzol behandelt; 20 gr. Bromide wurden also im ganzen mit 1.5 Liter siedendem Benzol behandelt und es wurden der ungelöst gebliebene Anteil B getrennt aufgefangen. Die vereinigte Benzollösung wurde auf ca. 500 c. c. eingeengt und dann 3 Stunden bei 40° stehen gelassen. Der dabei abgeschiedene Niederschlag C wurde abfiltriert; aus dem Filtrat wurde nach dem Abdestillieren des Benzols der Rückstand A erhalten. Vermutlich trat bei der obigen Behandlung mit Benzol geringe Zersetzung der Bromide ein, weil die bei 40° abgeschiedenen Bromide C und die in Benzol löslichen Bromide A dunkelbraunlich gefärbt waren. Beim erneuten Auswaschen mit Aether wurden die beiden Anteile nicht ganz weiss, während merkliche Mengen derselben in Aether verloren gangen.

Insgesammt 1340 gr. der niederen Fraktion wurden bromiert und aus den erhaltenen ätherunlöslichen Bromiden folgende Anteile getrennt aufgefangen. Da der Anteil C als eine Mischfraktion der Anteile A und B angesehen werden kann, haben wir nur die Anteile A und B weiter verarbeitet.

A.	Bei 40° in Benzol löslicher Anteil	265 gr.
B.	In siedendem Benzol unlöslicher Anteil	172 gr.

C. In siedendem Benzol löslicher, aber bei
40° darin unlöslicher Anteil 57 gr.

III. Entbromung der in Benzol löslichen Bromide A und Fraktionieren des entbromten Produktes. Die in Benzol löslichen Bromide stellten etwas braunlich gefärbte Pulver mit einem Bromgehalt von 66.52 % dar, sie sinterten bei etwa 165° und schmolzen bei 198°. Sie wurden mit der 2-fachen Menge Zinkstaub und der 10-fachen Menge Eisessig versetzt und unter Durchleitung von Kohlensäurestrom 5 Stunden am Rückflusskühler auf dem Wasserbade erhitzt. Hierauf wurde die Lösung abdekantiert; der ungelöst gebliebene Niederschlag erneut mit Eisessig versetzt, wieder 5 Stunden erhitzt, abfiltriert und mit Eisessig ausgewaschen. Aus der vereinigten Eisessig-Lösung wurde der Eisessig unter vermindetem Druck zum grossten Teil abdestilliert, der Rückstand mit Petroläther aufgenommen, mit Wasser ausgewaschen und mit Natriumsulfat getrocknet. Nach dem Vertreiben des Petroläthers blieb das entbromte Produkt als orangegelbes Oel. Aus 264 gr. der Bromide wurden 65 gr. des entbromten Produktes erhalten; die Ausbeute betrug rund 74 % der Theorie. Bei obiger Behandlung mit Zinkstaub und Eisessig trat wahrscheinlich ausser Entbromung noch andere Nebenreaktionen ein. Das entbromte Produkt schien ausser den Methylestern auch ihre polymerisierten Produkte und einige unverseifbare Zersetzungsprodukte zu enthalten.

65 gr. des entbromten Produktes wurden unter 15 mm. Druck destilliert. Es ergaben sich dabei Vorlauf bis 180° wenige Tropfen, Fraktion von 180-215° 36 gr. und Fraktion von 215-220° 7 gr.; über 220° hinaus gang nur geringe Menge Nachlauf über, während im Destillierkolben beträchtliche Menge Rückstand hinterblieb. Die Fraktion von 180-215° wurden weiter fraktioniert und es wurden zwei Fraktionen getrennt aufgefangen: 1. Sdp. 180-190° (15 mm.), 2. Sdp. 205-215° (15 mm.).

Fraktion 1, Sdp. 180-190° (15 mm.). Diese Fraktion ist eine hellgelbe Flüssigkeit mit folgenden Zahlen. Das daraus gewonnene ätherunlösliche Bromid schmolz bei 180° zu einer gelben Flüssigket.

$d_4^{15}=0.9160$, $d_4^{20}=0.9125$, $n_D^{15}=1.4792$, $n_D^{20}=1.4771$, Verseifungszahl 206.9, Jodzahl (Rosenmund u. Kuhnhenn) 280.2, Jodzahl (Wijs) 296.8, Ausbeute an ätherunlösl. Bromid 56.67%, Bromgehalt des ätherunlösl. Bromides 64.95%.

Ber. für $C_{16}H_{25}O_2CH_3$: Verseifungszahl 212.4, Jodzahl 288.2, Bromgehalt des Bromides $C_{16}H_{25}O_2CH_3Br_6$ 64.47%.

Diese Fraktion wurde verseift und nach Entfernung vom beigemischten Unverseifbaren die freie Säure dargestellt. Sie stellte eine gelbe Flüssigkeit mit folgenden Zahlen dar. Das daraus gewonnene ätherunlösliche Bromid schmolz bei 190° zu einer gelben Flüssigkeit.

$d_4^{15}=0.9324$, $d_4^{20}=0.9288$, $n_4^{15}=1.4876$, $n_D^{20}=1.4855$, Neutralisationszahl 221.6, Verseifungszahl 222.6, Jodzahl (Rosenmund u. Kuhnhenn) 298.5, Jodzahl (Wijs) 310.7, Ausbeute an ätherunlösl. Bromid 56.80%, Bromgehalt des ätherunlösl. Bromides 66.10%.

Ber. für $C_{16}H_{26}O_2$: Neutralisationszahl 224.2, Jodzahl 304.4, Bromgehalt des Bromides $C_{16}H_{26}O_2Br_6$ 65.71%.

Nach obigen Zahlen stimmt diese Säure auf die Formel $C_{16}H_{26}O_2$. Diese Säure wurde hydriert und das hydrierte Produkt durch fraktionierte Fällung mit Magnesiumacetat zerlegt. Hierbei zeigte sich, dass obwohl das hydrierte Produkt von geringen Mengen der Säuren mit mehr als 16 C-Atomen beigemengt war, der Hauptanteil nach Reinigung durch Umkristallisieren Kristalle von Neutralisationszahl 218.2 und Schmp. 62-62.5° lieferte, welche sich durch Mischprobe als reine Palmitinsäure erwiesen. Daher hat die ursprüngliche Säure $C_{16}H_{26}O_2$ eine unverzweigte Kohlenstoffkette. Wir schlagen für diese Säure den Namen Hiragonsäure vor.

Fraktion 2, Sdp. 205-215° (15 mm.). Diese Fraktion zeigte folgende Zahlen. Das daraus gewonnene ätherunlösliche Bromid wurde über 200° stark dunkel gefärbt und schmolz bei etwa 215° zu einer teerartigen Substanz.

$d_4^{15}=0\ 9168$, $d_4^{20}=0.9133$, $n_D^{15}=1.4856$, $n_D^{20}=1.4837$, Verseifungszahl 190.6, Jodzahl (Rosenmund u. Kuhnhenn) 268.2, Jodzahl (Wijs) 283.9, Ausbeute an ätherunlösl. Bromid 48.61%, Bromgehalt des ätherunlösl. Bromides 65.94%.

Ber. für $C_{18}H_{29}O_2CH_3$: Verseifungszahl 192.0, Jodzahl 260.6.
Ber. für $C_{18}H_{29}O_2CH_3Br_6$: Bromgehalt 62.13%.
Ber. für $C_{18}H_{27}O_2CH_3Br_8$: Bromgehalt 68.78%.

Die aus dieser Fraktion abgeschiedenen, vom Unverseifbaren befreiten Säuren (a) zeigten folgende Zahlen. Das daraus gewonnene ätherunlösliche Bromid schmolz bei etwa 215° zu einer teerartigen Substanz.

$d_4^{15}=0.9329$, $d_4^{20}=0.9294$, $n_D^{15}=1.4935$, $n_D^{20}=1.4915$, Neutralisationszahl 198.3, Verseifungszahl 200.3, Jodzahl (Rosenmund u. Kuhnhenn) 280.4, Jodzahl (Wijs) 297.3, Ausbeute an ätherunlösl. Bromid 49.30%, Bromgehalt des ätherunlösl. Bromides 67.00%.

Ber. für $C_{18}H_{30}O_2$: Neutralisationszahl 201.7, Jodzahl 273.7.
Ber. für $C_{18}H_{30}O_2Br_6$: Bromgehalt 63.28%.
Ber. für $C_{18}H_{.8}O_2Br_8$: Bromgehalt 69.83%.

Diese Säuren wurden hydriert und das hydrierte Produkt näher untersucht. Es wurde hierbei gefunden, dass das hydrierte Produkt in der Hauptsache aus Stearinsäure besteht, obwohl es von geringen Mengen der C_{16}– und C_{20}–Säuren begleitet ist. Somit wurde bestätigt, dass die ursprünglichen Säuren hauptsächlich aus C_{18}–Säuren bestehen. Ihre Jodzahl steht mit dem berechneten Wert für $C_{18}H_{30}O_2$ nahe, während der

Bromgehalt des ätherunlöslichen Bromides zwischen den berechneten Werten für $C_{18}H_{30}O_2Br_6$ und $C_{18}H_{28}O_2Br_8$ liegt. Demnach sind die Säuren (a) nicht einheitlich ; sie enthalten ausser der Säure $C_{18}H_{30}O_2$ auch einerseits stärker ungesättigte Säure $C_{18}H_{28}O_2$, anderseits schwächer ungesättigte Säuren, welche niedrigere Jodzahl als die Säure $C_{18}H_{30}O_2$ zeigen und keine ätherunlösliche Bromide liefern. Wenn man aber berücksichtigt, dass die Säuren (a) ursprünglich aus den ätherunlöslichen Bromestern regeneriert worden sind, und dass in diesen ätherunlöslichen Bromestern das Vorkommen irgendwelcher Bromester von schwächer ungesättigten Säuren als $C_{18}H_{30}O_2$ ganz ausgeschlossen werden kann, so muss man annehmen, dass die in Säuren (a) beigemischten, schwächer ungesättigten Säuren keine ursprüngliche Bestandteile des Sardinenöls, sondern einige Umwandlungsprodukte, welche bei der Entbromung der Bromide entstanden worden waren.

IV. Entbromung der in siedendem Benzol unlöslichen Bromide B und Fraktionieren des entbromten Produktes. Die in siedendem Benzol unlöslichen Bromide stellten weisse Pulver mit einem Bromgehalt von 69.25 % dar, sie wurden über 200° stark dunkel gefärbt und schmolzen bei etwa 240° zu einer teerartigen Substanz. Aus 170 gr. dieser Bromide wurden durch Behandlung mit Zinkstaub und Eisessig, wie beim Abschnitt III beschrieben, 40 gr. entbromtes Produkt erhalten ; die Ausbeute betrug 76.5 % der Theorie. Das entbromte Produkt schien etwas Unverseifbares beigemengt zu enthalten ; zwecks Entfernung vom Unverseifbaren wurde das entbromte Produkt verseift, mit Aether behandelt und die abgeschiedenen freien Säuren wieder in die Methylester übergeführt. 38 gr. der so gewonnenen Methylester wurden unter 15 mm. Druck fraktioniert, wobei folgende Fraktionen erhalten wurden : Fraktion bis 200° nur 0.5 gr., Fraktion von 200-215° 15 gr. und Fraktion von 215-230° 17 gr. (Verlust und Rückstand 5.5 gr.). Der Siedepunkt der Methylester ist also etwas höher als derjenige der aus benzollöslichen Bromiden A dargestellten Methylester.

Die Fraktion von 200-215° (15 mm.) wurde weiter fraktioniert und eine bei 205-215° (15 mm.) übergehende Fraktion mit folgenden Zahlen getrennt aufgefangen. Das daraus gewonnene ätherunlösliche Bromid schmolz bei etwa 215° zu einer teerartigen Substanz.

$d_4^{15}=0.9172$, $d_4^{20}=0.9139$, $n_D^{15}=1.4862$, $n_D^{20}=1.4842$, Verseifungszahl 196.8, Jodzahl (Rosenmund u. Kuhnhenn) 314.3, Jodzahl (Wijs) 323.1, Ausbeute an ätherunlösl. Bromid 52.56%, Bromgehalt des ätherunlösl. Bromides 68.58%.

Ber. für $C_{18}H_{27}O_2CH_3$: Verseifungszahl 193.3, Jodzahl 349.8, Bromgehalt des Oktobromides $C_{18}H_{27}O_2CH_3Br_8$ 68.78%.

Ber. für $C_{18}H_{29}O_2CH_3$: Verseifungszahl 192.0, Jodzahl 260.6, Bromgehalt des Hexabromides $C_{18}H_{29}O_2CH_3Br_6$ 62.13%.

Die aus dieser Fraktion gewonnenen freien Säuren (b) zeigten folgende Zahlen, das daraus gewonnene ätherunlösliche Bromid schmolz bei etwa 220° zu einer teerartigen Substanz.

$d_4^{15}=0.9332$, $d_4^{20}=0.9298$, $n_D^{15}=1.4942$, $n_D^{20}=1.4921$, Neutralisationszahl 202.5, Verseifungszahl 206.4, Jodzahl (Rosenmund u. Kuhnhenn) 327.8, Jodzahl·(Wijs) 340.8, Ausbeute an ätherunlösl. Bromid 53.82%, Bromgehalt des ätherunlösl. Bromides 69.67%.

Ber. für $C_{18}H_{28}O_2$: Neutralisationszahl 203.1, Jodzahl 367.6, Bromgehalt des Oktobromides $C_{18}H_{28}O_2Br_8$ 69.83%.

Ber. für $C_{18}H_{30}O_2$: Neutralisationszahl 201.7, Jodzahl 273.7, Bromgehalt des Hexabromides $C_{18}H_{30}O_2Br_6$ 63.28%.

Das hydrierte Produkt der Säuren (b) wurde aus Alkohol fraktioniert kristallisiert und es wurde gefunden, dass obwohl das hydrierte Produkt von geringen Mengen der C_{16}-Säuren begleitet ist, der Hauptanteil nach der Reinigung durch Umkristallisieren Kristalle mit der Neutralisationszahl 196.6 und dem Schmp. 69.5–70° lieferte, die sich durch Mischprobe als reine Stearinsäure erwiesen. Somit bestehen die Säuren (b) hauptsächlich aus C_{18}-Säuren. Die Jodzahl der Säuren (b) ist erheblich kleiner als der berechnete Wert für $C_{18}H_{28}O_2$, während der Bromgehalt des daraus gewonnenen ätherunlöslichen Bromides mit dem berechneten Wert für $C_{18}H_{28}O_2Br_8$ nahe steht. Diese Tatsache lässt darauf schliessen, dass die Säuren (b) ausser der Säure $C_{18}H_{28}O_2$ auch eine gewisse Menge der schwach ungesättigten Säuren, die keine ätherunlösliche Bromide ergeben, enthalten. Diese schwach ungesättigten Säuren sind, wie vorher beim Abschnitt III gesagt worden war, wahrscheinlich einige intramolekulare Umwandlungsprodukte, welche bei der Entbromung der Bromide entstanden worden waren. Es liegt jedenfalls keines Zweifel darüber, dass die Säuren (b) in der Hauptsache aus $C_{18}H_{28}O_2$ bestehen, obwohl sie nicht reine Individuum sind.

Zusammenfassung.

1. Japanisches Sardinenöl wurde durch die Natriumseife-Aceton Methode behandelt und es wurden aus den acetonlöslichen Natriumseifen die rohen hochungesättigten Säuren dargestellt. Diese wurden in die Methylester übergeführt und die Ester unter vermindetem Druck destilliert, wobei die niedere Fraktion, Sdp. bis 215° (15 mm.), getrennt aufgefangen wurde. Aus dieser Fraktion wurden die ätherunlöslichen Bromide dargestellt, die letzteren wurden mit Benzol behandelt und es wurden zwei Anteile getrennt aufgefangen: a. bei 40° in Benzol löslicher Anteil, b. in siedendem Benzol unlöslicher Anteil.

2. Der in Benzol lösliche Anteil (a) wurde entbromt und die regenerierten Ester fraktioniert. Aus einer Fraktion von 180-190° (15 mm.) wurde eine neue Säure $C_{16}H_{26}O_2$ isoliert, die wir Hiragonsäure nannten.

3. Aus dem in Benzol unlöslichen Anteil (b) wurden die entbromten Ester dargestellt und diese fraktioniert. Wir haben dabei eine Fraktion von 205-215° (15 mm.) getrennt aufgefangen und festgestellt, dass diese Fraktion in der Hauptsache aus dem Methylester der Säure $C_{18}H_{28}O_2$ besteht.

4. Unter den ätherunlösliche Bromide ergebenden C_{18}-Säuren scheint auch die Säure $C_{18}H_{30}O_2$ vorzukommen.

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THE RADIOACTIVE CONSTITUENTS OF HOKUTOLITES AND OTHER MINERALS IN JAPAN.

By Jun YOSHIMURA.

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The radioactivity of the hokutolite from the Hokuto hot-spring in Taiwan has been studied by several investigators since its discovery in 1906 by Y. Okamoto. M. Hayakawa and T. Nakano⁽¹⁾ pointed out the presence of ionium, radium and polonium as its radioactive constituents, examining merely the characteristics of the decay curves of radioactivity shown by the particular fractions separated by chemical processes. On the hokutolite from the Shibukuro hot-spring in Akita Prefecture, R. Ohashi⁽²⁾ determined its radium-content, and recently I. Suganuma⁽³⁾ proved qualitatively that the radioactive constituents of this mineral consists of radium, polonium and thorium. Majority of these previous investigations have, however, been wholly deficient in the quantitative examination of the radioactive constituents, hence in the present work the author has determined the amounts of radium and thorium in the above mentioned hokutolites as well as those in the allanite from Shirakawa near Kyoto and the radium-content of the xenotime from Ishikawa, Fukushima Prefecture, by the accurate measurements of the emanations given out from these minerals.

Samples Used for Analyses. *Hokutolite from the hot-spring of Hokuto, Taiwan.*—This mineral occurs as a crystalline crust which grows on the bottom of the river, where runs hot-spring water gushed out. Thickness

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(1) M. Hayakawa and T. Nakano, *Z. Anorg. Chem.*, **78** (1912), 183.

(2) R. Ohashi, *Min. Mag.*, **19** (1920), 73; *J. Chem. Soc.*, **118** (1920), Abs. ii, 550.

(3) I. Suganuma, this Bulletin, **3** (1928), 69.

7—8 mm. Yellowish brown and translucent. This crystalline crust was carefully taken from its mother-rock and analyzed.

Hokutolite from the hot-spring of Shibukuro, Akita Prefecture.—This specimen is also a thick crystalline crust similarly produced as that from Hokuto, and thicker than the latter. On the surface of this crust, there are recognized some minute crystals and the fracture shows a zonal structure consisting alternately of brown and white ingredients. An average portion of these ingredients was taken for analysis.

Allanite from Shirakawa, Kyoto Prefecture.—The allanite is a black prismatic crystal taken out from the granite occurring in this locality. The crystals measure about 5—6 mm. in length and 1—2 mm. in diameter.

Xenotime from Ishikawa, Fukushima Prefecture.—Xenotime occurs in this quarter usually intermingled with zircon, the former always developing around the crystal of the latter. A special form of aggregate consisting of such intermingled crystals is sometimes called " Kikukwa-seki " in this district. It is almost impossible to obtain pure xenotime entirely free from zircon, and so the lumps of such intermingled crystals were employed for analysis, a special care having been taken in the disintegration process, so as not to decompose the zircon, of which will be described latter.

Treatment of Minerals. *Hokutolite.*—The finely ground sample was fused with a quantity of fusing mixture, and the melt was extracted with water and filtered. For the extraction of emanations, the solution obtained by dissolving the residue in nitric acid was called the "first solution," and the filtrate acidified with nitric acid, the "second solution."

Allanite.—The sample was pulverized and fused with fusing mixture. The melt was lixiviated with water containing hydrochloric acid and filtered. The residue was very small in quantity. In the filtrate, the silica was removed by usual method and the solution thus obtained was called the "first solution". The insoluble residue was then fused with potassium pyrosulphate, and brought to a solution being dissolved in water acidified with sulphuric acid. The clear solution thus obtained was chiefly used for the determination of thorium, being called the "second solution".

Xenotime.—The finely powdered mineral was left for more than a month to let the radium emanation come into equilibrium. The sample, thus prepared, was directly employed for the estimation of radium emanation, so that a quantity of the sample was transferred into a large test-tube made of quartz-glass and an excess of concentrated sulphuric acid was then added. Having been boiled this mixture over a moving flame, all the radium emanation contained in the sample was evolved. The latter was collected by a suitable means in an emanation reservoir and then introduced into an electroscope for the measurement. There is no doubt in this treatment, about the fact that the xenotime alone is completely decomposed whilst the zircon may hardly be attacked. It may, therefore, be safely asserted that the emanation measured in this case is wholly derived from the xenotime.

Determination of Radium. For the measurement of radium, the electroscope and accessory apparatuses formerly deviced by F. Soddy⁽¹⁾ were employed. Each solution for the examination was kept in a sealed emanation bottle under a little reduced pressure. After having been left for more than a month in this sealed state, the solution was used for the determination. The electroscope was calibrated by the radium standard solutions prepared from the Cornish pitchblende, which was previously analyzed by Dr. S. Iimori and determined the amount of uranium as to be 44.37% U_3O_8, accordingly 1.28×10^{-5}% radium.

Using the above standards, the constant of the electroscope was determined as follows :—

Standard solution	Radium-Content (gr.)	Activity (div./min.)	Constant of Electroscope (10^{-12} gr. Ra per div./min.)
I	1.73×10^{-10}	5.77	30.0
II	,,	5.71	30.3
			mean, 30.2

The results are shown in tabular form in the rear.

Determination of Thorium. The determination of thorium was carried out by the constant current method.⁽²⁾ According to G. H. Cartledge,⁽³⁾ the degree of accuracy of this method is said to be about 1.5%. Before the measurement, the radium emanation in the sample solution was always completely expelled by boiling and letting air bubble through the solution. A steady current of air from a Mariotte's bottle being then bubbled in the sample solution, the thorium emanation was continuously conveyed into the emanation chamber of the electroscope through a drying tube filled with calcium chloride. The readings were taken when the rate of discharge in the electroscope had come to constant under a steady flow of air through the apparatus.

As the standard of thorium, the thorianite from Ceylon was used. The amount of thorium of this mineral was previously determined by gravimetric analysis to be 52.92% ThO_2. A definite quantity of the thorianite,

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(1) F. Soddy, *Phil. Mag.*, (6) **18** (1909), 846.
(2) R. J. Strutt, *Proc. Roy. Soc.*, A, **76** (1905), 88; J. Joly, *Phil. Mag.*, (6) **17** (1909), 760.
(3) G. H. Cartledge, *J. Am. Chem. Soc.*, **41** (1919), 42.

viz. in the experiment 0.1199 gr. was dissolved in concentrated nitric acid and diluted to about 150 c.c. with water, small insoluble parts, which did not contain any radiothorium and thorium X, having been filtered off. In this method of measurement, it is important to keep the standard solution and sample solutions in the same comparable condition throughout the whole experiment, which is, however, rather difficult in practice. Hence the calibration of the standard solution was made every time as soon as the measurement of a sample solution was finished, as will be seen in the results given in Table 2.

Experimental Results. The results obtained in the measurements of the amounts of radium and thorium in the minerals are given in the following tables.

Table 1. Radium-Content.

Mineral	Sample taken (gr.)		Activity (div./min.)	Radium-Content			Uranium-content (as U_3O_8) (%)
				of each soln. (gr.)	Total (gr.)	Total (%)	
Hokutolite (Hokuto, Taiwan)	(I) 1.0194	The 1st soln.	58.9	1778×10^{-12}	1.78×10^{-9}	1.75×10^{-7}	—
		The 2nd soln.	0.03	0.9×10^{-12}			
	(II) 1.0211	The 1st soln.	57.3	1740×10^{-12}	1.74×10^{-9}	1.70×10^{-7}	—
		The 2nd soln.	— *	—			
						mean, 1.73×10^{-7}	
Hokutolite (Shibukuro, Akita Pref.)	1.1487	The 1st soln.	46.3	1398×10^{-12}	1.40×10^{-9}	1.22×10^{-7}	—
		The 2nd soln.	0.03	0.9×10^{-12}			
Allanite (Shirakawa, Kyoto Pref.)	0.8112	The 1st soln.	1.11	33.5×10^{-12}	3.95×10^{-11}	4.87×10^{-9}	0.017
		The 2nd soln.	0.20	6.0×10^{-12}			
Xenotime (Ishikawa, Fukushima Pref.)	(I) 0.7157		168.1	—	5.08×10^{-9}	7.09×10^{-7}	
	(II) 0.1228		27.8	—	0.839×10^{-9}	6.83×10^{-7}	
	(III) 0.1438		33.5	—	1.01×10^{-9}	7.03×10^{-7}	
						mean, 6.98×10^{-7}	2.42

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*The measurement was omitted, since the activity of the second solution was very little as seen in the case of the sample (I).

In the above table, the amount of uranium was calculated from that of radium, taking the equilibrium-ratio of radium to uranium to be 3.4×10^{-7}.

Table 2. Thorium-Content.

Mineral	Sample taken (gr.)		Constant of Electroscope (gr. ThO_2 per div./hr.)	Activity (div./hr.)	Thorium-Content (as ThO_2)		
					of each soln. (gr.)	Total	
						(gr.)	(%)
Hokutolite (Hokuto, Taiwan)	1.0194	The 1st soln.	3.54×10^{-4}	0.4	1.4×10^{-4}	2.1×10^{-4}	0.02
		The 2nd soln.	,,	0.2	0.7×10^{-4}		
Hokutolite (Shibukuro, Akita Pref.)	1.1487	The 1st soln.	3.56×10^{-4}	0.3	1.1×10^{-4}	1.1×10^{-4}	0.01
		The 2nd soln.	—	—**	—		
Allanite (Shirakawa, Kyoto Pref.)	0.8112	The 1st soln.	3.78×10^{-4}	14.5	0.0055	0.0085	1.05
		The 2nd soln.	3.41×10^{-4}	8.8	0.0030		

Summary.

As to the uranium in hokutolite, there is no analytical evidence, hitherto, of its presence in this mineral, and it is thought quite useless to calculate it from the amount of radium, as the mineral is obviously of the secondary nature.

The radium- and thorium-contents of the two kinds of hokutolites mentioned above are respectively of the same order and quite similar. The comparatively large content of radium, however, in comparison with the poorer content of thorium shows that the radioactivity of this mineral is mainly ascribed to radium and its disintegrating products and very little to the members of thorium-series.

It is seen that the allanite from Shirakawa, Kyoto Prefecture contains 1.05% ThO_2 and 0.017% U_3O_8.

The uranium-content of the xenotime-portion of the xenotime-zircon from Ishikawa was determined to be 2.42% U_3O_8. According to K. Kimura⁽¹⁾, the average amount of uranium in the "Kikukwa-seki" is said as being

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**It has shown almost no activity.

(1) K. Kimura, *Japan. J. Chem.*, **2** (1925), 73.

1.92% UO_2. These results indicate that the amount of uranium in the zircon-portion of the latter mineral is probably less than that in the xenotime portion.

In conclusion, the author wishes to express his hearty thanks to Dr. S. Iimori for his kind direction during the course of this experiment.

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SORPTION OF GAS BY MINERAL. I. HEULANDITE AND CHABAZITE.

By Jitsusaburo SAMESHIMA.

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It is already known that the minerals of zeolite group have some special chemical properties.(1) G. Tammann(2) observed that the dissociation pressures of zeolite minerals change continuously with the change of their water contents. By the dehydration of them over sulphuric acid no change was perceptible on the appearance as well as the transparency of the crystals. Tammann attributed this to the formation of solid solution of the hydrated and the dehydrated minerals.(3) G. Stoklossa,(4) however, stated that the water evaporates somewhat step by step. The sorption capacities of chabazite was measured by R. Seeliger,(5) F. Simon,(6) O. Schmidt(7) and others,(8) of gases, O. Weigel and E. Steinhoff(9) of organic vapours.

I have measured the quantities of gases sorped by heulandite and chabazite. The procedure of the measurement is as follows. A known quantity of the air-dry mineral is put in a glass tube, which is then connected to a phosphorus pentoxide tube and a Toepler vacuum pump successively. The tube is heated to 360–400°C. and evacuated simultaneously until no evolution of vapour is perceptible. Now the tube is hermetically sealed and weighed. The tube is then filed and opened, and the dehydrated mineral is transferred into the measuring apparatus. The emptied glass

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(1) Doelter, "Physikalisch-Chemische Mineralogie" (1905), p. 168 or "Handbuch der Mineralchemie" II, 3 (1921).

(2) Tammann, *Z. physik. Chem.*, **27** (1898), 323.

(3) See O. Weigel, *Chem. Abstracts*, **17** (1923), 3151.

(4) Stoklossa, *Neues Jahrb. Mineral. Geol., Beilage-Band*, **42** (1919), 1.

(5) Seeliger, *Physik. Z.*, **22** (1921), 563.

(6) Simon, *Z. physik. Chem.*, **132** (1828), 456.

(7) Schmidt, *Z. physik. Chem.*, **133** (1928), 263.

(8) For earlier literatures, see Doelter's books.

(9) Weigel and Steinhoff, *Z. Krist.*, **61** (1924), 125.

tube and the pieces of glass are weighed and subtracted from the former value, the correction for the bouyancy of air being applied. Thus the weight of the dehydrated mineral can be known exactly.

From the weight decrease, the percentage content of volatile matter in the air-dry mineral can be estimated. These volatile matter has not been analysed, so its composition is not known, but it can be supposed from the composition of mineral that the volatile matter is composed mostly of water. If the mineral is contaminated with $CaCO_3$, $MgCO_3$ etc., then carbon dioxide may be contained in the evolved vapour. I have selected transparent well defined pure crystals for the experiments.

The measuring apparatus is the same which was described in this Bulletin, 2 (1927), 2, except the measuring burette. In the present experiment, an ordinary 100 c.c. gas-burette has been used instead of the special burette used on that time.

Now the vessel containing the mineral is evacuated and heated to 300°C. by an electric furnace. After a thermostat was brought in place of furnace, the vessel is communicated to the gas-burette which contains a known quantity of gas. The room temperature and the barometric pressure are noted. The temperature of the mineral has been fixed to 25.0°C. The volume of gas sorped has always been reduced to those at 0°C. and 760 mm. pressure, and the values thus calculated are recorded in the present paper.

Heulandite. The composition of heulandite is considered to be $CaAl_2Si_6O_{16}5H_2O$⁽¹⁾ The mineral from Ogasawara-jima, Japan, has been used.⁽²⁾ The mineral has an appearance like mica, and the crystal is translucent and easily separable in thin, colourless, transparent lamellæ from the cleavages.

On the dehydration by heating to 350°C., the crystal became somewhat opaque and white. 0.8459 gr. air-dry heulandite gave 0.7543 gr. dehydrated substance by evacuation and heating to 350°C. Percentage of the water evaporated is 10.8, or one gram of dehydrated substance combines with 0.0067 mol H_2O, assuming the volatile matter is consisted merely of water.

The amounts and the velocities of sorptions of ammonia, carbon dioxide and ethylene have been measured and the results are shown in the following tables.

By the sorption of ammonia, the mineral becomes chalky in its appearance and expands its volume. After the first measurement had been finished, the vessel was evacuated and heated to 300°C. By this treatment,

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(1) Doelter, "Handbuch der Mineralchemie" II, 3 (1921), p. 188.

(2) K. Jimbo, *J. Coll. Sci. Imp. Univ. Tokyo*, **11** (1899), 278.

the expanded mineral has given up its sorped ammonia and shrinked and collapsed into small pieces. Then ammonia has been fed again, and measured the sorption capacity, the result of which is given in Table 2.

Table 1.

Sorption of ammonia by heulandite at 25.0°C.

Time after the contact of subst. to gas in min. t	Vol. of NH_3 sorped by 1 gr. of dehydrated subst. in c.c. (N.T.P.) x	Pressure of gas in mm. Hg.
0.5	8.1	770.0
1	13.2	”
2	20.9	”
3	28.5	”
5	36.1	”
10	51.6	770.0
15	61.9	”
20	69.4	”
30	80.1	”
45	91.0	”
60	98.6	770.0
90	108.2	”
1340	134.8	765.3
2730	137.6	751.2

Table 2.

Second sorption of ammonia by heulandite at 25.0°C.

Time after the contact of subst. to gas in min. t	Vol. of NH_3 sorped by 1 gr. of dehydrated subst. in c.c. (N.T.P.) x	Pressure of gas in mm. Hg.
0.5	26.6	754.0
1	40.7	”
2.7	74.3	”
5	97.7	”
10	120.5	”
15	128.2	754.0
20	131.9	”
47	137.6	”
60	138.3	”

These values are depicted in Fig. 1. In this figure the logarithm of time in minutes is taken in abscissa and the sorped volume of ammonia in

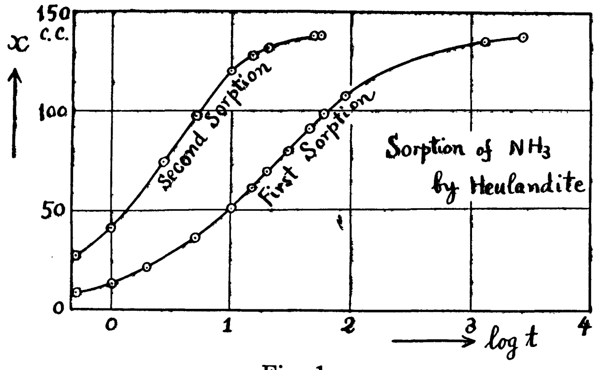

Fig. 1.

c.c. in ordinate. We see, from the figure, that the first sorption proceeds more slowly than the second one. As has already been described, the first sorption is done by the crystallised mineral while the second by the powdered one, so the difference in sorption velocities is expected. The sorption amounts, however, are quite the same in both cases.(1)

The sorption amounts by heulandite of carbon dioxide and ethylene have been measured. But it has sorped no considerable amounts of these gases. One gram of dehydrated heulandite sorped 0.5 c.c. of carbon dioxide and 0.2 c.c. of ethylene in 60 minutes under nearly one atmosphere and at 25.0°C. respectively.

From the fact that the dehydrated heulandite absorbs only ammonia in large amount, this substance may combine chemically with ammonia. There are numerous cases where the ammonia combine with dehydrated salt, for example calcium chloride, copper sulphate or cobalt chloride, etc.

One gram of our dehydrated mineral absorbs 138 c.c. of ammonia at normal temperature and pressure, or 0.0062 mol NH_3. This value is identical with the number of mols of water (0.0067) combines with the same quantity of dehydrated mineral, some allowance for the volatile matters other than water being made. Thus we have known that H_2O can be replaced by the same number of mols of NH_3 in the molecule of heulandite. The composition of the substance obtained in the present experiment may be $CaAl_2Si_6O_{16}\cdot 1.5H_2O\cdot 3.5NH_3$. Or if we assume the formula of heulandite to be $Ca_2Al_4Si_{12}O_{32}.11H_2O$,(2) then the substance corresponds to $Ca_2Al_4Si_{12}O_{32}\cdot 4H_2O\cdot 7NH_3$. It may be interesting to study from the standpoint of the silicate complex theory that whether any molecule of water can be replaced by ammonia or not, or how many ammoniacal heulandites can be synthesised.

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(1) Cf. Sameshima, this Bulletin, **2** (1927), 5.

(2) Stoklossa, *Neues Jahrb. Mineral. Geol., Beilage-Band,* **42** (1919), 1.

Chabazite. The composition of chabazite is considered to be (CaNa$_2$) Al$_2$Si$_4$O$_{12}$·6H$_2$O. The minerals from Mitaka in Izu⁽¹⁾ and from Takashima in Hokkaido have been used. The former is transparent crystals of 1–2 mm. and the latter translucent crystals of 3–5 mm. On dehydration by heating to 350–400°C. the crystals do not change their appearance. Thus the transparent crystals keep their transparency unaltered.

0.2089 gr. air-dry chabazite from Izu gave 0.1669 gr. dehydrated substance by evacuation and heating to 400°C. Percentage of the water evaporated is 20.1. The amounts of sorptions of carbon dioxide, ethylene and ammonia have been measured and the results are shown in Table 3.

Table 3.

Sorption of gases by chabazite from Izu at 25.0°C.

Gas	Time after the contact of subst. to gas in min. t	Vol. of gas sorped by 1 gr. of dehydrated subst. in c.c (N.T.P.) x	Pressure of gas in mm. Hg.
CO_2	0.25	75.4	769.5
	1	109.0	,,
	2	115.4	,,
	5	116.4	,,
	23	116.8	,,
	30	117.4	,,
	60	117.7	,,
C_2H_4	0.25	7.1	768.5
	1	11.9	,,
	3	19.7	,,
	5	23.1	,,
	10	29.8	,,
	15	33.8	768.5
	30	40.3	,,
	60	46.7	,,
	90	50.3	,,
	1270	57.7	765.5
NH_3	0.25	129.3	764.5
	1	175.5	,,
	2	196.8	,,
	5	205.8	,,
	10	207.7	764.3
	30	209.3	764.0
	70	211.0	763.5
	360	212.3	761.3
	1460	213.0	760.2

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(1) K. Jimbo, *J. Coll. Sci. Imp. Univ. Tokyo*, **11** (1899), 279.

0.3344 gr. air-dry chabazite from Hokkaido gave 0.2725 gr. dehydrated substance by evacuation and heating to 360°C. Percentage of the water evaporated is 18.5. The sorption amounts are shown in Table 4.

Table 4.

Sorption of gases by chabazite from Hokkaido at 25.0°C.

Gas	Time after the contact of subst. to gas in min. t	Vol. of gas sorped by 1 gr. of dehydrated subst. in c.c. (N.T.P.) x	Pressure of gas in mm. Hg.
CO_2	0.5	70.9	757.6
	2	105.2	"
	5	111.6	"
	10	111.7	757.7
	30	111.9	757.9
	60	112.0	758.2
C_2H_4	0.5	8.9	758.6
	2	13.9	"
	5	18.9	"
	16	26.9	758.7
	22	29.0	"
	30	31.9	758.8
	60	37.0	759.0
	1200	53.7	760.7
NH_3	0.3	115.6	767.4
	1	149.1	"
	2.5	181.7	"
	5	194.9	"
	10	197.2	767.3
	30	198.4	767.2
	68	198.5	767.0
	270	199.9	766.2
	1430	200.4	765.0

The data in Table 3 and Table 4 are depicted in Fig. 2.

The amounts of gases sorped by chabazite from Izu is a little larger than those by that from Hokkaido. These differences probably due to the purities of samples and the degrees of dehydrations. It is noteworthy that the carbon dioxide and the ammonia are sorped very rapidly, while ethylene is sorped rather slowly. The velocities of sorptions of carbon dioxide and ammonia are nearly the same with the velocity of sorption of gas by charcoal.(1) We see, in the paper of Seeliger(2) that the velocity of

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(1) Sameshima, this Bulletin, 2 (1927), 1.

(2) Seeliger, *Physik. Z.*, **22** (1921), 563.

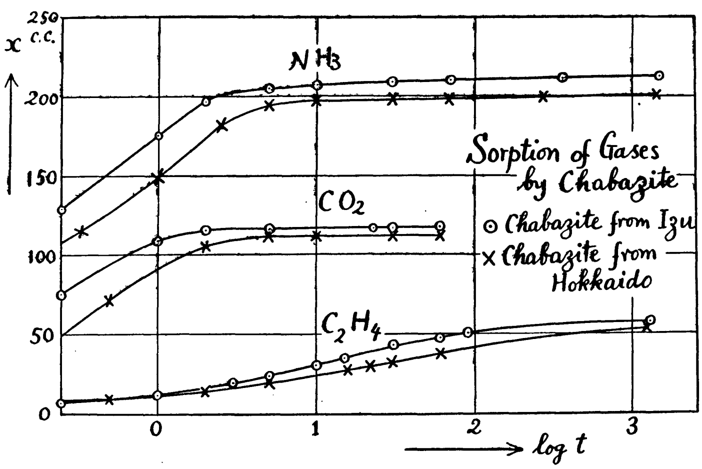

Fig. 2.

sorption by chabazite of acetylene is much smaller than those of ammonia, carbon dioxide and nitric oxide. Further studies on this point may give interesting results on the mechanism of sorption.

Seeliger described that one gram of his chabazite sorped 82.22 c.c. of hydrogen at 0°C., while Schmidt's chabazite⑴ sorped only 1.5 c.c. of hydrogen at 20°C. The author measured the amount sorped by one gram of chabazite from Hokkaido at 25.0°C. of hydrogen and obtained the value 1.1 c.c. Thus our chabazite absorbs no considerable amount of hydrogen.

The author wishes to express his cordial thanks to Professor S. Tsuboi who kindly placed some of the minerals on the author's disposal, and identified some others by the mineralogical testing.

Summary.

1. The amounts and the velocities of sorptions by partially dehydrated heulandite of ammonia, carbon dioxide and ethylene have been measured.

2. It was known that the heulandite absorbs only ammonia in considerable amount.

3. The number of mols of ammonia sorped are nearly identical with that of water evaporated in the process of dehydration. So the ammonia is considered to combine chemically with the dehydrated heulandite. The composition of the substance obtained in the present experiment is probably $Ca_2Al_4Si_{12}O_{32}\cdot 4H_2O\cdot 7NH_3$.

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(1) Schmidt, *Z. physik. Chem.*, **133** (1928), 263.

4. The amounts and the velocities of sorptions by dehydrated chabazites of carbon dioxide, ethylene and ammonia have been measured.

5. Chabazite absorbs carbon dioxide and ammonia rapidly, but ethylene slowly.

6. Chabazite absorbs hydrogen only in small quantity.

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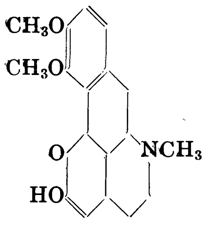
SINOMENINE AND DISINOMENINE. PART VIII.(1) ON COLOUR REACTIONS OF SINOMENINE AND SINOMENOL.

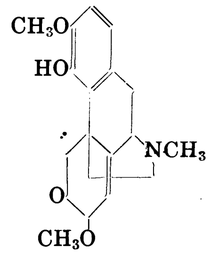
By Kakuji GOTO.

Received March 25, 1929. Published April 28, 1929.

At the time when I proposed the provisional formula for sinomenine (I), the materials to determine the position of hydroxyl, methoxyl and ketone groups were very scanty. The relative position of these groups were assumed mainly from the colour reaction of sinomenine.(2)



[I]



[II]

Sinomenine gives a purple colour with alkaline potassium ferricyanide solution, which is taken up by chloroform. This reaction reminds one of that of apomorphine. And the sinomenol, which is the decomposition product of sinomenine by potash fusion, and is determined to be dioxy-dimethoxy-phenanthrene, gives a beautiful blue colour, when treated with ammoniacal silver in an acetone solution. The author regarded that this

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(1) The former papers of this series were published in *Journal of the Agricultural Chemical Society of Japan*, **1** (1924), 3; **1** (1925), 50 and 89; others in Japanese.

(2) *Proc. Imp. Acad.*, **2** (1926), 7.

blue colour, might have come from the formation of an ortho-chinone from sinomenol by the oxidising agent.

The provisional formula could explain the formation of sinomenol from sinomenine by potash fusion, etc. very easily, but it was not without its difficulties. The principal one was that it could not explain the formation of dihydro-sinomenine, which is a phenol as well as a ketone, as the original sinomenine itself. The author, admitting these deficiencies, expected to reform it in future.

Meantime, Kondo and Ochiai[1] converted sinomenine into dihydrothebakodin by a series of reduction and moreover synthetised the dimethylsinomenol by Pschorr's method, proving that it is 3, 4, 6, 7-tetramethoxyphenanthrene.[2] From these two facts, they withdrew their former views and assigned to sinomenine the formula (II), retaining the linking position of ethanamine chain in 5 or 13.

It seemed, therefore, very desirable to compare the ferri-cyanide reaction of sinomenine with that of thebainon and the reaction of sinomenol with that of 3-methoxy-4, 6-dioxy phenanthrene. The results in this respect are given in the following (The figure shows the dilution of the alkaloids, at which the colour is still visible).

	Ferri-cyanide reaction (chloroform)	Diazo-reaction
Sinomenine	1 : 500,000	1 : 2,000,000
Thebainon	1 : 1,000,000	1 : 1,500,000
Morphothebain	weak	1 : 2,000,000

Ammoniacal silver reaction in acetone (blue colour).

	Cold	Warmed
Sinomenol	1 : 10,000	1 : 50,000
3-Methoxy-5, 6-dioxyphenanthrene .	1 : 10,000	1 : 50,000
Morphol	—	—

From these results, it may be assumed that the relative position of the hydroxyl, and the ketone group in sinomenine is quite analogous to that of thebainone. The author, in cooperation with H. Sudzuki, synthetised dimethyl-sinomenol (this will be published later) and found also that it is 3, 4, 6, 7-dimethoxy-phenanthrene. The Kondo and Ochiai's sinomenine formula must, therefore, be admitted to be superior to my provisional one, even from the side of my investigation.

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(1) *J. Pharm. Soc. Japan*, No. 538, p 1015.

(2) Ibid., No. 539, p. 20.

As regards the linking point of methyl-aminoethyl group and the position of the double bond, Kondo and Ochiai assumes that they must be same with those in thebainon, in supposing that sinomenine is an optical antipode of a hypothetical 7-methoxythebainone. But the present author wishes to reserve this question for future, since there is some discrepancy in the reactions of sinomenine and thebainone, as for instance, sinomenine is easily decomposed by acetic anhydride into diacetyl-sinomenol and methylethyl-amine, whereas thebainone is very resistant to this treatment. The linking point of the side chain in morphine alkaloids is now rather the centre of the discussions, than to be regarded as determined. And the author hopes that sinomenine might give some clew in this problem in future.

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STUDIES ON BIMOLECULAR ALKALOIDS. PART I. ON DISINOMENINE AND Ψ-DISINOMENINE.

By Kakuji GOTO and Hideo SUDZUKI.

Received March 25, 1929. Published May 28, 1929.

The milder action of oxidising agents, such as $AuCl_3$, $AgNO_3$, $K_3Fe(CN)_6$, $KMnO_4$, $FeCl_3$ and H_2O_2, on sinomenine leads to the formation of two isomeric, bimolecular substances, disinomenine and ψ-disinomenine in a nearly equal proportion. These two alkaloids are very similar in their behaviour, but are distinguished by the following characteristics.

	Disinomenine	ψ-Disinomenine
M. p. of free base	222°	227°
Dec. p. of free base	245°	243°
Crystal form	plates	hairy needles
M. p. of hydrochloride	>290°	>290°
Solubility of hydrochloride . . .	0.6%	∞
Dec. p. of methiodide	263°	268°
M. p. of oxim	265° (dec.)	>290°
M. p. of semicarbazone	>290°	>290°
$[\alpha]_D$	+149.98°	-127.03°
Formaldehyde-H_2SO_4.	pink	yellow

The acetolysis of the two substances gives the identical tetraacetyldisinomenol, which is converted into the identical tetramethoxy-, tetraethoxy- and tetrabenzoyl-derivatives respectively, and these derivatives of disinomenol are again quite identical with those prepared from disinomenol, obtained by the linking together of sinomenol by the action of boiling 66% potash.(1)

Thus, the two new alkaloids seems to be stereoisomeric, but not enantiomorphic, since they are quite easily separated from each other by the recrystallisation of their hydrochlorides. The isomerism here may have been caused by the difference in the third nucleus of phenanthrene, i.e. perhaps by the difference in the linking position of the ethanamine chain. Spectrographic study gives little clew in this respect, the curve of the absorption of ψ-disinomenine being almost identical with that of disinomenine.

As regard to the linking position of two sinomenine molecules in these substances, the position 2, opposite to the free phenolic hydroxyl may be

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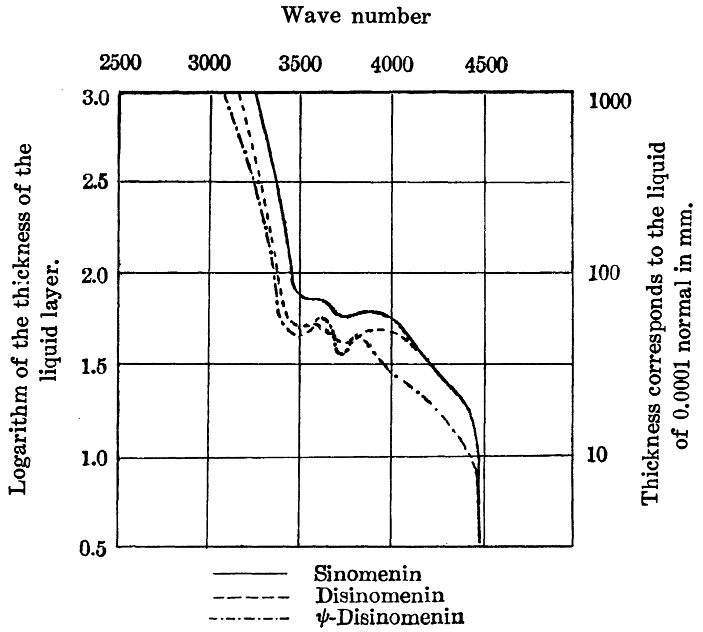
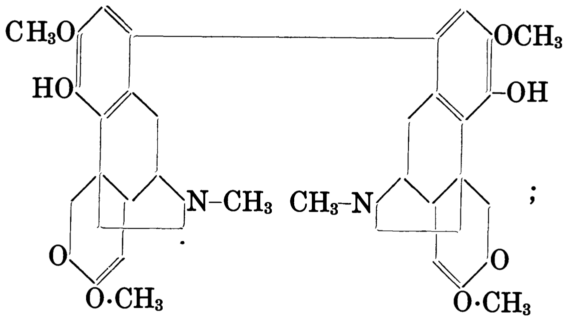
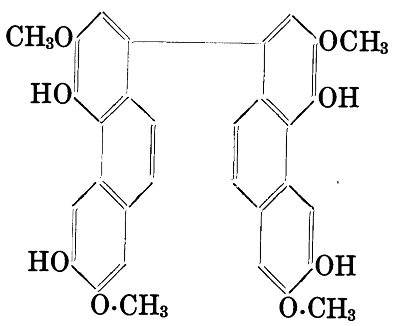
(1) See *Proc. Imp. Acad.*, **2** (1926), 414.



assumed with some certainty from the following two facts. In the first place, the strong diazoreaction of sinomenine (sensitiveness 1:2,000,000) is greatly diminished in these two substances (1:50,000). Secondly, the monobrom-sinomenine, in which the diazoreaction is similarly diminished (1 : 50,000) and on that account the bromine atom seems to occupy the position 2, does not give a bimolecular substance by the same oxidising agent and treatment.



Disinomenine



Disinomenol

Disinomenine occurs in nature, accompanying sinomenine, but ψ-disinomenine has not been isolated from sinomenium acutum up to present.

Experimental.

Preparation of Disinomenine and ψ-Disinomenine. *With potassium ferri-cyanide and sodium carbonate.*—Potassium ferricyanide solution (1 mol.; 10.5 gr. in 300 c.c. water) is poured into an aqueous solution (300 c.c.) of sinomenine hydrochloride (12 gr.; 1 mol.) at 50°. The mixture is immediately made alkaline with sodium carbonate solution. The precipitates, richly formed, are collected on a filter-paper and after being washed with water, redissolved in a small quantity of dilute hydrochloric acid. After standing overnight, the hydrochlorides of disinomenine and ψ-disinomenine are deposited. By repeated crystallisation from water, the hydrochloride of disinomenine can be obtained in a pure state. From the united filtrates, the free base of ψ-disinomenine can be precipitated by ammonia, and recrystallised from methyl alcohol.

With silver nitrate. Free base of sinomenine (9 gr.) is dissolved in alcohol (100 c.c.) and water (200 c.c.) and is oxidised by silver nitrate (7 gr.) in aqueous solution (300 c.c.) The isolation of the bases, after the removal of metallic silver and silver ion, is carried out in the almost same way as above.

Properties of disinomenine.—Hexagonal plates from methyl alcohol (solubility 1:50 hot; 1:250 cold.) M. p. 222° and decomposes at 245°. With formaldehyde sulphuric acid, it takes a pink colour.

Anal. Found: C=70.07, 69,03; H=6.85, 6.89; N=4.69, 4.63%. Calc. for $(C_{19}H_{22}NO_4)_2$: C=69.68; H=6.47; N=4.28%.

Mol. wt. Found: (in glacial acetic acid) 670, 677; (in boiling acetone) 659. Calc. for $(C_{19}H_{22}NO_4)_2$: 656.

Hydrochloride: m. p. >290° (Cl=9.64, 9.66. Calc., 9.65%.)

Solubility in cold water: 0.6%; in boiling 3.3%.

Methiodide: m. p. 263° (dec.). Long prisms from water (solubility, 0.3%.)

Oxim: m. p. 265° (dec.).

Semicarbazone: m. p. >290°.

Properties of ψ-Disinomenine. Long hairy needles from methyl alcohol. It dissolves easily in cold methyl alcohol, but when once these hairy needles containing methyl alcohol are formed, it becomes as difficultly soluble as disinomenine. M. p. 228°, decomposing at 245°. In formaldehyde sulphuric acid, it dissolves with a yellowish brown colour.

Anal. Found: C=66.57, 66.99, 66.83; H=7.05, 6.56, 8.03; N=4.24%. Calc. for $(C_{19}H_{22}NO_4)_2+2CH_3OH$: C=66.66; H=7.02; N=3.78%.

Mol. wt. Found: (in glacial acetic acid) 696. Calc. for $(C_{19}H_{22}NO_4)_2$: 656.

Methoidide: Polyhedral crystal from water. M. p. 267~268° (dec.) (Found: I=26.83. Calc.: I=27.02%).

Oxim: m. p. >280°. (Found: N=7.76. Calc. for dioxim: N=8.16%).

Semicarbazone: m. p. <290°.

Acetolysis of Disinomenine and *ψ*-Disinomenine. Disinomenine (1 gr.) is heated with acetic anhydride (5 gr.) in a sealed tube at 180° for 8 hours. The contents are poured into water and the acetic anhydride is destroyed by boiling. The insoluble part is recrystallised from benzene (15 gr.) The crude tetracetyl-disinomenol thus obtained, amounts to 0.2 gr. and already melts at 253°. It is once more recrystallised for analysis.

The same treatment of *ψ*-disinomenine gives the identical tetracetyl-disinomenol.

Anal. Found: C=67.78; H=4.91%. Calc. for $C_{40}H_{34}O_{12}$: C=67.98; H=4.81%.
Mol. wt. Found: (by Rast's) 703. Calc. for $C_{40}H_{34}O_{12}$: 706.
Methoxyls. Found: 17.28%. Calc. for $4CH_3O-$: 17.56%.

Nitrogenous decomposition products were in both cases methyl-ethyl amine, as the case with sinomenine (Gold salt, m. p. 179°; Platinum salt, dec. p. 224°). Yield: 0.25 gr. as hydrochloride from 3 gr. of *ψ*-disinomenine, and 0.2 gr. from 3 gr. of disinomenine.

The acetyl groups are easily hydrolysed away by alcoholic sodium hydroxide, and, from the disinomenol thus formed, tetramethoxy-, tetra-ethoxy, and tetrabenzoyl-disinomenol can easily be prepared by the action of dimethyl- and diethyl-sulphate and benzoyl chloride respectively. In the following, these three derivatives were prepared from the tetracetyl-disinomenols obtained from disinomenine as well as from *ψ*-disinomenine.

Disinomenol: m. p. >310°. It takes a beautiful blue colour in an acetone solution, when oxidised by ammoniacal silver (Sensitiveness 1:50,000).

Anal. Found: C=70.24; H=5.21%. Calc. for $C_{32}H_{26}O_8$: C=71.37; H=4.83%.

Tetramethyl-disinomenol: m. p. 240°, Fine needles difficultly soluble in cold acetone.

Anal. Found: C=72.70; H=5.92%. Calc. for $C_{36}H_{34}O_8$: C=72.72; H=5.72%.
Mol. wt. Found: (by Rast's) 638. Calc. for $C_{36}H_{34}O_8$: 594.
Methoxyls. Found: 40.01%. Calc. for $8CH_3O-$: 41.75%.

Tetra-ethyl-disinomenol: m. p. 177° (184°, very pure specimen).

Anal. Found: C=74.10; H=6.64%. Calc. for $C_{40}H_{42}O_8$: C=73.84; H=6.46%.
Mol. wt. Found: (by Rast's) 624. Calc. for $C_{40}H_{42}O_8$: 650.
Methoxyls. Found: 18.70%. Calc. for $4CH_3O-$: 19.07%.

Tetrabenzoyl-disinomenol: m. p. 280°, long needles. Very difficultly soluble in ordinary solvents. Benzoylation of disinomenol can only be carried out smoothly in ethyl-benzoate solution by benzoyl chloride and aqueous sodium hydroxide. The same substance can be obtained by heating disinomenol (1 gr.) with benzoic anhydride (5 gr.) in a stoppered test-tube at 180°–200° for 6 hours.

Anal. Found: C=74.79; H=4.11%. Calc. for $C_{60}H_{42}O_{12}$: C=75.47; H=4.40%.
Mol. wt. Found: (by Rast's) 1010, Calc. for $C_{60}H_{42}O_{12}$: 954.

On Colour Reaction of Monomolecular and Bimolecular Phenanthrene. Sinomenol, 3,7-dimethoxy-4,6 dioxy phenanthrene, dissolves yellow in cold conc. sulphuric acid, but almost decolourised on the addition of water. On the contrary, disinomenol, bis-1,1′- (3,7-dimethoxy- 4,6-dioxy)-phenanthrene dissolves brown in cold conc. sulphuric acid, and gives intensely purple flocculations on diluting with water. The same behaviour was ascertained with dimethyl-, diethyl-, diacetyl- and dibenzoyl-derivatives of sinomenol and with corresponding tetravalent derivatives of disinomenol. This reaction can be utilised advantageously in the study of potash fusion of phenanthrene alkaloids, since some of them are expected to give rise to bimolecular phenanthrene derivatives in that treatment.

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THE DETERMINATION OF THE HELIUM CONTENT OF SOME JAPANESE MINERALS. II.

By Jirô SASAKI.

Received April 13, 1929. Published May 28, 1929.

On the minerals occurring in Japan, the determination of helium content was undertaken as a continuance of the former work.(1) The apparatus employed and so the method of extracting helium were the same as those described in the previous communication, special cares, however, sometimes having been taken for the sampling of the minerals. The results are given in the following table.

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(1) This Bulletin, **1** (1926), 253; *Sci. Pap. Inst. Phys. Chem. Res.*, **5** (1927), 258.

Mineral	Locality	Sample taken gr.	Helium yielded c.c. at N. T. P.	Helium c.c. per gr. of Mineral	Helium %
Conglomerate of Samarskite and Columbite	Ishikawa in Fukushima	12.43	2.44	0.20	0.0035
Naegite	Naegi in Gifu	19.29	0.55	0.028	0.00051
Ilmenite	Korea	62.27	<0.028	0.00044	0.000008
Ilmenite	Chôhakumen in Korea	41.22	No He	—	—
Sphene	Ishikawa in Fukushima	22.34	0.12	0.0054	0.000098
Sphene	Mozumi in Gifu	19.20	No gas evolved	—	—
Rutile(1)	Mayuyama in Kagawa	26.31	<0.00014	0.0000053	0.000000095
Apatite	Kurokura in Kanagawa	46.91	Small quantity of gas evolved	—	—
Apatite	Kuropira in Yamanashi	63.28	Fair quantity of H_2 evolved	—	—
Tourmaline	Ishikawa in Fukushima	52.11	Small quantity of gas evolved	—	—
Axinite	Obira in Ôita	67.16	Small quantity of H_2 evolved	—	—

The rutile of Mayuyama and the ilmenite of Korea showed no radioactivity, while the sphene from Ishikawa was feebly radioactive. As to the conglomerate of samarskite and columbite from Ishikawa the amount of uranium was determined to be 4.0% U_3O_8 by the Brearley's method and that of thorium 0.036% ThO_2 by the hydrogen peroxide method.

The geological age of the above stated mineral resembling ånnerödite and that of naegite were computed by the same way as has been shown in the previous paper. The age of samarskite accompanying columbite in some extent was thus calculated as to be 100 million years from the foregoing results. For the amounts of uranium and thorium in naegite from Naegi, however, the author has used of the analytical results formerly obtained by Prof. Y. Shibata and K. Kimura(2) and has found them to be 2.69% UO_2 and 2.85% ThO_2. The age was found to be 17 million years. It showed a somewhat less value in comparison with the age of the fergusonite from the same district as has been given in the previous paper. This difference might probably be ascribed to the inequality of the amount of radioactive constituents contained in the two samples used by Prof. Y. Shibata and the author.

In conclusion, the author wishes to express his best thanks to Dr. S. Iimori for his kind advice and constant guidance; his thanks are also due to Mr. T. Yoshimura who was kind enough in supplying some of the samples to him.

The Institute of Physical and Chemical Research.
Hongo, Tokyo.

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(1) The volume was measured under the reduced pressure.

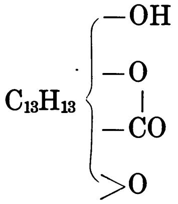
(2) *J. Chem. Soc. Japan*, (in Japanese), **42** (1921), 1.

UEBER DIE KONSTITUTION DES NODAKENINS, EINES NEUEN GLUCOSIDS VON PEUCEDANUM DECURSIVUM MAXIM. II.(1)

Von Junzo ARIMA.

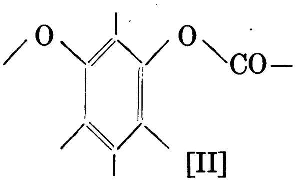
Eingegangen am 20, April 1929. Ausgegeben am 28, Mai 1929.

In der vorigen Mitteilung(2) ist gezeigt worden, dass das Nodakenetin, das Aglykon des Nodakenins, das Formelbild (I) besitzt und in seinem Moleküle den Kern (II) enthält, und dass sein Verhalten gegen Alkalien dem der Cumarinreihen sehr ähnlich ist.



$$C_{13}H_{13}\left\{\begin{array}{l}-OH\\ -O\\ \ \ |\\ -CO\\ >O\end{array}\right.$$

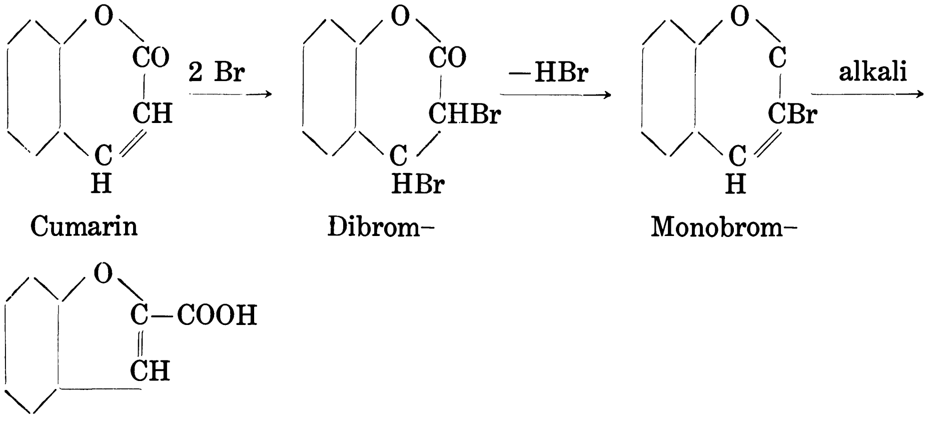
[I]



[II]

In dieser Mitteilung kann der Verfasser die weiteren Aehnlichkeiten des Nodakenetins mit den Cumarin-reihen beweisen.

Das Nodakenetin absorbiert 1 Mol. Brom unter Bildung einer Monobromverbindung, und diese Bromverbindung wird durch Erwärmen mit alkoholischem Alkali in eine einbasische Säure, die die Formel $C_{14}H_{14}O_5$ hat und ein Atom Sauerstoff mehr als das Nodakenetin enthält, die aber keine Lacton- oder Phenolhydroxyl-gruppe besitzt. Diese Reaktions-reihen sind den folgenden Reaktionen-reihen des Cumarins analog :



Cumarin Dibrom- Monobrom-

Cumarilsäure

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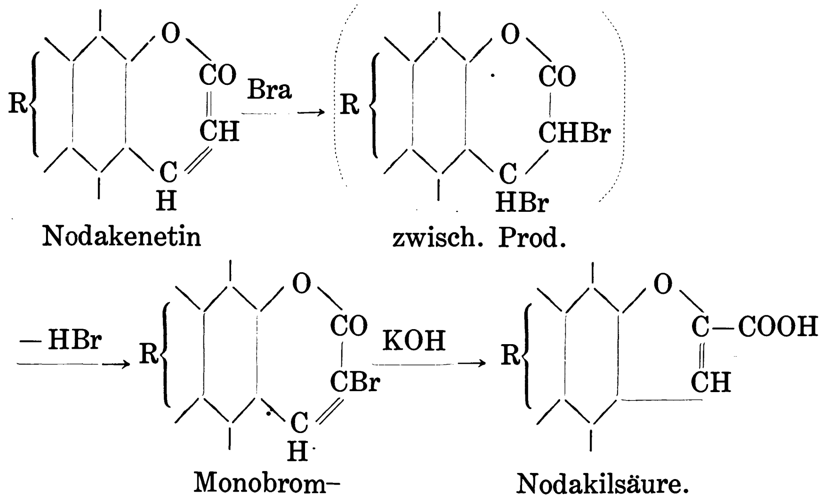
(1) Vorläufige Mitteilung in *J. Chem. Soc. Japan,* **49** (1928), 110 u. 415.

(2) Dieses Bulletin, **4** (1929), 16.

Daher kann man die Reaktions-reihen vom Nodakenetin sehr wahrscheinlich in folgender Weise erläutern:

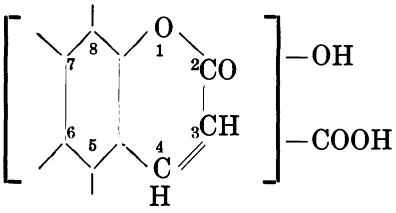


Das Monobrom-nodakenetin schmilzt bei 230-231°. Diese der Cumarilsäure entsprechende Säure wird "Nodakilsäure" bezeichnet und schmilzt bei 214–215°, es gibt durch Diazomethan eine Monomethyl-verbindung vom Schmp. 133–134°, die durch Alkali verseift werden kann.

Wegen oben erwähnter Resultate kann man also das Nodakenetin mit guten Grunde als ein Derivat der Cumarin-reihen auffassen; ja diese Ansicht kann man durch unter beschriebene Untersuchungen endgültig beweisen und auch die Konstitution des Nodakenetins grössten Teils erklären.

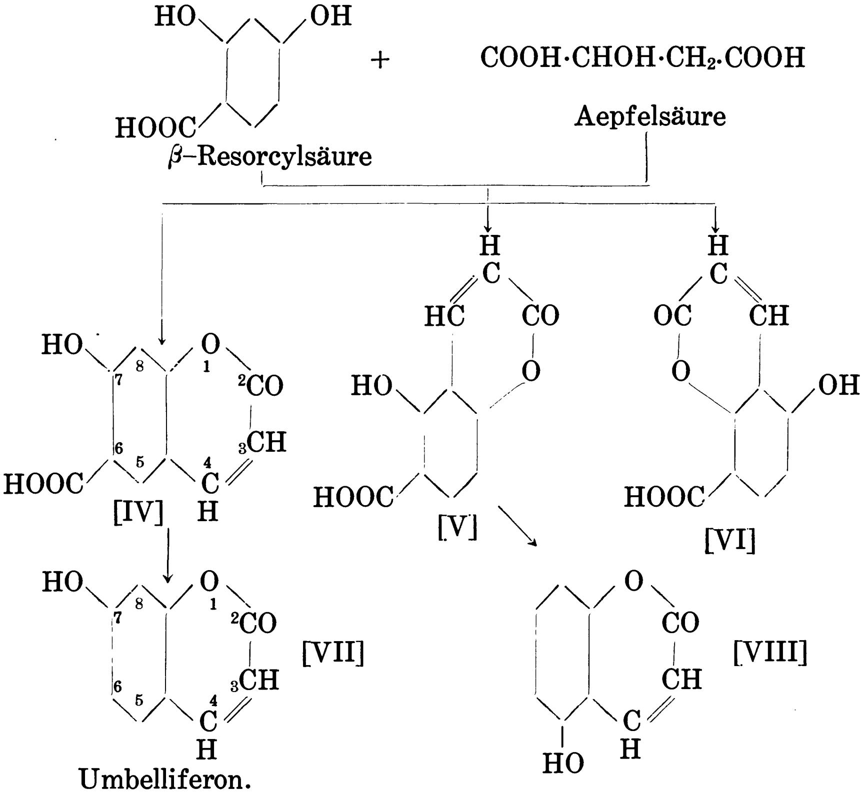
Durch Oxydation mit verd. Chromsäure gibt das Nodakenetin eine Phenolcarbonsäure, die die Formel $C_{10}H_6O_5$ mit dem Schmp. 244–246° (Zersetzt.) hat. Diese Phenolsäure ist einbasisch, enthält eine Lactongruppe, und zeigt mit Eisenchlorid eine violette Farbenreaktion wie die Salicylsäure. Und mit Diazomethan gibt es eine Dimethyl-verbindung vom Schmp. 165–166°. In Anbetracht der eben erwähnten Eigenschaften dieser Säure liegt die Vermutung sehr nahe, dass sie eine Oxycumarincarbonsäure ist und das Formelbild (IV) besitzt.

[IV]



Aber sind alle die bisher bekannten Oxy-cumarin-carbonsäuren,—7-Oxy-cumarin-carbonsäure-3(1), 7-Oxy-cumarin-carbonsäure-4(2), 6-Oxy-cumarin-carbonsäure-4(3), und 4-Oxy-cumarin-carbonsäure-3(4),—von dem vom Verfasser erhaltenen Säure entschieden verschieden. Um daher die Konstitution der Säure zu ermitteln wurden synthetische Versuche vorgenommen. Und glücklicherweise konnte der Verfasser dieselbe Oxycumarin-carbonsäure aus β-Resorcylsäure und Aepfelsäure nach Pechmannscher Methode(5) aufbauen. Die durch die Synthese erhaltene Oxy-cumarin-carbonsäure, die bei 244–246° schmilzt (Zersetzt.), stimmt mit de durch den Abbau erhaltenen vollkommen überein; auch stimmen die beiden Dimethyl-verbindunden der beider Säuren vollkommen überein, und die Mischprobe zeigt keine Depression. Die Identität beider Säuren liegt ohne Zweifel vor.

Daher muss die Oxycumarincarbonsäure nach dem Aufbau aus β-Resorcylsäure und Aepfelsäure einer der unten bezeichneten drei Formeln, (IV), (V), und (VI) entsprechen.



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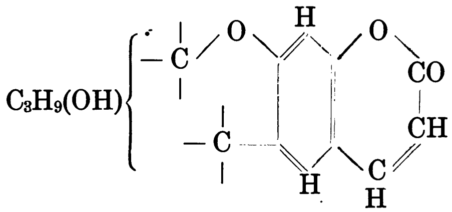
(1) H. v. Pechmann, *Ber.* **34**, 385.
(2) Ibid, 381.
(3) P. Biginelli, *Ber.* **28**, R, 155; *Gazz. Chim.* **24**, 11, 491.
(4) R. Anschutz, *Ann.* **379**, 335.
(5) H. v. Pechmann, *Ber.* **17**, 932.

Diese Oxycumarincarbonsäure wird aber durch Erhitzen über ihren Schmp. unter Abspaltung von Kohlendioxyd in eine Oxycumarin ubergeführt, das bei 230° schmilzt. Dieses Oxycumarin stimmt mit dem 7-Oxycumarin vom Schmp. 230–231°, das nach Pechmannscher Synthese aus Resorcin und Aepfelsäure erhalten wird, vollkommen überein, und die Mischprobe zeigt keine Depression.

Also dieses durch Decarboxylierung erhaltene Oxycumarin ist nicht anders als 7-Oxycumarin (VII) d.h. Umbelliferon.

Daher muss die Oxycumarincarbonsäure die Konstitution (IV), d. h. 7-Oxycumarin-carbonsaure-6, haben, da die anderen zwei, (V) und (VI), durch Decarboxylierung das 5-Oxy-cumarin (VIII) geben müssen.

Aus diesen Resultaten kann man schliessen, dass das Nodakenetin das Formelbild (IX) besitzen muss:



[IX]

Beschreibung der Versuche.

Brom-nodakenetin. Zu einer Lösung von 1 gr. Nodakenetin in 4 c.c. Chloroform wurden unter Kühlung 0.7 gr. Brom, das mit 2 c.c. chloroform verdünnt wurde, langsam zugetropt. Das Reaktionsgemisch, das zu einen Krystallbrei erstarrt war, gasst man in eine Schale und lässt freiwillig verdunsten, wobei sich Bromwasserstoffgas entwickelte. Der Rückstand wurde mit wenig Aether umgerührt und freiwillig verdunsten lassen, dies mehrmals wiederholt bis kein Bromwasserstoffgas sich entwickelte. Den Rückstand digeriert man mit etwas Aether, filtriert und trocknet auf der Tonplatte, und krystallisiert aus Chloroform um. Die Ausbeute ist eine fast quantitative. Es bildet farblose, prismatische Krystalle vom Schmp. 230–231°. Es ist löslich in Alkohol, unlöslich in Wasser und Aether.

Best. des Broms. 4.653 mg. Sbst.; 2.671 mg. AgBr. Gef.: 24.41%. Ber. für $C_{14}H_{13}O_4Br$: 24.60%.

Nodakilsaure. 1 gr. Brom-nodakenetin wurde in einer Lösung von 2 gr. Kaliumhydroxyd in 20 c.c. absol. Alkohols eingetragen. Nach dem Umschütteln wurde die Reaktionsmasse auf dem Wasserbade bis zum Sieden erhitzt und 15 Minuten im Sieden erhalten. Dabei erstarrte sie zu einem Krystallbrei. Man verdünnte nun mit demselben Volumen Wasser und dampfte den Alkohol ab. Nach dem Erkalten wurde die Lösung mit verd. Schwefelsäure angesäuert. Die ausgeschiedenen Krystalle wurden abfiltriert und auf der Tonplatte getrocknet. Die Ausbeute betrug 0.7 gr. Es krystallisiert aus verd. Alkohol in kleinen farblosen Prismen vom Schmp. 214–215°. Es enthält kein Brom. Es ist löslich in wässerigen Alkalien und Natriumbicarbonat, die Lösungen zeigen keine Fluorescenz.

Anal. 5.332, 5.337 mg. Sbst.; 12.472, 12.571 mg. CO_2; 2.722, 2.786 mg. H_2O. Gef.: C=64.21, 63.80; H=5.71, 5.84 %. Ber. für $C_{14}H_{14}O_5$: C=64.09, H=5.38%.

Krystallwasser. 5.706, 5.711 mg. Sbst.; 0.374, 0.374 mg. H_2O. Gef.: 6.57, 6.56 %. Ber. für $C_{14}H_{14}O_5 + H_2O$: 6.94 %.

Saurezahl. 7.81 mg. Sbst. (Krystallwasserhaltige); 1.35 c.c. 0.0208 N. KOH. Gef. (in Alkohol mit Phenolphtalein als Indikator): 199. Ber. für $C_{13}H_{13}O_3 \cdot COOH \cdot H_2O + 1$ Mol. KOH: 200.

Es ist keine Verseifungszahl.

Nodakilsäure-methylester. 0.1 gr. gepulverte Nodakilsäure wurde in wenig Aether suspendiert und in üblicher Weise mit Diazomethan methyliert.

Der aus Aether umkrystallisierte Ester bildet farblose Prismen vom Schmp. 133–134°. Ausbeute 0.085 gr. Es ist unlöslich in kalten wässerigen Alkalien.

Best. der Methoxyls. 2.447, 2.588 mg. Sbst.; 2.007, 2.166 mg. AgJ. Gef.: 10.84, 11.06 %. Ber. für $C_{13}H_{13}O_3 \cdot COOCH_3$: 11.22%.

Mol.-Gew. 0.407 mg. Sbst. in 3.87 mg. Campher: Δ=14.4°. Gef. (Rast): 292. Ber. für $C_{15}H_{16}O_5$: 276.

Verseifungszahls. 10.08 mg. Sbst.: 1.82 c.c. 0.0191 N.KOH Verbrauch. Gef. (in 2 c.c. Alkohol 1.00 c.c. 1/10 N.KOH gelöst und auf dem Wasserbade 3 Stunden lang erhitzt, und dann mit 1/50 N.KOH rucktitriert.): 195. Ber für $C_{13}H_{13}O_3 \cdot COOCH_3 + 1$ Mol. KOH: 203.

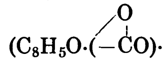
Oxydation des Nodakenetins mit Chromsäure. 7-Oxy-cumarin-carbonsäure-6. Zu einer Lösung von 1 gr. Nodakenetin in 200 c.c. siedender 2% iger Schwefelsäure wurde die Lösung von 2.4 gr. Kaliumbichromat in 40 c.c. Wasser portions-weise zugefügt, und noch auf dem Sandbade 3 Stunden lang gekocht. Nach dem Erkalten wurde das ausgeschiedene, unangegriffene Nodakenetin abfiltriert. Das Filtrat wurde dreimal mit Aether geschüttelt. Die wässerige Lösung wurde mit Natronlauge alkalisch gemacht und einige Stunden stehen gelassen. Dann wurde es nochmal mit verd. Schwefelsäure angesäuert und einige Tage stehen gelassen. Dann schieden sich gelbliche Krystalle aus. Die Ausbeute betrug 0.08 gr. Beim Konzentrieren des Filtrats erhielt man nochmals 0.13 gr. Krystalle. Die aus 50% igem Alkohol umkrystallisierte Säure bildet weisse Nadeln. Die Ausbeute an reiner Säure betrug 0.15 gr., Schmp. 244-246° (Zersetzt), beim langsamen Erhitzen stieg der Schmp. auf 260–261° (Zersetzt). Es ist löslich in Alkohol, verd. Alkalien und Natriumbicarbonat-lösung, wenig in Wasser und Chloroform, und schwer in Aether. Die wässerige Lösung reagiert sauer und zeigt mit Eisenchlorid eine violette Farbenreaktion wie die Salicylsäure. In verd. Alkalien gibt es eine blaue Fluorescenz wie die Cumarin-reihen.

Anal. 3.826, 5.375 mg. Sbst.; 8.142, 11.507 mg. CO_2; 1.137, 1.529 mg. H_2O. Gef.: C=58.06, 58.53; H=3.33, 3.19 %. Ber. für $C_{10}H_6O_5$: C=58.27; H=2.94 %.

Krystallwasser. 4.222, 5.857 mg. Sbst.; 0.346, 0.484 mg. H_2O. Gef.: 8.20, 8.25 %. Ber. für $C_{10}H_6O_5\cdot H_2O$: 8.04 %.

Saurezahl. 5.74 mg. Sbst. (krystallwasserhaltige); 1.26 c.c. 0.0208 N. KOH Verbrauch. Gef.: 256. Ber für $C_9H_5O_3\cdot COOH\cdot H_2O+1$ Mol. KOH.: 251.

Diese Säure enthält ein Phenolhydroxyl, aber es scheint fast keinen Einfluss auf die Titration zu haben.

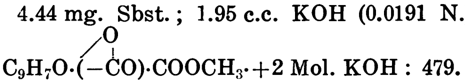


Verseifungszahl. 6.03 mg. Sbst. (krystallwasserhaltige): 295 c.c. 0.0191 N. KOH Verbrauch. Gef. (wie oben): Saurezahl+Verseifungszahl=526. Ber. für $(C_8H_5O\cdot(-\overset{\overset{O}{|}}{C}O)\cdot COOH\cdot H_2O\cdot+2$ Mol. KOH: S.-Z.+V.-Z.=502. Also: Verseifungszahl=524–256=268 (Ber.: 251).

Dimethyl-7-oxy-cumarin-carbonsäure-6. (Abbauprod.) 40 mg. 7-Oxy-cumarin-carbonsäure-6 wurde mit überschüssiger, ätherischer Lösung vom Diazomethan in üblicher Weise methyliert. Das Rohprodukt wurde aus Aether-Methylalkohol umkrystallisiert. Ausbeute 25 mg. Blassgelbe Nadeln vom Schmp. 165–166°. Es ist unlöslich in verd. kalten Alkalien.

Best. der Methoxyl. 1.799 mg. Sbst.; 3.653 mg. AgJ. Gef.: 27.07 %. Ber. für $C_{10}H_4O_3\cdot(OCH_3)_2$.: 26.50 %.

Mol.-Gew. 0.451 mg. Sbst. in 4.45 mg. Campher.: $\Delta=18.5°$. Gef. (Rast).: 222. Ber. für $C_{12}H_{10}O_5$.: 234.



Verseifungszahl. 4.44 mg. Sbst.; 1.95 c.c. KOH (0.0191 N.) Verbrauch. Gef. (wie oben): 471. Ber. für $C_9H_7O\cdot(-\overset{\overset{O}{|}}{C}O)\cdot COOCH_3\cdot+2$ Mol. KOH: 479.

Synthese der 7-Oxy-cumarin-carbonsaure-6. Eine innige Mischung von 10 gr. β-Resorcylsäure und 8.4 gr. Aepfelsäure in einem Rundkolben wurde mit 20 c.c. konz. Schwefelsäure übergossen und auf dem Drahtnetz rasch bis zum beginnenden Schäumen erhitzt. Entfernt man die Flamme, so vollzieht sich die Reaktion unter lebhaftem Aufschäumen und reichlicher Gasentwicklung binnen wenigen Minuten von selbst. Nach dem Abkühlen wurde die Schmelze in fünffacher Menge Eiswasser gegossen und die nach dem eintägigen Stehenlassen abgeschiedene Krystallmasse abfiltriert. Zur Entfernung von beigemengter β-Resorcylsäure wurde die auf den Tonplatten getrocknete Masse wiederholt mit etwas Aether gut gewaschen.

Das getrocknete Rohprodukt betrug 3.1 gr. Es wurde aus 50% igem Alkohol umkrystalliert. Die Ausbeute an reinen Krystallen betrug 1.8 gr. Farblose Nadeln vom Schmp. 244–246 unter Zerz., beim langsamen Erhitzten stieg der Schmp. bis auf 260–261°. Alle anderen Eigenschaften stimmen mit den der oben erwähnten Abbauprodukte überein.

Anal. 4.780 mg. Sbst.; 10.156 mg. CO_2; 1.326 mg. H_2O. Gef.: C=57.93; H=3.10 %. Ber. für $C_{10}H_6O_5$: C=58.27; H=2.94 %.

Krystallwasser. 5.200 mg. Sbst.; 0.420 mg. H_2O. Gef.: 8.08 %. Ber. für $C_{10}H_6O_5 \cdot H_2O$: 8.03 %.

Dimethyl-7-oxy-cumarin-carbonsäure-6 (synth.) 0.10 gr. synthetische Säure wurden mit Diazomethan methyliert. Aus Aether-Methylalkohol umkrystallisiert wurde die Substanz in farblosen Nadeln vom Schmp. 165–166° gewonnen.

Ausbeute 70 mg. Alle Eigenschaften der Substanz stimmen mit der durch Abbau erhaltenen Dimethyl-oxy-cumarin-carbonsäure überein, und die Mischprobe beider Verbindungen ergab keine Depression.

Best. der Methoxyl. 2.470 mg. Sbst.; 4.985 mg. AgJ. Gef.: 26.66 %. Ber. für $C_{10}H_4O_3 \cdot (OCH_3)_2$: 26.50 %.

Decarboxylierung der 7-Oxy-cumarin-carbonsäure-6. 100 mg. Oxy-cumarin-carbonsäure wurden in einer kleinem Reagenzglasse 20 Minuten lang auf 260–270° erhitzt, wobei lebhafte Kohlendioxydentwicklung eintrat. Nach dem Abkühlen wurde die Schmelze mit Alkohol extrahiert. Das Filtrat wurde auf dem Wasserbade eingedampft und der Rückstand mit Aether extrahiert. Der Aether des Filtrats wurde verdampft und die zurückgebliebenen Krystalle wurden aus Wasser unter Zusatz von Tierkohle umkrystallisiert. Ausbeute 25 mg. Der Schmp. 230°.

Anal. 5.253 mg. Sbst.; 12.757 mg. CO_3; 1.919 mg. H_2O. Gef.: C=66.23; H=4.09 %. Ber. für $C_9H_6O_3$: C=66.64; H=3.74 %.

Diese Substanz stimmt mit dem Umbelliferon ganz überein, das nach der Pechmannschen Synthese(1) aus Resorcin und Aepfelsäure gewonnen wirde und den Schmp. 231°(2) hat. Und die Mischprobe der beiden Substanzen zeigt keine Erniedrigung.

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und Kitasato-Institut für Infektions-krankheiten
zu Tokyo.

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(1) *Ber.* **17**, 932.

(2) Nach der Literatur ist der Schmp. des Umbelliferons 225°, aber mein Substanz, dreimal aus Alkohol, nacher noch einigemal aus Wasser umkrystallisiert, schmilzt bei 231° (unkor.).

STUDIES ON THE COAGULATION OF VON WEIMARN'S Au_F—SOLS. I.

By Eiichi IWASE.

Received April 20, 1929. Published May 28, 1929.

I. Introduction. The application of P. P. von Weimarn's(1) modification of the "formaldehyde method" makes it possible to produce large amounts of dispersoidal gold solutions of a *beautiful red* colour, which are *always reproducible*; the obtaining of dispersoidal gold solutions by this modification of the formaldehyde method, may be performed in laboratories possessing no expensive equipment; that is to say, without the use of gold condensers for the distillation of water, or of beakers of extra resistant glass, etc.

Of course, in spite of their all possessing the same beautiful red colour when observed with the naked eye, the quantitative properties of these dispersoidal gold solutions are dependent upon the conditions of their preparation; e.g. the coagulation values of these red dispersoidal solutions should vary more or less considerably, in accordance with the conditions of experimenting.

Prof. P.P. von Weimarn suggested to me(2) a systematic investigation of the coagulation phenomena in dispersoidal gold solutions, obtained by his method. The programme of this investigation comprises the elucidation of the influence upon the coagulation values for various electrolytes, of the following variables: 1). Of unreduced gold compounds; 2). Of the excess of KOH and K_2CO_3 in the solution; 3). Of water different in purity; 4). Of the materials the vessels are made of; 5). Of the purity of the reagents, and especially of the formaldehyde solutions (redistilled and non-redistilled formaldehyde, its age, etc.) etc.

I wish also to express here to Prof. P.P. von Weimarn my sincere gratitude for giving me the theme of this investigation; in this brief paper are presented certain of the results obtained by me, of the coagulation values for NaCl and $BaCl_2$.

II. The Dispersoidal Gold Solutions were Prepared in Beakers of Ordinary Laboratory Glass A, with Ordinary Distilled Water; The Measuring Vessels Used were of Ordinary Laboratory Glass C. In the same

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(1) P.P. von Weimarn, *Kolloid-Z.*, **33** (1923) 74 & 228; **36** (1925) 1; **39** (1926) 166 & 278; **45** (1928), 203 & 366. This Bulletin, **4** (1929), 34. *Japanese Journal of Chemistry*, **3** (1929), 165.

(2) P.P. von Weimarn, *Japanese Journal of Chemistry*, **3** (1929), 201.

Room, Simultaneously with the Dispersoidal Gold Synthesis, were Carried out Other Chemical Experiments.(1) Dispersoidal solution "Sol B_1" was obtained by boiling a mixture of 500 c.c. distilled water (20°C.) + 10 c.c. $AuCl_3HCl4H_2O$-solution (0.6%) + 3.5 c.c. reagent $F^{10}_{0.2KOH}$. Immediately after the beginning of boiling (it required about 10 minutes' heating) into this mixture were poured, in portions, 150 c.c. distilled water. After about 30 minutes' boiling, the volume of the solution equalled 500 c.c. (at room temperature). The $AuCl_3HCl4H_2O$ and KOH were *extra pure.* The formaldehyde solution was *redistilled.*

In Table 1 are given data of *one* experiment with NaCl (*extra pure*) and in Table 2 of *one* experiment with $BaCl_2$ (*extra pure*).

Table 1. "Sol B_1."

Concentration of NaCl per litre (in millimols): Colour of sol:	12	14	17	19	22	24	26
at the time of addition:	red	red	red	red	violettish-red	violettish-red	violettish-red
after 5 min.	red	red	red	violettish-red	violettish-red	violettish-red	*violet.*
after 15 min.	red	red	red with a violet tinge	reddish-violet	reddish-violet	reddish-violet	violet.
after 2 hours:	red	red	red with a violet tinge	reddish-violet	violet	violet	turbid, the intensity of colour falls off.
after 20 hours:	red	red	red with a violet tinge	*violet.*	*violet slightly turbid.*	the intensity of colour falls off markedly	almost colourless.

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(1) Glass C is more sensitive to a weak solution of alkalies than is glass A; see P.P. von Weimarn, l.c. The determination of the coagulation values was always carried out in a separate room, which was heated by electricity and in which no other chemical work was performed. The NaCl and $BaCl_2$-, KOH- and $AuCl_3HCl4H_2O$- solutions were prepared with water, redistilled through Jena glass.

Table 2. "Sol B_1."

Concentration of $BaCl_2$ per litre (in milli-mols): / Colour of sol:	0.06	0.09	0.11	0.14	0.16–0.17	0.18
at the time of addition:	red	red	red	red	red	violettish-red
after 5 min.	red	red	red with a violet tinge	violettish-red	*violet*	violet
after 15 min.	red	red	red with a violet tinge	violettish-red	violet.	violet
after 2 hours:	red	red	violettish-red	violet with a red nuance	violet	the intensity of colour falls off, the sol is slightly turbid
after 20 hours:	red	red	violettish-red	*violet*	*violet, slightly turbid.*	almost colourless.

In Tables 3 and 4 are shown similar data for "Sol B_1+150 c.c. KOH, 0.02 norm.; the method of preparation of this sol was quite similar to that of "Sol B_1," the only difference being that, instead of 150 c.c. distilled water, there were added, for a more complete reduction, 150 c.c. of KOH-solution, 0.02 norm. *extra pure.*

Table 3. "Sol B_1+150 c.c. KOH, 0.02 norm."

Concentration of NaCl per litre (in milli-mols): / Colour of sol:	4	5	7	10	12	14	16
at the time of addition:	red	red	red	red	red	red with a violet tinge	red with a violet tinge
after 5 min.	red	red	red	red	red with a violet tinge.	violet-tish-red	*violet.*
after 15 min.	red	red	red with a violet tinge	violet-tish-red	reddish-violet	reddish-violet	violet
after 2 hours:	red	red	red with a violet tinge	reddish-violet	violet	violet	violet
after 20 hours:	red	red with a violet nuance	violet-tish-red.	*violet.*	violet	*violet, turbid,*	the intensity of colour falls off, the sol is turbid.

Table 4. "Sol B_1+150 c.c. KOH, 0.02 norm.

Concentration of $BaCl_2$ per litre (in millimols): / Colour of sol:	0.006	0.011	0.016	0.021	0.026	0.030	0.035
at the time of addition:	red	red	red	red	red	red	red
after 5 min.	red	red	red	red	red	violettish-red	*violet*
after 15 min.	red	red	red	red with a violet tinge	violettish-red	violet	violet
after 2 hours:	red	red with a violet tinge	red with a violet tinge	reddish-violet	violet	violet	violet
after 20 hours:	red	*violet.*	violet	violet	*violet, slightly turbid.*	violet, turbid	almost colourless.

In Table 5 are summed up the results of different experiment (by I, II, III, and IV are designated dispersoidal gold solutions prepared at different times; by a, b and c are designated the coagulation values for different portions of one and the same dispersoidal gold solution).

Table 5. (Red→violet after 5 minutes).

	"Sol B_1"		"Sol B_1+150 c.c. KOH, 0.02 norm."	
	NaCl	$BaCl_2$	NaCl	$BaCl_2$
I	27	0.16	a. 16, b. 16	0.03
II	a. 26, b. 26	0.16	a. 16, b. 16	between 0.03–0.035
III	a. 28, b. 28	a. 0.18, b. 0.17, c. 0.17	a. 16, b. 16	between 0.03–0.035
IV	——	——	——	0.04
Mean	27	0.17	16	0.03

III. The Dispersoidal Gold Solutions were Prepared with Ordinary Distilled Water, in Beakers of Glass A; the Measuring Vessels were of Jena Glass and of Glass A; no Other Chemical Experiments were Performed in the Room. Under these conditions, the intensity of colour (at room temperature), of "Sol B_1+150 c.c. KOH. 0.02 norm." when compared with "Sol B_1," showed a much smaller increase, than in similar experiments described in Section II.

Table 6. (Red→violet after 5 minutes).

	"Sol B_1"		"Sol B_1+150 c.c. KOH, 0.02 norm."	
	NaCl	$BaCl_2$	NaCl	$BaCl_2$
I	between 27-28	0.21	19	0.06
II	——	——	17	0.06
III	——	——	19	0.08
Mean	27.5	0.21	18	0.07

In Table 6 are summed up the data, pertaining to the coagulation values for NaCl and $BaCl_2$; these values are considerably greater than those obtained in dispersoidal synthesis carried out in a room where other chemical experiments are being performed at the same time, and with measuring vessels made of glass C, which is more sensitive to weak solutions of alkalies.

IV. The Dispersoidal Gold Solutions were Prepared in Beakers of Jena Glass, with Water Redistilled Through a Condenser of Jena Glass.

Table 7. (Red→violet after 5 minutes).

	"Sol B_1".		"Sol B_1+150 c.c. KOH, 0.02 norm."	
	NaCl	$BaCl_2$	NaCl	$BaCl_2$
I	between 24-25	between 0.17-0.18	13	0.03
II	25	0.18	a. 14, b. 14	0.03
III	a. 24, b. 24	0.17	——	——
Mean	24	0.17	14	0.03

From the data given in Table 7, it is clearly seen that the coagulation values for NaCl and $BaCl_2$ are *not* increased by using, instead of ordinary distilled water, water redistilled through a Jena glass condenser, nor are they by using Jena glass beakers, instead of those made of glass A.

V. Conclusion. The above coagulation numbers for NaCl and $BaCl_2$ admit of the following conclusions:

A. By varying the conditions of obtaining "Sol B_1," the coagulation values are changed relatively little; for NaCl the changes are within the limits of 27.5 and 24, or 14 per cent, and for $BaCl_2$, between 0.21 and 0.17, or 23 per cent.

B. By varying the conditions of obtaining "Sol B_1+150 KOH, 0.02 norm.," the coagulation values become changed considerably; viz. for NaCl they are between 18 and 14, or 28 per cent. For $BaCl_2$ the changes in coagulation values are very great; they are expressed between 0.03 and 0.07, or 133 per cent.

C. The greatest difference in the coagulation values for "Sol B_1" and "Sol B_1+150 c.c. KOH, 0.02 norm.," is for NaCl between 27.5 and 14, a difference of 96 per cent; and for Ba Cl_2 between 0.21 and 0.03, a difference of 600 per cent.

D. Dispersoidal solutions "Sol B_1+150 c.c. KOH, 0.02 norm." although the difference in their coagulation values for $BaCl_2$ rises up to 600 per cent. preserve their *pure red* colouring; only the colour becomes darker (more intense) and the brownish opalescence in reflected light increases. Other conditions being equal, the darker the red colour, and the stronger the opalescence, the less is the coagulation value for $BaCl_2$.

I shall devote my future papers to the consideration of the influence of separate variables upon the coagulation values, now I wish only to point out that the intensity of the red colour of "Sol B_1+150 c.c. KOH, 0.02 norm." prepared in a gold beaker, with water redistilled through a gold condenser, differs very little from that of "Sol B_1" (prepared also in a gold beaker and with the same *extra pure* water); in this case, the coagulation numbers of "Sol B_1+150 c.c. KOH, 0.02 norm.," for NaCl are 20 and for $BaCl_2$, 0.08.

In conclusion, I wish to extend my hearty thanks to Prof. P. P. von Weimarn for kindly guiding me into the world of Dispersoidology, during my stay in his laboratory, from September 1926 to April 1929.

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SORPTION OF GAS BY THE POROUS MATTER.

By **Jitsusaburo SAMESHIMA.**

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Sorption of the gases by the porous matters such as charcoal, silica gel etc. are generally considered to be one of the adsorption phenomena. Thus the molecules of the gas condense on the surface of the charcoal. Some authors consider that the gas molecules condense to liquid in the capillary. But it is highly improbable that, except the easily condensable vapours, the gas liquefies at a temperature so appart from its normal boiling point. McBain considered that a small part of the gas diffuse into the mass of charcoal while the most part are adsorbed on the surface of the charcoal, and he used the term "sorption" for such a case.(1)

The author measured the sorption amount by various kinds of charcoals of air(2) and of carbon dioxide as well as the sorption velocity by sugar charcoal of carbon dioxide.(3) It was known that the sorption velocity of gas by the granular charcoal is smaller than that by the powder one, while the sorption amounts by both charcoals are quite the same. We saw, moreover, that the amounts of sorptions of carbon dioxide by various kinds of charcoals are not so different each other notwithstanding the divergence of the materials from which the charcoals were made. According to the results of these observations, the author concluded that the sorption of gas by charcoal is to be ascribed to the dissolution and not to the adsorption.

By the experiments of the sorption of gases by chabazite,(4) it can naturally be supposed that the gas molecules enter into the crystal of the dehydrated chabazite in the places where the water molecules has formerly situated. There are vacant cavities in the dehydrated chabazite crystal, each of which was formerly filled with water molecule. If such dehydrated chabazite is brought in contact with gas, the gas molecules enter into the mass of the crystal and take possession of the cavities which were left unoccupied. Thus the crystal is still a homogeneous phase in the sence used in phase rule.

The author consider that the same can be said in the case of charcoal and silica gel. Charcoal has a great number of molecular cavities which were left when it was produced by the decomposition of carbohydrate etc. Silica gel has also molecular cavities left by the departure of water molecules in the process of dehydration.

Now the gas molecule dash into one of these molecular cavities and it is attracted and captured by the surrounding charcoal atoms or silica molecules. The gas molecule settles into the molecular cavity and make a homogenous solid solution. So the sorption process is not quite the same with the ordinary dissolution process, while the product is a solid solution. The phenomena neither be called "absorption" nor "adsorption." We will use the term "sorption" for this case, having the different meaning

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(1) McBain, *Z. physik. Chem.*, **68** (1909), 471.

(2) Sameshima and Hayashi, *Science Reports of the Tohoku Imperial University*, **12** (1924), 289.

(3) Sameshima, this Bulletin, **2** (1927), 1.

(4) Sameshima, this Bulletin, **4** (1929), 96.

from that used by McBain. Our " sorption " means the entering of the gas molecule into the molecular cavities and forming a solid solution.

It is well known fact that the more easily condensable gas are sorped the more, and this is considered to be one of the reasons of the adsorption hypothesis. This relation, however, hold never strictly but only approximately. According to the author's theory, the easily condensable gas molecule is liable to be captured more easily than the non-condensable gas molecule. In other words, the more active gas molecule is the more difficult to be prisoned. In the process of the ordinary dissolution, the solute molecule push aside the solvent molecules, or the solvent molecules make room for the solute molecule. So the molecular affinity between solute and solvent molecules is the most important factor for the ordinary dissolution.

Some authors describe that the rapidity of sorption of gases by the porous matters is to be due to the surface adsorption. They said that if it be a diffusion phenomena, then the sorption will proceed more slowly.(1) This statement is correct, however, only in the case of the diffusion into a compact solid body. In a case of the porous body such as charcoal, the contact surface between gas and solid is very large, and therefore, the "diffusion" goes on very rapid. By powdering the charcoal, the surface area will increase so the sorption velocity will also increase. This was already proved experimentally.(2)

Other reason of the adsorption hypothesis consists in the non-expansion of the adsorbent body. The expansions of charcoals by the sorptions of carbon dioxide and water vapour are observed recently by Meehan,(3) and Bangham and Fakhoury.(4) The amounts of expansions of charcoals determined by these authors are rather small, i.e. in the order of 0.1%. This can be explained by the present author's theory that the CO_2 molecules enter into the cavities of charcoal.

It is known that the sorption isotherm generally deviates from the Henry's law. This can easily be understood from the difference between the author's theory and the ordinary dissolution process. In the case of the sorption of hydrogen by charcoal, the Henry's law is applicable.(5) Recently, Magnus and co-workers(6) have determined the sorption isotherms by purified charcoal and silica gel of carbon dioxide at low pressures and known that the Henry's law is applicable.

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(1) Zsigmondy, " Kolloidchemie," 4ed. (1924), p. 85.

(2) Sameshima, this Bulletin, **2** (1927), 1.

(3) Meehan, *Proc. Roy. Soc.* (London), A, **115** (1927), 199.

(4) Bangham and Fakhoury, *Nature*, **122** (1928), 681.

(5) Titoff, *Z. physik. Chem.*, **74** (1910), 641.

(6) Magnus and co-workers, *Z. anorg. allg. Chem.*, **174** (1928), 142; **179** (1929), 215.

Summary.

The mechanism of the sorptions of gases by charcoal, silica gel and chabazite etc. are discussed. The author's theory for these cases is as follows: The gas molecules enter into the molecular cavities in the solid body and form a homogeneous solid solution.

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STUDIES ON BIMOLECULAR ALKALOIDS. PART II. REDUCTION OF DISINOMENINE AND Ψ-DISINOMENINE.

By **Kakuji GOTO.**

Received March 25, 1929. Published June 28, 1929.

In the preceding article,(1) the author, in cooperation with H. Sudzuki, reported the formation of disinomenine and ψ-disinomenine by the mild oxidation of sinomenine, and put forward the view that the isomerism of these two alkaloids might be due to the difference of the constitution of the third nucleus of phenanthrene, namely, to the difference of the linking position of the ethanamine group. It is of some interest, therefore, to see whether these two bimolecular alkaloids would give, on reduction, the same hydrogenated substance or not. The results of hydrogenation were the production of two different bimolecular substances, tetrahydro-disinomenine and tetrahydro-ψ-disinomenine, which are characterised by the following properties.

	Tetrahydro-disinomenine	Tetrahydro-ψ-disinomenine(2)
M. p. of free base	247°–252° (dec.)	271° (dec.)
M. p. of hydrochloride	>295°	not crystalline
Solubility of ,, ...	ca. 10%	∞
Form of ,, ...	hexagonal plates	——
M. p. of methiodide	275° (dec.)	285° (dec.)
M. p. of oxim	227°	242° (dec.)
M. p. of semicarbazone . . .	>290°	>290°
$[\alpha]_D$	+264°.41	+167°
Diazo reaction	50,000	25,000
$K_3Fe(CN)_6$ reaction	500,000	500,000
Formalin-sulphuric Acid . . .	weakly pink	faintly yellow

Tetrahydro-disinomenine and tetrahydro-ψ-disinomenine can also be obtained from dihydrosinomenine by mild oxidation with silver nitrate or potassium ferricyanide. And these two bases can easily be separated by alcohol, for tetrahydro-ψ-disinomenine is very difficultly soluble even in boiling alcohol. The tetrahydro-disinomenine can be purified through its hydrochloride, which crystallises well in hexagonal plates.

It is interesting to note that the colour reaction of disinomenine (pink) and ψ-disinomenine (brownish yellow) when dissolved in formaldehyde sulphuric acid is retained in the tetrahydro-derivatives in a diminished degree,

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(1) This Bulletin, **4** (1929), 107.

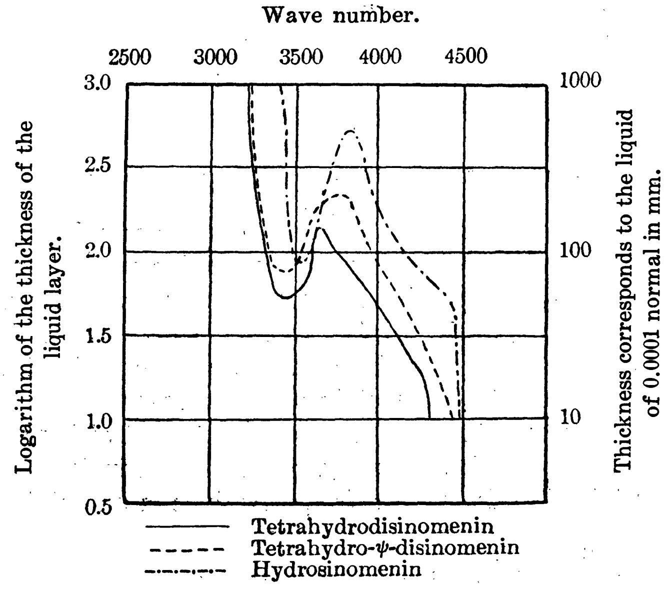
(2) Compare Kondo and Ochiai, *J. pharm. Soc. Japan*, **549** (1927), 124 (in German).

whilst that of hydrosinomenine (yellow, green, then blue with red fluorescence) is quite lost.

That in these two tetrahydro-derivatives, the original linking of two sinomenine molecules found in disinomenine and ψ-disinomenine, as was proved in Part I, must be remained untouched, is shown quite clearly from the decrease of the diazoreaction in these two alkaloids compared with sinomenine and hydrosinomenine. The fact that disinomenine and ψ-disinomenine give rise to two different tetrahydro-derivatives, seems to enforce the author's view regarding to the isomerism of the two alkaloids, given at the beginning of this article, since otherwise they might have given in all probability the identical tetrahydro-derivative in the same method of reduction. But, the final elucidation would be given only when these two alkaloid were decomposed into phenanthrene derivatives with side chain attaching to different position.

The mild oxidation and reduction of sinomenine are thus summarised in the following.

$$\begin{tikzcd}
\begin{array}{c}\text{Sinomenine}\\ C_{19}H_{23}NO_4\\ \text{m. p. } 159^\circ\ (-)\end{array} \arrow[r, "AgNO_3 \text{ or } K_3Fe(CN)_6"] \arrow[d, "PdCl_2+H_2"] & \begin{array}{cc}\text{Disinomenine} + & \psi\text{-disinomenine}\\ (C_{19}H_{22}NO_4)_2 & (C_{19}H_{22}NO_4)_2\\ \text{m. p. } 222^\circ\ (+) & \text{m. p. } 229^\circ\ (-)\end{array} \arrow[d, "PdCl_2+H_2"] \\
\begin{array}{c}\text{Hydro-}\\ \text{sinomenine}\\ C_{19}H_{25}NO_4\\ \text{m. p. } 202^\circ\ (+)\end{array} \arrow[r, "AgNO_3 \text{ or } K_3Fe(CN)_6"] & \begin{array}{cc}\text{Tetrahydro-} + & \text{Tetrahydro-}\\ \text{disinomenine} & \psi\text{-disinomenine}\\ (C_{19}H_{24}NO_4)_2 & (C_{19}H_{24}NO_4)_2\\ \text{dec. p. } 252^\circ\ (+) & \text{dec. p. } 271^\circ\ (+)\end{array}
\end{tikzcd}$$



Absorption curves show very little difference in these two alkaloid, as seen from the annexed diagram.

The author expects to decompose these two alkaloids for the purpose of deciding the constitution.

Experimental.

Tetrahydro-disinomenine. Disinomenine hydrochloride (1.7 gr.) was shaken in an aqueous solution (100 c.c.) with 100 c.c. colloidal palladium (0.1 gr. + 0.1 gr. gummi arabic) in hydrogen atmosphere (absorbed, 125 c.c. in one hour.) Tetrahydro-derivative was isolated in a usual way and recrystallised from alcohol. Prisms of m. p. 252°; yield 1.1 gr. With naturally occurring disinomenine, the same result was obtained.

Anal. Found: C=68.75; H=7.69; N=4.68%. Calc. for $(C_{19}H_{24}NO_4)_2$: C=69.09; H=7.27; N=4.24%.

Mol. wt. Found (in glacial acetic acid): 714 (suspected to be associated slightly). Calc.: 660.

Methiodide: m. p. >275°. (Found: I=27.63%. Calc.: I=26.91%).

Oxim: m. p. 227°, dec. p. 245°. (Found: N=8.06%. Calc. for dioxim: N=8.11%).

Tetrahydro-ψ-disinomenine. ψ-Disinomenine (1.6 gr.) was reduced in the same way as above and 0.9 gr. tetrahydro-ψ-disinomenine was isolated. Long needles of dec. p. 271°. $[\alpha]^{7}_{D} = +167°$. Difficultly soluble in ordinary organic solvents (0.13% in cold acetone; 1% in hot chloroform). The hydrochloride is not obtained in crystalline form.

Anal. Found: C=68.16; H=7.45; N=4.25%. Calc. for $(C_{19}H_{24}NO_4)_2$: C=69.09; H=7.27; N=4.24%.

Mol. wt. Found (in glacial acetic acid): 753 (a slight association is suspected). Calc.: 660.

Methiodide: m. p. 285° (dec.). (Found: I=28.23%. Calc.: I=26.90%).

Oxim: m. p. 242° (dec.). (Found: N=6.53%. Calc.: N=8.11%).

Linking of Dihydrosinomenine by Mild Oxidation.

With alkaline ferri-cyanide solution. To the solution of hydrosinomenine (9.5 gr. in 450 c.c. of 0.33% hydrochloric acid) potassium ferri-cyanide solution (9.5 gr. in 300 c.c. water) was added, followed by 150 c.c. of saturated soda solution. The bases were extracted with a large amount of chloroform and the residue of chloroform was boiled out with alcohol (60 c.c.). The insoluble part is tetrahydro-ψ-disinomenine (yield, 4.2 gr.; ca 45%). The soluble part was purified through its hydrochloride (yield, 1.2 gr.; ca 15%). The remainder was not crystallisable.

With silver nitrate. Hydrosinomenin (3 gr.) was dissolved in alcohol (50 c.c.) and water (200 c.c.) and was added with silver nitrate (1.5 gr.) in an aqueous solution (200 c.c.). After several minutes, the brine was added to the mixture (almost no precipitation) and then made alkaline with sodium carbonate solution. The treatment hereafter was carried out as in the preceding experiment. Yield: Tetrahydro-ψ-disinomenine (1.4 gr.; ca. 48%) and tetrahydro-disinomenine hydrochloride (1.0 gr.; ca. 30%).

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ON THE OXIDATION OF SODIUM SULPHITE BY AIR IN THE PRESENCE OF FERROUS HYDROXIDE AND A THEORY OF NEGATIVE INDUCED REACTION.

By Susumu MIYAMOTO.

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Introduction. The present research was undertaken with an expectation that the oxidation of the mixture of sodium sulphite and ferrous hydroxide in sodium hydroxide solution in a vessel will be an example of negative induced reaction favourable to the author's theory,(1) in connection with the former study on the oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide(2) solution or in sodium carbonate(3) solution by air, which was found to be a kind of negative induced reaction.

A Theory of Negative Induced Reaction. When two independent chemical reactions take place simultaneously in a same vessel, sometimes the primary reaction has an accelerating or an inhibiting action on the secondary reaction. In the former case, the phenomenon is usually called induced reaction, and in the latter case, it will be probable to be called negative induced reaction.

According to the modern theory of the kinetics of chemical reaction, the velocity of a reaction is accelerated by the appropriate activation of the molecules of the reacting substances. It is then quite probable to consider

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(1) S. Miyamoto, *Sci. Papers Inst. Phys. Chem. Research*, **4** (1926), 259.

(2) S. Miyamoto, this Bulletin, **2** (1927), 191; *Sci. Papers Inst. Phys. Chem. Research*, **7** (1927), 195.

(3) S. Miyamoto, this Bulletin, **3** (1928), 95; *Sci. Papers Inst. Phys. Chem. Research*, **8** (1928), 237.

that the phenomenon, called induced reaction, is no other than the activating action of the primary reaction, which can proceed by itself, on the molecules of the reacting substances of the secondary reaction, whose own reaction velocity is extremely small.

Various kinds of possible activating processes can be considered. It was proposed by the author,⁽¹⁾ that the direct transference of the appropriate active states of the reaction products of the primary reaction to the molecules of the reacting substances of the secondary reaction can be regarded as one of the possible processes of activation at least for some induced reactions.

The phenomenon, called negative induced reaction, can be considered to be the reverse process. In this case, the active states of the molecules of the reacting substances of the secondary reaction, already activated, lose their activity, before they react each other, by some means in the presence of the primary reaction.

The direct transference of active states will also be one of the possible mechanisms for this phenomenon. According to this consideration, the existence of three kinds of negative induced reactions can be considered. The active states of the molecules of the reacting substances of the secondary reaction can transfer firstly to the molecules of the reacting substances, secondly to the molecules of the reaction products and thirdly to the molecules of both of the reacting substances and reaction products of the primary reaction. It should be considered that the direct transference of active states depends upon the mutual specific nature of the colliding molecules. Then the negative induced reaction of the third kind will scarcely occur in the actual case.

In the case of the negative induced reaction of the first kind, the velocity of the secondary reaction will be very small at the beginning, and increase with time as the concentration of the reacting substances of the primary reaction decreases.

In the case of the negative induced reaction of the second kind, the velocity of the secondary reaction will not be small at the beginning, but decreases with time as the concentration of the reaction products of the primary reaction increases. Then in this case, the phenomenon can be regarded as the negative catalytic action of some of the reaction products of the primary reaction, whose concentrations increase with time.

The oxidation of the mixture of sodium sulphite and stannous hydroxide in sodium hydroxide⁽²⁾ or in sodium carbonate⁽³⁾ solution by means of air was

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(1) S. Miyamoto, *Sci. Papers Inst. Phys. Chem. Research,* **4** (1926), 259.
(2) Loc. cit.
(3) Loc. cit.

found to be an example of negative induced reaction of the first kind. The inhibiting action of the oxidation of stannous hydroxide on the oxidation of sodium sulphite, and the increase of the oxidation velocity of the mixture in sodium hydroxide solution with the suitable elapse of time, when the initial concentration of stannous hydroxide is small, are the principal evidences that it is the negative induced reaction of the second kind.

With the expectation that the oxidation of the mixture of sodium sulphite and ferrous hydroxide in sodium hydroxide solution by means of air will also be the same kind of phenomenon, the present research was undertaken. Favourable result to the author's theory, above described, was obtained. The oxidation velocity of the mixture was found to be an example of negative induced reaction of the second kind.

The oxidation velocity of ferrous hydroxide⁽¹⁾ or sodium sulphite⁽²⁾ in sodium hydroxide solution by means of air was already studied under certain conditions. They are considerably great and the observed oxidation velocity of each shows the dissolution velocity of oxygen into the solution. In the present research, the mixture was treated under the same conditions, and the rate of the oxidation of sodium sulphite alone was observed. The experimental results, which will be given in the later, show that it is a negative induced reaction of the second kind, the oxidation of ferrous hydroxide and that of sodium sulphite being considered as the primary and the secondary reactions respectively. It was unnecessary for the present purpose to observe the oxidation velocity of ferrous hydroxide in the mixture, which will be expressed by

(The oxidation velocity of $Fe(OH)_2$ in the mixture) $\leqq$
(The dissolution velocity of oxygen)—(The oxidation velocity of Na_2SO_3 in the mixture).

Experimental.

The experimental procedure was almost the same as that employed in the previous studies.⁽³⁾

A large test tube (diameter $\fallingdotseq$ 3 cm.) was used for the reacting vessel, the total volume of the mixture being made to 40 c.c. in each case. After t—minutes, the air current, which was passed into the mixture through a glass tube (inside diameter $\fallingdotseq$ 4 mm., outside diameter $\fallingdotseq$ 6 mm.) after being washed by acidic solution of potassium bichromate and sodium hydroxide

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(1) S. Miyamoto, this Bulletin, **3** (1928), 137; *Sci. Papers Inst. Phys. Chem. Research*, **9** (1928), 203.

(2) S. Miyamoto, this Bulletin, **2** (1927), 74; *Sci. Papers Inst. Phys. Chem. Research*, **7** (1927), 40.

(3) Loc. cit.

solution, was stopped, and the total amount of the mixture was quickly filtered and washed under reduced pressure into a known amount of iodine solution, acidified with hydrochloric acid. The excess of iodine was titrated back by means of sodium thiosulphate solution. In the following tables, v is the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the quantity of sodium sulphite, remained in the mixture after the t—minutes passage of air. The amount of ferrous hydroxide, initially present in the mixture, was determined separately by the titration by means of 0.1000 normal solution of potassium permanganate, the values of $v_{0\,Fe(OH)_2}$ in the following tables being the volume of potassium permanganate solution, equivalent to the amount of ferrous hydroxide, present in the mixture at $t=0$.

Thus the oxidation velocity of sodium sulphite in the mixture was only observed. The results were quite sufficient for the present purpose, above descrived.

Table 1.

Temp. = 20°C. $C_{NaOH} = 0.2000$ normal

Air = 7.78 litres per hour.

$v_{0\,Fe(OH)_2}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v'(=v_0-0.260\,t)_{(Na_2SO_3)}$ c.c.
10.90	0	13.69	—
	10	12.41	11.09
	30	12.21	5.89
	120	12.02	—
9.20	0	13.90	—
	10	12.94	11.30
	30	12.47	6.10
	120	12.13	—
9.20	0	13.46	—
	10	12.55	10.86
	30	12.23	5.66
	120	12.08	—
5.45	0	9.53	—
	10	8.48	6.93
	30	8.25	1.73
	120	8.09	—
5.45	0	18.71	—
	10	17.35	16.11
	30	17.22	10.91
	120	16.78	—

Table 1. (*continued*)

$v_{0\,Fe(OH)_2}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v'(=v_0-0.260\,t)_{(Na_2SO_3)}$ c.c.
2.30	0	13.15	—
	10	11.83	10.55
	25	11.55	6.65
	50	11.50	0.15
2.30	0	22.00	—
	10	21.18	19.40
	25	21.00	15.50
	120	20.06	—
2.30	0	13.37	—
	10	12.26	10.77
	25	12.11	6.87
	120	11.79	—
0.109	0	12.59	—
	10	9.90	9.99
	30	8.62	4.79
	120	7.37	—
0.058	0	10.35	—
	10	8.16	7.75
	25	7.12	3.85
	120	5.73	—
0.044	0	14.11	—
	10	11.54	11.51
	30	9.71	6.31
	120	7.82	—
0.022	0	12.46	—
	10	9.87	9.86
	30	7.80	4.66
	120	6.33	—

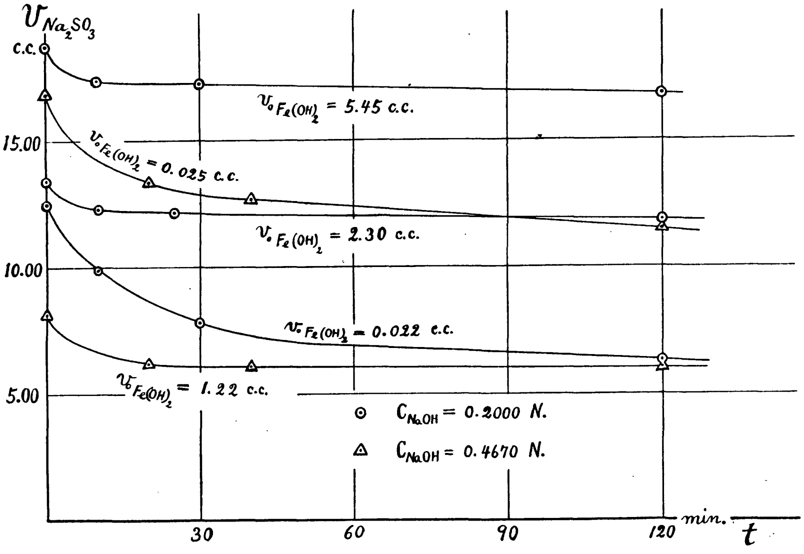
Table 2.

Temp. = 20°C. $C_{NaOH}=0.4670$ normal.
Air = 7.78 litres per hour.

$v_{0\,Fe(OH)_2}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v'=(v_0-0.234\,t)_{(Na_2SO_3)}$ c.c.
12.23	0	12.96	—
	20	11.80	8.28
	40	11.72	3.60
	120	11.63	—
6.12	0	18.84	—
	21	17.02	13.93
	40	16.85	9.48
	120	16.77	—

Table 2. (*continued*)

$v_{0\,Fe(OH)_2}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v' = (v_0 - 0.234\,t)_{(Na_2SO_3)}$ c.c.
2.45	0	20.69	—
	20	19.18	16.01
	40	19.03	11.33
	120	18.68	—
1.22	0	8.13	—
	20	6.19	3.45
	40	6.09	—
	120	6.05	—
0.122	0	10.44	—
	20	6.47	5.76
	40	5.42	1.08
	120	4.87	—
0.050	0	14.70	—
	20	10.42	10.02
	40	8.74	5.34
	120	7.42	—
0.025	0	16.81	—
	20	13.32	12.13
	40	12.63	7.45
	120	11.46	—



As is shown in Table 1 and 2, the oxidation velocity of sodium sulphite in the presence of ferrous hydroxide by means of air decreases rapidly with time; a few of the results being graphically shown in the accompanying figure. The values of v', given in the last column of the tables are calculated by an equation,

$$v' = v_0 - kt,$$

k being the velocity constant of the oxidation of sodium sulphite(1) in the absence of ferrous hydroxide, obtained in the previous study. When the initial concentration of ferrous hydroxide is very small, the values of v and v' are almost the same at the beginning; that is, sodium hydroxide oxidizes in the first stage almost at the same velocity as it is oxidized alone, but the velocity decreases gradually with time. It is not diminished so rapidly as in the other cases, since ferric hydroxide is formed at a very slow rate, when the initial concentration of ferrous hydroxide is very small.

The experimental results show that it is an example of negative induced reaction of the second kind, and the direct transference of the active states of the molecules of sodium sulphite to the molecules of ferric hydroxide, the reaction product of the primary reaction, will be one of the proper interpretations for this phenomenon.

The Effect of Ferric Hydroxide. The observed results on the oxidation of the mixture, an example of negative induced reaction of the second kind, should be considered to be the negative catalytic action of ferric hydroxide, according to the theory, above described. To ascertain this consideration, the oxidation velocity of sodium sulphite in the presence of ferric hydroxide was studied under the same conditions, quite the same way as was above described. The amount of ferric hydroxide was determined by the usual method of iodometry, the value of $v_{0\,Fe(OH)_3}$ in Table 3 and 4 being the volume of sodium thiosulphate solution of 0.0996 normal, equivalent to the amount of ferric hydroxide, present in the reacting mixture.

Table 3.

Temp. = 20°C. $C_{NaOH} = 0.2000$ normal.

Air = 7.78 litres per hour.

v_0 $Fe(OH)_3$ c.c.	t min.	v (Na_2SO_3) c.c.	$v'(=v_0)-0.260\,t)$ (Na_2SO_3) c.c.
10.65	0	12.86	—
	10	12.59	10.26
	30	12.50	5.06
	120	12.35	—

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(1) Loc. cit.

Table 3. (*continued*)

v_0 Fe(OH)$_3$ c.c.	t min.	v (Na$_2$SO$_3$) c.c.	$v'(=v_0-0.260\,t)$ (Na$_2$SO$_3$) c.c.
4.26	0	13.77	—
	10	13.44	11.17
	30	13.31	5.97
	120	13.27	—
2.13	0	19.01	—
	10	18.48	16.41
	30	18.40	11.21
	120	18.33	—
2.13	0	17.43	—
	10	16.94	14.83
	30	16.73	9.63
	120	16.72	—
2.13	0	9.32	—
	10	8.82	6.72
	30	8.75	1.52
	120	8.73	—
0.213	0	18.45	—
	10	17.86	15.85
	30	17.37	10.65
	120	17.12	—
0.210	0	10.90	—
	10	10.53	8.30
	30	10.17	3.10
	120	9.87	—
0.085	0	15.85	—
	10	15.13	13.25
	30	14.89	8.05
	120	14.62	—
0.085	0	13.06	—
	10	12.34	10.46
	30	12.19	5.26
	120	12.06	—
0.043	0	13.50	—
	10	12.73	10.90
	30	12.46	5.70
	120	11.82	—
0.021	0	13.31	—
	10	12.13	10.71
	30	11.78	5.51
	120	11.49	—

Table 4.

Temp. = 20°C. $C_{NaOH} = 0.4670$ normal.

Air. = 7.78 litres per hour.

$v_{0\,Fe(OH)_3}$ c.c.	t min.	$v_{(Na_2SO_3)}$ c.c.	$v' = (v_0 - 0.234\,t)_{(Na_2SO_3)}$ c.c.
13.20	0	16.92	—
	15	16.62	13.41
	45	16.58	6.39
	120	16.58	—
6.60	0	16.50	—
	20	16.29	11.82
	40	16.29	7.14
	120	16.25	—
2.64	0	15.90	—
	20	15.77	11.22
	40	15.70	6.54
	120	15.60	—
1.32	0	12.88	—
	20	12.84	8.20
	40	12.68	3.52
	120	12.66	—
0.65	0	11.70	—
	20	11.60	7.02
	40	11.57	2.34
	120	11.41	—
0.132	0	19.66	—
	20	19.46	14.98
	40	19.43	10.30
	120	19.27	—
0.053	0	10.00	—
	20	9.54	5.32
	40	9.41	0.64
	120	9.19	—
0.026	0	16.69	—
	20	15.88	12.01
	40	15.62	7.33
	120	15.36	—

As was shown in the Tables a favourable result to the author's considerations was obtained: the oxidation velocity of sodium sulphite in the presence of ferric hydroxide is very small.

The Effect of Sodium Sulphate. Though it is almost certain that sodium sulphate formed by the oxidation of sodium sulphite has a negligible effect on the oxidation velocity of sodium sulphite under the conditions of the author's measurements by the previous studies, it was ascertained by measuring the oxidation velocity in the presence of a considerable amount of sodium sulphate.

$v_{0\,Na_2SO_4}$ in Table 5 is the volume of 0.1000 normal solution of sodium sulphate initially present in the mixture.

Table 5.

Temp. = 20°C. C_{NaOH} = 0.2000 normal.

Air = 7.78 litres per hour.

$v_{0\,Fe(OH)_2}$ c.c.	$v_{0\,Fe(OH)_3}$ c.c.	$v_{0\,Na_2SO_4}$ c.c.	t min	v c.c.
2.30	—	10.00	0	12.77
			10	11.63
			25	11.52
			60	11.23
0.116	—	10.00	0	12.49
			11	10.16
			25	9.27
			120	7.86
—	0.085	10.00	0	14.79
			10	14.06
			30	13.63
			120	13.32

By comparing Table 5 and Table 1—4, it will be seen that sodium sulphate has no appreciable effect on the oxidation velocity of sodium sulphite.

The experimental error of the present measurements is considerably great owing to the slowness of the reaction velocity, and it will be of no use to try to obtain any quantitative relation from the values, given in the tables.

Summary.

1. A theory of negative induced reaction was proposed. Three kinds of negative induced reactions was considered according to the proposed theory. The oxidation of the mixture of stannous hydroxide and sodium sulphite in sodium hydroxide or in sodium carbonate solution by means of air, the results of which being already reported in the previous papers, can be regarded as an example of negative induced reaction of the first kind, and the oxidation of the mixture of ferrous hydroxide and sodium sulphite

in sodium hydroxide solution, here reported, as an example of negative induced reaction of the second kind.

2. The oxidation of the mixture of sodium sulphite and ferrous hydroxide in sodium hydroxide solution by means of air was studied, with an expectation, that it will give an example of negative induced reaction. The oxidation velocity of sodium sulphite in the mixture was only measured, which was sufficient for the present purpose. The velocity decreases rapidly with time, and the result was interpreted as a negative induced reaction of the second kind.

3. To ascertain that the decrease of the observed oxidation velocity of sodium sulphite in the mixture is due to the formation of ferric hydroxide, the reaction product of the primary reaction, the oxidation velocity of sodium sulphite in the presence of ferric hydroxide was studied under the same conditions. The expectation was fulfilled.

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STUDIES ON ASYMMETRIC OXIDATION.

(Preliminary Note.)

By Yuji SHIBATA and Ryutaro TSUCHIDA.

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Introduction. The cause of the well known fact that organic substances containing one or more asymmetric carbon atoms in their molecules occur in the nature always in optically active forms, while the same substances synthesised in vitro are of racemic compounds, has long been discussed and various experiments, physical as well as chemical, have been attempted(1)* for the purpose of finding any reasonable theory on this subject. Notwithstanding those efforts, we are not able, up to the present time, to arrive to a conclusion which will definitively explain this fundamental fact in the nature.

On the other hand, we are acquainted with many examples of such facts that certain organic ferments extracted from living bodies act selectively upon racemic compounds, that is to say, either *d*- or *l*-form of the

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(1) Compare Byk, *Z. physik. Chem.*, **49** (1904), 641; *Ber.*, **37** (1904), 696; and Bredig: Ueber absoluter asymmetrische Synthese, *Z. angew. Chem.*, No. 62 (1923).

* The asymmetric syntheses which were attempted on the standpoint of pure synthetic chemistry without any biochemical consideration have often been succeeded by Marckwald, Mckenzie and others.

latter substances is attacked more easily than the other by ferments: for example, pancreas extracts act upon *d*, *l*-tyrosine ethyl ester, decomposing the *l*-form of this compound more quickly than the *d*-form⑴; pancreatine hydrolyses only *l*-form of carboethoxyl-glycyl-*d*, *l*-leucine⑵ and intestinal erepsine decomposes asymmetrically *d*, *l*-leucyl tyrosine⑶ and so on. It appears, therefore, to be quite logical to conclude that the syntheses in living bodies are asymmetric by the reason that they are carried out by ferments which are themselves asymmetrically constructed.

But it will soon be found that this explanation is by no means conclusive, because there is, up to the present time, no experimental evidence as to the assimmetricity of nuclear molecules (or active centre) of ferments.

One of the present authors, Yuji Shibata together with Keita Shibata has found some years ago an interesting phenomenon exhibited by some metallic complex salts: it deals with namely the oxidase-like oxidising actions which differ entirely from the oxidation of the electrochemical nature shown often by stannic- or ferric salts. A series of investigations on this subject executed by Y. and K. Shibata and their collaborators⑷ have proved that those oxidation reactions carried out by some metallic complex salts must be regarded to have a catalytic nature and resemble closely to enzyme actions from the point of view of chemical kinetics. Now, among those complex salts which possess the oxiding action, there are some ones, the molecules of which are asymmetrically constructed, such as $[\mathrm{Co}\ \underline{en}_2\ \mathrm{NH_3Cl}\substack{(1)\\(2)}]\ \mathrm{X_2}$, $[\mathrm{Co}\ \underline{en}_2\ \mathrm{H_2OCl}\substack{(1)\\(2)}]\ \mathrm{X_2}$, $[\mathrm{Co}\ \underline{en}_2\ \mathrm{Cl_2}\substack{(1)\\(2)}]\ \mathrm{X}$, &c. When a certain racemic organic compound (preferably polyphenol containing an asymmetric carbon atom in the side chain) is put under the action of an optically active cobalt complex salt, it will be suggested that the oxidation of the former substance proceeds asymmetrically, i.e., one of the *d*- or *l*-form is more easily oxidised than the other by *d*- or *l*-form of cobalt complex salts above mentioned. If this is experimentally realised, it will be of no less interest,

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⑴ E. Abderhalden, H. Sickel and H. Ueda, *Fermentforschung*, **7** (1923), 91.

⑵ E. Fischer and P. Bergell, *Ber.*, **36** (1903), 2592.

⑶ E. Abderhalden and E. Schwab, *Fermentforschung*, **9** (1927), 252.

⑷ Yuji Shibata and Keita Shibata: On the Oxydase-like Oxidising Action of Certain Metallic Complex Salts, *Journ. Chem. Soc. Japan*, **41** (1920), 35; *Chem. Abst.*, **14** (1920), 2590. Yuji Shibata and Hideo Kaneko: Chemical Kinetics of Oxidation by the Catalytic Action of Some Complex Salts of Metals, *Journ. Chem. Soc. Japan*, **43** (1922), 833; *Chem. Abst.*, **17** (1923), 2811. Yuji Shibata and Hideo Kaneko: Decomposition of Hydrogen Peroxide by Complex Salts of Metals, *Journ. Chem. Soc. Japan*, **44** (1923), 166; *Chem. Abst.*, **17** (1923), 2812. Hideo Kaneko: On the properties of Aqueous Solutions of Some Cobalt Complex Salts Which Show the Oxidase-like Actions, Part 1 and 2, *Journ. Chem. Soc. Japan*, **48** (1927), 391; **49** (1928), 380. Keita Shibata: The Vital Oxidising Reaction, *Toyo Gakugei-Zasshi*; *Chem. Abst.*, **16** (1922), 1443. Atsushi Watanabe: Über die vitale Oxydation in den Pflanzenzellen mit den Kobaltammin-komplexsalzen, *Japan. Journ. Bot.*, **4** (1928), 31. Atsushi Watanabe: Oxidation of Metallic Iodides by Complex Salts of Metals, *Journ. Chem. Soc. Japan*, **49** (1928), 476.

because the further analogy between the behaviours of enzymes and some metallic complex salts is thus established and, on the other hand, the supposed asymmetrical structure of essential molecules of enzymes will be revealed on an experimental basis.

The present investigation of the authors has, as will be briefly described below, positively proved that the asymmetric oxidation, as the phenomenon is so called by the authors, is really the case, at least in the interaction between the substances now studied, namely racemic 3,4-dioxyphenyl-alanine as the substance to be oxidised and optically active ammonio-chloro-diethylenediamine cobaltic bromide as the oxidiser.

Experimental.*

Racemic ammonio-chloro-diethylenediamine cobaltic bromide was first synthesised and resolved into optically active components by the method of fractional crystallisation of its bromocamphersulfonate⁽¹⁾; the results of the determinations of rotatory powers of the *d*- and *l*-components are as follows:

$$d\,[\mathrm{Co}\,\underset{\sim}{en}_2\,\mathrm{NH_3Cl}]\text{-}d\,(\mathrm{C_{10}H_{14}O\ BrSO_3})_2,\ \ [\alpha]^{18.5^\circ}_{\mathrm{red}} = +68.3^\circ$$
$$l\,[\quad ,, \quad]\text{-}d\,(\quad ,, \quad)_2,\ \ [\alpha]^{18.5^\circ}_{\mathrm{red}} = +32.2^\circ$$

The *d*- and *l*-bromocamphersulfonate were then transformed again into the respective bromides by dissolving in hydrobromic acid; the rotatory powers of these bromides were as follows:

$$d\,[\mathrm{Co}\,\underset{\sim}{en}_2\,\mathrm{NH_3Cl}]\,\mathrm{Br_2},\ \ [\alpha]^{11^\circ}_{\mathrm{red}} = +45.8^\circ$$
$$l\,[\quad ,, \quad]\ ,,\ ,\ \ [\alpha]^{10^\circ}_{\mathrm{red}} = -45.5^\circ$$

The racemic 3, 4-dioxyphenyl-alanine⁽²⁾ was, on the other hand, synthesised in starting from glycine anhydride, according to the method given by K. Hirai.⁽³⁾

In order to save the materials, the preparations of which are fairly laborious and expensive, the authors have only determined in definite time intervals, the change of rotatory power of dilute solutions containing the reacting substances, without isolating and examining the oxidation products. The experiments were carried out in the following manner:

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(1) A. Werner, *Ber.*, **44** (1911), 1887.

(2) The authors chose at first dioxymandelic acid as the substance to be oxidised, dioxyphenyl-alanine has afterwards been preferred to the former for the sake of its larger yield in the syntheses.

(3) K. Hirai, *Biochem. Zeitsch.*, **114** (1921), 67.

* One of the authors, Y. Shibata with his collaborators is continuing this work using racemic catechin as the substance to be oxidised and at the same time is studying chemical kinetics in the case of interaction between both optically active polyphenol, such as dioxyphenyl-alanine and catechin, and metallic complex salts.

1. To 100 c.c. of a saturated solution of racemic 3, 4-dioxyphenyl-alanine, there were added 25 c.c. of a solution of *l*-ammonio-chloro-diethylene-diamine cobaltic bromide, in which 0.3030 gr. of this complex salt is contained, and 5 c.c. of a buffer solution of phosphate (1/5 mol, PH=6.2). This solution mixture was put in a thermostat of 20°; 10 c.c. of the solution was then taken out from time to time and its rotatory power was observed in adding about 2 c.c. of acetic acid solution (1 normal), in order to arrest the course of the oxidation. The three-field polariscope of Adam-Hilger, and the monochromater of Leitz as the light source were used; the observations were made with 10 cm. tube in red light. The results of the determinations are shown in Table 1 and Figure 1:

Table 1.

Time (hour)	Angle of rotation	Time (hour)	Angle of rotation
0.0	-0.03	6.5	-0.05
0.5	-0.06	8.5	-0.07
1.5	-0.07	10.0	-0.07
2.0	-0.08	13.0	-0.07
2.5	-0.05	17.0	-0.08
3.5	-0.04	26.0	+0.02
4.5	-0.04	29.0	+0.07
5.5	-0.08		

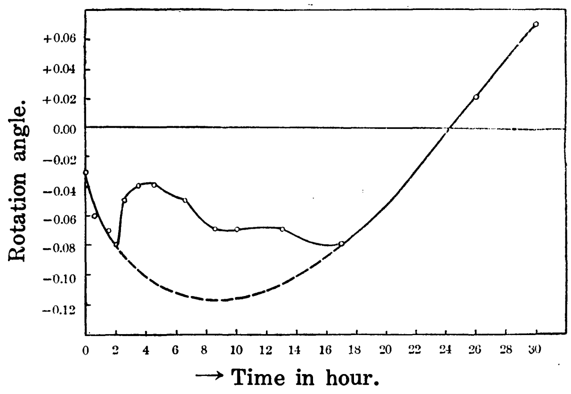


Fig. 1.

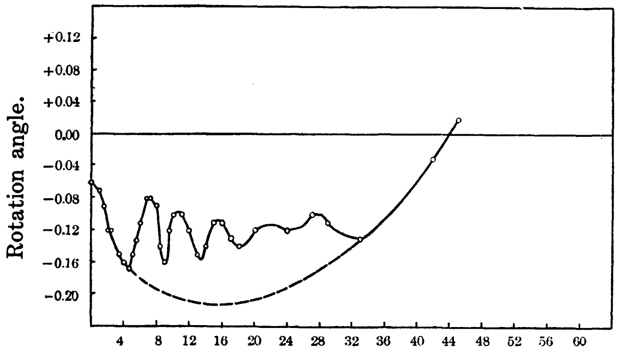
From the above figure, it is easily seen that the solution changes its rotatory power in such a manner that in the early stadium of the oxidation reaction, the *l*-rotation increases by and by, and after tracing a somewhat irregular course for a while, the *l*-rotation begins to decrease in its amount, until it reaches to the zero-point; the sign of the rotatory power is then changed, the *d*-rotation being henceforth again increased.*

2. Racemic 3, 4-dioxyphenyl-alanine: 0.6157 gr. in 200 c.c. water; *l*-ammonio-chloro-diethylenediamine cobaltic bromide: 0.4371 gr. in 50 c.c. water. The other conditions are similar as in the former experiment.

In this second experiment, the time interval of the determination of rotatory power was considerably shortened, for the purpose of studying more closely the part of the time-rotation curve, where there was observed some irregularity in the former experiment. The results of this observation are given in Table 2 and Fig. 2.

Table 2.

Time (hour)	Angle of rotation	Time (hour)	Angle of rotation
0.0	−0.06	5.0	−0.15
1.0	−0.07	5.5	−0.13
1.5	−0.09	6.0	−0.11
2.0	−0.12	6.5	−0.08
2.5	−0.12	7.0	−0.08
3.5	−0.15	8.0	−0.09
4.0	−0.16	8.5	−0.14
4.5	−0.17	9.0	−0.16
9.0	−0.12	18	−0.14
10	−0.10	20	−0.12
11	−0.10	24	−0.12
12	−0.12	27	−0.10
13	−0.15	29	−0.11
14	−0.14	33	−0.13
15	−0.11	42	−0.03
16	−0.11	45	+0.02
17	−0.13		



→ Time in hour.

Fig. 2.

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* A control experiment, in which dioxyphenyl-alanine was omitted, the other condition being the same as the experiment above mentioned, showed that the rotatory power of the solution stayed constant within 320 hours.

By this study, it was shown that the change of the rotatory power of the solution begins to take a zig-zag-formed course several hours after since the reacting substances were mixed; this zig-zag-shape is then gradually flattened until the curve become finally smooth. It appears, anyhow, that the general form of the time-rotation curve which is represented by broken lines in the figures is almost the same in both cases of the experiments (1) and (2).*

Let us now theoretically consider various possible cases of the interaction between the substances in question. The following four figures representing also the time-rotation curve are given to illustrate the courses of those possible reactions: if, for example, the *d*- and *l*-components of a racemic organic compound are oxidised with an equal easiness by an optically active complex salt, say *l*-salt, and the oxidation product thus formed possess no optical activity, the rotation-change of the solution should be represented by the curve in Fig. 3,(1) while if only the *l*-component of the racemic organic compound is attacked by the *l*-complex salt, the *l*-activity of the solution will be gradually diminished and after some times the solution will become dextro-rotatory due to the unattacked *d*-component of

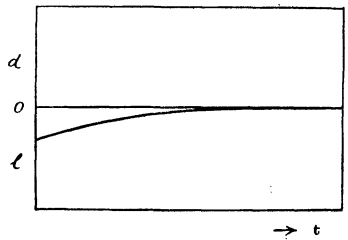

Fig. 3.

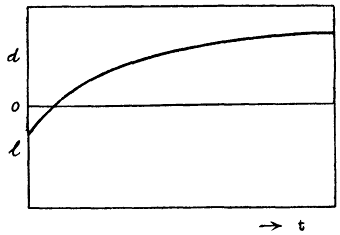

Fig. 4.

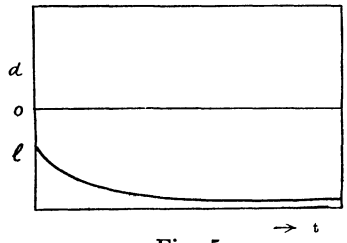

Fig. 5.

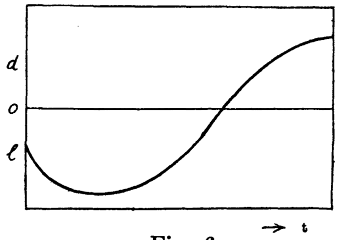

Fig. 6.

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* One more series of observation, similarly arranged as the experiment (2), was carried out by the authors, but the results of this measurement were not described here, for the data thus obtained were proved to be in good accordance with those of the former.

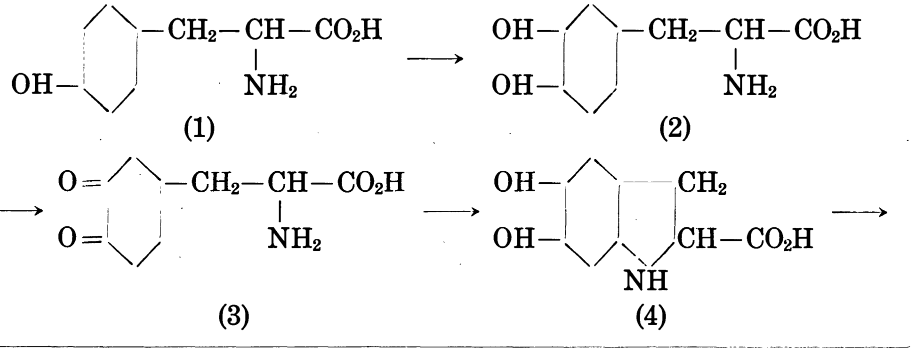
(1) In considering quite theoretically, the curve must be parallel to the zero-line, but, in fact, metallic complex salt itself, after some times, gradually undergo a certain change, losing its optical activity.

the organic compound (curve in Fig. 4), provided that the *d*-rotation of the latter substance is higher than the *l*-rotation of the complex salt.. If, in the latter case, a *l*-rotatory compound, a quinone for example, is produced by the oxidation, the *l*-activity of the solution will be increased by degrees, the activity of the oxidation product superposing with that of the oxidising agent. The curve of Fig. 5 represents this sort of reaction. Finally, if the *l*-rotatory quinone, just now supposed to be produced, is then decomposed by the further oxidation and lose its own activity, the solution will become by and by less *l*-rotatory and finally *d*-activity will take its appearance, as is shown in Fig. 6.

Now, if the curves (Fig. 1 and 2) which were obtained by the authors as the results of the present investigation are compared with those above discussed, it may easily be found that the former curves show a close resemblance with that of Fig. 6. From this experimental fact, it might reasonably be concluded that *l*-ammonio-chloro-diethylenediamine cobaltic bromide oxidises the *l*-component of racemic 3, 4-dioxyphenyl-alanine more easily than its *d*-component and a *l*-rotatory substance, probably quinonic compound, is intermediately produced. This latter substance undergo further oxidation and is transformed into an inactive compound (perhaps by a decomposition or polymerisation) thus the solution becomes gradually less *l*-rotatory and finally *d*-rotatory owing to the remaining *d*-dioxyphenyl-alanine.

Consideration on the Reaction Mechanism.

As is well known, dioxyphenyl-alanine is oxidised by tyrosinase,(1) and the same enzyme act upon *l*-tyrosine, giving intermediately *l*-dioxyphenyl-alanine and finally melanine.(2) Raper explained the mechanism of this oxidation reaction as follows :(3)



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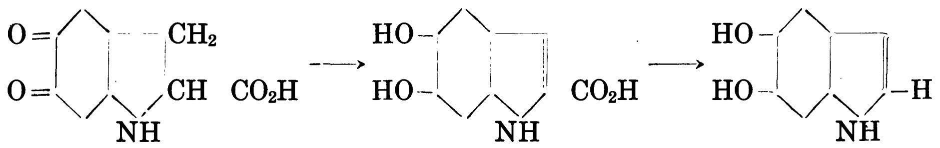
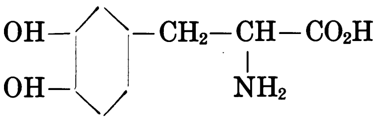
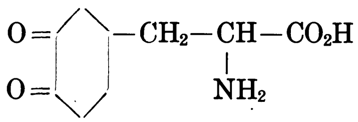
(1) H. Prigbaum, *Arch. Entwickl. Org.*, **48** (1921), 140.

(2) H. S. Raper, *Biochem. Journ.*, **20** (1926), 735.

(3) *Fermentforsch.*, **9** (1927), 206.



(5) (6) (7)

If the oxidation of racemic 3, 4-dioxyphenyl-alanine by *l*-ammonio-chloro-diethylenediamine bromide follows too the reaction mechanism above stated, the solution should contain *d*  and *l*  in the early stage of the reaction; the quinonic compound will then be further oxidised and, passing (4) and (5), lose its activity at (6). The transition of (6)——→(7) will be accompanied by separation of carbonic acid and consequently the acidity of the solution augments at this moment, resulting temporary retardation of the reaction velocity; the repetition of the latter chemical changes might perhaps be regarded as the cause of giving the zig-zag shape in a part of the time-rotation curve, as was observed by the authors.

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A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. III.(1)

By Tetsuya ISHIKAWA.

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Viscosity and molecular structure. It was discovered by Dunstan and Wilson(2) that the viscosity coefficient and molecular weight of a liquid are related by the simple law :

$$M = A + B \log \eta \, ,$$

where M is the molecular weight, A and B are constants depending on the

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(1) The former papers of this series have been published in this Bulletin, **4** (1929), 5 and 25.

(2) A. E. Dunstan & R. W. Wilson, *J. Chem. Soc.*, **91** (1907), 90.

particular series to which the liquid belongs, and η is the viscosity coefficient. They further noticed that B is almost the same in the various series, and has therefore a general nature, A being the specific constant for each family.

A mere transformation of the expression into

$$\log \eta = a + b\,M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

brings us the following another noticeable result. The experimental data applied in the present calculation are quoted from the values obtained by Thorpe and Rodger.⁽¹⁾

Paraffins.

t°C.	C_5H_{12}	a	b	C_6H_{14}	a	b	C_7H_{16}	a	b	C_8H_{18}
0	0.00283	−3.30	0.01044	0.003965	−3.12	0.00835	0.00519	−3.23	0.00940	0.00703
20	0.00232	−3.35	0.00996	0.00320	−3.16	0.00772	0.004105	−3.23	0.00838	0.00538
30	0.00212	−3.37	0.00971	0.00290	−3.18	0.00746	0.00369	−3.24	0.00805	0.004785

t°C.	i−C_5H_{12}	a	b	i−C_6H_{14}	a	b	i−C_7H_{16}
0	0.00273	−3.25	0.00950	0.00371	−3.10	0.00778	0.00477
20	0.00223	−3.31	0.00919	0.00300	−3.15	0.00724	0.00379
30	0.00204	−3.34	0.00897	0.002725	−3.17	0.00699	0.003415

Iodides.

t°C.	CH_3I	a	b	C_2H_5I	a	b	C_3H_7I
0	0.005945	−3.06	0.00589	0.00719	−3.43	0.00824	0.00938
20	0.00487	−3.10	0.00558	0.00583	−3.37	0.00726	0.00737
40	0.00409	−3.13	0.00521	0.00484	−3.34	0.00659	0.005985

t°C.	i−C_3H_7I	a	b	i−C_4H_9I
0	0.008785	−3.53	0.00870	0.011625
20	0.00690	−3.38	0.00718	0.00870
40	0.00559	−3.36	0.00654	0.006905

Monobromides.

t°C.	C_2H_5Br	a	b	C_3H_7Br
0	0.00478	−3.33	0.00929	0.00645
20	0.00392	−3.34	0.00857	0.00517
30	0.00357	−3.35	0.00832	0.00467

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

t°C.	i−C_3H_7Br	a	b	i−C_4H_9Br
0	0.006045	−3.40	0.00958	0.008235
20	0.00482	−3.39	0.00869	0.00638
30	0.00435	−3.38	0.00832	0.00569

Sulphides.

t°C.	$(CH_3)_2S$	a	b	$(C_2H_5)_2S$
0	0.00354	−3.33	0.01416	0.00559
20	0.00293	−3.34	0.01291	0.004445
30	0.002685	−3.34	0.01243	0.00401

Fatty alcohols.

t°C.	CH_3OH	a	b	C_2H_5OH	a	b	n-C_3H_7OH
0	0.00813	−2.86	0.02411	0.01770	−2.87	0.02433	0.03882
20	0.00591	−2.92	0.02173	0.01192	−2.83	0.01976	0.02255
40	0.004505	−2.95	0.01884	0.008275	−2.84	0.01635	0.01403

a is regarded to be a universal constant, almost independent of temperature, while b which varies with temperature seems to be a particular constant for each homologous series.

Taking the mean value of a at 20°C. from the above figures, we obtain a reduced formula:

$$\log \eta = -3.22 + b\,M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Relationship between b and the field-constant k. So far as a can be put to be a universal constant for all liquids, the factors which particularize a liquid are b and the molecular weight, and therefore b may well be said to play a great rôle in the molecular constitution of the liquid.

The writer, in his earlier papers,(1) defined the field-constant k of a liquid which presumably depends on the molecular structure, and evaluated those values of more than ten liquids by putting that of C_6H_6 as unity.

It is the purpose in this paper to find the relationship between k and b thus calculated. Two examples are taken below.

For benzene as we have η at 25°C=0.00599,

$$\log 0.00599 = -3.22 + b \times 78.05$$

$$b \text{ of } C_6H_6 = 0.0128.$$

And for water at the same temperature

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(1) This Bulletin, **4** (1929), 5; **4** (1929), 25.

$$\log 0.00891 = -3.22 + b \times 18.02$$
$$b \text{ of } H_2O = 0.0649.$$

In the writer's opinion it is not likely to include water into a member of alcohol series and benzene into a member of substitutions of CH_3- or other groups.

b of other liquids can be estimated by the same method, the results of calculation from the viscosity data at 25°C. being recorded in the following table.

Substance	η_{25°	b	$\frac{b_{C_6H_6}}{b}$	k
C_6H_6	0.00599	0.0128	1	1
$C_6H_5CH_3$	0.00541	0.01035	1.23	1.23
CH_3COOCH_3	0.003594	0.0105	1.22	1.67
$CHCl_3$	0.00540	0.00798	1.60	1.50
CCl_4	0.00883	0.00758	$1.69=\frac{1}{0.59}$	0.63
CS_2	0.003656	0.0103	$1.24=\frac{1}{0.80}$	0.76
CH_3OH	0.00557	0.0302	0.42	0.36
H_2O	0.00891	0.0649	0.20	0.21
$HCONH_2$	0.03359	0.0388	0.33	0.35
CH_3COOH	0.01121	0.0212	0.60	0.57

A simple test of comparison between k and b relative to that of C_6H_6 results in the fact that they are fairly concordant with each other as shown in this table.

As already observed, k or b being an important factor which characterizes a liquid, there may be introduced a "hypothetical or ideal liquid" which displays no particular nature as any real liquid does. For such liquid we may put $b=0$ in formula (2), so obtain

$$\log \eta = -3.22 = \bar{4}.78$$
$$\text{or} \qquad \eta = 0.00060.$$

This values is far less than the viscosity coefficients of all liquids.

It will also be noticed that the degree of association has no important meaning in treating the viscosity of a single liquid.

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ZUR ACETYLIERUNG DER STÄRKE. EINIGE VERSUCHE ZUR LÖSUNG DER STÄRKE.

Von Yojiro TSUZUKI.

Eingegangen am 22. Mai 1929. Ausgegeben am 28, Juli 1929.

Neuerdings ist die Acetylierung der Stärke beträchtlich erleichtert worden durch eine Vorbehandlung, dass die Stärke in Wasser gelöst und dann mit Alkohol gefällt wird.(1) Inzwischen wurde eine noch erfolgreichere Arbeitsweise veröffentlicht, die auf einem Prinzip beruht, dass die Stärke in möglichst wenig Lösungsmittel gelöst und—ohne das Lösungsmittel zu entfernen—die ganze Masse vom Acetylierungsmittel angegriffen wird; als Lösungsmittel für Stärke sind bisher nur konzentrierte *wässerige* Lösungen einiger Salze gebraucht worden.(2)

Es ist mir nicht ohne Interesse, zu versuchen, ob die in *wasserfreiem* Medium gelöste Stärke auch nach diesem Prinzip leicht acetyliert werde; dieselbe Methode wäre vorteilhafter, weil in diesem Falle die Stärke ohne Gefahr der Hydrolyse acetyliert werden soll. Als wasserfreies Lösungsmittel bisher bekannt ist Glycerin,(3) welches an sich aber leider nicht stark befähigt ist, die Stärke zu lösen; doch durch Zusatz von etwas Chlorzink kann man die Stärke in wenig Glycerin auflösen. Die so hergestellte Kleistermasse wird nun durch Einwirkung von Essigsäureanhydrid zur Acetylierung gesetzt. Zuerst reagiert das vorhandene Glycerin auf Essigsäureanhydrid, wobei Acetine gebildet werden, deren Anwesenheit aber die Acetylierung keinesweges stört, vielmehr die Reaktion glatt verlaufen lässt. Die entstehende, völlige Lösung wird in Wasser gegossen und das ausgeschiedene Produkt mit Wasser wiederholt verrieben (die Acetine werden in Wasser gelöst). Ausbeute fast theoretisch. Die Reinigung erfolgt durch Lösen in Chloroform und Ausfällen mit Alkohol.

Diese Acetylstärke löst sich in verschiedenen Lösungsmitteln leichter und klarer als die, die ich erhielt bei der Acetylierung der Stärke mit Chlorzinklösung als Lösungsmittel,(4) liefert weniger viskose Lösungen, zeigt ein kleineres Drehungsvermögen, und besitzt einen niederen Schmelzpunkt, also liegt eine etwas depolymerisierte Acetylstärke vor, jedoch

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(1) E. Peiser, *Z. physiol. Chem.* **161** (1926), 210. H. Pringsheim und P. Meyersohn, *Z. physiol. Chem.*, **173** (1928), 221. Haworth, Hirst und Webb, *J. Chem. Soc.*, **1928**, 2681. P. Brigl und R. Schinle, *Ber.*, **62** (1929), 99.

(2) Y. Tsuzuki, dieses Bulletin, **3** (1928), 276; **4** (1929), 21.

(3) K. Zulkowski, *Ber.*, **13** (1880), 1395; **23** (1890), 3295.

(4) Y. Tsuzuki, loc. cit.

löst sich das entacetylierte Produkt in Wasser schwach opalescierend, die wässerige Lösung scheidet beim Stehen einen wolkigen Niederschlag ab, wie die Amyloselösung, reduziert nicht und wird mit Jod charakteristisch gefärbt.

Jedenfalls, beim Lösen der Stärke in Glycerin, infolge der hohen Temperatur, kann einige Depolymerisation der Stärke nicht vermieden werden, und zwar wenn bei noch höheren Temperaturen gelöst, wird die Stärke beträchtlich depolymerisiert. Es wäre daher uns wünschenswert, irgendwelches noch bequemeres, wasserfreies Lösungsmittel für die Stärke zu finden. Zu diesem Zwecke habe ich versucht, die Stärke in einigen Alkoholen zu lösen, aber ohne glücklichen Erfolg. Es ergab sich, dass Erythrit die Stärke ziemlich leicht löst, Mannit(1) etwas schwerer, aber Glykol sehr wenig und Methylalkohol fast gar nicht.(2)

Beschreibung der Versuche.

Acetylierung der Stärke. 20 gr. getrocknete Kartoffelstärke wurden mit 30 gr. Glycerin und 2 gr. Chlorzink vermischt und im Glycerinbad unter Umrühren erhitzt. Bei 150° (Badtemperatur) löste sich die Stärke zum Teil und bildete eine sehr konsistente Masse, die, auf 160-170° unter Kneten noch 15 Min. erhitzt, dickflüssig und halbdurchsichtig wurde (die Stärke ist jetzt fast völlig gelöst). Zu diesem Kleister, nach dem Erkalten auf 70°, wurden 140 c.c. Essigsäureanhydrid in kleinen Portionen vorsichtig gegeben, so dass die Temperatur bei 70–80° blieb (40 Min.).

Die entstandene, durchsichtige Lösung wurde noch 30 Min, auf derselben Temperatur erwärmt, noch vorhandene Klümpchen abzentrifugiert (auch durch Glasfilter filtrierbar) und in Wasser gegossen, das ausgeschiedene Produkt mehrmals mit Wasser zerrieben und getrocknet. Ausbeute 34 gr. (95% d. Th.). Reinigung, durch Lösen in heissem Chloroform und Zusatz von Alkohol bis zur bleibenden Trübung. Weisses Pulver. Mit Vorsintern schmilzt es bei 240–245° (korr.) und bräunt sich über 270°. Löslich in Eisessig, Chloroform, Essigsäureanhydrid, Pyridin, Aceton, Essigester und konzentrierter Schwefelsäure.

Anal. 0.1921 gr. Subst. gaben 0.3501 gr. CO_2 und 0.0965 gr. H_2O. Gef.: C=49.70; H=5.62%. Ber. für $C_6H_7O_5(CH_3CO)_3$: C=49.98; H=5.60%. Asche 0.1%.

Acetylbestimmung: Die Substanz wird in 10 c.c. Aceton gelöst, erwärmt und mit 15 c.c. n/4-NaOH versetzt. Völlige Lösung wird gegeben

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(1) Es sei erwähnt, dass der Versuch zur Lösung der Stärke in Mannit etwas früher von Dr. A. Nishimura, meinem Kollegen unternommen wurde.

(2) So scheint mir, dass von den Alkoholen nur die mit sekundären Alkoholgruppen die Stärke (in denen auch dieselben Gruppen vorhanden sind) auflösen können.

durch Erwärmen einige Min. auf dem Wasserbade, und überschüssiges Natron mit n/10-HCl titriert.

0.1562 gr. Subst. verbrauchten 6.52 c.c. n/4-NaOH. Gef.: $CH_3CO=44.8$ %. Ber. für $C_6H_7O_5$ $(CH_3CO)_3$: $CH_3CO=44.8$ %.

Molekulargewicht: Ebullioskopisch in Aceton bestimmt. Konz. 4.6-9.2 %. Gef. Mol.-Gew. 4000-6000.

$[\alpha]^{18}_{D}=3.17° \times 100/1.937 \times 1=164°$ (in Chloroform).

Verseifung: 2 gr. Triacetylstärke werden in 20 c.c. heissem Aceton gelöst und 14 c.c. 2n-NaOH hinzugefügt, Verseifungsprodukt sofort abgeschieden. Dies wird in Wasser gelöst. Die Lösung wird filtriert, mit Essigsäure neutralisiert, in Methylalkohol gegossen, und das ausgeschiedene Produkt mit Methylalkohol gekocht, zentrifugiert und getrocknet. Etwas hygroskopisches, weisses Pulver, löslich in Wasser; die Lösung ist schwach opalescierend, scheidet bei längerem Stehen einen wolkigen Niederschlag ab, wie die Amyloselösung, reduziert nicht und färbt sich mit Jodlösung prachtvoll blau.

$[\alpha]^{15}_{D}=2.46° \times 100/1.300 \times 1=189°$ (in Wasser).

Depolymerisierte Triacetylstärke. 20 gr. getrocknete Kartoffelstärke wurden mit 30 gr. Glycerin und 5 gr. Chlorzink vermischt und durch 25 Min. langes Erhitzen auf 180–190° unter Kneten verkleistert, und nach dem Erkalten 150 c.c. Essigsäureanhydrid zugegeben. Während der Acetylierung wurde die Temperatur auf 70–80° gehalten (1.5 Stdn.). Ausbeute 95%. Diese Triacetylstärke ist in verschiedenen Lösungsmitteln leichter löslich als die oben angegebene Triacetylstärke und ihre Lösungen sind weniger zähe und leichter filtrierbar. Schmp. 141–144° (korr.).

Anal. 0.2068 gr. Subst. gaben 0.3787 gr. CO_2 und 0.1028 gr. H_2O. Gef.: C=49.94; H=5.56 %. Ber. für $C_6H_7O_5$ $(CH_3CO)_3$: C=49.98; H=5 60 %. Asche 0.1 %.

0.2100 gr. Subst. verbrauchten 8.90 c.c. n/4-NaOH. Gef.: $CH_3CO=45.5$ %. Ber. für $C_6H_7O_5$ $(CH_3CO)_3$: $CH_3CO=44.8$ %.

Molekulargewicht: Ebullioskopisch in Aceton bestimmt. Konz. 5.6-8.8%. Gef. Mol.-Gew. 3100-3200.

$[\alpha]^{12}_{D}=2.26° \times 100/1.550 \times 1=146°$ (in Chloroform).

Verseifungsprodukt: Etwas hygroskopisches, weisses Pulver, löslich in Wasser. Die Lösung reduziert nicht und färbt sich mit Jod blau-violett.

$[\alpha]^{18}_{D}=2.70° \times 100/1.460 \times 1=185°$ (in Wasser).

Unvollständig acetylierte Acetylstärke. 20 gr. getrocknete Weizenstärke (Merck) wurden mit 30 gr. Glycerin und 2 gr. Chlorzink vermischt und durch 15 Min. langes Erhitzen auf 160–165° unter Kneten gelöst und nach dem Erkalten mit 140 c.c. Essigsäureanhydrid versetzt. Temperatur auf 70–80° gehalten (1 Stde.). Die entstandene, fast klare Lösung, die viskoser und schwerer filtrierbar war als die bei der Darstellung des Acetylderivats aus Kartoffelstärke, wurde in Wasser gegossen, das Produkt in Wasser zerrieben und getrocknet. Ausbeute 32 gr. Reinigung wie vor. Weisses Pulver, welches mit Vorsintern gegen 190° (korr.) unscharf schmilzt. Löslich in Eisessig, Chloroform, Pyridin, Aceton, Essigester u.a. aber die Lösungen sind schwach trübe.

0.1590 und 0.1724 gr. Subst. verbrauchten respektive 6.40 und 6.98 c.c. n/4-NaOH. Gef.: $CH_3CO=43.4$ und 43.5 %. Ber. für $C_6H_7O_5(CH_3CO)_3$: $CH_3CO=44.8$ %. Ber. für $C_6H_8O_5(CH_3CO)_2$: $CH_3CO=34.9$ %.

0.2024 gr. Subst. gaben 0.3664 gr. CO_2 und 0.1034 gr. H_2O. Gef.: C=49.37; H=5.71%. Ber. für $C_6H_7O_5(CH_3CO)_3$: C=49.98; H=5.60 %. Ber. für $C_6H_8O_5(CH_3CO)_2$; C=48.78; H=5.73 %. Asche 0.2 %.

Ebullioskopie in Aceton: Keine messbare Erhöhung wurde beobachtet.

$[\alpha]_D^{15}=2.99° \times 100/1.755 \times 1=170°$ (in Chloroform).

Verseifungsprodukt: Weisses Pulver, löslich in Wasser. Die Lösung ist opalescierend, reduziert nicht und färbt sich mit Jod blau.

$[\alpha]_D^{15}=0.82° \times 100/0.432 \times 1=190°$ (in Wasser).

Zur Auflösung der Stärke in Alkoholen. Die Stärke löste sich bei 150–160° in geschmolzenem Erythrit ziemlich reichlich (etwa 10%) unter Bildung eines halbdurchsichtigen Kleister. In geschmolzenem Mannit löste sich die Stärke, wenn auch auf 180–190° erhitzt, beträchtlich schwerer; eine trübe Gallerte wurde gebildet. In Äthylenglykol, auf 190° 20 Min. erhitzt, quoll die Stärke in geringem Masse; die obere stehende, klare Flüssigkeit wurde mit Jodlösung schwach rot-violett gefärbt. In Methylalkohol, selbst wenn auf 185° 1.5 Stdn. im geschlossenen Gefäss erhitzt, wurde die Stärke weder gelöst noch aufgequollen.

Es ist mir eine angenehme Pflicht, Herrn Prof. T. Soda für sein wohlwollendes Interesse an diesen Arbeiten meinen besten Dank auszusprechen.

Chemisches Institut, Kaiserliche Universität zu Tokyo.

KOLLOIDES CHROMSAURES CHROMOXYD. BILDUNGSMÖGLICHKEIT AUF DER KATHODE BEI DER ELEKTROLYTISCHEN REDUKTION DER CHROMSÄURE.

Von Shiro TAKEGAMI.

Eingegangen am 30. Mai 1929. Ausgegeben am 28. Juli 1929.

Bei der elektrolytischen Abscheidung des Chroms aus wässrigen Chromsäure-Lösungen spielt nach den Ergebnissen verschiedener Untersuchungen

Chromsaures Chromoxyd insofern eine wichtige Rolle, als es durch Reduktion der Chromsäure an der Kathode entstanden, letztere in Gestalt eines Films oder Diaphragmas überziehen und dadurch die weitere Reduktion der Chromsäure unterbinden soll. Das Festhaften dieses Films auf der Kathode, seine semipermeable Natur, die ihn nur für Wasserstoffionen durchlässig macht und anderes mehr, lassen sich kaum anders erklären, als durch eine kolloide Beschaffenheit. Es war deshalb von Interesse, unter welchen Bedingungen kolloides Chromichromat entsteht und wie es sich verhält.

Bei der Elektrolyse konzentrierter wässriger Lösungen der Chromsäure, wie sie zwecks Abscheidung vom metallischen Chrom ausgeführt wird, findet stets neben der Metallbildung die Reduktion zu Cr(3) statt gemäss

$$H_2CrO_4+2H_2O-3F=Cr^{\cdot\cdot\cdot}+6OH' \ldots\ldots\ldots\ldots \quad (1)$$

ein Vorgang, der an der Anode—wenigstens wennsie aus Blei besteht—wieder rückgängig gemacht wird. Es bildet sich mit der Zeit ein angenähert konstantes Verhältnis von Cr (3): Cr (6) heraus, wobei die Lösung sauer bleibt. Wie besondere, später mitzuteilende Versuche gezeigt haben, ist unter solchen Verhältnissen das Cr (3) wesentlich als $Cr^{\cdot\cdot\cdot}$ in Lösung, und diese enthält nicht, wie vielfach behauptet wird, kolloides Chromichromat. Cr (3) und Cr (6) bilden erst dann einen schwer löslichen Niederschlag, wenn die Lösung nicht mehr sauer, wenn das Verhältnis Cr (3): Cr (6) 1:1.5 ist, was zu einer basischen Verbindung führen muss.

Um zu sehen bis zu welchem Verhältnis Cr(3): Cr (6) man bei der Reduktion der Chromsäure kommen kann, ohne dass ein Niederschlag entsteht, und von welchem Verhältnis ab die Lösungen kolloiden Charakter haben, wurden wässrige Lösungen von Chromsäure mit überschüssigem Aethylalkohol versetzt, wobei sich die Reaktion nach folgender Gleichung abspielt:

$$2H_2CrO_4+3CH_3CH_2OH=2Cr^{\cdot\cdot\cdot}+6OH'+2H_2O+3CH_3CHO \ldots \quad (2)$$

Um den Fortschritt der Reaktion zu verfolgen, wurden von Zeit zu Zeit Proben entnommen und in ihnen das Verhältnis Cr(3) zu Cr(6) bestimmt. Da die verwendeten Lösungen sehr konzentriert waren, wurden jeweils 10 c.c. auf 1 Liter verdünnt und davon je 20 c.c. zur Analyse entnommen.

Zwecks Ermittelung des Gesamtchroms(1) (Cr(3)+Cr(6)) wurde mit Alkohol und Schwefelsäure auf dem Wasserbad eingedampft, mit starker

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(1) Wegen der Anwesenheit des Alkohols musste diese umständliche Bestimmung angewendet werden.

Kalilauge gelöst und nach Hahn⁽¹⁾ mit Ferricyankalium titriert. Um den Gehalt an Cr (3) zu finden, wurde die Lösung unter Zusatz von Ammoniumnitrat mit Ammoniak schwach alkalisch gemacht, das ausgefällte Chromhydroxyd in Kalilauge gelöst und ebenfalls nach Hahn mit Ferricyanid titriert.

Der Zusatz des Alkohols zur Chromsäurelösung erfolgte langsam unter Kühlen.

Vers. 1.

Ansatz: 40 gr. CrO_3, 100 gr. H_2O, 60 gr. Alkohol.

Stunden nach Ansatz	C.c. $K_3Fe(CN)_6$		Cr(3)/Cr(6)	Bemerkung
	für Cr(3)	für Cr(6)		
5	5.70	13.85	1:1.43	Lösung klar
26	7.90	13.80	1:0·75	,,
47	9.55	13.80	1:0.53	,,
52	—	—	—	Lösung gelatiniert
120	7.25	10.10	1:0.39	

Die Lösung wurde mit der Zeit immer tiefer braunrot. Da das 52 Stunden gelatinierte Produkt sich nicht vollständig in Wasser löste, wurde von einer Dialyse abgesehen und ein Ansatz mit verdünnterer Chromsäure gemacht,

Vers. 2.

Ansatz: 20 gr. CrO_3, 140 gr. Wasser, 40 gr. Alkohol.

Stunden nach Ansatz	C.c. $K_3Fe(CN)_6$		Cr(3)/Cr(6)	Bemerkung
	für Cr(3)	für Cr(6)		
1/4	4.10	13.3	1:2.2	Lösung klar
27	6.65	13.25	1:0.99	,,
93	8.20	13.25	1:0.62	,,
117	8·75	13.30	1:0.52	,,
124	1 Stunde auf 50° erwärmt			
125	8.80	13.25	1:0.505	,,
148	8.85	13.30	1:0.503	,,

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(1) *Z angew. Chem.*, **40** (1927), 349.

Nach Erreichung des Verhältnisses Cr(3): Cr(6) 1:0.5 hörte die Reduktion praktisch auf. Eine Fällung mit K_2SO_4 konnte nicht beobachtet werden. Die Lösung wurde nun mit der zweifachen Menge destillierten Wassers versetzt und im destillierten Wasser, zunächst in Pergamentpapier 4 Tage, und anschliessend im Kollodiumbeutel der Dialyse unterzogen. Dabei gingen grosse Mengen Lösung heraus. Erst nach 3 tägigem Verbleiben im Kollodiumbeutel hörte dieses auf. Die klare, so erhaltene braune Lösung liess sich nun durch K_2SO_4 fällen. Das Verhältnis Cr(3): Cr(6) war stark angestiegen und betrug 1:0.203.

Der nächste Versuch mit demselben Ansatz zeigt, dass bei Anwendung höherer Temperatur auf längere Zeit die Reduktion der Chromsäure noch etwas weiter getrieben werden kann.

Vers. 3.

Ansatz: 20 gr. CrO_3, 140 gr. Wasser, 40 gr. Alkohol.

Stunden nach Ansatz	C.c. $K_3Fe(CN)_6$		Cr(3)/Cr(6)	Bemerkung
	für Cr(3)	für Cr(6)		
19	—	—	—	2 Std. auf 50°C.
114	9.05	13.25	1:0.464	
137	—	—	—	2 Std. auf 50°C.
141	9.55	13.25	1:0.384	
170-185	—	—	—	Lösung koaguliert
187	8.35	11.7	1:0.413	

Die koagulierte Lösung löste sich in Wasser unter Verbleib einer geringen Trübung. Diese Lösung war fast unempfindlich gegen K_2SO_4; erst nach 6 Stunden trat durch reichliche Mengen Fällung auf. Die Gallerte wurde mit der 2 fachen Mengen Wasser gelöst und im Kollodiumbeutel der Dialyse unterzogen, bis nichts mehr in das Aussenwasser überging, was ähnlich lange dauerte, wie bei Vers. 2. Das Verhältnis Cr(3): Cr(6) war durch die Dialyse wieder stark gestiegen. Es betrug 1:0.229. K_2SO_4 fällte sofort.

Die nach der Dialyse verbleibenden Sole der Versuche 2 und 3 (Sol 2 und 3 genannt) hiterlassen beim langsamen Verdunsten auf dem Uhrglas zunächst eine lackartige Haut, die unter dem Mikroskop keine besondere Struktur erkennen lässt und beim weiteren Trocknen staubförmig wird. Der Rückstand löst sich nicht wieder in Wasser.

Gegen Erhitzen zum Sieden waren sie beständig. Beim Abkühlen auf 8°C. und Wiedererwärmen blieb der grösste Teil als flockiger Niederschlag ungelöst.

Sol 2 ist vollständig klar durchsichtig, Sol 3 dagegen, welches aus der koagulierten Lösung hergestellt war, zeigte schwache Opaleszenz. Sol 3 zeigte im Ultramikroskop Teilchen, Sol 2 nur einen hellen Kegel mit einer kleinen Zahl von Teilchen.

Ihr Verhalten gegen K_2SO_4 verschiedener Konzentration ergibt sich aus folgender Uebersicht. Es wurden jeweils 10 c.c. Sol mit 10 c.c. Kaliumsulfatlösung verschiedener Konzentration versetzt. Die dadurch entstehende Konzentration an K_2SO_4 findet sich in der ersten Vertikalreihe verzeichnet.

Tabelle 1.

Konzentration an K_2SO_4	Sol 2	Sol 3
1/100	Flocken	Flocken
1/200	,,	,,
1/250	,,	,,
1/300	,,	keine Flocken
1/400	,,	,,
1/500	,,	,,
1/600	keine Flocken	,,

Unter dem Einfluss eines elektrischen Potentialgefälles wandert das Kolloid nach der Kathode. Der sich hier abscheidende gallertartige Körper haftet nicht fest und löst sich nicht wieder in Wasser. Das Verhältnis Cr(3) : Cr(6) ist in ihm noch weiter gestiegen-auf 1:0.159, was aber wohl auf eine reduzierende Wirkung des Stromes zurückzuführen sein wird. Die gefällten Produkte lösen sich in den n/2—Lösungen von KOH und H_2SO_4 und selbst in 20% iger Chromsäure nur langsam.

Um zu sehen, wie weit ein solches Sol konzentriert werden kann, versuchte ich, Sol 3 auf dem Wasserbad einzudampfen. Dabei schied sich aber an der Oberfläche eine nicht wieder lösbare Haut ab. Ich verdampfte deshalb das Wasser im Vakuum bei 50°C. unter gutem Rühren. Dabei wurde erreicht, dass das Sol, welches ursprünglich 8.249 gr. Cr im Liter enthielt, auf 18.40 gr./Liter stieg. Das so konzentrierte Sol stellt bei 25°C. eine klare Flüssigkeit vor, welche aber, längere Zeit auf 20°C. gehalten, gelatinös erstarrt, um beim sofortigen Erwärmen wieder flüssig zu werden.

Die gelatinöse Struktur verschwindet beim verdünnen mit Wasser. Hatte das gelatinierte Sol indessen 3 Monate gestanden, so war es durch Erwärmen nicht mehr zu verflüssigen. Tabelle 2 enthält Daten über das Verhältnis Cr (3) : Cr (6), Leitfähigkeit und Zähigkeit der beiden Sole verschiedener Konzentration.

Tabelle 2.

Konzentration des Sols gr. Cr/Liter	Cr(3) : Cr(6)	Spez. Leitfähigkeit $\varkappa^{25°}$	Zähigkeit $\eta^{25°}$
8.249	1:0.229	0.0002639	0.01522
18.409	1:0.218	0.0009443	0.3046

Sol 3 wurde dann noch auf sein Verhalten verschiedenen Elektrolyten gegenüber untersucht. Die Resultate bringt Tabelle 3.

Tabelle 3.

Elektrolyte	Kritische Fällungskonzentration
KCl	beständig
KNO_3	,,
K_2SO_4	1/250–1/300 n
K_2CrO_4	1/1250–1/1500 n
Na_2HPO_4	1/20–1/25 n
$K_4Fe(CN)_6$	1/1500–1/1750 n

Zum Schluss sei noch eine Messungsreihe an demselben Ansatz wie bei Vers. 2 und 3 mitgeteilt, aus dem die mit fortschreitender Reaktion zwischen Chromsäure und Alkohol auftretenden Änderungen nicht nur des Verhältnisses Cr (3) : Cr (6), sondern auch der Zähigkeit und spez. Leitfähigkeit nebst dem ultramikroskopischen Befund zu erkennen ist.

Auch hier zeigt sich, wie bei Versuch 3, dass die Reduktion durch den Alkohol bei einem Verhältnis Cr (3) : Cr (6) von etwa 1:0.4 halt macht. Etwa bei diesem Verhältnis tritt unter diesen Konzentrationsbedingungen Koagulation auf. Mit dem Fortschritt der Reduktion sinkt die spez. Leitfähigkeit und steigt die Zähigkeit. Bei einem Verhältnis Cr (3) : Cr (6) 1:0.5 treten nach dem ultramikroskopischen Befund Anzeichen des kolloiden Zustandes auf, obgleich eine Fällung durch K_2SO_4, wie oben erwähnt, noch

Vers. 4.

Ansatz: 20 gr. CrO_3, 140 gr. Wasser, 40 gr. Alkohol.

Stunden nach Ansatz	Cr (3) : Cr (6)	Spez. Leitf. $\varkappa=\frac{1}{\omega}C$ $C=0,33584$	Zähigkeit(1) $\eta=\eta_0\frac{st}{s_0t_0}$	Ultramikr. Befund
1	1:2.15	0.01702	0.02069	keine Teilchen wahrnehmbar
4	30 Minuten auf 50° erwärmt			
21	1:0.772	0.00883	0.02168	„
23	60 Minuten auf 50° erwärmt			
26	1:0.606	0.00721	0.02272	„
28	60 Minuten auf 50° erwärmt			
45	1:0.514	0.00536	0.02808	schwach heller Kegel
47	60 Minuten auf 50° erwärmt			
51	1:0.415	0.00434	0.0520	heller Kegel mit wenig Teilchen
52	30 Minuten auf 50° erwärmt			
69	1:0.407	0.00395	0.085	zahlreiche Teilchen
72	10 Minuten auf 50° erwärmt			
73	1:0.401	0.00371	0.177	„
Zwischen der 75 und 92 Stunde trat Koagulation auf.				

nicht zu beobachten ist. Die Lösung enthält offenbar noch Elektrolyte, als welche nur $Cr^{\cdots}$ und CrO_4'' in Betracht kommen können. Dies zeigt der hohe Wert der spez. Leitfähigkeit der nach 73 Stunden entstandenen Lösung, und der geringe der Zähigkeit im Vergleich mit dem konzentrierten Sol der Tabelle 2; obgleich die Konzentration des Chroms in Vers. 4 etwa 50 gr. Cr/Liter, die des konzentrierten Sols in Tabelle 2 nur 18.4 gr. Cr/Liter ist, sind die Zähigkeitswerte 0.177 und 0.304. Dies zeigt auch der Umstand, dass bei der Dialyse unter Entfernung grosser Mengen von Chromverbindungen im verbleibenden Sol das Verhältnis Cr (3) : Cr (6) bis auf 1:0.2 steigt.

Welcher Art nun die im Sol enthaltene kolloide Verbindung ist, lässt sich nicht angeben, jedenfalls handelt sich um eine solche stark basischer Natur. In einer Verbindung $Cr_2(CrO_4)_3$ ist das Verhältnis Cr (3) : Cr (6) 1:1.5 in einer $(Cr(OH)_2)_2\ CrO_4$ 1:0.5. Dem im dialysierten Sol enthaltenen Verhältnis 1:0.2 ist durch eine Formel schwer Rechnung zu tragen, obgleich sich Verbindungen wie

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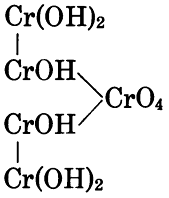
(1) η_0: Zähigkeit des Wassers bei 25°C. = 0.00894. t_0 u. S_0: Ausflusszeit und spez. Gew. bei Wasser, bei 25°C. = 0.99707.



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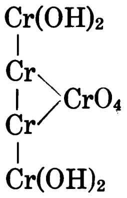

denken lassen.

Jedenfalls folgt, da erst Lösungen mit einem Verhältnis Cr(3) : Cr (6) >0.5 kolloide Eigenschaften zeigen, dass bei der Elektrolyse der Chromsäure an der Kathode kolloides chromsäures Chromoxyd nur dann entstehen kann, wenn hier alkalische Reaktion herrscht. Diese Möglichkeit erscheint aber durchaus gegeben zu sein. Denn bei der Reduktion der Chromsäure nach Gleichung 1 entstehen $3OH'$ mehr als zur Fällung des gleichzeitig gebildeten $Cr^{\cdots}$ als $Cr(OH)_3$ nötig sind.

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

Institut für Elektrochemie und physikalische Chemie,
März 1929. Dresden, Deutschland.

SINOMENINE AND DISINOMENINE. PART X.(1)
ON SYNTHESIS OF DIMETHYLSINOMENOL AND ON SINOMENOL-CHINONS.

By Kakuji GOTO and Hideo SUDZUKI.

Received June 21, 1929. Published July 28, 1929.

Sinomenol was first obtained by one of the authors (K.G.) from sinomenine by heating it with 66% potash at 180° for 1–2 hours. It was determined to be dioxy-dimethoxy-phenanthrene, from the analysis of the substance as well as of its derivatives. Moreover, dimethylsinomenol was obtained by the Hofmann's decomposition of sinomenine through caustic alkali and dimethyl-sulphate, diacetyl-sinomenol by the acetolysis, and dibenzoyl-sinomenol by the fusion with benzoyl-anhydride of sinomenine. As regards the relative position of the hydroxyl and methoxyl groups, K.G. assumed, from the colour reactions of sinomenol and of sinomenine, that sinomenol must be 3, 4- dimethoxy -5, 6- dioxy-phenanthrene. But, as was already cited, Kondo and Ochiai's synthesis of dimethylsinomenol after Pschorr's method proved that it is 3, 4, 6, 7-tetramethoxy-phenanthrene.

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(1) This Bulletin, **4** (1929), 103. Part IX will be published later.

The present authors have repeated the synthesis of dimethylsinomenol and could verify Kondo and Ochiai's result. Considering the closely analogous colour reaction of sinomenol and 3-methoxy —4, 6— dioxy-phenanthrene against ammoniacal silver in acetone solution, sinomenol itself may be regarded to be 3, 7- dimethoxy —4, 6— dioxy-phenanthrene.

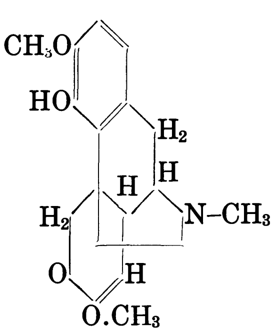
By way of this investigation, four chinons from sinomenol derivatives were prepared and ascertained as phenazines. These are summarized in the following table.

	M.p.	M.p. of phenazine
Sinomenol-chinon	259–263°	272°
Diacetyl- ,, ...	217–219°	255°
Diethyl- ,, ...	174°	188°
Dimethyl- ,, ...	266°	184°
Dibenzoyl- ,, ...	213°	254°

NOTE BY KAKUJI GOTO.

On the Revised Formula of Sinomenine. The synthesis of dimethylsinomenol necessitated to revise the provisional constitutional formula of sinomenine, which I advanced four years ago, chiefly on the ground of the colour reaction of sinomenine and sinomenol.

As sinomenine gives a strong diazo-reaction (sensitiveness 1:2,000,000), it is clear that the free phenol hydroxyl must lie in position 4. This position may be kept in sinomenol and hence the one methoxyl group in 3. The close analogy of the colour reaction of sinomenol and 3-methoxy -4, 6-dioxy-phenanthrene against ammoniacal silver in acetone solution leaves no doubt that the second phenol hydroxyl must lie in position 6 and hence the second methoxyl group in 7. This deduction is further supported by the fact that dihydro-sinomenine is transformed into d-form of Speyer's dihydro-thebainon by the reduction of Na-amalgam. From these reasons, as well as those, which will be enumerated afterwards, I should like to assign to the sinomenine $C_{19}H_{23}NO_4$ the following constitution.



This constitutional formula is somewhat similar to one which was proposed by Kondo and Ochiai two years ago, but there is a fundamental difference between them. For, in my formula, the double linkage is taken in C_7–C_8, regarding sinomenine to be an enol-ether and to the linking position of ethanamine chain C_{13} is selected decidedly.

The chief reasons, which let the author to assign C_7–C_8 position to the double linkage and C_{13} to the attaching point of the ethanamine group, will be explained in the following. The experimental data of the compounds here concerned will be published in the next communication.

(A) In contrary to the supposition of Kondo and Ochiai, sinomenine is not an optical antipode of a hypothetical 7-methoxy-thebainone.

1. Sinomenine dissolves yellow in dilute caustic alkali; this indicates that the double linking is conjugated with the ketone group. But, sinomenine does not give the halochromie with conc. hydrochloric acid. The double linking of sinomenine thus seems not to be in the same position with that of thebainone.

2. Sinomenine is far more easily decomposed by acetic anhydride than thebainone. This fact can not be explained, if we assume the same linking point of the ethanamine chain in sinomenine and in thebainone.

3. By boiling sinomenine with 66% alkali or by its acetolysis only the amine isolated hitherto was methyl-ethyl-amine, whereas ethanol-amine or its condensation product was met with in the same decomposition of thebainone. This fact also suggests that the constitution of the third nucleus in these two alkaloids is different.

(B) From the following three facts, the double linking of sinomenine is assumed to situate between C_7–C_8.

1. It was recently found that the double linking of sinomenine could be reduced with Zn-amalgam and hydrochloric acid or with Zinc and hydrochloric acid, both in the cold. The product is dihydro-sinomenine. This fact clearly indicates that sinomenine is an α, β-unsaturated ketone.

2. By the reduction with Na-amalgam, sinomenine gives a bimolecular substance, each molecule losing one methoxyl group at the same time. The linking of the two molecules of this kind was sometimes met with in α, β-unsaturated ketone, as Harries and Müller have first noticed. The linking point was determined to be β-position in relation to the ketone group in case of coumarine by Asahina and Fujita.(1)

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(1) Asahina and Fujita, *J. Pharm. Soc. Japan*, No. 444 (1919), 97.

3. By heating sinomenine with 2N hydrochloric acid on a steam-bath for 2 hours and liberating the base with caustic ammonia, the author could isolate a bimolecular substance, which contained one methoxyl group less in each sinomenine molecule. The new ketone group, which must have been introduced by the hydrolysis of the enol-ether seems to cause the condensation of the two molecules of the substance newly formed, as is the case with diacetyl.*

(C) The C_{13} position for ethanamine chain was selected by the following reasons:

1. In the reaction, where sinomenol or its derivative is formed, the ethanamine chain of sinomenine is very easily removed. This fact indicates, as R. Robinson and Rucizka have often remarked, that the chain is attached to the tertiary carbon atom.

2. If sinomenine has thus two hydrogen atoms on C_5, then the ketone group in C_6 may enolise rather easily. Although the author can not yet prepare this substance with sinomenine itself, yet the desazoted substance, which was given on p. 168, Proc. Imp. Acad. 2 (1926) and afterwards proved to be bimolecular, is a tetramethoxy derivative, in spite of the fact that its side-chain is preserved.

3. Sinomenine seems to form a piperonyliden derivative, but the scanty yield and the difficulty of its purification makes the author to defer the investigation for future.

Experimental.

Synthesis of Dimethyl-sinomenol. This need not to be given in details, since it was carried out exactly in the same manner with Pschorr's original method. Only the melting point and yield of intermediates may be here summarily given.

(1) Acetvanillin (83%), m.p. 77°.
(2) Nitro-acetvanillin (78%), m.p. 85°.
(3) 2-Nitro-vanillin (65%), m.p. 138°.
(4) 2-Nitro-veratrumaldehyd (65%), m.p. 65°.
(5) Veratrumaldehyde (85%), m.p. 42°.

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* Pechmann, *Ber.*, **21** (1888), 1417.

(1), (2), (3), (4), Pschorr and co-workers, *Ber.*, **32** (1899), 3407.

(5) Rosemund, *Ber.*, **43** (1910), 3415. Without heating.

(6) Azlacton of 3, 4-dimethoxy-phenylacetic acid (49%).
(7) 3, 4-Dimethoxy-phenyl-pyruvic acid (75%).
(8) Homoveratric acid (85%), m.p. 88°.
(9) 6-Br-veratrum-aldehyde (80%), m.p. 149°.
(10) Azlacton of 3, 4-dimethoxy-6-brom-phenyl-acetic acid (73%), m.p. 211°.
(11) 3, 4-Dimethoxy-6-bromphenyl-pyruvic acid (78%), m.p. 217°.
(12) 6-Brom-homoveratric Acid (90%), m.p. 113°.

(4)+(8) makes

(13) α-[3, 4-Dimethoxy-phenyl]-2-nitro-3, 4-dimethoxyl-cinnamic acid (48%), m.p. 193°.
(14) α-[3, 4-Dimethoxy-phenyl]-2-amino-3, 4-dimethoxy-cinnamic acid (86%), m.p. 146°.

For (15) and (16) see further down.

(17) 3, 4, 5, 6-Tetramethoxy-phenanthrene-9-carbonic acid (6%), m.p. 240°.
(18) α-[3, 4-Dimethoxy-6-bromphenyl]-2-nitro-3, 4-dimethoxy-cinnamic acid (45%), m.p. 216–218°.
(19) α-[3, 4-Dimethoxy-6-brom-phenyl]-2-amino-3, 4-dimethoxy-cinnamic acid (85%), m.p. 189°.
(20) 8-Brom-3, 4, 5, 6-tetramethoxyl-phenanthrene-9-carbonic acid (27%), m.p. 190°.
(15) 3, 4, 6, 7-Tetramethoxy-phenanthrene-9-carbonic acid (13%), m.p. 210°.

Anal. Found: C=67.05; H=5.21%. Calc. for $C_{19}H_{18}O_6$: C=66.66; H=5.26%.
Methoxyls. Found: 36.68%. Calc. for 4 CH_3O-: 36.25%.

Decarboxylation of this substance was carried out by heating it in a sealed tube with glacial acetic acid at 230° for 20 hours.

(16) 3, 4, 6, 7-Tetramethoxy-phenanthrene (24%), m.p. 123°—125°.

Admixture with the dimethylsinomenol originated from sinomenine did not lower the melting point.

Anal. Found: C=72.88; H=5.86%. Calc. for $C_{18}H_{18}O_4$: C=72.48; H=6.04%.
Methoxyls. Found: 41.79. Cal. for 4 methoxyls: 41.61%.

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(6), (7), (9), (10), (11), Pschorr and co-workers, *Ann.*, **391** (1912), 33.

(8), (12), Perkins and co-workers, *J. Chem. Soc.*, 1925, 1693. Compare Kondo and Ochiai, *Ann.*, **470** (1929), 247.

Picrate. m.p. 124–125°. Admixture with dimethyl-sinomenol picrate (m.p. 124–128°) melted at 128°.

Anal. Found: N=7.88%. Calc. for $C_{24}H_{21}O_{11}N_3$: N=7.96%.

(21) 3, 4, 5, 6-Tetramethoxy-phenanthrene-9-carbonic acid. Prepared by reducing its 8-brom-derivative by Wohl's method.

Yield 50%. m.p. 240°. By decarboxylation, no crystalline substance was obtained.

Anal. Found: C=66.85; H=5.32%. Calc. for $C_{19}H_{18}O_6$: C=66.66; H=5.26%.
Methoxyls. Found: 36.87%. Calc. for $4CH_3O-$: 36.25%.

Sinomenol-chinon. Prepared by the hydrolysis of diacetyl-sinomenol-chinon in alcoholic solution with caustic soda in an atmosphere of hydrogen. Purified through ethyl-acetate. Brown needles of m.p. 259–263°. Yield scanty.

Anal. Found: C=63.97; H=3.99%. Calc. for $C_{16}H_{12}O_6$: C=64.00; H=4.00%.
Methoxyls. Found: 21:06%. Calc. for $2CH_3O-$: 20.66%.

This chinon gives the sinomenol reaction.

Sinomenol-chinon-phenazine. Prepared by ordinary method. m.p. 272.° Yield not very small.

Anal. Found: N=7.56%. Calc. for $C_{22}H_{16}O_4N_2$: N=7.52%.

Diacetyl-sinomenol-chinon. Prepared by the oxidation of diacetyl-sinomenol in glacial acetic acid by chromic acid. Purified through ethyl acetate. Orange red needles. Yield 10%. m.p. 217–219°.

Anal. Found: C=62.21; H=4.36%. Calc. for $C_{20}H_{16}O_8$: C=62.50; H=4.16%.
Methoxyls. Found: 16.06%. Cal. for $2\ CH_3O-$: 16.14%.

Diacetyl-sinomenol-chinon-phenazine. Yellow needles of m.p. 256°.

Anal. Found: N=5.83%. Calc. for $C_{20}H_{20}O_6N_2$: N=6.14%.

Diethyl-sinomenol-chinon. Prepared by the ethylation of the hydrolysed dibenzoyl-sinomenol-chinon with diethyl sulphate and caustic soda. Orange red needles of m.p. 174°. Yield 40%.

Anal. Found: C=67.76; H=5.59%. Calc. for $C_{20}H_{20}O_6$: C=67.41; H=5.61%.
Methoxyls. Found: 17.43%. Calc. for $2CH_3O-$: 17.41%.

Diethyl-sinomenol-chinon-phenazine. Yellow needles of m.p. 188°.

Anal. Found: N=6.06%. Calc. for $C_{20}H_{24}O_4N_2$: N=6.54%.

Dimethyl-sinomenol-chinon. Prepared in the same manner as diethyl sinomenol-chinon. Recrystallised from hot ethyl acetate, its forms beautiful red needles collected in rosettes.

Anal. Found: C=65.72; H=4.92%. Calc. for $C_{18}H_{16}O_6$: C=65.85; H=4.87%.
Methoxyls. Found: 37.31 %. Calc. for $4CH_3O-$: 37.80 %.

Dimethyl-sinomenol-chinon-phenazine. M.p. 184°; yellow needles.

Anal. Found: N=7.42 %. Calc. for $C_{24}H_{20}O_4N_2$: N=7.00%.

Dibenzoyl-sinomenol-chinon.(1) Prepared by the oxidation of dibenzoyl-sinomenol. Stout, cinnober red prism of m.p. 211°, yield 30%.

Anal. Found: C=75.48; H=5.27%. Calc. for $C_{30}H_{24}O_6$: C=75.00; H=5.00%.

Dibenzoyl-sinomenol-chinon-phenazine. Yellow needles of m.p. 254°, yield 70%.

Anal. Found: N=5.5 %. Calc. for $C_{36}H_{24}O_6N_2$: N=4.83%.

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(1) See, *Journal of the Agricultural Chemical Society of Japan*, **1** (1925), No. 5.

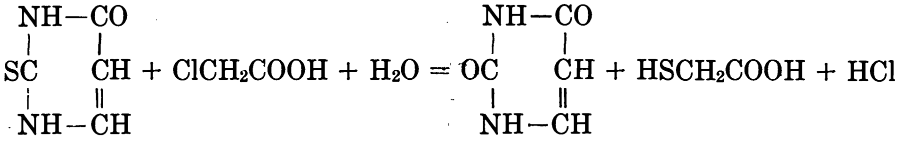
CHEMISTRY OF THIO-CHOLINE HALIDE (TRIMETHYL THIO-ETHYL AMMONIUM HALIDE). NEW THIO-CHOLINE BROMIDE AND ITS DERIVATIVES. I.

By Taichi HARADA.

Received June 22, 1929. Published August 28, 1929.

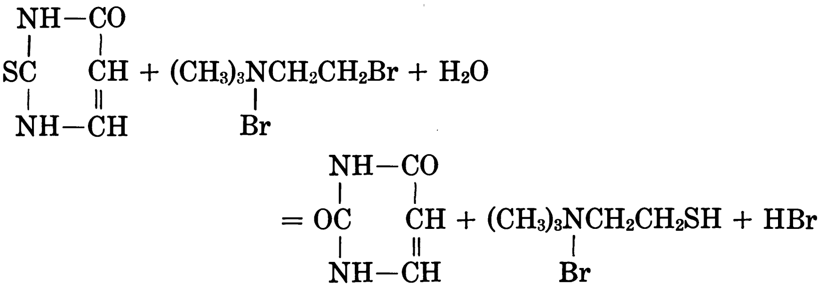
In 1882 Nencki and Sieber⁽¹⁾ obtained 4-methyl-2-thio-uracil by the condensation of thio-urea and acetic ester. List⁽²⁾ has shown that 4-methyl-2-thio-uracil gives 4-methyl uracil, when heated with concentrated hydrochloric acid for a few hours at 150°—160° C.

Recently Wheeler and Bristol⁽³⁾ have found that when 2-thio-uracil, like other compounds of this class, is boiled with an aqueous solution of chloracetic acid, in slight excess, sulphur is easily removed with the formation of uracil and thio-acetic acid, the reaction being in accordance with the following equations:



$$\begin{array}{ll}\text{NH}-\text{CO} & \\ | \qquad | & \\ \text{SC} \quad \text{CH} & \\ | \qquad \| & \\ \text{NH}-\text{CH} & \end{array} + \text{ClCH}_2\text{COOH} + \text{H}_2\text{O} = \begin{array}{ll}\text{NH}-\text{CO} & \\ | \qquad | & \\ \text{OC} \quad \text{CH} & \\ | \qquad \| & \\ \text{NH}-\text{CH} & \end{array} + \text{HSCH}_2\text{COOH} + \text{HCl}$$

This reaction gives an important means for the replacement of the halogen atom by the —SH group. This exchange takes place with more difficulty between 4-methyl-2-thio-uracil and bromo-choline bromide than between 2-thio-uracil and the bromide. Almost the theoretical yields of the corresponding uracils were obtained. The reaction may be formulated as follows, for example, in the case of 2-thio-uracil:



$$\begin{array}{ll}\text{NH}-\text{CO} & \\ | \qquad | & \\ \text{SC} \quad \text{CH} & \\ | \qquad \| & \\ \text{NH}-\text{CH} & \end{array} + \begin{array}{l}(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{Br} \\ \;| \\ \text{Br}\end{array} + \text{H}_2\text{O}$$

$$= \begin{array}{ll}\text{NH}-\text{CO} & \\ | \qquad | & \\ \text{OC} \quad \text{CH} & \\ | \qquad \| & \\ \text{NH}-\text{CH} & \end{array} + \begin{array}{l}(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{SH} \\ \;| \\ \text{Br}\end{array} + \text{HBr}$$

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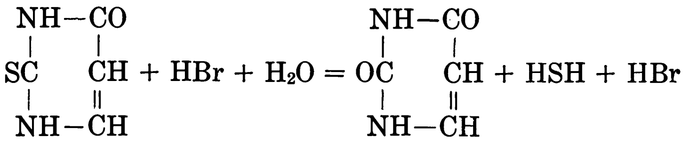
(1) *J. Prakt. Chem. N. F.*, **25** (1882), 72; Behrend, *Ann.*, **229** (1885), 13.

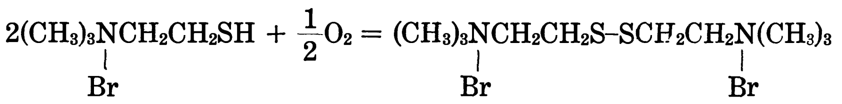
(2) List, *Ann.*, **236** (1886), 18.

(3) *Am. Chem. J.*, **33** (1905), 458.

However, quantitative thio-choline bromide was not obtained, owing to partial formation of the following reaction and also formation of its oxidation product; the disulphide, ammonium bromide and a silver derivative of the compound in the following purification method.

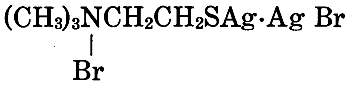


The compound is very hygroscopic in nature, and is very soluble in both alcohol and water. The compound is easily oxidized on heating with hydrobromic acid yielding the disulphide.



$$2\underset{\text{Br}}{(CH_3)_3\overset{}{N}}CH_2CH_2SH + \frac{1}{2}O_2 = \underset{\text{Br}}{(CH_3)_3N}CH_2CH_2S\text{-}SCH_2CH_2\underset{\text{Br}}{N(CH_3)_3}$$

Its decomposition begins slowly at above 220°C., On continuous heating it boils at 243°C. (uncorr.) with a dark brown coloration. The isoelectric point of this compound was found to be P_H 7.00 by the colorimetric method.⁽¹⁾ It is interesting to note that the compound with an excess of silver oxide resulted in a solution containing a strong base, which on neutralizing with hydrobromic acid, gave an insoluble, white asbestos-like crystalline salt. This salt decomposes into silver bromide and the original type of compound on boiling with a strong acid. The mechanism of the formation was not clear. However, it appears to be the following formula:



$$\underset{\text{Br}}{(CH_3)_3N}CH_2CH_2SAg\cdot AgBr$$

It decomposes slowly at above 211°C., and melts and boils at 214°C. (uncorr.) with a dark brown coloration, similar to thio-choline bromide. The base, in a brown syrup, on drying was supposed to be a hydroxyl compound containing silver bromide in the same molecule. With acid the aqueous solution precipitates silver bromide. This subject was not studied further.

Experimental Part.

2-Thio-uracil. The sodium salt of ethyl formylacetate was prepared according to Wislicenus' directions⁽²⁾ as follows: 42 gr. metallic sodium dis-

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(1) Clarke, "The determination of hydrogen ions," (1925).
(2) *Ber.*, **20** (1887), 2931.

solved in 500–600 c.c. of dry ether containing 150 gr. of ethyl formate and 150 gr. of ethyl acetate. The solution was kept cool with running water. The reaction took place slowly at the beginning and later it became more or less violent, the solution becoming turbid and light brown in color. This was permitted to stand over night and the condensation product was filtered through filter paper. The yellow powder-like substance, $NaOCH=CHCOOC_2H_5$, was obtained, washed with ether and dried in a dessicater. It yielded about 100 gr. 75 gr. of this salt was treated with 25 gr. of thiourea according to Wheeler and Bristol(1) in saturated aqueous solution form. After standing in the cold one hour, it was heated on the steam bath for a short time, and then cooled. A yellowish white precipitate weighing about 25 gr. was separated by acidifying with acetic acid. It was crystallized from ammonium hydroxide by boiling with a small quantity of "norit" to decolorize it. A portion of this material was crystallized from water until it was obtained in colorless monoclinic plates. When heated, it effervesces at above 300°C. It is difficultly soluble in water and alcohol but its solubility increases by heating the solvents. A second run, for the preparation of this material was carried out according to Wheeler and Liddle(2) as follows: 70 gr. of saturated aqueous thio-urea solution was added directly to the condensation product, $NaOCH=CHCOO-C_2H_5$, in the ethereal solution, instead of powdered form, as in the preceding case. About 70 gr. of 2-thiouracil was obtained by this method.

Bromo-choline bromide. This compound(3) was prepared according to the directions of Hutckiss(4) by the condensation of trimethylamine with ethylene bromide. Trimethylamine (b.p. 3.5°C.) was generated by dropping a saturated solution containing 30 gr. of trimethylamine hydrochloride slowly into granulated sodium hydroxide. The evolved gas dried over KOH, was liquefied at a low temperature by means of ice and salt and collected in a cooled pressure bottle containing 50 gr. of redistilled ethylene bromide at 130°C. and 15 c.c. of toluene. The toluene was added merely to prevent the condensation product forming in a hard cake. The pressure bottle was corked tightly, placed in an iron frame and allowed to come slowly to room temperature. The bottle was placed in a water bath and the temperature raised gradually to about 50°C. and held at this temperature for three hours or more. Upon cooling, the product was removed, and recrystallized from hot 95% alcohol, then washed with ether. It yielded about 55 gr. Its decomposition begins at 235°C., and melts and boils at 238°C.

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(1) *Am. Chem. J.*, **33** (1905), 458.
(2) Wheeler and Liddle, ibid., **40** (1908), 547.
(3) Krüger and Bergell, *Ber.* **36** (1903), 2901.
(4) Thesis, Now York University, 1926.

Thio-choline bromide. One molecular proportion, or slightly an excess, 9.6 gr. of bromo-choline bromide, was mixed with one molecular proportion 5 gr. of 2-thio-uracil or 5.5 gr. of 4-methyl-2-thio-uracil⁽¹⁾ in powdered state. This was sealed with 25 c.c. of water in a closed tube or pressure bottle whose capacity was about 150 c.c. The pressure bottle was framed with an iron cage and heated in an oil bath. In order to get a complete reaction it was found necessary to heat it for more than two hours at around 150°C. or in the case of 4-methyl-2-thio-uracil for several hours at around 170°C. At these temperatures the mixtures became a transparent yellowish colored solution. On cooling, uracil deposits almost quantitatively. About 4.2 gr. of uracil and 4.3 gr. of 4-methyl-uracil were obtained respectively. In these reactions, a considerable amount of hydrogen sulphide was evolved. In order to purify this compound, the mixture of reaction products was washed down into a beaker with 95% alcohol, then filtered with suction to remove the uracil and the other unreacted insoluble substances. The filtrate was evaporated down to about 30 c.c. on the steam bath, then cooled with ice for a while, and then filtered again to remove further impurities. The filtrate was made up to about 300 c.c. with water. The solution thus obtained was slightly yellow in color and strongly acidic owing to the formation of hydrobromic acid in the reaction.

It was neutrallized with a base, such as ammonium hydroxide, or carefully with silver oxide, until the solution became slightly acidic. However, an excess of silver oxide leads to the formation of a double salt of silver derivative of thio-choline bromide and silver bromide, as an insoluble white asbestos-like crystalline substance. Therefore, the solution was treated with the amount of silver oxide obtained from about 6.6 gr., (one molecular proportion) or slightly less, to the HBr acid formed in the above reaction of silver nitrate with sodium hydroxide, and then filtered. The filtrate was light yellow in color. In order to remove further colored impurities it was on some occasions heated with 0.5 gr. of "norit" for a short time and filtered. With evaporation on the steam bath, and cooling, it gave colorless crystals. It may be re-crystallized out from hot butyl alcohol by repeating with or without a small amount of 95% alcohol. In this way an average of about 1.5 gr., or 19% of thio-choline bromide was obtained as beautiful colorless transparent monoclinic plates. It decomposes slowly at above 220°C. On continuous heating it boils at 243°C. with a dark brown coloration. If the temperature is maintained at 234°C. it also gives the same results using paraffin as the liquid for heating the bath.

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(1) The author wishes to express his thanks to Dr. R.R. Renshaw for his kindness in supplying this material.

10 c.c. of 0.005 N. (0.2%) solution of this compound, with water of P_H 6.80, or with water having P_H 7.20, containing a trace of NaOH, gave the same P_H value, 7.00. Likewise with water of P_H 7.00, there was no change in its value, using bromo-thymol blue as the indicator.

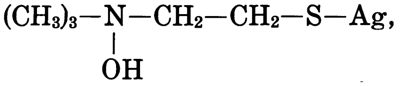
The compound is very hygroscopic in nature, 0.2314 gr. of the dried substance over P_2O_5 increased to 0.2326, 0.2339 and 0.2352 gr. respectively after one, two and three hours standing in the air.

Anal. Subst.=0.2314, 0.2010; AgBr=0.2173, 0.1891 gr. Subst.=0.2163 (Carius' method); $BaSO_4$=0.2541 gr. Found: Br=39.92, 40.07; S=16.14%. Calc. for $C_5H_{14}NSBr$: Br=39.94; S=16.02%.

Disulphide. When thio-choline bromide was heated for a prolonged period with hydrobromic acid, the disulphide was formed, which is a slightly yellowish colored syrup and is hygroscopic in nature. It does not form any silver derivative and is a less ionizable substance than thio-choline bromide in aqueous solution. It may be purified with butyl alcohol.

Anal. Subst.=0.2286; AgBr=0.2148 gr. Found: Br=40.27%. Calc. for $C_{10}H_{26}N_2S_2Br_2$: Br=40.20%.

Silver derivatives. The formation of a silver derivative of thio-choline bromide usually occurred, when the strongly acidic bromide solution was treated with an excess of silver oxide and was brought back to a neutral or slightly acidic point with HBr acid in alcoholic solution, as stated before. The compound is an insoluble white asbestos-like crystalline substance. It becomes brown in color at above 211°C., and on continuous heating, melts and boils at 214°C. with a dark brown coloration. The compound, like silver bromide, is slightly soluble in ammonium hydroxide but is insoluble in acid and alcohol. The compound was also obtained when pure thio-choline bromide solution was treated with silver oxide and hydrobromic acid, as before. However the compound of the basic type,



$$(CH_3)_3-\underset{\displaystyle OH}{\underset{|}{N}}-CH_2-CH_2-S-Ag,$$

was not isolated.

The compound precipitated silver bromide completely on boiling with strong acid such as hydrobromic, nitric acid, etc.

The following analytical results were obtained by the following methods.

1. The substance was decomposed by strong hydrobromic acid on boiling, into silver bromide. It was found that the filtrate did not precipitate silver bromide on heating with concentrated nitric acid.

Anal. Subst. = 0.2095; AgBr. = 0.1601 gr. Found: AgBr = 76.42%. Calc. for $C_5H_{13}NSAg_2Br_2$: AgBr=75.91; S=6.48%.

2. The compound was decomposed by nitric acid on boiling. The filtrate did not give silver bromide with silver nitrate solution.

Anal. Subst. = 0.2252, 0.2088; AgBr = 0.1703, 0.1582 gr. Found: AgBr = 75.62, 75.77%.

3. Carius' method.

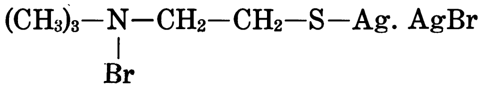
Anal. Subst. = 0.2874; AgBr = 0.2178; $BaSO_4$ = 0.1377 gr. Found: AgBr = 75.78; S = 6.57%.

Summary.

1. Thio-choline bromide was prepared by heating bromocholine bromide with 2-thio-uracil or 4-methyl-2-thio-uracil with water in a closed tube or pressure bottle at 150° and 170°C. for two and five hours respectively. The compound is hygroscopic in nature, and is very soluble in both alcohol and water. It decomposes at 243°C. on heating. Its isoelectric point was found to be 7.00.

2. By heating with hydrobromic acid the compound is easily oxidized to its disulphide, which is a syrupy and less pronounced ionizable substance, in aqueous solution.

3. On treating an aqueous solution of this compound, with an excess of silver oxide, and neutrallizing with hydrobromic acid and heating on the steam bath, an insoluble white asbestos-like crystalline substance was formed. It appears to be the following formula:



$$(CH_3)_3-\underset{\substack{|\\ \mathrm{Br}}}{N}-CH_2-CH_2-S-Ag.\ AgBr$$

The compound is slightly soluble in alkaline solution. It decomposes at 214°C.

In conclusion the author wishes to express his appreciation to Prof. Renshaw of New York University, who suggested this researth, for his advice rendered during this investigation.

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ON THE THERMAL DECOMPOSITION OF FATTY PRIMARY ALCOHOLS.

By Kozo KASHIMA.

Received June 26, 1929. Published August 28, 1929.

M. Berthelot⁽¹⁾ studied the thermal decomposition of ethyl alcohol in 1851. Since then many works on the line have been done by many different researchers. The main reactions may be expressed by the following formulas:

$R.CH_2OH = R.CHO + H_2$, ... (1)
$R.CH_2OH = R'\!:CH_2 + H_2O$, and .... (2)
$2R.CH_2OH = (R.CH_2)_2O + H_2O$. .... (3)

Also the effects of many kinds of the catalysts on the reaction have been studied. Some of them having intimate relations with the present experiment may be mentioned as references. Sendrens⁽²⁾ perceived the formation of methyl ether and water by passing methyl alcohol upon alumina heated at 300-350° and Inoue⁽³⁾ reported the formation of ethylene, carbon dioxide and para-formaldehyde by passing the alcohol with air or carbon dioxide upon heated Japanese acid clay.

Ethylene and water were produced from ethyl alcohol by passing the alcohol on aluminium oxide at 400°,⁽⁴⁾ while ethyl ether and water were produced by using alumina heated at 240-260° on the reaction.⁽⁵⁾ When Japanese acid clay was used as the catalyst on the reaction, ethylene, ethyl ether, ester and aldehyde were produced⁽⁶⁾; the catalyst was used in the manufacture of ethylene in a semi-industrial scale.⁽⁷⁾

n-Propyl alcohol behaves similar to ethyl alcohol on the reaction. On passing upon aluminium oxide heated at 560°, n-propyl alcohol gave propylene and water as the decomposition products⁽⁸⁾; and propyl ether was the additional product to the above ones, when the reaction was conducted under high temperature and pressure.⁽⁹⁾

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(1) *Ann. chim. phys.*, [3] **33** (1851), 295; *Ann.*, **81** (1852), 108.
(2) *Compt. rend.*, **148** (1909), 928; *Bull. soc. chim.*, [4] **5** (1909), 480.
(3) This Bulletin, **1** (1926), 197.
(4) Sabatier and Mailhe, *Compt. rend.*, **146** (1908), 1376; **147** (1908), 106.
(5) Sendrens, *Compt. rend.*, **148** (1909), 228; *Bull. soc. chim.*, [4] **5** (1909), 480.
(6) Inoue, this Bulletin, **1** (1926), 198.
(7) Kashima, Mihara and Takahashi, Japanese Patent, 81,337 (1929).
(8) Ipatiew, *Ber.*, **36** (1903), 1997.
(9) Ipatiew, *Ber.*, **37** (1904), 2997.

LeBel and Greene⁽¹⁾ obtained a mixture of two butylenes by dropping n-butyl alcohol upon strongly heated zinc chloride and Sendrens⁽²⁾ gained the mixture by passing the alcohol on aluminium phosphate.

Lemoine⁽³⁾ proved the formation of n-amylene by passing n-amyl alcohol upon a coal (*braise de boulanger*) heated at 430°.

From the above results and others, the reactions may be summarised as follows: When aliphatic primary alcohols are thermally decomposed, aldehyde are formed after dehydrogenation and olefines or ethers after dehydration. And the formation of ethers seems to occur at lower temperature than that of olefines.

It was presumed, from the standpoint of thermochemistry, that ethers were produced firstly in the thermal decomposition of the alcohols and then they were further decomposed into olefines and water. The writer therefore attempted to make clear the mechanism of the thermal decomposition of the alcohols by using Japanese acid clay as the catalyst and methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols as the materials.

The heat effects, Q_1, Q_2, and Q_3, in the following three reactions, (4), (5) and (6), may be calculated by the succeeding three formulas, (7), (8) and (9), respectively:

$$2R.CH_2OH=(R.CH_2)_2O+H_2O+Q_1, \quad \text{(4)}$$
$$R.CH_2OH=R':CH_2+H_2O+Q_2, \text{ and} \quad \text{(5)}$$
$$(R.CH_2)_2O=2R':CH_2+H_2O+Q_3. \quad \text{(6)}$$
$$Q_1=(\text{ether})+(\text{water})-2\,(\text{alcohol}), \quad \text{(7)}$$
$$Q_2=(\text{olefine})+(\text{water})-(\text{alcohol}), \text{ and} \quad \text{(8)}$$
$$Q_3=2\,(\text{olefine})+(\text{water})-(\text{ether}). \quad \text{(9)}$$

Where, (ether), (water), (alcohol) and (olefine) represent the heats of formation of ethers, water, alcohols, and olefines, respectively.

The heats of formation of organic compounds are intensively described in Berthelot's work⁽⁴⁾ or in Stohmann's papers.⁽⁵⁾ But those of the five alcohols and ethers and the four olefines mentioned in this paper are not given by a series of the experiment and there are some differences according to the authors. J. Thomsen's values are therefore adopted from his work⁽⁶⁾

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(1) *Amer. Chem. J.*, **2** (1880), 24.

(2) *Compt. rend.*, **144** (1907), 1110; *Bull. soc. chim.*, [4] **1** (1907), 692.

(3) *Bull. soc. chim.*, [4] **3** (1908), 940.

(4) "Essai de mécanique chimique," I, p. 406. Paris, Dunod, 1879.

(5) *Z. physik. Chem.*, **6** (1890), 334.

(6) "Thermochemistry," translated by K.A. Burke, pp. 369, 467, etc. London, Longman, Green & Co., 1908.

and those not obtained experimentally are calculated by his formulas. Those values and the calculated Q_1, $2Q_2$ and Q_3 are given in Table 1;

Table 1.

Substance	Heat of formation, Cal.	Q_1, Cal.	$2Q_2$, Cal.	Q_3, Cal.
Methyl alcohol	50.58	—	—	—
Dimethyl ether	48.19	4.67	—	—
Ethyl alcohol	57.02	—	—	—
Diethyl ether	67.43	11.03	—	—
Ethylene	−3.29	—	−5.34	−16.37
n-Propyl alcohol	63.66	—	—	—
Di-n-propyl ether	76.37	16.54	—	—
n-Propylene	2.06	—	−7.92	−4.76
n-Butyl alcohol	69.51	—	—	—
Di-n-butyl ether	90.39	18.86	—	—
n-Butylene	6.49	—	8.94	9.90
n-Amyl alcohol	74.64	—	—	—
Di-n-amyl ether	104.41	22.52	—	—
n-Amylene	12.43	—	10.56	12.06

The thermal effect, Q_1, in the case of ether-formation is always larger than $2Q_2$ and Q_3. It is therefore assumed that when the alcohols are passed over the heated Japanese acid clay, corresponding ethers are firstly produced and then the ethers decompose into olefines and water by the further action of the heated clay. Figs. 2, 3 and 4 show the mutual quantitative relations between the decomposition products at different reaction temperatures from ethyl, propyl and butyl alcohols; that the amounts of olefines and water produced increase with the rise in the reaction temperature, while that those of ethers and alcohols in the decomposition products decrease with the rise in temperature will sufficiently explain the above assumption.

The Japanese acid clay used as the catalyst in the experiment is produced in the Province of Niigata, giving the following analytical result:

Table 2.

Composition of Japanese Acid Clay, per cent.

H_2O	Loss on ignition	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
10.15	5.28	63.78	5.94	14.63	0.48	0.82

The clay is well mixed with about 80 per cent. water and pressed through a 8-mesh sieve obtaining prisms having wrinkles on the sides. They are dried at 100°, cut into cubes and filled in a combustion tube of 15 mm. diameter to the length of 450 mm., the weight of the clay being about 55 grams. The glass tube is inserted into a porcelain tube to be heated electrically. The clay is previously heated in the glass tube at about 350–400° for getting rid of water and for making active. When the clay thus treated attains a desired temperature, a sample is gradually dropped into a space in one end of the glass tube from a burett, which vaporises and is decomposed by the heated clay. A Liebig condenser, a special receiver for liquid and a gas-holder are attached to the other end of the tube. When the reaction is completed, the products in the receiver and the gas-holder are analysed. In the case of methyl alcohol, a washing bottle containing concd. sulphuric acid is inserted between the receiver and the gas-holder for absorbing methyl ether produced by the reaction, which will naturally also absorb one part of the olefine, though it is not desired.

Generally, when the alcohols are passed over heated Japanese acid clay, corresponding ethers, olefines, aldehydes, water and sometimes esters are produced as the decomposition products. The amounts of olefines increase with the rise in the reaction temperature, which is shown in Fig. 1. Above a certain temperature the amounts of olefines and water become almost constant, which shows the steady progress of the reaction.

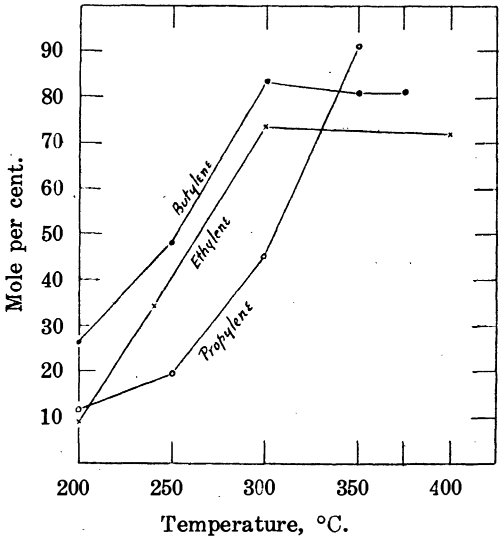

Fig. 1.

The double bond of the olefine produced belongs to the carbon atom linked with the hydroxyl group:

$$R.CH_2.CH_2OH \longrightarrow R.CH:CH_2.$$

However, in the case of n-butyl alcohol, the olefine produced is a mixture of ethyl ethylene ($C_2H_5.CH:CH_2$) and dimethyl ethylene ($CH_3.CH:CH.CH_3$), the latter being predominated (cf. Table 15). It may be assumed that the former is produced firstly and is changed into the latter stable form by the moving of the double bond by the further action of the heated clay. LeBel and Greene(1) and Sendrens(2) obtained the mixture by dropping n-butyl alcohol upon heated zinc chloride or passing the alcohol over aluminium phosphate, which may be ascribed to the same cause. The ratio of the two olefines varies according to the reaction temperature, dimethyl ethylene being 2–6.5 times of ethyl ethylene.

The amounts of ethers in the decomposition products decrease with the rise in the reaction temperature and almost zero at high temperature (cf. Figs. 2, 3 and 4). They also decrease as the molecular weights of the alcohols increase. From the fact that the values of Q's are proportional to the molecular weights of the alcohols, the degree of olefine-formation from ethers will become easier according to the increasing molecular weights.

It may also be mentioned that esters are produced at generally low temperature. In the case of ethyl alcohol, the ester is formed in comparatively larger amount than the cases of the other alcohols.

Methyl Alcohol. Pure methanol of Merck free from aldehyde and distilled over quick lime is used as the material, boiling point of which being 65°. As the general procedure throughout the series, the alcohol is gradually dropped into a space of one end of the reaction tube previously heated at a certain temperature and the decomposition products are collected in a receiver and a gas-holder attached to the other end of the reaction tube through a Liebig condenser. In the case of methyl alcohol, a washing bottle containing concd. sulphuric acid is inserted between the receiver and the gas-holder. The gas produced is analysed according to the ordinary method. The identification of the olefine is generally done through its bromide. After testing some qualitative properties of the liquid part of the decomposition products, it is fractionally distilled with caution and the each fraction is examined by proper methods.

The experimental conditions, the decomposition products and the analytical results are summarised in Tables 3, 4 and 5:

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(1) Loc. cit.

(2) Loc. cit.

Table 3.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Increase of weight of H_2SO_4-bottle, gr.	C_nH_{2n} yield, mole %
				Liquid, gr.	Gas, L.		
1	51.3	200	0.4	19	0.5	29	0.51
2	41.8	200	0.4	24	0.5	15	0.62
3	149.0	270	0.6	130	1.0	11	—
4	64.0	270	0.5	26	0.5	19	—
5	46.0	270	0.9	18	0.8	19	0.65
6	135.1	400	0.4	64	12.7	60	1.18
7	83.0	400	0.4	36	5.4	9	1.73

Table 4.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
1	36.2	1.7	0	11.2	12.8	18.8
2	36.4	2.2	0	10.0	7.5	23.7
3	—	—	—	—	—	—
4	—	—	—	—	—	—
5	26.3	0	0.4	11.9	22.4	22.6
6	8.8	3.2	15.5	1.2	37.6	33.7
7	18.6	2.8	10.0	1.4	30.9	36.3

Table 5.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Aldehyde
1	31.6	52.6	0.09
2	52.1	25.0	0.09
3	74.2	9.2	—
4	59.6	26.9	0.07
5	27.2	63.9	0.06
6	32.8	56.3	0.40
7	31.7	60.6	0.68

A bromide obtained by carefully passing the gas of No. 5 into bromine water is washed, dried and distilled, two fractions being obtained. The one boils at 130–131° and the other at 140–141°. The former boiling point corresponds to that of ethylene dibromide and the latter to that of propylene dibromide. The olefine obtained is therefore a mixture of ethylene and propylene.(1)

When the sulphuric acid solution of the 7th column of Table 3 is dropped into about same amount of water, a colourless gas is produced. The gas collected over mercury dissolves into water and condenses into a colourless liquid by introducing it into a small U-tube loosely filled with glass-wool and cooled at -35°, the liquid boils at -23.5°. It is therefore dimethyl ether.

When methyl alcohol is passed over Japanese acid clay heated at 400°, a small amount of crystalline mass condensed at the inlet part of the Liebig condenser, which melted at 162-163°, after purified from alcohol, it will therefore be hexamethyl benzene.(2)

In No. 7, a washing bottle containing water is used instead of a sulphuric acid one, which resulted the increasing percentages of olefine, carbon monoxide and hydrogen in the produced gas.

Ethyl Alcohol. Pure ethyl alcohol is used after distilling over quick lime and silver oxide, boiling point of which being 78°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 6, 7 and 8 and the mutual relation of the main products (in percentages to the sample) is shown in Fig. 2:

Table 6.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %
				Liquid, gr.	Gas, L.	
8	43.3	200	0.12	28	4.5	6.81
9	37.4	200	0.13	23	2.3	3.69
10	44.6	200	0.14	31	2.0	3.27
11	86.2	200	0.11	58	9.2	8.68
12	56.8	240	0.19	30	11.5	21.51
13	57.0	240	0.18	25	11.0	21.02
14	48.7	300	0.13	19	22.6	46.46
15	54.6	300	0.15	22	22.6	43.21
16	51.6	400	0.17	20	23.5	45.83
17	42.9	400	0.12	18	17.4	41.42

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(1) LeBel and Greene, loc. cit.

(2) LeBel and Greene, loc. cit.

Table 7.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
8	52.4	0.1	0.7	9.6	1.8	3.2
9	47.8	0.5	1.2	11.2	1.3	3.0
10	58.4	0.6	0.8	9.4	4.2	6.2
11	64.9	3.2	0.3	7.2	3.8	8.6
12	84.9	3.6	0.3	3.7	2.2	3.1
13	87.0	2.0	0.4	3.4	2.3	3.7
14	80.0	5.5	0.2	10.9	1.0	2.4
15	83.4	5.2	0.2	6.2	1.4	3.6
16	80.4	6.1	0.4	7.3	3.3	2.5
17	81.6	5.0	0.2	9.3	1.5	0.8

Table 8.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Ether	Aldehyde	Ester
8	41.4	14.6	42.1	0.16	0.89
9	33.0	10.4	36.5	0.56	0.43
10	35.8	11.6	37.1	0.40	0.32
11	30.0	8.6	31.0	0.34	0.17
12	31.7	37.0	15.3	0.17	0.16
13	40.8	47.2	12.0	0.19	0.60
14	2.6	92.1	trace	0.09	—
15	2.7	92.7	0	0.05	—
16	trace	96.0	0	0.10	—
17	trace	94.4	0	0.06	—

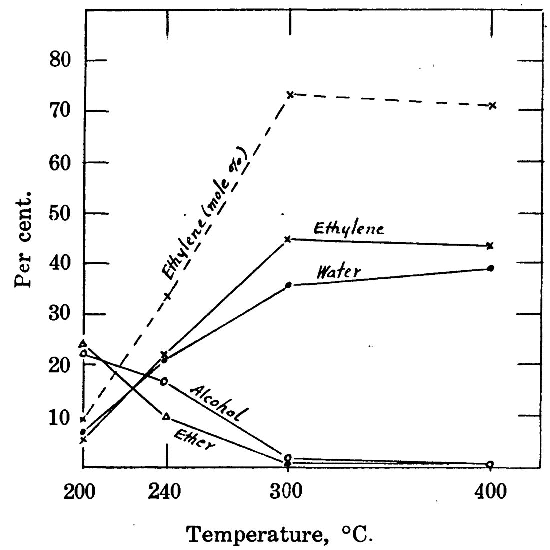

Fig. 2.

The amounts of the gas, ethylene and water produced increase with the rise in temperature and they become almost constant at above 300°. The purity of ethylene increases also with the rise in temperature. The amounts of ether and of the remaining undecomposed alcohol in the decomposition products decrease as the temperature rises.

As stated above, the above facts prove that ether is firstly produced in the reaction when the temperature is not high, one part of which being decomposed into ethylene and water, but it is almost completely changed into ethylene and water as the temperature rises and the reaction proceeds in the same mode.

n-Propyl Alcohol. Pure n-propyl alcohol of Eastman Kodak Co. was used after purifying with distillation, boiling point of which being 94°. The experimental conditions, the decomposition products and the analytical results of the products are summarised in Tables 9, 10 and 11 and the mutual relation of the main products (in percentages to the sample) is shown in Fig. 3:

Table 9.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Propylene yield, %
				Liquid, gr.	Gas, L.	
18	80.8	200	0.75	70	10.5	5.6
19	80.5	200	0.76	68	5.8	11.0
20	151.0	250	1.67	118	14.0	14.7
21	111.0	300	1.23	63	22.4	32.5
22	53.0	350	0.75	12	19.0	65.2

Table 10.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
18	23.0	0	0.2	17.0	6.0	7.2
19	81.5	7.4	0.2	3.7	2.0	1.3
20	84.0	—	—	—	—	—
21	86.0	—	—	—	—	—
22	97.0	0	1.8	1.1	—	—

Table 11.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Ether	Aldehyde	Ester
18	77.6	3.5	12.9	0.17	+
19	68.2	7.8	17.7	0.19	+
20	79.7	5.2	3.5	0.24	—
21	46.5	—	—	—	—
22	8.3	84.2	2.5	0.09	—

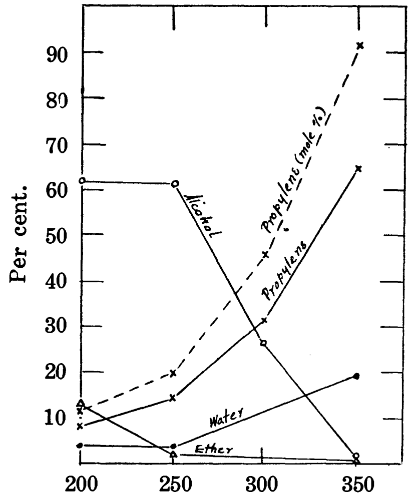

Fig. 3.

The amounts of the gas and of propylene produced increase with the rise in temperature. When the reaction temperature is not high, the amount of n-propyl ether in the decomposition products is large, but small at higher temperature. The purity of propylene increases as the reaction temperature rises, it being 97 per cent. at 350°; the method is therefore applied to the preparation of the olefine, the yield being about 93 per cent.

n-Butyl Alcohol. Pure n-butyl alcohol of Eastman Kodak Co. was used after distillation, boiling point of which being 117°. The experimental conditions, the decomposition products and the analytical results of the products are summarised in Tables 12, 13 and 14 and the mutual relation of the main products (in percentages to the sample) is shown in Fig. 4.

Table 12.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Butylene yield, %
				Liquid, gr.	Gas, L.	
23	193.0	200	0.40	165	18.3	19.9
24	48.2	250	0.40	25	7.5	36.1
25	49.9	250	0.42	28	7.8	36.8
26	64.3	300	0.53	23	16.5	62.3
27	46.6	300	0.39	15	12.8	65.1
28	51.5	350	0.47	16	13.1	60.6
29	45.0	350	0.47	14	11.8	60.6
30	52.3	370–380	0.44	16	13.5	60.9
31	48.2	370–380	0.40	14	12.3	60.4

Table 13.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2
23	83.7	0	0	3.0
24	92.7	0	0	1.6
25	94.2	0	0	1.2
26	96.9	0	0.4	0
27	94.7	0	0	1.1
28	95.2	0.9	0.8	1.8
29	92.4	0	0	2.0
30	94.2	0	0	1.3
31	96.1	0	0	0.8

Table 14.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Ether	Aldehyde	Ester
23	67.0	29.2	1.2	0.37	trace
24	38.5	45.5	trace	—	trace
25	54.1	42.4	trace	—	—
26	12.7	65.6	0	—	—
27	16.7	70.0	0	—	—
28	14.1	48.4	0	—	—
29	11.6	67.0	0	—	—
30	15.6	65.6	0	—	—
31	17.3	68.6	0	—	—

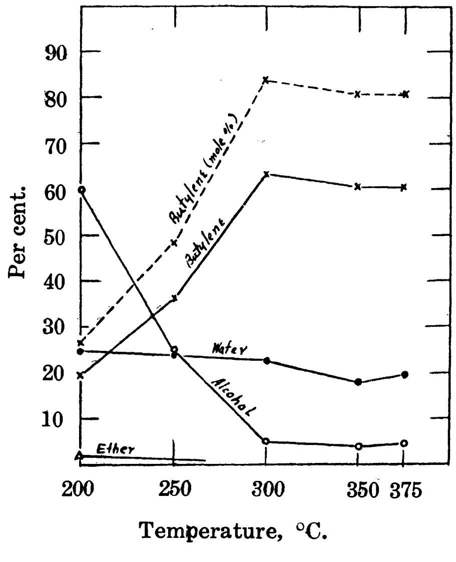

Fig. 4.

When bromine is reacted carefully at low temperature, the produced gas absorbs it. The dibromide thus obtained is washed, dried and fractionally distilled, the result being shown in Table 15:

Table 15.

Composition of Butylene Dibromide, per cent.

No.	Reaction temperature	Low-boiling fraction	α-Compd.	β-Compd.	β/α
24	250	10.2	12.8	76.9	5.9
25	250	3.8	19.2	76.9	3.9
26	300	10.0	12.0	78.0	6.5
27	300	3.1	21.8	75.0	3.4
28	350	9.6	25.8	64.5	2.5
29	350	11.7	11.7	76.4	6.5
30	370–380	8.6	30.4	60.9	2.0
31	370–380	12.7	12.7	74.5	5.9

In each case, the gas is therefore a mixture of dimethyl ethylene and ethyl ethylene; the former being about 2–6.5 times of the latter. This fact shows that the latter is produced first and is changed into the former by the action of the heated clay:

$$CH_3.CH_2.CH{:}CH_2 \longrightarrow CH_3.CH{:}CH.CH_3$$

The amounts of butylenes increase with the rise in temperature and become almost constant at above 300°. The amounts of ether and of butyl alcohol in the products decrease as the temperature rises. It is therefore assumed that the reaction proceeds steadily at above 300°.

n-Amyl Alcohol. Pure n-amyl alcohol of Kahlbaum is used after distillation, boiling point of which being 137–138° and $n_D^{13.8}$: 1.415. The experimental conditions and the decomposition products are shown in Table 16.

Table 16.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition Products		Amylene yield, %
				Liquid, gr.	Gas. L.	
32	66	260–270	0.33	55	5.2	32.0

The liquid part of the decomposition products was of two layers, the lower one was water containing a small amount of amyl alcohol. The upper layer was fractionally distilled with care first under ordinary pressure and then under reduced one, three fractions being obtained. The first boils at 35–39°, from which n-amylene is isolated, the dibromide of which boils at 187-189°. The second boils at 138-139° ($n_D^{13.8}$: 1.417) and is undecomposed amyl alcohol. And the third boils at 68-71°/12 mm. ($n_D^{13.8}$: 1.430) and is di-n-amyl ether. The above result and the gas-composition are shown in Table 17.

Table 17.

Composition of the Products.

No.	Gas, volume per cent.				Liquid, per cent.			
	C_nH_{2n}	CO_2	CO	O_2	Alcohol	Water	Ether	Amylene
32	1.6	0	0.85	15.85	14.2	19.5	4.5	38.4

June, 1929. Tokyo.

ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART I. SILVER CYANIDE COMPLEX RADICAL.

By Kosaku MASAKI.

Received July 8, 1929. Published August 28, 1929.

As early as 1904 it was stated by Richard Lucas,(1) Morgan,(2) and Kunschert(3) that when a silver salt is dissolved in a cyanide solution, the molal ratio of combined cyanide to silver is usually two to one, though sometimes one to one, corresponding to the formulas $Ag(CN)_2^-$ and $AgCN^-$. In the literature generally, even in recent text books, the complex ion is

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(1) *Z. anorg. Chem.*, **41** (1904), 193.

(2) *Z. physik. Chem.*, **17** (1865), 513.

(3) *Z. anorg. Chem.*, **41** (1904), 359.

almost universally given as $Ag(CN)_2^-$. This may be due to the fact that the simplest of the double salts of potassium cyanide and silver cyanide is $KAg(CN)_2$.

Kunschert assumed that the e.m.f. of the concentration cell of copper cyanide in potassium cyanide solution was solely due to the difference in KCN concentration. It is probable, however, that at least an equally important source of potential difference in silver ion concentration was produced through the equilibrium $Ag(CN)_2^- \rightleftarrows Ag^+ + 2CN^-$ by the change in concentration of cyanide.

The works of Kunschert, Morgan and Richard Lucas are only necessary for me to add that their experiment were not well adapted to revealing the composition of the complex ion in solution.

Bonner and Kaura⁽¹⁾ found that in KCN solutions saturated with CuCN the ratio of bound cyanide is always three and the ratio of KCN to CuCN is therefore two instead of 2.5.

Bonner and Kaura determined the ratio of bound cyanide by simple titration method. I tried with this method to determine the ratio of bound cyanide about silver complex ion.

Composition of the silver cyanide ion. In order to determine the ratio of combined cyanide to silver in the complex ion, I have employed a simple titration method. Varying quantities of the desired silver salt were dissolved in 100 c.c. portions of an approximately moral sodium cyanide solution. The "free" cyanide which was not combined with silver to form the complex ion, was determined by titrating with silver nitrate solution using potassium iodide to facilitate the detection of the end point. The difference between the total cyanide, as determined in the original sodium cyanide solution, and the free cyanide in a particular sample, gave the amount of cyanide combined with the silver to form the complex ion. The result are summerized in the following tables.

Table 1.

Sodium Cyanide and Silver Cyanide.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.4660	0.0000	—
0.2061	0.2389	1.21
0.1422	0.1571	1.12
0.1031	0.1089	1.05
0.0770	0.0791	1.02
0.0559	0.0591	1.04
0.0301	0.0289	0.98

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(1) *Chem. Met. Eng.*, **34** (1927), 84.

Table 2.

Sodium Cyanide and Silver Chloride.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.1868	0.0000	—
0.1549	0.1669	1.04
0.1134	0.1218	1.06
0.0999	0.1050	1.05
0.0883	0.0903	1.02
0.0738	0.0782	1.07

Note: I have determined the concentration of silver nitrate by means of pure sodium chloride solution. In this case, I used potassium bichromate as the indicator.

Table 3.

Sodium Cyanide and Silver Thiocyanate.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.2318	0.0000	—
0.0908	0.0983	1.07
0·0676	0.0739	1.07
0.0560	0.0615	1.09
0.0463	0.0516	1.08
0.0309	0.0323	1.04
0.0193	0.0195	1.01
0.0097	0.0103	1.05

Table 4.

Sodium Cyanide and Silver Oxide.

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.1852	0.0000	—
0.0445	0.0486	1.09
0.0129	0.0138	1.07
0.0039	0.0048	1.24

Table 5.

Sodium Cyanide and Silver Chromate.(1)

Bound cyanide mol per liter	Silver mol per liter	Ratio
0.1882	0.0000	—
0.0357	0.0370	1.04
0.0231	0.0263	1.13
0.0217	0.0251	1.15
0.0179	0.0186	1.03

In all the above solutions the molal ratio of combined cyanide to silver is one to one, indicating the formula $AgCN^-$.

Yokohama Higher Technical School,
Yokohama.

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(1) Prepared by the method given in *Z. anorg. Chem.*, **41** (1904), 69.

SINOMENINE AND DISINOMENINE. PART XIII.(1)
ON THE REDUCTION OF BROMSINOMENINE.

By **Kakuji GOTO** and (Miss) **Teruko NAKAMURA.**

Received July 23, 1929. Published September 28, 1929.

In 1923, one of the authors reported(2) that the bromination of sinomenine in acetic acid leads to two different monobromsinomenines, viz. monobromsinomenine and isobromsinomenine. The properties of these two substances may, for the sake of convenience, be given here in the following table.

	Bromsinomenine	Isobromsinomenine
Yield	8 %	20%
Solubility in alcohol	soluble in cold	insoluble in hot
M. p. of free base	153°	214°
Sp. rotation: free base	$[\alpha]^{25}_{D} = -2.62°$	$[\alpha]^{25}_{D} = +14.65°$
Sp. rotation: hydrochloride	$[\alpha]^{25-5}_{D} = -30.19°$	$[\alpha]^{25}_{D} = +51.79°$
M. p. of HBr salt	110° (with 3 Aq.) 231° (anhydrous)	229 (anhydrous)
M. p. of ICH_3	80°	210~211°
Methoxyls	(not determined)	14.22% (calc. 15.19%)
M. p. of semicarbazone	270° (dec.)	amorphous.
$FeCl_3$	1,250(3)	400
Diazo-reaction	5,000	800
$K_3Fe(CN)_6$	100,000	no
Formaline—H_2SO_4	same as sinomenine.	reddish violet.

As regards the position occupied by the bromine atom, it may be reasonably assumed to be the position (1), opposed to the free phenol hydroxyl, since the diazo-reaction is remarkably diminished in the both brom-sinomenines. In isobromsinomenine, moreover, the third nucleus of the phenanthrene may have been undergone some change, as it does not give the potassium ferricyanide reaction.

This assumption, in regard to the position of bromine atom, is enforced by the following two facts.

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(1) Parts XI and XII will be published later.

(2) *J. Chem. Soc. Japan,* **44** (1923), 815; *J. Agr. Chem. Soc. Japan,* **1** (1924), 3.

(3) The figures show the dilution, at which the reactions are still visible.

KATALYTISCHE UEBERTRAGUNG VON WASSERSTOFF ZWISCHEN ORGANISCHEN VERBINDUNGEN. I.

Von Shiro AKABORI und Tazo SUZUKI.

Eingegangen am 9. August 1929. Ausgegeben am 28. September 1929.

In seinen Untersuchungen über den Mechanismus der Oxydationsvorgänge kam H. Wieland(1) auf den Gedanken, dass bei der biologischen Oxydation der organischen Substanzen nicht der Sauerstoff, sondern der Wasserstoff aktiviert wird. Der Sauerstoff würde dann nur als Akzeptor für den Wasserstoff fungieren. Dieser Gedanke erwies sich als überraschend fruchtbar und führte Wieland zu seiner Theorie der Wasserstoffaktivierung. Er liess Palladiumschwarz unter Ausschluss von Sauerstoff auf mehrere organische Substanzen einwirken und erhielt die entsprechenden dehydrierten Produkte. Leicht reduzierbare Substanzen wie Chinon, können dabei, an Stelle des Sauerstoffs, die Rolle des Wasserstoffakzeptors spielen.

Wir möchten diese Theorie der Wasserstoffaktivierung anwenden, um eine einfache katalytische Reduktions- und Dehydrierungsmethode zu erhalten. Wenn man auf ein Gemisch aus zwei Bestandteilen, von denen der eine durch Abspalten von Wasserstoff und der andere durch Anlagern von Wasserstoff in die stabilere Form übergeht, eine den Wasserstoff aktivierende Substanz wie Palladiumschwarz einwirken lässt, so muss der Wasserstoff vermutlich aus dem ersten in den letzten sich umwandeln. Gäbe es irgendeine billige und den Wasserstoff leicht spaltende Substanz, so würde man auf die eben besprochene Weise eine einfache katalytische Reduktionsmethode gewinnen. Falls die Dehydrierung hydrozyklischer Verbindungen, die man mehrfach bei den Natursubstanzen trifft, erzielt ist, würde diese Methode wieder bequem anwendbar sein. Für den ersten Zweck wandten wir als Wasserstoffdonator Tetralin (Tetrahydronaphtalin) an, das neuerdings als Lösungsmittel technisch dargestellt wird. Zimtsäure, Oelsäure, Eugenol und Cumarin wurden durch Behandlung mit Tetralin und Palladiumschwarz zu Hydrozimtsäure, Stearinsäure, Hydroeugenol und Melilotsäure mit befriedigender Ausbeute reduziert. Die Reaktion mit den drei erstgenannten geschah, mit grossem Uberschuss an Tetralin, durch Kochen oder durch Schütteln bei 115–120° und die mit Cumarin durch Kochen in Toluol-Lösung. Benzoylchlorid wurde jedoch mit

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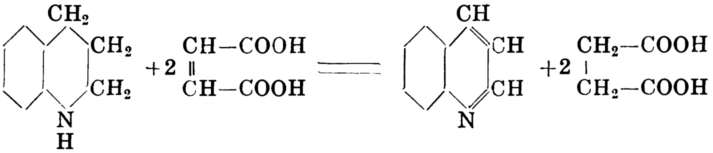
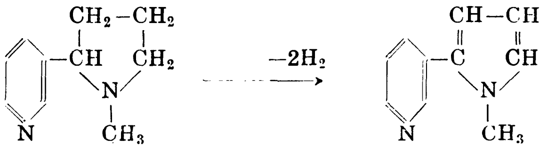
(1) *Ber.*, **45** (1912), 484, 679, 2606; **46** (1913), 3327; **47** (1914), 2085; *Ann.*, **432** (1923), 301; **439** (1924), 196; *Ber.*, **59** (1926), 1180; Zusammenfassung *Ber.*, **55** (1922), 3639; *Ergeb. d. Physiol.*, **20** (1922), 477.

Schwierichkeit enthalogeniert und gab nur eine geringe Menge von Benzaldehyd.

Die experimente betreffend der Dehydrierung hydrozyklischer Verbindungen gaben folgende Resultaten. 1 Mol Tetrahydrochinolin und 2 Mol Maleinsäure wurden in Wasser gelöst und mit Palladiumschwarz 4 Stunden lang gekocht. Die Wasserstoffübertragung war dabei fast quantitative, wie es die nachfolgende Gleichung fordert.



Ersetzt man Maleinsäure durch Bernsteinsäure, so findet die Wasserstoffabspaltung des Tetrahydrochinolins gar nicht statt, selbst nicht bei Anwesenheit von Palladiumschwarz. Aus dieser Tatsache ist ersichtlich dass für die Dehydrierung des Tetrahydrochinolins bei 100° nicht nur der Wasserstoffaktivator, sondern auch der Wasserstoffakzeptor nötig ist. Piperidin wird in wässeriger Lösung durch Maleinsäure und Palladium bei Siedehitze nicht dehydriert, durch Safrol und Palladium bei 175° jedoch fast vollkommen. Die Ausbeute war dabei 88% der Theorie. Tetrahydroisochinolin wurde durch Anethol und Palladium in Xylol-Lösung bei 145° zu Isochinolin dehydriert. Tetrahydropapaverin dagegen wurde unter denselben Bedingungen nicht dehydriert. Kocht man Nikotin (1 Mol) und Anethol (2 Mol) in Xylol-Lösung mit Palladiumschwarz (Temperature der Reaktionsflüssigkeit 150–152°, Kochdauer 2 Stunden), so erhält man Nikotyrin mit geringerer Ausbeute (0.4 gr. aus 4.9 gr. Nikotin). Das Nikotyrin wurde durch Umwandlung in Pikrat (Schmp. 164–165°) sowie Jodmethylat (Schmp. 211–212°) identifiziert.



Beschreibung der Versuche.

Reduktion der Zimtsäure. 1.0 gr. Zimtsäure, in 15 c.c. Tetralin gelöst, wurde mit 0.5 gr. Palladiumschwarz 5 Stunden lang gekocht. Die Ausbeute an Hydrozimtsäure betrug 0.8 gr. Schmp. 45–47°.

Reduktion der Olsäure. 5 gr. Oelsäure, in 13.5 gr. Tetralin gelöst, wurden mit 0.9 gr. Palladiumschwarz $5\frac{1}{2}$ Stunden lang gekocht. Nach Abdestillation von Naphtalin und Tetralin mit Wasserdampf blieb Stearinsäure zurück, die aus Alkohol umkrystallisiert wurde. Die Ausbeute an gereinigter Stearinsäure betrug 3.65 gr. Schmp. 69–70°.

Gef.: C=76.13; H=12.80%. Ber. für $C_{18}H_{36}O_2$: C=75.98; H=12.77%.

Reduktion des Eugenols. 16.4 gr. Eugenol (1 Mol) und 26.4 gr. Tetralin (2 Mol) wurden mit 0.9 gr. Palladiumschwarz $6\frac{1}{2}$ Stunden lang gekocht. Temperatur der Reaktionsflüssigkeit 213–214°. Während der ersten 4 Stunden entwickelte sich kein Wasserstoff, danach erst wurde anfangs langsame, allmählich zunehmende Entwicklung des Gases beobachtet. Nach 5-stündigem Erhitzen entwickelte sich mit konstanter Geschwindigkeit Wasserstoff (75 c.c. in einer Viertelstunde). Die aus dem Reaktionsgemisch isolierte phenolische Substanz wurde durch Vakuumdestillation gereinigt. Sdp. 126–129.6°/16 mm. Ausbeute 13.4 gr. $d_4^{25}=1.0331$, $n_C^{25}=1.51714$.

Gef.: C=72.38; H=8.79%. Ber. für $C_{10}H_{14}O_2$: C=72.24; H=8.49%.

Das benzoylderivate schmilzt bei 73.5–74.5°. Nach M. H. Fournier⁽¹⁾ bei 73°.

Gef.: C=75.66; H=7.31%. Ber. für $C_{17}H_{18}O_3$: C=75.52; H=6.72%.

Reduktion der Zimtsäure bei niedriger Temperatur. 3.0 gr. Zimtsäure (1 Mol) und 26.0 gr. Tetralin (10 Mol) wurden mit 0.5 gr. Palladiumschwarz ca. 15 Stunden lang geschüttelt. Die Temperatur der Reaktionsflüssigkeit wurde dabei konstant auf 115–120° gehalten. Bei dieser Temperatur entwickelt Tetralin keinen Wasserstoff, selbst nicht bei Anwesenheit von Palladiumschwarz. Die isolierte Hydrozimtsäure betrug 2.7 gr. Schmp. 47°.

Reduktion des Cumarins. 2.0 gr. Cumarin (1 Mol) und 4.5 gr. Tetralin (2.6 Mol) wurden in 12 c.c. Toluol gelöst und 4 Stunden lang mit 0.5 gr. Palladiumschwarz gekocht. Hydrocumarin wurde als Melilotsäure isoliert und aus Benzol umkrystallisiert. Schmp. 85–86° Ausbeute 2.2 gr., 97% der Theorie.

Gef.: C=65.30; H=5.94%. Ber. für $C_9H_{10}O_3$: C=65.03; H=6.07%.

Reduction von Benzoylchlorid zu Benzaldehyd. 2.8 gr. Benzoylchlorid (1 Mol) und 26.4 gr. Tetralin (10 Mol) wurden mit 0.9 gr. Palladiumschwarz bis zum Sieden erhitzt und die Reaktionsflüssigkeit langsam destilliert (Destillationsdauer 2 Stunden). Das Destillat wurde mit einer Essigsäure-

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(1) *Bull. Soc. Chim. France,* [4] **7** (1910), 27.

Lösung von *p*-Nitrophenylhydrazin geschüttelt und 0.34gr. zitronengelbe Krystalle gewonnen, die nach dem Umkrystallisieren aus Alkhol bei 189–190° schmolzen und sich als *p*-Nitrophenylhydrazon des Benzaldehyds erwiesen.

Gef.: N=17.21%. Ber. für $C_{13}H_{11}O_2N_3$: N=17.43%.

Dehydrieren des Tetrahydrochinolins durch Maleinsäure. 2.2 gr. Tetrahydrochinolin (1 Mol) und 3.9 gr. Maleinsäure (2 Mol) wurden in 25 c.c. Wasser gelöst und 4 Stunden lang mit 0.5 gr. Palladiumschwarz gekocht. Aus dem Reaktionsprodukte wurden 2.2 gr. Rohchinolin und 3.7 gr. bei 184–185° schmelzende Bernsteinsäure isoliert. Die ausbeute an Chinolin, die aus dem gereinigten Pikrat vom Schmp. 201° berechnet wurde, betrug 77% der Theorie. Ein Parallelversuche mit Bernsteinsäure anstatt der Maleinsäure wurde unter ganz gleichen Bedingungen wie oben ausgeführt, wobei sich wieder unverändertes Tetrahydrochinolin ergab.

Dehydrieren des Piperidins zu Pyridin. 3 gr. Pyridin (1 Mol) und 18 gr. Safrol (3 Mol) wurden mit 0.5 gr. Palladiumschwarz 4 Stunden lang gekocht. Temperatur der Reaktionsflüssigkeit 175°. Das isolierte Pyridin wurde in Form des Pikrats gereinigt und identifiziert. Die Ausbeute an Pikrat (Schmp. 164–165°) betrug 9.54 gr., 88% der Theorie.

Dehydrieren des Tetrahydroisochinolins. Tetrahydroisochinolin wurde durch Reduktion des Isochinolins mit Natrium und absolutem Alkohol dargestellt. 2 gr. Tetrahydroisochinolin (1 Mol) und 4.45 gr. Anethol (2 Mol) wurden in 15 c.c. Xylol gelöst und mit 0.5 gr. Palladiumschwarz 5 Stunden lang gekocht. Temperatur der Reaktionsflüssigkeit 149°. Aus dem Reaktionsgemisch wurde das gebildete Isochinolin in gewöhnlicher Weise isoliert. Ausbeute 1.8 gr. 93% der Theorie. Schmp. 25–26.5°. Goldchloriddoppelsalz Schmilzt bei 236–239°.

Gef.: Au=45.94%. Ber. für $C_9H_7N.AuCl_3$: Au=45.58%.

Dehydrieren des Nikotins. 4.9 gr. Nikotin (1 Mol) (Sdp. 240.2–241.5°) und 8.9 gr. Anethol (2 Mol) wurden in 20 gr. Xylol gelöst und mit 1.0gr. Palladiumschwarz bis zum Sieden erhitzt. Temperatur der Reaktionsflüssigkeit 151–152°. Nach 2-Stundigem Erhitzen wurde der Basische Teil herausgenommen und in Vakuum destilliert. Unter vermindertem Druck von 16 mm. ging 1.1 gr.der Base zwischen 136–152° über. Nach F. Blau⁽¹⁾ ist der Sdp. des Nikotins 123°/15 mm. und der des Nikotyrins 150°/17 mm. Das Destillat wurde in 25 c.c. 10-prozentiger Essigsäure gelöst und mit der wässerigen Lösung von 4.0 gr. Pikrinsäure umgesetzt. Das gebildete Pikratgemisch wurde mit 150 c.c. heissem Benzol behandelt; die darin

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(1) *Ber.*, **27** (1894), 2537.

ungelösten Krystalle wurden abfiltriert und erwiesen sich als Nikotindipikrat. Nach dem Erkalten der Benzol-Lösung krystallisierte das Nikotyrinpikrat in gelben Nadeln aus (1.2 gr.). Diese wurden aus heissem Wasser und dann nochmals aus heissem Benzol umkrystallisiert. Schmp. 164–165°. Nach F. Blau(1) ist der Schmp. des Nikotyrinpikrats 163–164° und nach J. P. Wibaut und J. Overhoff(2) 168–169°.

Gef.: C=49.78; H=2.92%. Ber. für $C_{10}H_{10}N_2 \cdot C_6H_3O_7N_3$: C=49.59; H=3.39%.

Das von dem gereinigten Pikrat befreite Nikotyrin (0.4 gr.) wurde mit 0.5 gr. Methyljodid in Benzol gelöst und übernacht stehen gelassen. Das anfangs harzig ausgeschiedene Jodmethylat veränderte sich allmählich in eine krystallinische Masse, welche nach zweimaligem Umkrystallisieren aus absolutem Alkohol schöne, glänzende, bräunlichgelbe Nadeln vom Schmp. 211–212° bildete.

Gef.: C=43.96; H=4.04; N=9.24%. Ber. für $C_{10}H_{10}N_2 \cdot CH_3J$: C=43.99; H=4.37; N=9.34%.

Zum Schluss möchten wir Herrn Prof. Riko Majima für seine überaus freundliche Leitung bei unseren Versuchen bestens danken.

Chemisches Institut, Tohoku Kaiserliche Universität, Sendai.

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(1) Loc. cit.
(2) *Rec. Trav, Chim. Pays-Bas*, **47** (1928), 935.

SPECTROCHEMICAL STUDY OF AMINO-ACID ANHYDRIDES.(3)

III. LIGHT ABSORPTION OF SOME N-SUBSTITUTED DIKETOPIPERAZINES AND SOME OTHER AMINO-ACID ANHYDRIDES.(4)

By Tei-ichi ASAHINA.

Received August 20, 1929. Published September 28, 1929.

In the preceeding paper,(3) Y. Shibata and the author have reported on the ultra-violet absorption of some C-substituted derivatives of diketopiperazines. The light absorption of these substances was almost coincident with that of the amino-acids from which the anhydrides are derived. An

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(3) The 1st and 2nd reports, see this Bulletin, **1** (1926), 71; and **2** (1927), 324.
(4) Read before the Chemical Society of Japan, May 11th, 1929.

exceptional case was, however, found in C,C’-dibenzylderivatives, which showed no selective absorption, although the substance contains effective chromophore groups in its molecule. Further studies of the ultra-violet absorption and the behaviour of some N-substituted diketopiperazines were now attempted. Sarcosine anhydride, which is an N,N’-dimethyldiketopiperazine shows too no selective absorption and moreover its spectrogram is quite identical with that of diketopiperazine⁽¹⁾ (Fig. 3). If the substituents in the N,N’ position of diketopiperazines are phenyl or benzyl group, no selective absorptions are either observed in the compound produced, though phenylamino and benzylamino-acetic acids which are regarded to be the mother substances of the former show more or less distinct absorption bands in the ultra-violet region (Fig. 1 and Fig. 2). The relation between the optical behaviours of N,N’-diphenyldiketopiperazine and N-phenylglycine is exactly comparable to that between acetanilide and aniline. Thus it may probably be concluded that the ring formation of diketopiperazine is

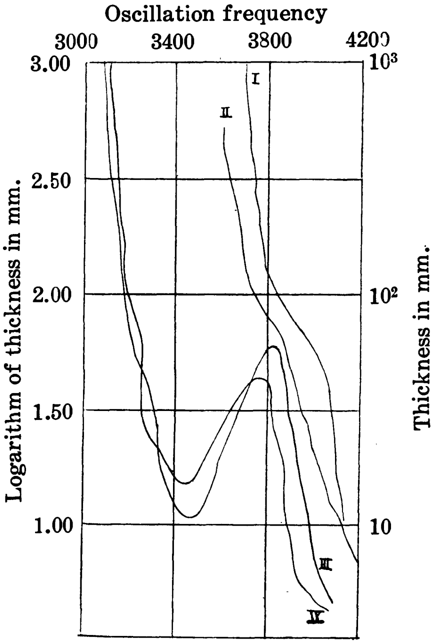

Fig. 1.

I Acetanilide 0.001 mol
II N, N’-diphenyldiketopiperazine
III Aniline
IV N-phenylglycine and its ethyl ester

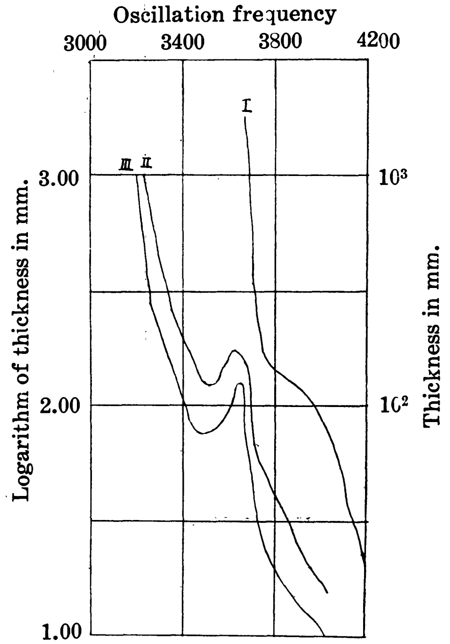

Fig. 2.

I N, N’-dibenzyldiketopiperazine
II Benzylamine 0.001 mol
III Benzylaminoacetic acid ethyl ester 0.001 mol

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(1) Ibid., **1** (1926), 71.

due to the acylation of amino groups of amino-acids. It seems further that the introduction of acyl groups in N-atoms of diketopiperazine causes the displacement of its end absorption in the ultra-violet regularly towards the region of longer wave-lengths according to the augmentation of molecular weight of substituted products, only with the exception of N,N'-dichloracetyl-diketopiperazine which absorbs light less than N,N'-diacetyl-diketopiperazine (Fig. 3). Hydantoin, which may be regarded as another kind of amino-acid anhydride, and its corresponding acid or acid ester show nearly the identical absorption to each other. Neither γ-phenylhydantoin nor phenyl-urea, both of which are acylated products of aromatic groups, was found to give any selective absorption, while aniline possesses a remarkable absorption band in the ultra violet (Fig. 4).

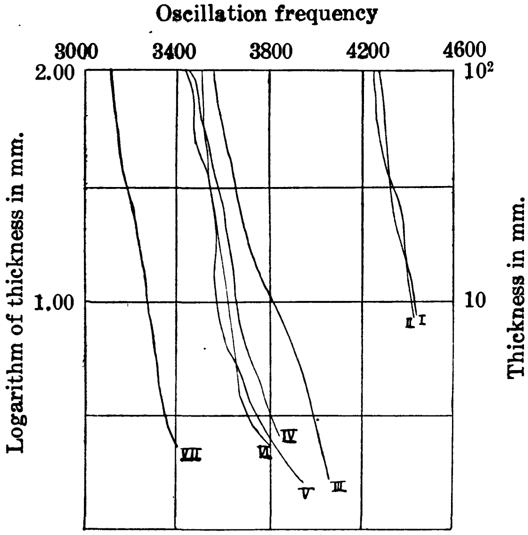

Fig. 3.

I	Sarcosine anhydride	0.01 mol	
II	Glycine anhydride	„	
III	N, N'dichloracetyl-diketopiperazine	„	(in CH_3COOH)
IV	N, N'diacetyl-diketopiperazine	„	(in alcohol)
V	Hippuric acid	„	(„)
VI	N, N'dipropionyl-diketopiperazine	„	(„)
VII	N, N'dibenzoyl-diketopiperazine	„	(in CH_3COOH)

Azlactones are also amino-acid anhydrides derived from hippuric acid and they have generally distinct yellow colour. The azlactones of benzaldehyde and furfural were also studied; they showed analogous absorption with each other, but by the closer comparison of these absorption curves it was

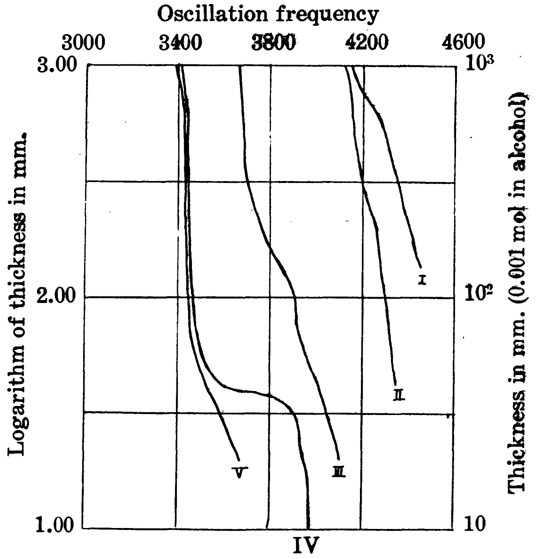

Fig. 4.

I Hydantoic acid ethyl ester
II Hydantoin
III γ-Phenylhydantoin
IV Phenylurea
V γ-Phenylhydantoic acid

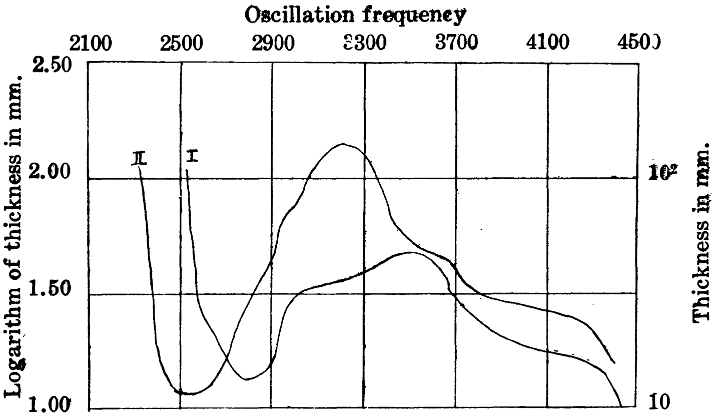

Fig. 5.

I Benzazlactone 0.0001 mol (in alcohol)
II Furfuralazlactone ,, (,,)

known that azlactone of furfural absorbs more bathochromic and hyperchromic than the other (Fig. 5), the fact being quite coincident with that observed by Dr. I. Kasiwagi in his study of furyl ketones.(1)

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(1) Ibid., 1 (1926), 150.

Experimentals.

N-phenylglycocoll. Commercial product was repeatedly recrystallised from water and alcohol alternately (m.p. 123.5–124.5°) and its alcoholic solution (0.001 mol) was spectroscopically examined (see Fig. 1.)

N-phenylglycocoll ethylester. The preparation method given by Bischoff and Hausdörfer(1) was followed, starting from monochloracetic ester and aniline; the product was recrystallised thrice from petroleum ether (m.p. 55.5–56.5°). The absorption curve of its 0.001 mol alcoholic solution was identical with that of the free acid, the maxima of the absorption being observed at $\lambda = 3450 \text{Å}$. The spectrograms are also nearly identical with that of aniline in the alcoholic solution, the absorption maximum of which is shown at $\lambda = 3460$ Å (Fig. 1).

N,N'-diphenyl-diketopiperazine. N-phenylglycocoll was heated in an oil-bath at the temperature of 140°. On cooling, the dark solid mass was obtained, which was washed with small quantity of luke-warm alcohol and recrystallised from glacial acetic acid (m.p. 265°).(2) The 0.01 mol glacial acetic acid solution gave only an end absorption which is identical with that of acetanilide, while its corresponding amino-acid shows a distinct absorption band (Fig. 1). From this remarkable fact it will most probably be concluded that the diketopiperazine takes the acid-amide constitution.

Benzylamino-acetic Acid. Instead of the free acid, its ethyl ester was synthesized from benzylamine and monochloracetic ester (b.p. 137±1° under 8 mm. pressure).(3)

Benzylamine. Commercial product was purified by fractional distillation and the portion boiling at 182–183° was dissolved in alcohol which was previously boiled (to expel the dissolved carbon dioxide). The absorption maximum of the amino-acid (ester) in alcoholic solution was observed at $\lambda = 3490$ Å and that of the benzylamine at $\lambda = 3500$ Å (Fig. 2).

N,N'-dibenzyl-diketopiperazine. The sample was afforded by Dr. T. Sasaki.(4) In 0.01 mol glacial acetic acid solution, no absorption band was observed except an inflection in the absorption curve (Fig. 2).

Diacetyl-diketopiperazine. Glycine anhydride was boiled with 10 times acetic anhydride for about 6 hours, then the latter was expelled in vacuo,

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(1) *Ber.*, **25** (1892), 2270.

(2) P. Meyer, *Ber.*, **10** (1877), 1967.

(3) Mannich and Kuphal, *Ber.*, **45** (1912), 313.

(4) T. Sasaki and T. Hashimoto, *Ber.*, **54** (1921), 2692.

and the product was three times recrystallized from alcohol (m.p. 102.5°).⑴ The curve showing its end absorption is situated in the spectrum region of longer wave-length than that of glycine anhydride (Fig. 3)

Dipropionyl-diketopiperazine. Well powdered glycine anhydride (1.1 gr.) was heated with 10 gr. propionic anhydride at 130–140° for about five hours, the liquid part was then distilled off in vacuo on a water bath and the dark coloured crystalline residue was then drained on a porous plate; yield 2 gr. (98% of the theor. amount). Twice recrystallizations from alcohol suffice to render the raw product quite pure as crystals with silverly lustre of m.p. 114.5°. Sasaki's reaction and sodium nitroprusside reaction are both positive.

Anal. Subst. = 4.925 mg.; N_2 = 0.541 c.c. (27°, 761.8 mm.) Subst. = 0.0988 gr.; CO_2 = 0.1907 gr.; H_2O = 0.0536 gr. Found: N = 12.5; C = 52.6; H = 6.1%. Calc. for $C_{10}H_{14}N_2O_4$; C = 53.1; H = 6.2; N = 12.39%.

The substance has a peculiar form of crystal: when the alcoholic solution is left for free evaporation, we obtain very thin square plates which are often as large as 1 cm^2. just like a cover-glass of microscopy. Like the acetyl product it has a tendency to decompose, on standing for a long time in the air and with sodium alcoholate it gives the odour of ethyl propionate. The end absorption was coincident with that of the acetyl derivative (Fig. 3).

Dichloracetyl-diketopiperazine. This substance was first obtained by E. Abderhalden and E. Klarmann⑵ by heating the glycine anhydride and chloracetyl chloride in nitrobenzene at 140°. The present author synthesized it by the interaction of glycine anhydride and chloracetic anhydride.⑶ Glycine andride 1.1 gr. was well mixed with 15 gr. of chloracetic anhydride and warmed on a water-bath for an hour (when an oil bath of 140–145° is used instead of a water-bath, a quarter of an hour is sufficient to complete the reaction, prolonged heating giving rather worse result). The cooled reaction mass was washed with small quantities of warm ether to remove chloracetic acid and anhydride completely; the brown crystalline residue which weighed 2.3 gr. (yield: 84% of the theor. amount) was three times recrystallised from boiling glacial acetic acid (m.p. 169°). The substance is very difficultly soluble in cold water, ether, alcohol, ethyl acetate,

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(1) A.P.N. Franchimont and H. Friedmann, *Rec. trav. chim. Pays-bas*, **27** (1908), 192; E. Abderhalden and E. Komm, *Z. physiol. Chem.* **139** (1924), 181.

(2) *Z. physiol. Chem.*, **129** (1923), 320.

(3) Chloracetic anhydride can easily be prepared by heating the mixture of chloracetic acid (freshly distilled) and phosphorus pentoxide for a short time and the successive vacuum distillation (Bischoff and Walden, *Ber.*, **27** (1894), 2949). A considerable part of the chloracetic acid remains unaltered and goes over in the distillate. This fraction is again treated with the pentoxide just as in the preparation of chloracetyl chloride.

benzene and a little soluble in xylene, amyl alcohol, amyl acetate, nitrobenzene and glacial acetic acid; the latter three solvents can be used for recrystallization of this substance. The Abderhalden and Klarmann's process was also followed by the author and the reaction product was found identical with that described just above.

Anal. Subst. = 4.388 mg.; N_2 = 0,395 c.c. (12.6°, 755.9 mm.) Found: N = 10.64%. Calc. for $C_8H_8O_4N_2Cl_2$: N = 10.49%.

Subst. = 4.72 mg., 0.0870 gr.; AgCl = 5.02 mg., 0.0950 gr. Found: Cl = 26.3, 27.0%. Calc.: Cl = 26.6%.

Abderhalden and Klarmann have not succeeded in obtaining diglycyl-diketopiperazine by treating the product with alcoholic ammonia.(1) This process was tried again by the present author, but in vain; and the further trial of obtaining diphthalylglycyl-diketopiperazine by the interaction between potassium phthalimide and the chloracetyl derivative has been also without success, only potassium chloride, phthalimide and somewhat complicated decomposition products being given in the reaction.

Dibenzoyl-diketopiperaine. This substance was prepared according to Sasaki's description(2) and the product was recrystallized from glacial acetic acid (m.p. 137°). The end absorption of the substance was found at the spectrum region of comparatively longer wave-length. Moreover the absorption was not coincident with that of the corresponding amino-acid—hippuric acid (Fig. 3).

Diacetyl-leucine-anhydride. Leucine anhydride (0.5 gr.) was heated with 5 c.c. acetic anhydride at 150° for 6 hours, the liquid part was then distilled off in vacuo and the residue was washed with ether and recrystallised from alcohol; yield 0.3 gr., m.p. 138.5°.

Anal. Subst. = 4.318 mg.; N_2 = 0.337 c.c. (14.2°, 767.6 mm.). Found: N = 9.06%. Calc. for $C_{16}H_{26}N_2O_4$: N = 8.91%.

Hydantoin and Hydantoic Acid Ethyl Ester.(3) The ester was prepared from glycine ester hydrochloride and potassium cyanate (m.p. 137.5–138.5°), and by evaporating this substance with hydrochloric acid, hydantoin was prepared (m.p. 215°).

γ-Phenylhydantoin and γ-Phenylhydantoic Acid. This acid was prepared from glycocoll and phenyl isocyanate (m.p. 192°)(4) and then trans-

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(1) *Z. physiol. Chem.*, **135** (1924), 200.

(2) *Ber.*, **54** (1921), 2691.

(3) C. Harries and Weiss, *Ber.*, **33** (1901), 3418.

(4) Paal, *Ber.*, **27** (1894), 974.

formed into hydantoin by boiling with hydrochloric acid (m.p. 155°).⑴ From the absorption curves, we can possibly conclude that the ring formation in this case scarcely influences on the light absorption (Fig. 4).

Phenyl-urea. Aniline (hydrochloride) and potassium cyanate were coupled to monophenyl-urea (m.p. 146–7°).⑵ Phenyl-urea shows no selective absorption but in its absorption curve only a slight inflection is observed (Fig. 4). From the results of optical studies obtained with acetanilide, diphenyl-diketopiperazine, γ-phenyl-hydantoin and phenyl-urea, it may be concluded that the absorption band of aniline (also perhaps of other aromatic amido derivatives) vanishes by the introduction of acyl groups to the amido group.

Azlactone of Benzaldehyde. The substance was prepared by the condensation of benzaldehyde with hippuric acid, in the presence of acetic anhydride and fused sodium acetate (m.p. 164.5°).⑶

Azlactone of Furfural. By replacing benzaldehyde with furfural in the preceding condensation, the azlactone was obtained (m.p. 170.5°).⑷

Both azlactones are yellowish substances and they show wide absorption bands, absorption maximum of the former substance being observed at 2760 Å, while that of the latter at 2550 Å. (Fig. 5).

The author wishes to express his best thanks to Prof. K. Shibata and Prof. Y. Shibata for their kind guidances throughout the research. He is also much indebted to Dr. T. Sasaki for affording him some precious samples and finally he is thankful to the Imperial Academy of Science for being defrayed a part of the research cost.

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(1) Mouneyrat, *Ber.*, **33** (1900), 2393.
(2) Weith, *Ber.*, **9** (1876), 820.
(3) Erlenmeyer, jun., *Ann.*, **275** (1893), 1.
(4) Erlenmeyer, jun., *Ann.*, **337** (1904), 283.

ON THE PROMOTER ACTION IN THE CATALYTIC OXIDATION OF METHANE WITH STEAM.

By Bennosuke KUBOTA and Tatsuo YAMANAKA.

Received September 18, 1929. Published October 28, 1929.

It has been recently reported by several authors⁽¹⁾ that the reduced nickel or reduced nickel promoted by thoria is a very suitable catalyst for causing the reactions,

$$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2 \qquad (1)$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad (2)$$

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (3)$$

to approach in equilibrium with rapidity. The present investigation, however, has been undertaken with the view of examining whether or not the products, which consist of mainly either CO_2+H_2 or $CO+H_2$, could be obtained by employing different promoters under different conditions, and moreover of inquiring into the mechanism of the promoter action.

When methane was allowed to pass over the catalyst, which consisted of reduced nickel promoted with a metallic oxide (such as Al_2O_3, ZrO_2, ThO_2, CaO, CdO, ZnO or MgO etc), with an excess of water vapor at 1000°, the product with the largest quantity of CO_2 was obtained by employing the catalyst promoted with Al_2O_3, whilst when the catalyst promoted with MgO was employed and water vapour was regulated, the product containing the largest quantity of CO was obtained as shown in the following table. The ratio $\frac{\text{Vol. of } CO_2}{\text{Vol. of } CO}$ at 1000° calculated from the results is represented in Table 1.

Table 1.

	Catalyst				$Ni_{(atom)} : Me_x O_{y(molecule)} = 1:0.02$												
$Me_x O_y$	Al_2O_3	ZrO_2	ThO_2	BeO	Cr_2O_3	Fe_2O_3	SiO_2	WO_3	MnO_2	CeO_2	SnO_2	CdO	CaO	MgO	CuO	$Al_2O_3\left(\begin{smallmatrix}\text{poisoned}\\ \text{with}C_4H_4S\end{smallmatrix}\right)$	ZnO
$\frac{CO_2}{CO}$	49.0	38.0	19.1	11.7	8.5	5.9	5.2	4.3	3.3	3.5	3.2	3.8	3.0	2.2	1.4	1.02	0.8

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(1) Neumann & Jacob, *Z. Elektrochem.*, **30** (1924), 557; Pease & Chesebro, *J. Am. Chem. Soc.*, **50** (1928), 1464.

$Ni_{(atom)} : Al_2O_3 = 1:0.2$	$Ni_{(atom)} : MgO = 1:0.1$ **(Water vapour regulated)**
96.0	0.02

These results might possibly lead one to suppose that the reaction may be looked upon as taking place successively in the manner shown by the scheme below:

$$CH_4 \xrightarrow{H_2O} CO + 3H_2 \xrightarrow{H_2O} CO_2 + 4H_2,$$

and as the beneficial effect of promoters in these reactions is to transfer water molecules to the reaction centers of the catalyst where the action of water on methane is carried out, the product may be determined according to the adsorbing intensity of water molecules and the size of the promoter. Thus it seems to us that results we obtained are quite in good agreement with Balandin's "Multipletthypothese."(1)

According to his theory we may imagine, of course, a number of "Krystalkeimen (Multiplette)," of which the following is one:— $I_5(\mathrm{C_{CH_4}},(\mathrm{H_C{-}H_O})_3,\mathrm{O_{H_2O}})$. In Fig. 1 A(Ni atom, radius=1.237Å)(2) denotes an adsorption center of methane molecule M(radius of C=0.77Å),(2) R_1R_2 and R_3 (Ni-atoms) reaction centers which attract hydrogen molecules, and P (metallic oxide for instance MgO, Mg=1.593Å)(2) an adsorption center of water molecule (w). Although this model is, naturally, quite hypothetical, it nevertheless serves to show that the yield of CO_2, as may be seen in the above table, increases successively in order of promoters, ThO_2, ZrO_2, Al_2O_3 (polyvalent metallic oxides) as the radius of the atom of promoter becomes smaller (Th=2.833Å, Zr=1.57 (1.61)Å,(2) Al=1.430Å), and also the yield of CO, in order of promoters CaO, CdO, MgO and ZnO (bivalent metallic oxides)(3) (Ca=1.97Å, Cd=1.714Å, Mg=1.597Å, Zn=1.329Å,)(2) for the distance (Δ) between H-atom in water molecule (w) and the reaction center (R) ($\Delta = f$(radius of P)) as shown by Balandin)(4) will be shorter according to the radius of promoter atom decreasing.

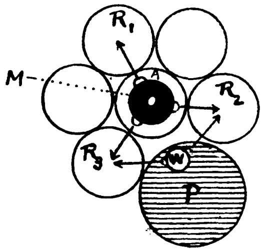

Fig. 1.

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(1) Balandin, *Z. physik. Chem.*, (B) **2** (1929), 289.

(2) W. P. Davey, "The Radii of Atoms and Ions," *Chem. Rev.*, **2** (1926), 356.

(3) BeO give an exception, because its radius is extraordinary small 1.106 Å and CuO is subjected somewhat to the reduction.

(4) Loc. cit.

Increasing the amount of promoter, for instance MgO, for a given amount of the catalyst, the rate of decomposition of methane rises up very rapidly which is represented graphically in Fig. 2.

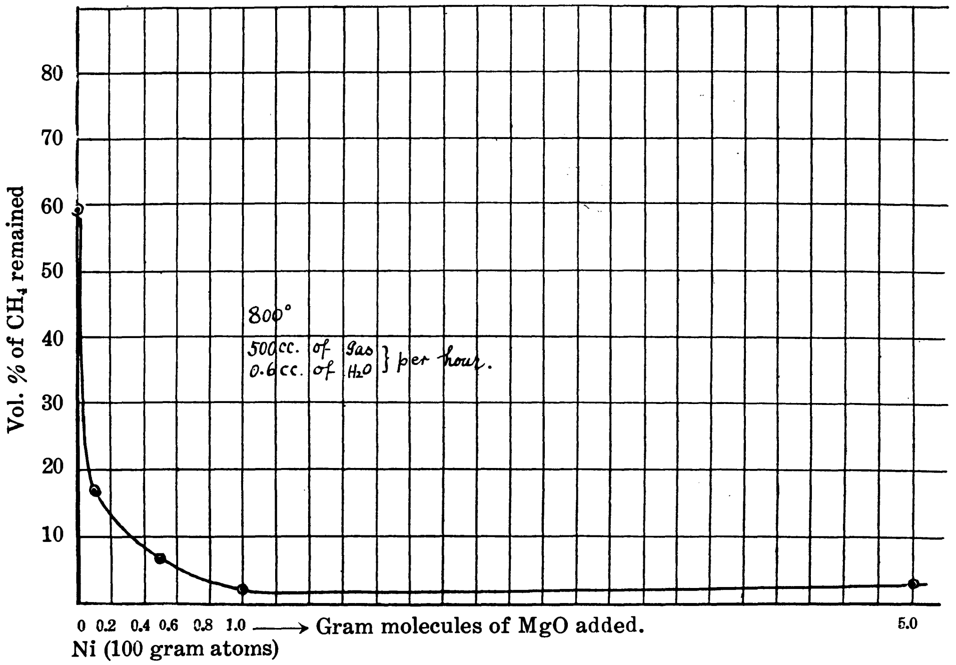
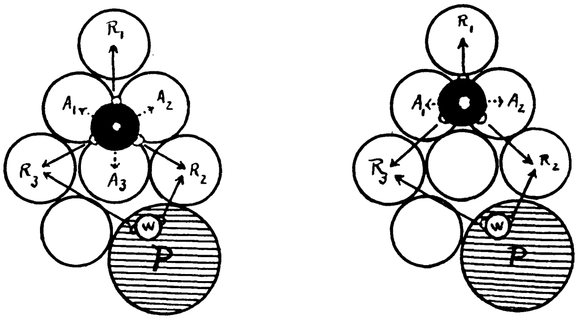


Fig. 2.

This fact may be explained clearly by the hypothesis in the following manner: The reduced nickel which composes the reaction centers and the adsorption centers for methane molecule, does not produce perfect multiplets for decomposing methane with water till it gets a supply of metallic oxide which composes the adsorption center for water molecule, and vice versa. Thus the minute quantity of MgO added to the comparatively large quantities of nickel may give rise to the rapid decomposition of methane.

There may exist, of course, multiplet and multiplet in addition to that shown in Fig. 1, and a sort of active centers giving rise to the hydrogenation of benzene nucleus, forms also a kind of very active multiplet with metallic oxide.

The fact that the nickel catalyst promoted with Al_2O_3 produces CO_2 and CO at 1000° in the ratio of $\frac{CO_2}{CO}=49.0$ (Table 1), but that it produces $\frac{CO_2}{CO}=1.02$ (Table 1) after it is subjected to the poisoning action of thio-



Before poisoning After poisoning

Fig. 3.

phene, shows us that the activity of this multiplet is weakened or is even lost by the poisoning action of thiophene by such a manner as shown in Fig. 3.

Experimental.

Catalysts were prepared by reducing with hydrogen at about 300° in the reaction tube the intimate mixture of nickel oxide and an other metallic oxide which is put on small grains of pumice. The intimate mixtures of metallic oxides were obtained by calcinating the fused mass of pure nickel nitrate and a calculated quantity of another metallic nitrate, for instance 29.1 gr. of $Ni(NO_3)_2.6H_2O$ and 3.75 gr. of $Al(NO_3)_3.\ 9H_2O$ ($Ni : Al_2O_3 = 1$ atom : 0.01 mol), (in the case of CaO and MgO the acetates were used).

The natural gas obtained at the Kashiwazaki Province, compressed in bombs, consisting of 80.3% of CH_4, 15.8% of N_2, 3.6% of O_2, 0.2% of unsaturated hydrocarbon and 0.1% of CO_2, was allowed to pass over the catalyst (volume about 10 c.c.) in the velocity of 500 c.c. per hour with an excess (5–10 times for calculated quantity) of water vapour which was produced in a small flask in an oil bath heated at 125–150°, and was carried by the natural gas in form of bubbles.

The product was collected on mercury and was analysed.

Table 2.

Catalyst	Temperature	Products in %						
		CO_2	CO	H_2	CH_4	unsat. H. C.	O_2	N_2
Ni:Al_2O_3 1:0.02	800°	18.5	1.2	75.9	0.5	0.0	0.1	3.8
	900	19.4	0.6	76.6	0.0	0.0	0.1	3.3
	1000	19.6	0.4	76.8	0.0	0.0	0.1	3.2
Ni:Al_2O_3 1:0.05	800	19.2	2.1	75.3	0.0	0.0	0.1	3.3
	900	19.2	0.7	77.0	0.0	0.0	0.1	3.0
	1000	19.6	0.2	77.0	0.0	0.0	0.1	3.1
Ni:Al_2O_3 1:0.1	800	19.7	2.8	73.9	0.0	0.0	0.1	3.5
	900	20.0	0.4	76.4	0.0	0.0	0.1	3.1
	1000	19.2	0.2	77.4	0.0	0.0	0.1	3.1
Ni:Al_2O_3 1:0.2	800	19.6	0.7	76.4	0.0	0.0	0.1	3.2
	900	19.1	0.4	77.1	0.0	0.0	0.1	3.3
	1000	19.2	0.2	77.5	0.0	0.0	0.1	3.0
Ni:Al_2O_3 1:0.3	800	19.8	1.2	75.9	0.0	0.0	0.1	3.0
	900	19.0	0.5	77.3	0.0	0.0	0.1	3.1
	1000	19.0	0.3	77.6	0.0	0.0	0.1	3.0
Ni:Al_2O_3 0.1:1	800	1.8	3.3	21.5	66.4	0.0	0.3	6.7
	900	9.5	3.9	49.4	32.4	0.0	0.2	4.6
	1000	11.0	5.0	62.4	17.2	0.0	0.2	4.2
Ni:ZrO_2 1:0.02	800	18.1	1.2	76.5	0.0	0.0	0.1	4.1
	900	19.1	0.7	76.7	0.0	0.0	0.1	3.4
	1000	19.0	0.5	76.9	0.0	0.0	0.1	3.5
Ni:ThO_2 1:0.02	800	18.6	1.5	77.0	0.0	0.0	0.2	3.0
	900	19.3	1.0	76.4	0.0	0.0	0.2	3.1
	1000	19.1	1.0	76.5	0.0	0.0	0.1	3.3
Ni:BeO 1:0.02	800	18.7	0.8	74.2	0.0	0.0	0.1	6.2
	900	18.3	0.9	71.2	2.1	0.0	0.1	7.4
	1000	17.6	1.5	72.5	1.5	0.0	0.1	6.8

Table 2.—(*Continued*)

Catalyst	Tem-perature	Products in %						
		CO_2	CO	H_2	CH_4	unsat. H. C.	O_2	N_2
Ni:Cr_2O_3 1:0.02	800	19.0	1.7	74.7	0.5	0.0	0.1	3.5
	900	18.2	1.6	75.3	1.0	0.0	0.2	3.7
	1000	16.2	1.9	72.4	5.1	0.0	0.1	4.3
Ni:Fe_2O_3 1:0.02	800	13.2	1.8	48.6	30.2	0.0	0.2	6.0
	900	15.4	3.8	61.5	11.1	0.0	0.2	8.0
	1000	16.6	2.8	75.9	1.0	0.0	0.2	3.5
Ni:SiO_2 1:0.02	800	16.9	2.5	72.8	1.0	0.0	0.1	6.7
	900	15.6	2.3	75.9	1.1	0.0	0.1	5.1
	1000	15.6	3.0	71.4	3.1	0.0	0.1	6.8
Ni WO_3 1:0.02	800	14.1	3.9	69.8	6.8	0.0	0.1	5.3
	900	14.6	4.4	71.0	4.8	0.0	0.1	5.1
	1000	14.9	4.8	72.8	2.6	0.0	0.1	4.8
Ni:MnO_2 1:0.02	800	18.3	2.3	74.0	2.0	0.0	0.2	3.2
	900	16.5	3.6	71.6	4.0	0.0	0.2	4.1
	1000	15.7	4.7	74.2	1.5	0.0	0.2	3.7
Ni:CeO_2 1:0.02	800	17.8	1.6	75.8	0.0	0.0	0.1	4.7
	900	15.9	3.9	74.5	0.0	0.0	0.1	5.6
	1000	15.6	4.4	74.0	0.0	0.0	0.1	5.9
Ni:SnO_2 1:0.02	800	8.5	1.7	21.5	60.8	0.0	0.4	7.1
	900	10.0	3.2	46.8	33.7	0.0	0.2	6.1
	1000	17.4	5.5	67.8	4.6	0.0	0.1	4.6
Ni:CdO 1:0.02	800	10.6	3.1	41.0	41.0	0.0	0.2	4.1
	900	8.6	7.5	43.2	35.2	0.0	0.2	5.5
	1000	15.8	4.1	74.3	1.2	0.0	0.1	4.5
Ni:CaO 1:0.02	800	15.4	4.6	71.2	4.6	0.0	0.2	4.0
	900	12.3	9.5	73.5	0.6	0.0	0.2	3.9
	1000	16.0	5.2	74.8	0.5	0.0	0.2	3.3

Table 2.—(*Continued*)

Catalyst	Temperature	Products in %						
		CO_2	CO	H_2	CH_4	unsat. H. C.	O_2	N_2
Ni:MgO 1:0.02	800	14.0	5.9	75.8	0.5	0.0	0.1	3.7
	900	14.6	5.3	76.1	0.0	0.0	0.1	3.9
	1000	14.0	6.4	75.9	0.0	0.0	0.1	3.6
Ni:CaO 1:0.02	800	2.0	3.5	20.8	61.2	0.0	0.1	12.4
	900	7.6	5.0	45.5	32.2	0.0	0.1	9.6
	1000	13.8	5.5	62.2	9.9	0.0	0.1	8.5
Ni:ZnO 1:0.02	800	11.6	5.2	56.2	20.6	0.0	0.2	6.2
	900	13.0	3.9	77.4	1.1	0.0	0.2	4.4
	1000	10.0	12.4	73.2	0.0	0.0	0.2	4.4

Results with the natural gas ($CH_4 = 95.4\%$, $C_nH_{2n} = 0.1\%$, $CO_2 = 0.2\%$, $H_2 = 0.0\%$, $O_2 = 0.8\%$ & $N_2 = 3.5\%$) and regulated water vapour (0.8—0.6 c.c. H_2O per hour).

Ni:MgO 1:0.01	800	1.8	22.7	74.1	0.0	0.0	1.4	0.081
	900	1.2	23.1	74.4	0.0	0.0	1.3	0.052
	1000	0.5	24.0	74.4	0.0	0.0	1.1	0.021

The products obtained at 800° when Ni and MgO are present in various proportions are shown in the following table (Table 3), where the composition of the natural gas is 82.7% of CH_4, 16.3% of N_2, 0.7% of O_2, 0.2% of unsaturated hydrocarbons and heavy hydrocarbons, and 0.1% of CO_2; the velocity of methane gas is 500 c.c. per hour and the volume of the catalyst which is put on small grains of pumice is 10 c.c.

Table 3.

Catalyst Ni:MgO	Volume of H_2O used at 17° c.c.	Products in %						
		CO_2	CO	H_2	CH_4	O_2	N_2	Methane* remained
100:0.0	6.0	8.7	2.2	43.0	36.1	0.1	10.9	76.8
	0.6	2.2	13.8	50.8	23.9	0.0	9.3	59.9
99.9:0.1	6.0	12.0	8.2	70.5	3.5	0.1	5.7	14.8
	0.6	0.8	18.8	68.5	4.0	0.0	7.9	16.9
99.5:0.5	6.0	14.8	3.5	73.0	1.0	0.1	7.6	5.2
	0.6	1.6	20.8	68.6	1.5	0.0	7.5	6.3
99.0:1.0	6.0	14.3	5.9	73.0	0.0	0.1	6.7	0.0
	0.6	1.8	22.0	69.2	0.5	0.0	7.5	2.1
95.0:5.0	6.0	12.4	5.4	74.2	0.3	0.1	7.6	1.6
	0.6	1.7	19.3	69.5	0.7	0.0	8.8	3.2
90:10	6.0	14.6	5.6	73.1	0.5	0.1	6.1	2.4
	0.6	2.5	20.4	68.1	0.9	0.0	8.1	3.8
80:20	6.0	16.3	3.3	73.5	1.0	0.1	5.9	4.9
	0.6	3.8	19.3	68.8	1.0	0.1	7.0	4.3
70:30	6.0	14.4	6.3	71.5	1.2	0.1	6.5	5.5
	0.6	1.2	18.8	69.0	1.5	0.0	9.5	6.9
60:40	6.0	15.1	3.8	70.9	1.5	0.1	8.6	7.6
	0.6	2.1	17.6	68.1	2.7	0.1	9.4	12.1
50:50	6.0	15.8	3.3	72.4	1.5	0.1	6.9	7.3
	0.6	2.5	15.9	68.9	4.2	0.1	8.4	18.6
40:60	6.0	15.3	2.8	73.2	2.8	0.1	7.1	7.7
	0.6	2.3	15.3	65.1	8.1	0.1	9.1	31.9
30:70	6.0	16.2	2.4	72.4	1.5	0.1	7.4	7.5
	0.6	2.2	14.7	62.1	10.6	0.0	10.4	38.5

Table 3.—(*Continued*)

Catalyst Ni:MgO	Volume of H_2O used at 17°	Products in %						
		CO_2	CO	H_2	CH_4	O_2	N_2	Methane* remained
	c.c.							
20:80	6.0	8.1	4.2	30.1	47.5	0.0	10.1	79.4
	0.6	1.0	12.4	41.2	12.8	0.0	12.6	48.8
10:90	6.0	3.8	3.6	25.2	53.2	0.0	14.2	87.8
	0.6	0.6	13.4	58.0	17.6	0.0	10.4	55.7
0:100	6.0	3.2	2.0	14.0	63.2	0.0	17.6	92.4
	0.6	2.6	3.1	20.3	59.4	0.0	14.6	91.2

$$* \text{ Percentage of methane} = \frac{[CH_4] \times 100}{[CO_2]+[CO]+[CH_4]}.$$

The data shown in Table 3 show that the most effective mixture of catalyst and promoter for CO formation is about 1.0 gram-molecule of MgO

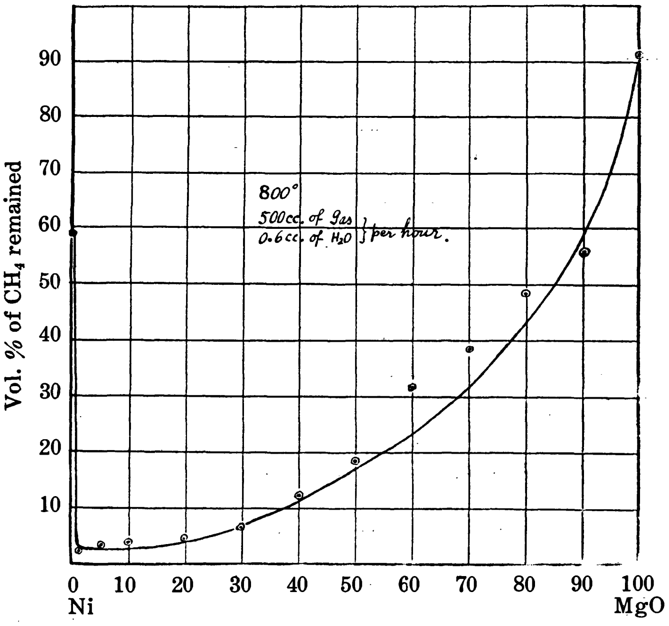


Fig. 4.

to 99.0 gram atom of Ni, and the volume percentage of methane which remained without changing, that is $\frac{[CH_4]\times 100}{[CO_2]+[CO]+[CH_4]}=2.1$, where bracket denotes the volume of the substance, are represented graphically in Fig. 4.

Summary.

In the catalytic oxidation of methane with steam in the presence of nickel, the promoter action of several metallic oxides were investigated.

It was found that the largest quantity of CO_2 was obtained by employing the catalyst promoted with Al_2O_3, whilst when water vapour was regulated the catalyst promoted with MgO gave the largest yield of CO.

These results might possively lead one to suppose that the reaction may be looked upon as taking place successively in the manner:

$$CH_4 \xrightarrow{H_2O} CO+3H_2 \xrightarrow{H_2O} CO_2+4H_2,$$

and as the beneficial effect of promoters in these reactions may be to transfer water molecules to the reaction centers of the catalyst where the action of water on methane is carried out, the products may be determined according to the adsorbing intensity of water molecules and the size of the promoter. Thus it seems to us that the results we obtained are quite in good agreement with Balandin's "Multipletthypothese."

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SINOMENINE AND DISINOMENINE.

PART IX. ON ACUTUMINE AND SINACTINE.

By Kakuji GOTO and Hideo SUDZUKI.

Received September 21, 1929. Published October 28, 1929.

Two new alkaloids were isolated from the root of *Sinomenium acutum Rehd et Wills*, so that the plant contains at least five well characterised alkaloids as the following.

1. Sinomenine $C_{19}H_{23}NO_4$
2. Diversine
3. Disinomenine $(C_{19}H_{22}NO_4)_2$
4. Acutumine
5. Sinactine

the latter three being first isolated by one of the authors (K.G.).

I.

Acutumine has the molecular formula $C_{20}H_{27}NO_8$ or $C_{21}H_{27}NO_8$ and its absorption spectra resembles rather that of narceine. It accumulated in chloroform solution, as free base, when weakly acidic diversine part of the extract of the drug was subjected to purification. The cystallisation was acceralated by addition of methyl alcohol. It forms pale yellow needles of m.p. 240° and very scarcely soluble in ordinary organic solvents. Its content in the root amounts to ca. 1/100 of the sinomenine.

No salt of acutumine has hitherto been obtained in crystalline form. The gold double salt is also amorphous and melts rather sharply at 199~200°. The specific rotatory power of the hydrochloride is $[\alpha]_D = +60.20°$.

The analytical date are the following. After Pregl. C=56.98, 56.89, 56.81, 57.46, 57.15; H=6.82, 5.81, 5.93, 6.51, 6.62%.

After Liebig C=56.88, 58.19, 58.20, 57.91; H=5.88, 6.42, 7.29, 6.34%.

After Dumas N=3.36, 3.38%.

From these results, the molecular formula $C_{20}H_{27}NO_8$ can be most plausibly assigned to it. Yet calculated as an alkaloid of narceine group, $C_{21}H_{27}NO_8$ may be preferred. The decision must be made only when the decomposing experiments were carried out, for which the materials is not sufficient at present.

Molecular weight. From the calcination of gold salt: 406. After Rast (this method is rather doubtful for some of the alkaloids): 381, 445, 393.

Functional groups.

1. Acutumine does not give ferric chloride reaction, potassium ferricyanide reaction and diazo-reaction. The existence of phenol hydroxyl is therefore excluded.

2. Methoxyls. Acutumine contains three methoxyl group, as are revealed by the Zeisel's method:

CH_3O=22.48, 22.70, 22.77, 22.80, 23.41%. Calc. for $3CH_3O$ in $C_{20}H_{27}NO_4$ (=409): 22.79%.

3. N-Methyl. After Herzig-Meyer's, found: N=4.34%. Calc: 3.66%.

4. Methylendioxy-group is not present in acutumine. (Controll: narcotine, narceine, berberine etc.).

5. Ketone group. One ketone group is existent in acutumine, since it forms a semicarbazone, which crystallises in beautiful, long needles. It does not melt even at 290°. (Found: N=11.66%. Calc. as monosemicarbazone: 12.06%).

6. Carboxyl group. Existence of a carboxyl group is suspected, since acutumine is very weakly basic, being precipitated from its hydro-chloride solution by sodium acetate (when its concentration reaches to ca. 5%.) Yet no definite proof has yet been given.

Constitution of acutumine. From what has been said above, the molecular formula of acutumine may be represented in the following way.

$$C_{14}H_{10} \text{ or } C_{15}H_{10} \left\{ \begin{array}{l} 3\ CH_3O \\ >CO \\ -\ COOH \\ N-\ CH_3 \\ 2\ H_2O \text{ (Crystall water ?)} \end{array} \right.$$

Assuming that acutumine has a skeleton of narcotine group, $C_{14}H_{10}$ are not sufficient for the construction of a protopapaverine skeleton and the molecular formula $C_{21}H_{27}NO_8$ is suspected to be better fitted for the alkaloid. The question will be decided by degradation, when we isolated a large quantity of the substance.

II.

Sinactine hydrochloride accumulates in chloroform, when the latter is repeatedly used in the extraction of the alkaloids without evaporation, but the base is removed by means of hydrochloric acid from it. Since this hydrochloride is very scarcely soluble in water (0.74%), it can be easily purified from sinomenine.

The free base is precipitated in needles from the solution of its hydrochloride by means of ammonia. It can be recrystallised from methyl alcohol. m.p. 174°.

The hydrochloride is yellow and decomposes at 272°.

The gold double salt is amorphous.

The platinum double salt is beautiful crystals and melts at 245~247°, darkening at 240°.

The specific rotation of free base in chloroform (C=ca. 1%) is $[\alpha]_D = -312°$.

Analysis. Found: C=71.03, 70.30, 70.52, 70.96; H=6.41, 6.68, 6.30, 6.41; N=3.87%. Calc. for $C_{19}H_{21}NO_4$(=327): C=69.73; H=6.40; N=4.28%.

Mol. Weight. Found: 309.2 (by the calcination of the platinichloride)

Functional groups.

1. Sinactine has no free phenol group, since it does not give the three reactions of phenol as were given with acutumine.
2. Sinactine has a methylendioxy group, as it gives much precipitates with phloroglucine-sulphuric acid.
3. Sinactine has two methoxyl groups. (Found: 18.87%. Calc. for $2CH_3O-$ in $C_{19}H_{21}NO_4$: 18.99%).
4. Sinactine has no N-methyl group. Heating for 2 hours at 300° or thereabout with $IH+INH_4$, it gave no precipitate with silver nitrate.

Constitution of Sinactine. The absorption spectra of sinactine almost coincide with that of laudanosine, and there can be no doubt that sinactine is an alkaloid belonging to tetrahydropapaverine group.

The molecular formula $C_{19}H_{21}NO_4$, in which two methoxyl, one (presumably) methylendioxy and no N—methyl groups are traced, makes sinactine an isomeride of veratryl-nor-hydro hydrastine, which W.H. Perkin jun. synthetised in 1924.(1)

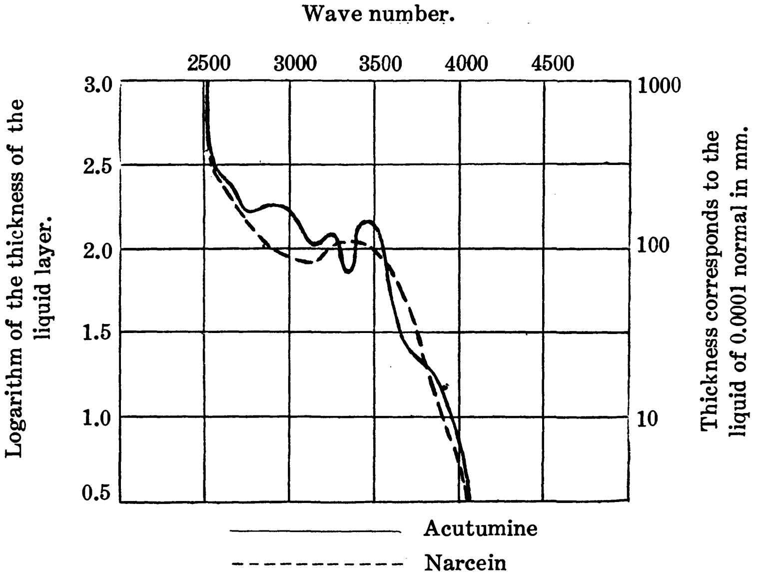

Fig. 1.

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(1) *J. Chem. Soc.*, **1924**, 1677 & 1696.

But there is a remarkable difference between sinactine, veratrylnorhydro-hydrastine and the epi-form of the latter in the melting points. The latter two melt at 84° and 96° respectively whilst sinactine melts at 174°, almost 100° degrees higher than they do. This difference we should like to explain by suspecting that the methoxyls and methylen-dioxy group are attached to the different positions from those in the synthesised alkaloids.

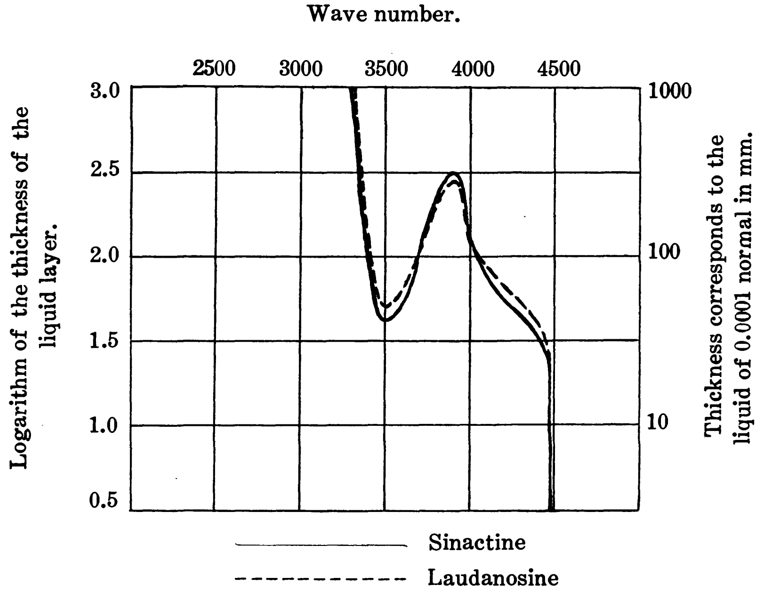

Fig. 2.

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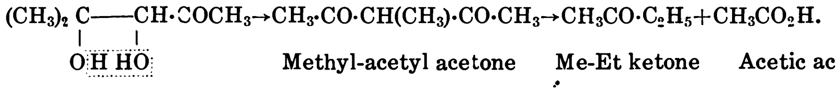
ELECTRONIC CONCEPTION IN ORGANIC CHEMISTRY.
III. DISSOCIATION AND SEMIHYDROBENZOIN REARRANGEMENT OF *αα*-DIMETHYL-*β*-ACETYL GLYCOL.

By Masao MIGITA.

Received September 24, 1929. Published October 28, 1929.

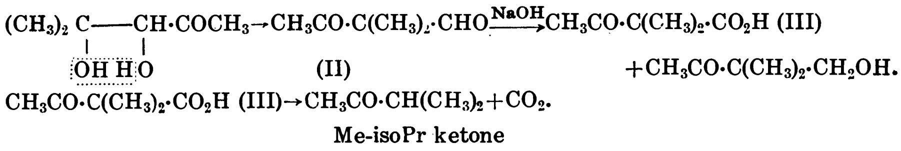
Numerous examples are known on dehydration and molecular rearrangement of pinacones and other hydroxy-compounds, closely related to them, but none has been known which deals with a glycol having substituents other than hydrocarbon-or substituted aromatic hydrocarbon-radicals. In order to see the effect exerted by carbonyl group, the author has studied the action of hot dilute and cold concentrated sulphuric acid on *αα*-dimethyl-*β*-acetyl glycol $(CH_3)_2C(OH)\cdot CH(OH)\cdot CO\cdot CH_3$ (I).

It is worthy of note that by the rearrangement of this glycol we cannot usually isolate the reaction products as such, owing to inevitableness of distilling them with acid and base during the analytical procedure, while they are very reactive to both acids and bases. Thus by the semipinacolinic rearrangement, the primary product is methyl-acetyl acetone, but the substances actually isolated will be its hydrolysis products, methyl-ethyl ketone and acetic acid.



$$(CH_3)_2\,\underset{\mathrm{O}\boxed{\mathrm{H}}}{\underset{|}{C}}\!-\!\!-\!\!\underset{\boxed{\mathrm{HO}}}{\underset{|}{C}}H\cdot COCH_3\rightarrow \underset{\text{Methyl-acetyl acetone}}{CH_3\cdot CO\cdot CH(CH_3)\cdot CO\cdot CH_3}\rightarrow \underset{\text{Me-Et ketone}}{CH_3CO\cdot C_2H_5}+\underset{\text{Acetic acid}}{CH_3CO_2H}.$$

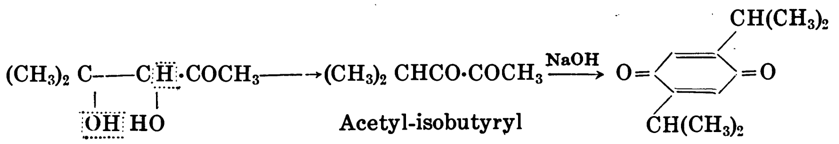
By the semihydrobenzoin rearrangement a tertiary keto-aldehyde (II) is formed, which, as a characteristic of a tertiary aldehyde, will give corresponding acid (III) and alcohol, when boiled with alkali. This *β*-keto-acid being unstable in free state, will readily lose carbon dioxide and will give methylisopropyl ketone.



$$(CH_3)_2\,\underset{\boxed{\mathrm{OH}}}{\underset{|}{C}}\!-\!\!-\!\!\underset{\boxed{\mathrm{H}}\mathrm{O}}{\underset{|}{C}}H\cdot COCH_3\rightarrow \underset{\text{(II)}}{CH_3CO\cdot C(CH_3)_2\cdot CHO}\xrightarrow{NaOH}CH_3CO\cdot C(CH_3)_2\cdot CO_2H\ \text{(III)}\ +CH_3CO\cdot C(CH_3)_2\cdot CH_2OH.$$

$$CH_3CO\cdot C(CH_3)_2\cdot CO_2H\ \text{(III)}\rightarrow \underset{\text{Me-isoPr ketone}}{CH_3CO\cdot CH(CH_3)_2}+CO_2.$$

By vinyl dehydration acetyl-isobutyryl is formed, which can be distilled from acidic solution, but when warmed with alkali, condensation into quinone, a specific reaction of an *α*-diketone, will take place.



In addition to these secondary reactions, possibility of a simultaneous reaction, the dissociation of the original glycol into acetone and acetol, is expected from the fact that in acetic acid solution this glycol does not give its own osazone but gives that of acetol.(1) In this way, a mixture of closely related compounds is likely to be obtained by the action of sulphuric acid on dimethyl-acetyl glycol, consequently the choice of analytical procedure must be the matter of the first importance. After careful study, it was ascertained that acetone can be successfully identified by indigo-reaction,(2) methyl-ethyl ketone by vanillin-hydrochloric acid test,(3) methylisopropyl ketone as its *p*-nitrophenyl-hydrazone, and acetol by the formation of 3-oxy-quinaldine,(4) even in case of their mixtures. All these methods are so sensitive that 1 c.c. of 1 % aqueous solution is sufficient for their identification.

Results. When dimethyl-acetyl gloycol was boiled with dilute sulphuric acid, acetone, methyl-isopropyl ketone and acetol were formed and isolated from the reaction products. When the glycol was treated with cold concentrated sulphuric acid, these two ketones were again formed, but no trace of acetol was detected. Acetol may be considered to be once formed and undergo subsequent condensation under the influence of concentrated sulphuric acid. Methyl-ethyl ketone and acetyl-isobutyryl were not found in both cases. Taking the secondary reactions into consideration, we can conclude from these results that dimethyl-acetyl glycol undergoes dissociation and semihydrobenzoin rearrangement simultaneously when treated either with hot dilute or cold concentrated sulphuric acid.

Interpretation of the results.

Semihydrobenzoin rearrangement of dimethyl-acetyl glycol. The oxygen of the carbonyl group being the most negative atom in the molecule of this glycol, it may be considered to act as a key atom when the molecule is placed

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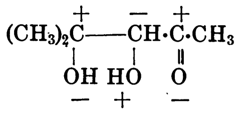
(1) Harries and Pappos, *Ber.*, **34** (1901), 2979.

(2) Baudisch describes on the indigo-reaction of acetol, but under my experimental conditions it gave negative test (see experimental part).

(3) Rosenthaler, *Z. anal. Chem.*, **44** (1904), 292.

(4) Baudisch, *Biochem. Z.*, **89** (1918), 279.

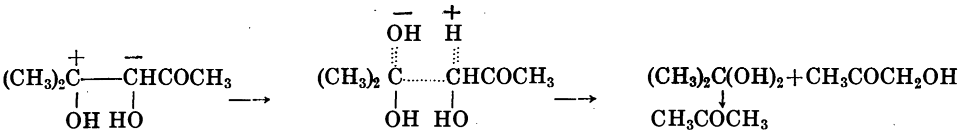
in an activated state.⁽¹⁾ Then the distribution of polarity in this molecule may be shown in the formula (IV), and this polarity being caused by the powerful key atom, it may be well considered to be strong enough to overcome the sterical factor in the substitutional action of cold concentrated sulphuric acid.⁽²⁾ Then it will be easily deduced from the electronic interpretation given in previous paper,⁽³⁾ that this keto-glycol undergoes semihydrobenzoin rearrangement either by hot dilute or by cold concentrated sulphuric acid.



$$(CH_3)_2\overset{+}{\underset{\substack{|\\ OH\\ -}}{C}}-\!\!-\overset{-}{\underset{\substack{|\\ HO\\ +}}{CH}}\cdot\overset{+}{\underset{\substack{\|\\ O\\ -}}{C}}\cdot CH_3$$

(IV)

Dissociation of the glycol. As above stated, the secondary carbon of this keto-glycol is induced strongly negative by the influence of carbonyl group. If this induced negativity is supposed to be sufficiently strong, electron pair which binds the secondary and tertiary carbon is drawn to the former so near that it can keep no longer the tertiary carbon in a stable bond. Under these circumstances, only very strongly-positive atom, say hydrogen, can form a stable union by this electron pair, for such an atom has, in stable state, its electron at distance from its proton. Therefore, under the influence of an acid, the secondary carbon is to be assumed to form a more stable bond with hydrogen ion than with tertiary carbon, resulting in the dissociation of the glycol.



$$(CH_3)_2\overset{+}{\underset{\substack{|\\ OH}}{C}}-\!\!-\overset{-}{\underset{\substack{|\\ HO}}{C}}HCOCH_3 \longrightarrow (CH_3)_2\underset{\substack{|\\ OH}}{\overset{\substack{\overset{-}{OH}\\ \vdots}}{C}}\cdots\cdots\underset{\substack{|\\ HO}}{\overset{\substack{\overset{+}{H}\\ \vdots}}{C}}HCOCH_3 \longrightarrow \underset{\substack{\downarrow\\ CH_3COCH_3}}{(CH_3)_2C(OH)_2}+CH_3COCH_2OH$$

If the above interpretation is allowable, the dissociation should be started also under the influence of alkali, for in this case a stable bond is considered to be formed first between hydroxyl ion and tertiary carbon atom. This was proved by the fact that dimethyl-acetyl glycol, when treated with *o*-amino-benzaldehyde in alkaline solution, gives 3-oxy-quinaldine, a condensation product of acetol and this reagent.

Dissociation of the glycol by distillation. Harries⁽⁴⁾ assumed that the dissociation of dimethyl-acetyl glycol takes place merely by distillation, how-

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(1) An analogy is found in the case of tertiary amino-alcohols. (This Bulletin, **3** (1928), 314.)

(2) It has been assumed that cold concentrated sulphuric acid acts substitutionally and that in substitution sterical factor is predominant over the effect of polarity, so long as the latter is not marked, elimination of the secondary hydroxyl group resulting. (This Bulletin, **4** (1929), 60).

(3) This Bulletin, **4** (1929), 58, 61.

(4) Loc. cit.

ever he could not prove it directly. In fact, when pure dimethyl-acetyl glycol (b.p. 114°/22 mm.) was subjected to two or three successive redistillations under reduced pressure, some measure of a fraction boiling under 100° was always obtained in every time. But the final solution of this question is possible only by finding a sharp method to identify acetone,⁽¹⁾ acetol and the keto-glycol in presence of one another. Formation of oxy-quinaldine, the excellent test for acetol, is inapplicable in this case, for during this procedure, the original glycol gives acetol by the action of alkali, as mentioned above. After various trials, it was found that Denigès' acid mercuric sulphate solution is very satisfactory reagent for this purpose (see experimental part), by virtue of which the presence of both acetol and the keto-glycol in the lower fraction obtained by the redistillation of pure dimethyl-acetyl glycol was proved. Thus the dissociation of the glycol by distillation was directly ascertained. A possible objection against this method that sulphuric acid contained in this reagent may start the dissociation of the glycol, can be overcome by the fact that the solution of pure dimethyl-acetyl glycol gives no crystal of acetol complex. Presumably this is due to the complex formation between the glycol and mercuric sulphate completed speedily enough not to give a chance for the dissociation of the glycol.

Experimental Part.

Dimethyl-acetyl glycol. This glycol was prepared by oxidation of mesityl oxide with potassium permanganate according to Harries.⁽²⁾ But the yield being extremely poor notwithstanding the original description, preparations were carried out under various conditions. The yield, however, could not exceed 37% of the weight of mesityl oxide used, which is only half of that claimed by Harries.

Exp. 1. The permanganate solution was dropped in the course of 6 hours at various temperature. The first fractions of the products obtained from 10 gr. mesityl oxide are given in Table 1.

Exp. 2. When the permanganate was added in 3 hours at 2–3°, following first fractions were obtained under the pressure of 22 mm.

27–31°, 6.15 gr., 50–65°, 1.25 gr., over 65°, 0.0 gr.

Exp. 3. After the reaction (temperature 2–3°, duration 6 hours), the solvent was removed by ordinary distillation, for by vacuum distillation only half of the acetone used was recovered. First fractions distilling under the pressure of 22 mm. was as follows:—

below 50°, 0.75 gr., 50–75° 2.15 gr., over 75°, 0.0 gr.

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(1) Taking the boiling points in consideration, acetone can be excluded.

(2) Harries and Pappos, loc. cit., "Zu einer gut gekühlten und stetig durchgerührten Mischung von 10 gr. Mesityloxyd in 20 c.c. Aceton lässt man langsam eine Lösung von 21. 6 gr. $KMnO_4$, 40 c.c. Wasser und 750 c.c. Aceton tropfen. . . ."

Table 1.

Fraction.	Reaction temperature.				Remarks.
	−8°	2-3°	7-8°	20-22°	
<50°/22 mm.	1.85 gr.	0.6 gr.	0.3 gr.	0.0 gr.	Mesityl oxide, (41°/23 mm.).
50-100°/22 mm.	2.45 gr.			0.15 gr.	Acetol, (54°/18 mm.).
>100°/22 mm.	0.00 gr.	3.7 gr.	3.7 gr.	2.4 gr.	Di-Me-acetyl glycol, (109°/19 mm.).

As is evident from these experiments, by the oxidation at too low temperature or in too short time, a considerable quantity of mesityl oxide remains unchanged, and by the treatment of the products at a temperature higher than room temperature, dissociation of the glycol into acetol takes place. Separation of the glycol from a fair quantity of mesityl oxide or acetol was proved to be a laborious and fruitless matter. The best conditions for the preparation were the reaction temperature 7—8°, and the duration 6 hours.

Methods of identification of the products.

Indigo-reaction. In dilute aqueous solution of acetone small quantity of *o*-nitro-benzaldehyde was dissolved at temperature not exceeding 50°. After cooling, add 15 % aqueous caustic soda solution, and the well-known precipitate of indigo will appear(1). Under these conditions, other ketones, acetol, and the keto-glycol did not interfere. In the case of acetol (1 and 10 % aqueous solutions were tested), long white needles crystallized from the solution in which *o*-nitro-benzaldehyde had been dissolved. On addition of caustic soda these crystals were dissolved again, and the solution turned reddish brown. On the other hand, Baudisch(2) has described that aqueous acetol solution, prepared from monochloro-acetone and freshly precipitated barium hydroxide, gives indigo-reaction by *o*-nitro-benzaldehyde and alkali even in the cold. However, it is worthy of notice what he had prepared was aqueous acetol solution, but not pure acetol, and what the present author dealt with was the aqueous solution of *pure acetol*, prepared, according to Nef,(3) from monochloro-acetone and fused potassium formate in dried methyl alcohol.

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(1) Rosenthaler, "Der Nachweiss der organishcer Verbindungen" p. 162.

(2) Baudisch, loc. cit.

(3) *Ann.*, **335** (1904), 259.

*Vanillin-hydrochloric acid test.*⑴ 1 % vanillin solution in concentrated hydrochloric acid was mixed, before use, with equal volume of concentrated sulphuric acid, to which 1 c.c. of dilute (1 %) aqueous solution to be examined was added. The colours produced in the instant when they were mixed, and these after heated in the boiling water bath were observed (Table 2).

Table 2.

Colour change	Acetone.	Me-Et ketone.	Me-isoPr ketone.	Acetol.	Di-Me-acetyl glycol.
Before heating.	No change.	Green.	No change.	No change.	Pink.
After heating.	Violet.	Blue.	Violet.*	Black brown.	Brown.

*Flourescence of green and purple is seen in the beginning.

The blue colour produced by methyl-ethyl ketone being extremely deep, this ketone can be detected by this method in presence of others. The typical colours given by acetone and methyl-isopropyl ketone are distinguished only when methyl-ethyl ketone is absent.

p-Nitrophenyl-hydrazones. Stress was placed upon properties of crystals, for the melting points of phenyl-hydrazones, as is known, are not often decisive for the purpose of identification. Some properties of crystals of *p*-nitrophenyl-hydrazones of the three ketones are given in Table 3.

Table 3.

	p-Nitrophenyl-hydrazone of		
	Acetone.	Me-Et ketone.	Me-isoPr ketone.
Crystal-form			
freshly prepared.	Prismatic needles.	Mossy.	Fibrous
recrystallized from aq. alcohol.		Long parallelogram.	Prismatic needles.
Dichroism.	Marked. Pale yellow(x′),* Brownish yellow(z′).	The same.	Weak. Pale yellow(x′), Yellow(z′).
Extinction.	Oblique.	The same.	The same.
Extinction-angle	Variable.	The same.	The same.
Mean values $\theta x'$**	34.0°	35.5°	40.0°
Mean values $\theta z'$	54.0°	51.1°	47.3°

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(1) Rosenthaler, *Z. anal. Chem.*, **44** (1904), 292.

*The crystal is pale yellow when observed by the ray which propagates with larger velocity through it, and brownish yellow by the slower ray.

**θ_x' and θ_z' represent angles between the prominent edge and the direction of the faster and slower rays respectively.

Solubilities. When 0.01 gr. *p*-nitrophenyl-hydrazones of three ketones are dissolved in 6c.c. of hot 50% alcohol, the hydrazone of methyl-ethyl ketone crystallizes out on cooling, but that of acetone separates out only very slowly, whereas the derivative of methyl. isopropyl ketone remains dissolved, this being soluble even in 3.6c.c. of 30% aqueous alcohol-

As is evident from the above table, acetone can be identified by freshly prepared crystals of its *p*-nitrophenyl-hydrazone, and methyl- isopropyl ketone by those recrystallized from aqueous alcohol.

A new test for Acetol. Insoluble complex of mercuric sulphate and a carbonyl compound is precipitated by heating dilute aqueous solution to be tested with equal volume of Denigès' reagent in boiling water bath.(1) Each carbonyl compound has its own complex and own velocity of complex formation. The results obtained from experiments on 1% aqueous solutions of several acetyl compounds are given in Table 4.

Table 4.

	Precipitates.	Precipitation takes place
Acetone.	White dense crystals.	After 1 min. all at once.
Me-Et ketone.	The same.*	After 2 min. gradually.
Me-isoPr ketone.	Faintly yellow dense crystals.	After 10 min. gradually.
Acetol.	White scaly crystals with pearly lustre.**	After 2 min. gradually.
Di-Me-acetyl glycol.	Yellowish brown dense crystals.	Within 1 min. all at once.

*This precipitate has been described as being yellow,(2) but the fresh precipitate formed from dilute aqueous solution of pure methyl-ethyl ketone was almost as white as the acetone complex.

**Mercury deposits by prolonged heating.

By this way, acetol can be detected in presence of the keto-glycol, but not in presence of acetone, for in this case only white heavy precipitates are formed.

Action of hot dilute sulphuric acid. 10 gr. of the glycol was boiled with 150 c.c. of dilute sulphuric acid (1:5) for 3 hours. The solution which had been opaque and yellow, gradually turned reddish brown and black oil

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(1) Denigès, *Ann. chim. phys.*, [7] **18** (1899), 384 & 399; Thorpe and Whitely, "Organic Chemical Analysis", p. 109.

(2) Thorpe and Whitely, "Organic Chemical Analysis", p. 110.

separated on the surface. Yellow liquid dropped from condenser and light greenish yellow vapour was observed in the neck of the flask.

Volatile Part. The raw product was subjected to rapid distillation. The first 10 c.c. of the distillate consisted of almost homogeneous yellow liquid lighter than water. The colour of the succeeding distillate turned lighter as distillation went on, and finally faded away. Distillation was stopped when the acidity of the distillate sank below 0.01 normal. However, even this last distillate reduced greedily cold Fehling's solution. This volatile part contained acidic substances equivalent to 4.3 c.c. of decinormal alkali, and was colored markedly yellow when rendered alkaline. By redistillation of this alkaline solution, it was separated into neutral and acidic fractions.

Neutral constituents. Neutral fraction was saturated with anhydrous potassium carbonate and separated oil was extracted with ether. After drying, the ethereal solution was subjected to fractional distillation, and following fractions were obtained: (a) 40–60°, 0.15 gr., (b) 60–80°, 0.0 gr., (c) 80–100°, 0.2 gr., (d) 140–155°, 0.2 gr.

As the fraction (a) contained considerable quantity of ether, it was shaken with equal volume of water, and this aqueous solution was tested for acetone and methyl-ethyl ketone. Acetone was identified by indigo reaction and by its *p*-nitrophenyl-hydrazone. The absence of methyl-ethyl ketone (b. p. 71°) was ascertained by vanillin-hydrochloric acid test. Fraction (c) was similarly tested for methyl-ethyl-and methyl-isopropyl ketones. The latter was isolated as its *p*-nitrophenyl-hydrazone, the former being proved to be absent also in this fraction. Fraction (d) was acidic for litmus, reduced cold Fehling's solution, and gave iodoform reaction by tincture of iodine and ammonia. It was identified to be acetol (b. p. 145–6°) by converting it into 3-oxy-quinaldine. It is not clear why this strongly acidic substance distilled out from alkaline solution and was found in this fraction.

The yellow vapour and condensed liquid observed during the reaction seem to indicate the presence of acetyl-isobutyryl (b. p. 115°), but no fraction distilling 100–140° was obtained, nor it was detected by the formation of quinones.

Acidic fraction. Acetol was easily identified. In order to detect other volatile acids, acetol was oxidized into little volatile lactic acid by Fehling's solution and the content was acidified and distilled. But the distillate was too slightly acidic to be fully analysed. Only the presence of minute quantity of lactic acid which escaped partly with water could be assumed by iodoform reaction.

Non-volatile Part. Though the residue of the first distillation was extracted with ether and treated as usual, nothing but black rosinous matter was obtained.

Action of cold concentrated sulphuric acid.

Under mechanical agitation, 100 c.c. of well cooled concentrated sulphuric acid was slowly dropped into 10 gr. of dimethyl-acetyl glycol, kept at the temperature below 0°. As sulphuric acid was added, the solution was colored crimson and turned reddish brown in the course of time. Cooling and stirring were kept for two hours after all the acid had been added, and the content, which smelled strongly of an essential oil, was poured into 1 litre of ice water. Black particles were observed suspended in the solution but the quantity being too small, the solution was distilled without being filtered. Subsequent separation and identification of the products were carried out exactly in the same way as in the previous case.

Volatile Part. *Neutral constituents.* Ethereal solution of neutral consistuents was fractionated into three fractions: (a) 40–50°, 1 c.c., (b) 90–110°, 0.1 gr. (c) over 110°, 0.1 gr. Acetone and methyl-isopropyl ketone were detected in (a) and (b) fractions respectively. Fraction (c) was tested for acetyl-isobutyryl by means of *o*-phenylene-diamine, but no precipitate was formed.

Acidic fraction. Though this fraction smelled strongly of the same smell as emitted by the raw product, it contained but a trace of acidic constituents, for only 0.1 c.c. of decinormal alkali was sufficient for neutralization of 50 c.c. of the distillate.

It must be mentioned that both neutral and acidic fractions were quite indifferent to Fehling's solution, thus no trace of acetol was detected. Under the assumption that acetol was once formed and underwent subsequent condensation, it was attempted, in vain, to find some relation between its consensation product and the smell emitted by the raw products and the acidic fraction.

Non-volatile Part. Non-volatile part consisted of a brown rosinous matter, soluble in ether and water, which reduced Fehling's solution very slowly when heated in boiling water bath, but not Schiff's reagent. Attempts to get a definite compound from this part ended in failure.

Summary.

In order to see the effect of the carbonyl group, action of hot dilute and cold concentrated sulphuric acid on $\alpha\alpha$-dimethyl-β-acetyl glycol was studied.

This keto-glycol was found to undergo semihydrobenzoin rearrangement and dissociation into acetone and acetol simultaneously. The primary product of the semihydrobenzoin rearrangement of this glycol being decomposed during the subsequent treatments, only the secondary products, methyl-isopropyl ketone, could be isolated. The dissociation of dimethyl-acetyl-glycol was started not only by acid, but also by alkali. These results can be easily deduced from the electronic interpretation given in previous papers.

That the dissociation of dimethyl-acetyl glycol takes place merely by distillation was directly proved by identifying acetol by a new method.

Methods to identify acetone, methyl-ethyl ketone, methyl-isopropyl ketone, acetol and dimethyl-acetyl glycol with limited quantity of the sample in presence of one another, were carefully studied and established.

I beg to tender my sincere thanks to Prof. K. Matsubara for his kind inspection of this paper.

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BEITRÄGE ZUR KENNTNIS DER ALLOTROPEN MODIFIKATIONEN VON SCHWEFEL.(1)

I. ZUR KRYOSKOPIE DES SCHWEFELS.

von C. R. PLATZMANN.

Eingegangen am 4. September 1929. Ausgegeben am 28. November 1929.

Die leichte Umwandlung in allotrope Modifikationen lässt den Schwefel als wenig geeignet erscheinen, um als Lösungsmittel bei kryoskopischen Versuchen Anwendung zu finden. Bei 119.25° schmelzender, monokliner Schwefel weist nach 6–8 stündigem Erhitzen bei der genannten Temperatur einen Erstarrungspunkt von 114.5°, also um 4.75° niedriger, auf, da offenbar eine oder mehrere neue Modifikationen entstehen, welche den Schmelzpunkt in gleicher Weise herabsetzen wie irgend ein fremder in Schwefel löslicher Stoff. Auch der Erstarrungspunkt von 114.5° ist nicht unveränderlich, sondern unterliegt mit Änderung der Aussenbadtemperatur entsprechenden Schwankungen. Wird die letztere erhöht, so tritt weitere Erniedrigung ein. Will man also möglichste Konstanz und Einheitlichkeit des Schmelzpunktes erreichen, so muss das Schmelzen in Badtemperaturen erfolgen, welche gerade über dem Schmelzpunkt des jeweilig bestehenden Gleichgewichts liegen, und umgekehrt darf das Erstarren nur bei Temperaturen, die gerade unter dem Gefrierpunkt des jeweilig bestehenden Gleichgewichts liegt, herbeigeführt werden.

Solche Versuche setzen voraus Konstanz der eingestellten Badtemperatur sowie die Möglichkeit, schnelle Änderungen dieser vorzunehmen, wenn Schmelzen oder Erstarren bewirkt werden sollen. Dampfbäder, die diesen Voraussetzungen sehr vollkommen entsprechen, sind die von E. Beckmann, W. Weber und O. Liesche(2) konstruierten Manostaten, bei denen die Badtemperatur einmal unabhängig von der Aussentemperatur ist, zum andern tagelang innerhalb einiger hundertstel Grade konstant erhalten werden kann.

Bei der für flüssigen Schwefel (110–125°) in Betracht kommenden Temperatur erwies sich Gärungsamylalkohol (Sp. 132°, 760 mm.) als Dampfbad besonders geeignet, da nur mit Hilfe einer gewöhnlichen an den Manostaten angeschlossenen Wasserstrahlluftpumpe die Siedetemperatur von 132° entsprechend herabgesetzt zu werden brauchte.

Um überhaupt eine Kryoskopie des Schwefels aufbauen zu können,

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(1) Ausführung dieser Versuche im Kaiser Wilhelm Institut für Chemie, Berlin-Dahlem auf Anregung und unter Leitung von Prof. Dr. E. Beckmann †.

(2) *Z. physik. Chem.*, **79** (1912), 565; **88** (1914), 13.

kam nur der natürliche Schmelzpunkt von 114.5° als Grundlage der Versuche in Frage. Der aus Schwefelkohlenstoff auskristallisierte und von diesem im Vakuum völlig befreite Schwefel wurde zunächst im Gefrierrohr durch den Manostaten auf eine Temperatur von 121° geschmolzen, die anfängliche bei 119° liegende Erstarrungstemperatur senkte sich mit der Zeit auf 114.5°.

Die Erstarrungstemperatur wurde ermittelt durch langsames Erniedrigen der Badtemperatur bei gleichzeitigem ständigen elektromagnetischen Rühren,(1) worauf durch das Einbringen eines 2½ mm. starken Platindrahts von Zimmertemperatur durch Wärmeentziechung Erstarren erfolgte.

Auf die Badtemperatur war besonders deswegen stets sorgfältig zu achten, weil bei der geringen latenten Schmelzwärme des Schwefels und der hoch viskosen Beschaffenheit der Schmelze der Wärmeausgleich zwischen Flüssigkeit und Kristallen nur langsam eintritt. Ist die Temperaturdifferenz zwischen Gefrierrohr und Bad zu gross, so wird die Ablesung der Gefriertemperatur leicht fehlerhaft.

Während in den folgenden Tabellen die Badtemperaturen sich auf Ablesungen am Normalthermometer bezeichen, sind die Erstarrungspunkte des Schwefels als direkte Ablesungen am Beckmannthermometer aufgeführt.

Die ersten Versuchsserien sollen zeigen, dass es bei Erhitzen über Nacht gelingt, ein festes Gleichgewichtsverhältnis herzustellen, dass also die Erstarrungspunkte im Rahmen experimenteller Fehlergrenzen Konstant bleiben.

Versuchsserie	Badtemperatur beim Schmelzen	Normalthermometer beim Erstarren	Zeit min.	Erstarrungspunkt Beckmannthermometer
I a	116	114	0	2.485
I b	116	114	25	2.467
I c	116	114	50	2.481
II a	116	114	0	3.838
II b	116	114	15	3.843
II c	116	114	30	3.841
III a	116–117	114	0	3.631
III b	116	114	20	3.630
III c	116	114	40	3.633

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(1) *Z. physik. Chem.*, **21** (1896), 241.

Um das Gleichgewichtsverhältnis in kürzerer Frist zu erreichen, wurde Schwefel in einem Aussenbad von 180° (siedendes Anilin) erhitzt und alsdann auf 115-116° abgekühlt, wobei das Wiederansteigen der Temperatur kryoskopisch geprüft wurde.

Versuchsserie	Badtemperatur beim Schmelzen	Normalthermometer beim Erstarren	Zeit min.	Erstarrungspunkt Beckmannthermometer
IV a	115.0	113.0	0	2.667
IV b	115.2	113.2	20	2.868
IV c	115.4	113.4	35	2.945
IV d	115.6	113.6	50	3.074
IV e	115.6	114.0	210	3.585
IV f	116.0	114.0	225	3.580
IV g	116.0	114.0	237	3.586

Solchermassen liess sich also in 3–4 Stunden Konstanz des Erstarrungspunkts erreichen. Diese Frist lässt sich auf 2 Stunden kürzen, wenn man zunächst den Schwefel 75 Minuten lang auf 140° in Dampf von siedendem *m*-Xylol erhitzt und ihn dann der Badtemperatur von 116° aussetzt.

Eine weitere Möglichkeit, die Konstanz zu beurteilen, besteht in der nach Smith⁽¹⁾ ermittelten Entstehung von amorphem, in Schwefelkohlenstoff unlöslichen Menge an Schwefel (S_μ), die als Ursache des um 4.75° mit der Zeit sinkenden Erstarrungspunktes für 114.5° 3.6% betragen soll und deren Bestimmung dergestalt erfolgt, dass die Schmelze in eine kalte Porzellanschale ausgegossen und nach 24 Stunden mit Schwefelkohlenstoff extrahiert wird. Bei verschieden langem Erhitzen auf 140° ergaben Versuche folgenden Gehalt für S_μ:

1 Stunde	2.31%
1 1/4 Stunden	3.56%
1 1/2 Stunden	4.20%
1 3/4 Stunden	6.90%.

Unter Berücksichtigung des von Smith angegebenen Werts von 3.6% S_μ für den natürlichen Schmelzpunkt von 114.5° war es also zweckmässig, wie oben angegeben, 1 1/4 Stunden zu erhitzen.

Wurden Beckmann- und Normalthermometer bei Gleichgewichtszustand miteinander verglichen, so ergaben sich folgende absolute Schmelzpunkte:

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(1) *Z. physik. Chem.*, **42** (1903), 469.

Badtemperatur	Erstarrungspunkt
115.18°	114.3°
115.31	114.4

Die erhaltenen Werte befinden sich mit den Angaben von Smith in Übereinstimmung, die Brauchbarkeit des natürlichen Schmelzpunkts als Grundlage für kryoskopische Versuche war demnach nicht zu bezweifeln.

Es blieb lediglich zu prüfen, ob das Gleichgewicht durch lösen fremder Stoffe verändert werde oder im wesentlichen erhalten bleibe. Im letzteren Falle mussten bei verschiedenen Stoffen übereinstimmende molekulare Erniedrigungen erhalten werden. Mit Rücksicht auf Löslichkeit, chemische Indifferenz, sowie Kenntnis der molekularen Assoziations-bezw. Dissoziationsverhältnisse wurden zunachst organische Stoffe und zwar nacheinander:

1. Naphtalin
2. Diphenyl
3. *β*-Naphthol
4. *α*-Naphtholsäure
5. Thymol
6. *p*-Kresol
7. Chinolin
8. Anilin
9. Phenylsenföl
10. *α*-Thiophencarbonsäure
11. Bromoform

gewählt.

Diese Versuche ergaben folgendes tabellarisch, zusammengestelltes Bild:

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim		K
			Erstarren	Schmelzen	
		1. Gelöst Naphtalin, $C_{10}H_8 = 128$.			
27.11	0.0287	0.202	112.2	115.0	244.2
	0.0500	0.269	111.8	114.8	186.7
	0.0559	0.349	111.6	114.5	206.6
	0.0431	0.254	111.3	114.2	214.5
				Mittel	213.0
25.12	0.0655	0.485	113.5	116.0	238.1
	0.0848	0.566	112.9	115.5	214.6
	0.0718	0.434	112.4	114.9	194.4
	0.0630	0.376	112.0	114.4	191.9
				Mittel	209.8

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim		K
			Erstarren	Schmelzen	
2. Gelöst Diphenyl $C_{12}H_{10}$=154.1.					
25.00	0.1119	0.620	113.5	115.5	213.5
	0.1179	0.607	112.9	114.9	198.3
	0.1165	0.645	112.2	114.3	213.3
	0.1391	0.678	111.5	113.5	187.8
	0.0824	0.401	110.8	112.8	187.5
				Mittel	200.1
25.00	0.1289	0.774	113.3	116.0	231.3
	0.1529	0.839	112.4	115.2	212.0
	0.1326	0.711	111.6	114.4	206.6
				Mittel	216.6
3. Gelöst β-Naphthol $C_{10}H_7OH$=144.1.					
25.00	0.0873	0.547	113.5	116.0	225.7
	0.0897	0.530	112.9	115.4	212.9
	0.0996	0.589	112.4	114.8	176.9
				Mittel	205.2
4. Gelöst α-Naphtholsäure $C_{10}H_7COOH$=172.1.					
25.00	0.0539	0.225	113.7	116.0	179.6
	0.0365	0.143	113.5	115.7	168.6
	0.0629	0.123	113.2	115.5	184.1

Die schwere Löslichkeit der Substanz und die abnorm niedrigen Konstanten lassen in diesem Falle deutlich Assoziation der Säuremoleküle erkennen.

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Erstarren	Schmelzen	K
5. Gelöst Thymol $C_{10}H_{13}OH$=150.1.					
25.00	0.0765	0.425	113.6	116.0	208.5
	0.0579	0.337	113.2	115.6	218.4
	0.0629	0.352	112.8	115.2	210.0
				Mittel	212.3
25.00	0.0705	0.395	113.6	115.5	210.2
	0.0731	0.394	113.2	115.2	202.3
	0.0711	0.358	112.8	114.8	188.9
				Mittel	200.5

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim		K
			Erstarren	Schmelzen	
6. Gelöst *p*-Kresol $C_7H_7OH = 108.1$.					
25.00	0.0840	0.648	113.7	116.0	208.4
	0.1658	1.165	112.5	115.4	189.8
	0.1548	0.871	111.4	114.2	136.3 (!)
				Mittel	178.1
25.00	0.0850	0.618	113.4	116.0	196.5
	0.0822	0.578	112.7	115.4	189.9
	0.0909	0.528	112.2	114.8	156.8
				Mittel	181.1
7. Gelöst Chinolin $C_9H_7N = 129.1$.					
25.00	0.0881	0.591	113.6	116.0	215.8
	0.1145	0.777	112.8	115.4	219.0
	0.1142	0.685	112.0	114.6	193.6
				Mittel	209.5
8. Gelöst Anilin $C_6H_5NH_2 = 93.1$.					
25.00	0.1038	0.970	113.4	115.7	217.5
	0.1074	0.927	112.4	114.8	200.9
	0.1061	0.853	111.5	113.8	187.1
				Mittel	201.8
9. Gelöst Phenylsenföl $C_6H_5NCS = 135.2$.					
25.00	0.1416	0.982	113.2	115.6	234.4
	0.1093	0.763	112.3	114.6	236.0
	0.1157	0.729	111.5	113.9	213.0
				Mittel	227.8
25.00	0.0974	0.695	113.3	115.7	241.2
	0.1015	0.702	112.6	115.0	233.8
	0.1009	0.665	111.9	114.3	222.8
	0.1032	0.623	111.2	113.6	204.0
				Mittel	225.5

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim		K
			Erstarren	Schmelzen	
10. Gelöst α-Thiophencarbonsäure $C_4H_3SCOOH = 128.1$.					
25.00	0.0981	0.467	113.3	115.3	152.5
	0.1001	0.329	113.0	114.8	105.3
	0.0987	0.307	112.6	114.5	99.6
				Mittel	119.1
25.00	0.0978	0.449	113.5	115.5	147.0
	0.0997	0.390	113.1	115.0	125.0
	0.0999	0.319	112.7	114.6	102.3
				Mittel	124.7

Wie bei der Verwendung von α-Naphtholsäure scheint auch in diesem Falle das Ergebnis auf eine Assoziation der Säuremoleküle hinzudenken.

11. Gelöst Bromoform $CHBr_3 = 252.9$.					
25.00	0.1958	0.637	113.2	115.5	205.7
	0.1602	0.592	112.5	115.0	233.6
	0.2533	0.910	111.8	114.5	227.1
				Mittel	222.1
25.00	0.1579	0.573	113.5	116.0	229.4
	0.1801	0.692	112.8	115.5	242.9
	0.1669	0.618	112.2	114.8	234.1
				Mittel	235.5
25.00	0.1872	0.705	113.2	115.0	238.1
	0.1866	0.653	112.5	114.2	221.3
	0.1655	0.623	111.9	113.5	238.0
	0.2071	0.733	111.0	112.8	223.8
				Mittel	230.3

Nach der Höhe ordnen sich die Konstanten folgendermassen:

Bromoform (11)	229.3
Phenylsenföl (9)	226.6
Naphtalin (1)	211.4
Diphenyl (2)	208.4
Thymol (5)	206.4
Chinolin (7)	205.7
β-Naphthol (3)	205.2

Anilin (8)	201.8
p-Kresol (6)	208–136
α-Naphtolsäure (4)	179–168.6
α-Thiophencarbonsäure (10)	152.5–102.3

Sieht man von den letzten drei Substanzen ab, deren Konstanten bei steigender Konzentration der Lösung stark abfallen, was auf den Gehalt an Hydroxyl und die Neigung zur Assoziation in dem nur schwach dissoziierenden Schwefel mit der kleinen Dielektrizitätskonstante 4.0 zurückgeführt werden darf, so erhält man für die übrigen Körper eine kryoskopische Konstante von im Mittel mit $K=213$.

Aus dieser berechnet sich die latente Schmelzwärme nach der van't Hoffschen Formel:

$$w = \frac{0.02 \times T^2}{K} = 14.1 \text{ gr.-Kal.}$$

im Gegensatz zu den bisher bekannten Werten für die Schmelzwärme des monoklinen Schwefels, die zwischen 9.368 und 12.5 gr.-Kal. schwankten.

Von besonderem Interesse erschien nach Ermittlung der Konstante $K=213$, das Molekulargewicht der analytisch viel verwendeten unlöslichen Sulfide zu bestimmen, obwohl gerade deren Löslichkeit in Schwefel beim natürlichen Schmelzpunkt nicht sehr gross ist.

Die zunächst mit Arsentrisulfid ($As_2S_3=246.2$) ausgeführten Versuche ergaben folgendes Resultat:

Schwefel gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim		Mol. Gew. (K=213)	Mol. As_2S_3
			Erstarren	Schmelzen		
25	0.0530	0.194	113.5	116.0	233	0.95
	0.0510	0.095	113.5	115.8	457	1.86
	0.0534	0.077	113.5	115.7	591	2.40
25	0.0540	0.194	113.8	116.0	309	1.25
	0.0364	0.070	113.7	115.8	443	1.80
25	0.0686	0.185	113.8	115.8	316	1.28
	0.0677	0.107	113.7	115.7	539	2.19

Die in sehr verdünnter Lösung vorhandenen Einzelmoleküle haben bei steigender Konzentration offenbar die Tendenz zur Polymerisierung.

Da weiter das Molekulargewicht von Selentetrachlorid experimentell noch nicht einwandfrei bestimmt wurde, erschien auch hiermit ein Versuch in Schwefel als kryoskopischem Lösungsmittel naheliegend, wobei sich folgendes Resultat ergab:

Schwefel gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim		Mol. Gew. (K=213)	Mol. bezogen auf $SeCl_4$
			Erstarren	Schmelzen		
25	0.1126	0.687	113.5	115.7	139.6	0.63
	0.1013	0.769	112.8	115.0	112.2	0.51
	0.1031	0.767	112.0	114.2	114.5	0.52
25	0.0894	0.511	113.3	115.6	149.1	0.67
	0.1106	0.862	112.8	115.1	109.3	0.49
	0.1137	0.948	111.9	114.2	102.1	0.46

Da das Molekulargewicht nur etwa halb so gross gefunden wurde, wie es der normalen Formel $SeCl_4 = 220.9$ entsprechen würde, hat das Selentetrachlorid offenbar auf den Schwefel wie folgt reagiert:

$$\underset{(2\ \mathrm{mol})}{2SeCl_4 + 6S} = \underbrace{Se_2Cl_2 + 3S_2Cl_2}_{(4\ \mathrm{mol})}$$

Zusammenfassung.

1. Beim natürlichen Schmelzpunkt 114.5° des Schwefels sind mit einer Reihe organischer Substanzen die kryoskopischen Konstanten des Schwefels bestimmt worden, wobei ein mittlerer Wert von K=213 resultierte, der einer latenten Schmelzwärme von 14.1 gr.-Kal. entspricht.
2. Auf Grund seiner kleinen Dielektrizitätskonstante besitzt der Schwefel nur geringe dissoziierende Kraft und lässt bei Säuren die Neigung zur Bildung von Doppelmolekülen erkennen.
3. Arsentrisulfid zeigte in verdünnten Lösungen Moleküle As_2S_3, während bei konzentrierteren Polymerisierung eintrat.
4. Selentetrachlorid ergab das halbe normale Molekulargewicht auf Grund der Bildung von Selenchlorür und Schwefelchlorür.

In einer zweiten Abhandlung sollen auf flüssigen Schwefel einwirkende katalytische Einflüsse behandelt werden, während die letzte Arbeit sich mit den Beziehungen von Jod zu Schwefel und Selen befassen soll.

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SINOMENINE AND DISINOMENINE.
PART XI. ON THE POSITION OF THE DOUBLE LINKING IN SINOMENINE.

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In Part X of this communication, the following three reasons were given in assigning C_7-C_8 position to the double linking of sinomenine.

1. The easy reducibleness of the double linking with nascent hydrogen.

2. The easy hydrolysis of the methoxylgroup, which situates on C_7, by the heating with dilute hydrochloric acid and the after-treatment with ammonia, viz., the formation of bis-[demethyl]-sinomenyliden.

3. The linking together of two sinomenine molecules by the reduction with Na-amalgam.

In the present paper, these three points, together with the formation of d-form of Speyer's dihydrothebainone, already mentioned, will be given in a detailed manner.

I.

When sinomenine is reduced with Na-amalgam in a dilute caustic soda solution, a substance $(C_{18}H_{22}NO_3)_2$ is formed in a 60% yield, besides a small quantity of a substance which is very similar to the desmethoxy-dihydro-sinomenine. (See section II).

The substance $(C_{18}H_{22}NO_3)_2$ has a great tendency to crystallize and it forms beautiful prisms in the course of the evaporation of its chloroform solution. As is given in Table 1, it melts at 304°, and has a double molecular weight. It has only two methoxyls, thus one methoxyl group of each sinomenine molecule being reduced away. It retains the original keton group and forms a disemicarbazone. The ferric chloride reaction and diazo-reaction are also retained in an undiminished degree.

Table 1.

	$(C_{18}H_{22}NO_3)_2$
Yield	ca. 60% (raw)
M. p.	304° (commonly 294°)
Crystal form	stout prisms
Mol. wt.	626 (calc. 600)
$[\alpha]_D$	−24.49°
M. p. of iodomethylate	>300°
M. p. semicarbazone	>300°
Methoxyls	two
$FeCl_3$-reaction	+ in alcohol
Diazo-reaction	+ in 2,500,000th dilution
$K_3Fe(CN)_6$-reaction	purple
Formaline-SO_4H_2	pure blue

As to the linking point of two sinomenine molecules in this substance, 1, 1′-position is excluded, since this substance gives diazoreaction in the same degree as sinomenine itself (disinomenine and ψ-disinomenine give the diazoreaction in a slightest degree).(1) The pinacone linking is also out of question, as the new substance forms a disemicarbazone and more especially, dihydrosinomenine does not give any double molecular substance by the reduction.

The formation of this double molecular compound can therefore only be explained by the parallelism with the reduction of the benzalacetone.

Harries and Muller(2) obtained, in 1902, a diphenyl-octadione by reducing benzal-acetone, and thus showed that α, ß-unsaturated ketone can be linked together by Na-amalgam reduction. The linking point was afterwards more thoroughly determined to be β-position to the ketone group with coumaline by Asahina and Shibata.(3)

From these considerations, it is most reasonable to assume that two melecules of sinomenine was linked together in the β—position to the keton group and that the double linking of the sinomenine must be conjugated to the keton group. This assumption is enforced through the fact that the double linking is reduced by the simple zinc dust and hydrochloric acid couple.

It is a difficult problem to determine whether the position of the ethanamine chain was dislocated or not by this reduction. Yet, the author

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(1) This Bulletin, **4** (1929), 129.

(2) *Ber.*, **35** (1902), 966.

(3) *J. Pharm. Soc. Japan*, (1918) p. 100 (in Japanese.)

feel to be justified to call this new double molecular substance "Bis-8,8′-demethoxy-dihydro-sinomenine".

II.

By the Na-amalgam reduction of dihydro-sinomenine, a monomolecular substance $C_{18}H_{23}NO_3$ was obtained in a yield about 65%. It crystallized in stout prisms from acetone. It has only one methoxyl group, retains the original keton group, and accordingly, it may be called demethoxy-dihydro-sinomenine.(1) As is seen from the following table, it is an optical antipode of Speyer's *l*-dihydrothebainone in all probability. The racemisation was carried out with the iodomethylates of the both substances.

Table 2.

	Demethoxy-dihydrosinomenine (from hydrosinomenine)	Speyer's dihydrothebainone (from thebain)
Yield	ca. 65%	ca. 20%
M. p.	138°	151° (Speyer) 138° (Skita)
Crystall form	prisms	prisms
In alcohol	easily soluble	easily soluble
In acetone	less soluble	less soluble
Mol. wt.	385 (calc. 301)	——
$[\alpha]_D$ (free base)	+59.17°	-80.12° (Skita)
$[\alpha]_D$ (hydrochloride)	+48.88°	-50.71° (Speyer)
Methoxyl	one	——
M. p. of iodomethylate	120°	120°
M. p. of semicarbazone	235°	(226° (Speyer) (237° (Goto)
$FeCl_3$-reaction	+in alcohol	+in alcohol
Diazo-reaction	+in 2,500,000th dilution	+in 2,500,00th dilution
$K_3Fe(CN)_6$-reaction	+in 500,000th dilution	+in 500,000th dilution
Formaline-SO_4H_2	+Yellow → green	yellow → green

The specific rotatory power of the free base of demethoxy-dihydro-sinomenine is somewhat lower than that given by Skita, yet that of the hydrochloride coincides fairy well with the figure given by Speyer.

As regards the melting point of the semicarbazone of Speyer's dihydro-thebainone, it is generally believed to be at 226°(2) Yet, the semicarbazone,

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(1) Reduction of an ether-group, which situates vicinally to a ketone, was also obtained by Wieland and Kotake in dihydro-des-N-methyl-dihydro-codeinon, *Ann.*, **444** (1925), 69.

(2) Gulland and Robinson. *J. Chem. Soc.*, **1923**, 1006.

which the author prepared from dihydro-thebainone and recrystallized from acetone melted at 237°, thus only two degrees higher than that of demethoxy-dihydrosinomenine. The mixed melting point of these two semicarbozone was at 235°.

III.

When sinomenine is reduced with zinc-amalgam in the hot, after the method of Clemmensen, it gives a substance of the composition $C_{18}H_{25}NO_2 + \frac{1}{2}H_2O$ in a yield about 20%. It melts at 148°, contains only one methoxyl group, but no keton group. The original phenol group seems to be intact, since it gives the strong ferric chloride reaction (in alcohol), the diazoreaction and ferri-cyanide reaction in an undiminished degree. This substance, which is to be called demethoxy-desoxo-dihydrosinomenine, is evidently the d-form of the ß-tetra-hydro-desoxy-codein, as is seen from the following table. This point was proved by the actual racemisation.

Table 3.

	Demethoxy-desoxo-dihydrosinomenine	β-Tetrahydrodesoxy-codein(1)
Yield	20%	——
M. p.	147~148°	147~148°
Cystall form	hexagonal plates	hexagonal plates
Mol. wt.	322 (calc. 287)	——
$[\alpha]_D^{19}$	+43.22°	weakly left
M. p. of iodomethylate	267°	263°
M. p. hydro-iodide	245°	240~241°
M. p. of hydrochloride	——	262
$FeCl_3$	+in alcohol	+in alcohol
Diazo-reaction	+in 2,000,000th dilution	+in 2,000,000th dilution
$K_3Fe(CN)_6$-reaction	+in 500,000th dilution	+in 500,00th dilution
Formaline-H_2SO_4	yellow → purple	yellow purple

Hydrosinomenine gives also the same substance by the Clemmensen's reduction.

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(1) Frennd, *J. prakt. Chem.*, **101** (1921), 1.

IV.

If sinomenine is, as we insists, an enol-ether, it may be hydrolysed on its enol-ether group and give rise to a new ketone, as is the case with thebaine. This is actually so. When sinomenine was heated on a steam bath with 2N, 4N, 6N, 8N or fuming hydrochloric acid for two hours, and the base was set free with ammonia, then a new substance of melting point >312° was obtained in a yield about 10%. This substance contained only one methoxyl group and one ketone group against each molecule of sinomenine. But the measurement of the molecular weight showed clearly that it had a double molecular weight. We propose to call this substance "Bis-[demethyl]-sinomenyliden." The property of this substance is given in Table 4.

Table 4.

Yield	10%
M. p.	>312°
Crystall form	prisms
Mol. wt.	650 (calc. 602)
$[\alpha]_D$ (hydrochloride)	+335.52°
M. p. of iodomethylate	>300°
Methoxyls	two (one against each sinomenine molecule)
M. p. of monosemicarbazone	>300°
M. p. of dioxim	>300°
$FeCl_3$-reaction	brown (weak)
Diazo-reaction	+in 2,000,000th dilution
$FeK_3(CN)_6$-reaction	transitory
Formaline-H_2SO_4	yellow → green → bordeau

The condensation of the two molecules of demethyl-sinomenine may be interpreted in the following way. The hydrolysis of the enol-ether may cause a new ketone group to be introduced and the original double linking to be eliminated. The third nucleus of the phenanthrene takes, therefore, the aspect of diacetyl. As Pechmann(1) has proved in 1888, diacetyl or similarily constituted diketones undergo the condensation by the action of alkali, and give substituted chinones. The same condensation may occur with the demethoxylated sinomenine through ammonia. As to the positions of the condensation, we should like to assume C_6 (ketone group) and C_8

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(1) *Ber.*, **21** (1888), 1417.

(methylen group) of each sinomenine molecule, thus giving a chinone like constitution to the new substance.

One uncertainty about this assumption is that this condensed substance is colourless, even in solution. Yet the fact that it forms a monoxim by the ordinary treatment with hydroxylamine hydrochloride seems to favour the chinone constitution.

V.

Throughout the preceeding sections, the author maintained the view that sinomenine must be an α, ß-unsaturated ketone. If this is correct, the double linking of sinomenine must be reduced by hydrogen in status nascendi.

The reduction of sinomenine with Na-amalgam can also be cited in this favour, yet the action of Na-amalgam does not exclude the might-be catalytic action of quicksilver.

After long fruitless trials, the author succeeded at last in reducing sinomenine by zinc dust and hydrochloric acid in the cold. The yield of dihydrosinomenine was, however, scanty (=about 15% in the experiment of a small scale). The reason why such experiments did not succeed for a long time can be sought in the fact that sinomenine is less resistant against hot dilute acid. The heating sinomenine with zinc dust and acetic acid, for example, might lead invariably to the derivative of sinomenine-hydrate,(1) and not that of sinomenine.

By the way, it may be added here that sinomenine can be reduced by Clemmensen's zinc-amalgam and hydrochloric acid in the cold into dihydrosinomenine (yield 60%). Here neither the trace of bis-8,8′-demethoxy-dihydrosinomenine nor demethoxy-desoxo-dihydrosinomenine was met with. This method may be advantageously applied to those α, β-unsaturated ketones, which by the reduction with Na-amalgam invariably undergo condensation.

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(1) Part XII of this communication, which will be published in the December number.

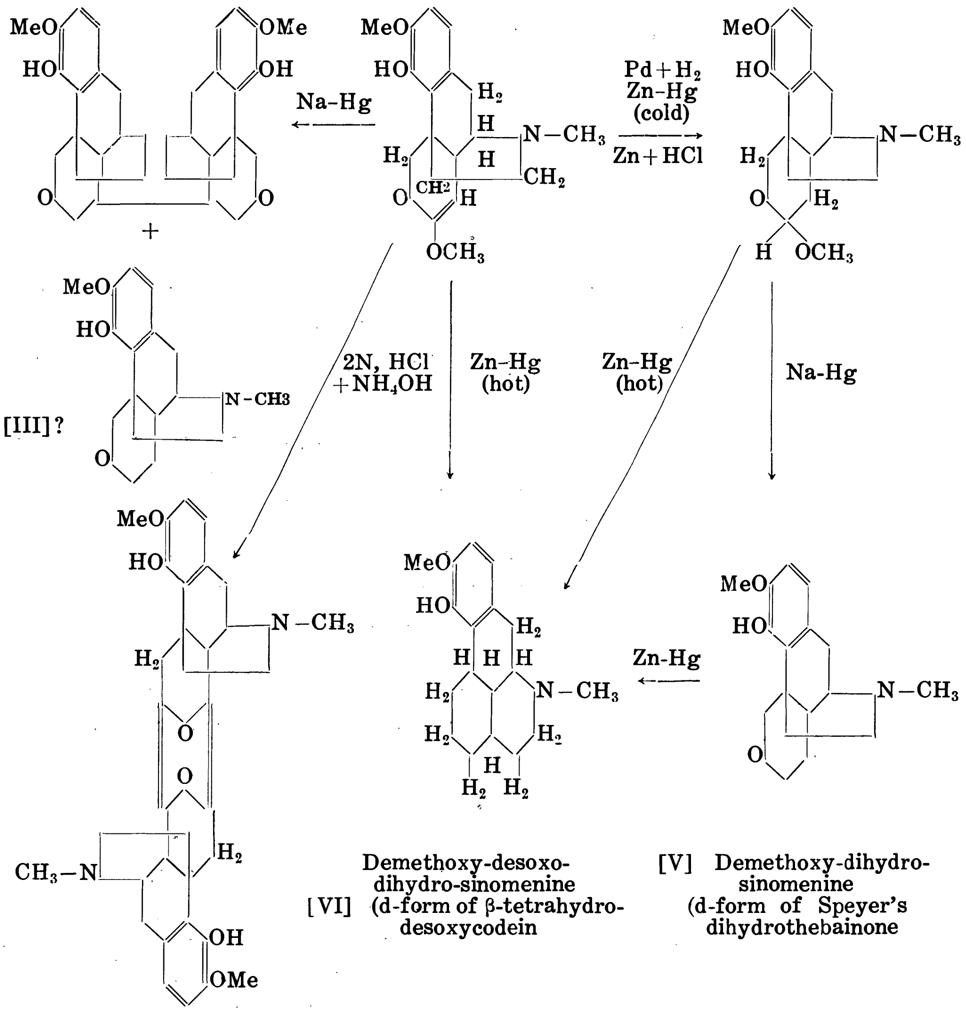
Note.—Reduction of sinomenine with sodium resp. zinc-amalgam was carried out by Kondo and Ochiai some time ago with totally different results. Compare, *Ann.*, **470** (1929), 224.

The above described transformation of sinomenine can be summarised in the following diagram.

[II] Bis-8, 8′-demethoxy-dihydrosinomenine.

[I] Sinomenine.

[IV] Dihydro-sinomenine.



Demethoxy-desoxo-dihydro-sinomenine
[VI] (d-form of β-tetrahydro-desoxycodein

[V] Demethoxy-dihydro-sinomenine
(d-form of Speyer's dihydrothebainone

[VII] Bis-demethyl-sinomenyliden.

Experimental.

Preparation and Properties of Bis-8, 8′-demethoxy-sinomenine. Sinomenine hydrochloride (5g.) is dissolved in 2% caustic soda (50 c.c.) and added with 40gr. 3% Na-amalgam (in four portions). Within 23 hours, the apueous part is saturated with carbon dioxide. The precipitate is collected and redissolved in chloroform. The crystalline residue, which remains on the evaporation of chloroform, is once boiled with a little acetone to remove impurities und recrystallised from a large quantity of alcohol. The pure substance crystallises in stout prisms, and melts at 304°. Yield about 1.5gr. (40%).

From the soluble part remaining in carbonic acid solution, a substance, melting at 134° was isolated. This seems to be very similar to the demethoxy-dihydro-sinomenine, which will be treated later.

As to the properties of bis-8,8′-demethoxy-hydrosinomenine, see the Table 1 in the theoretical part.

Anal. Found: C=70.95, 71.10, 71.94,; H=7.70, 7.77, 7.65; N=4.56%. Calc. for $(C_{18}H_{22}NO_3)_2=600$: C=72.00; H=7.33; N=4.66%.

Methoxyls Found: 11.37, 10.77. Calc. for one: 10.26%.

Mol. wt. Found (in glacial acetic acid): 650.

Sp. rotatory power: 0.8777gr. subst. was dissolved into 25 c.c. 1% hydrochloric acid solution. $l=1$ dm; $\alpha=-0.86$. $[\alpha]_D^{17}=-24.49°$

Semicarbazone: M. p. >300. (Found: N=14.07%. Calc. for disemicarbazone: N=15.68%).

Methiodide: M. p. $>305°$, needles. (Found: I=27.45%. Calc.: I=28.72%,)

Preparation and Properties of Demethoxy-dihydrosinomenine. The condition of the reduction is almost equal with the foregoing. The free base crystallises out from acetone slowly in prisms. It softens at 125° and melts at 138°. By drying at 100° over P_2O_5 in vacuum, it becomes syrupy. Yield: 3.9gr. from 6gr. of hydrosinomenine (65%).

The elimination of the methoxyl group seems to go on rather slowly and, even when a large quantity of Na-amalgam was used, the part, which crystallises afterwards, shows a little higher methoxyl number than calculated. The properties were given in Table 2.

Anal. Found: C=71.77; H=8.11; N=4.56%. Calc. for $C_{18}H_{23}NO_3=301$: C=71.76; H=7.64; N=4.65%. Methoxyl. Found: 10.91%. Calc. for one: 10.23%.

Mol. wt. Found (in glacial acetic acid): 358.

Sp. rotatory power. 1.0097gr. Subst. were dissolved into 25 c.c. alcoholic solution. $l=1$ dm. $\alpha=+2.39$, $[\alpha]_D^{19}=+59.17°$. 0.9718 gr. free base was dissolved into 25 c.c. 1% hydrochloric acid solution. $l=1$ dm. $\alpha=+1.90$, $[\alpha]_D^{19}=+48.88°$.

Semicarbazone. Prepared in the ordinary way, and recrystallised from acetone. M. p. 235°. (Found : N=15.66%. Calc : N=15.68%).

Methiodide : prisms collected in rosetts, (from water). M. p. 115° (Found: I=26.87%. Calc.: I=28.65%).

Racemisation of Demethoxy-dihydrosinomenine Iodomethylate with Dihydrothebainone Iodomethylate. Dihydrothebainone used in this experiment was prepared by the reduction of thebaine (10gr.) with Pd-H_2 and the sorption of hydrogen amounted to over two molecules (ca. 1600 c. c.). The mixture of the reduced bases was treated with 2% caustic soda solution (150 c. c.). The alkali soluble bases (yield : 2.8gr.) was tried to racemise with demethoxy-dihydrosinomenine, but, in contrary to the expectation, the crystalls obtained in this experiment turned the polarised light slightly left. The alkali soluble base thus seemed to have been still contaminated with dihydrothebainone.⑴

The alkali soluble part was, therefore, turned into its iodomethylate and the part, which directly crystallised out from methyl alcohol, was filtered away. The filtrate was evaporated and the residue crystallised from a little water. The fine crystalls thus obtained melted at 120°, viz. at the same point with the iodomethylate of desmethoxy-dihydrosinomenine. The specific rotatory power of the two iodomethylates is given below.

Demethoxy-dihydrosinomenine iodomethylate : $[\alpha]=+36.12°$ (0.3128 gr. subst, was dissolved into 10 c. c. water. $l=10$ cm., $\alpha=1.13$).

Dihydrothebainone iodomethylate : $[\alpha]=-34.36°$ (0.3148 gr. subst. was dissolved into 10 c. c. water. $l=5$ cm., $\alpha=0.54$).

To racemise the both iodomethylates, the above solutions were evaporated to a small bulk separately and mixed together in the hot. The beautiful prisms separated out instantly while hot, which melted at 231° sharply. The remarkable exaltation of the melting point might be due to the fact that recemic iodomethylate contained no crystal water. These crystalls did not rotate the polarised light.

0.5450 gr. subst. was dissolved into 10 c. c. water. $l=10$ cm., $\alpha=\pm 0$.

Preparation and Properties of Demethoxy-desoxo-dihydrosinomenine (d-form of β-Tetrahydro-desoxy-codein). Sinomenine hydrochloride (4 gr.) was added to the Clemmensen's zinc amalgam (prepared from 14gr. $HgCl_2$+ 7~10gr. Zn), poured on with hydrochloric acid (1 : 1; 10 c.c.) and heated on the steam bath for 6 hours. During the heating, the hydrochloric acid of the same concentration was added in small portions from time to time (the total amount 30 c.c.). After standing overnight, 25 c.c. of the filtrate

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⑴ Skita, *Ber.*, **54** (1921), 1561. This is presumably the iodomethylate of dihydrothebaine.

were obtained, from which separated a syrupy precipitate when added with the same amount of water. The precipitate was dissolved in acetone (10 c.c.) and poured into chloroform (100 c. c.). The chloroform was washed thoroughly with ammonia to decompose the zinc double salts. The dried chloroform was evaporated and a little acetone was added to the residue. On cooling it with tap-water, the substance crystallised out in prisms. The yield was scanty (0.1gr. from the above treatment and 0.1gr. from the not precipitated part). M.p. 148°. With hydrosinomenine, the yield was somewhat better (30%).

The properties of this substance were given in Table 3. The big hexagonal plates (as were described by Freund) are obtainable when recrystallised from a large quantity of hot acetone.

Anal. Found: C=73.10, 73.42; H=8.38, 8.33; N=4.53. Calc. for $C_{18}H_{25}NO_2\frac{1}{2}H_2O$ = 296: C=72.97; H=8.73; N=4.72%.

Methoxyl. Found: 10.15, 10.16%. Calc. for one: 10.47%.

Mol. wt. Found (in glacial acetic acid): 322. Calc.: 296.

Sp. rotatory power. 0.7982gr. substance was dissolved into 25 c.c. alcoholic solution. l=1 dm., $\alpha=+1.38$. $[\alpha]_D=+43.22°$.

Methiodide: M. p. 267° (long needles from alcohol). Found: I=28.30 Calc.: I=29.59%.

Hydro-iodide, (prepared after Freund)⁽¹⁾: Long needles, m. p. 245°.

The substance does not make a semicarbazone.

Racemisation of Demethoxy-desoxo-dihydrosinomenine with β-Tetrahydrodesoxy-codeine. The β-tetradesoxy-codeine used in this experiment was prepared from codeine by the method of M. Freund.⁽¹⁾ It melted at 148°. As regards the colour reactions, see the right-hand column of Table 3.

For the racemisation, ca. 0.5 gr. of each substance was mixed in acetone solution. The crystalls (ca. 0.7gr.), which separated out instantly on cooling, were collected and redissolved in hot acetone. When acetone was evaporated down to ca. 6 c.c. in a cool place, ca. 0.3gr. substance was deposited in beautiful crystals. This was collected and examined on its rotatory power.

0.2949 gr. substance was dissolved into 10 c.c. chloroform. l=10 dm., $\alpha=\pm 0$.

The racemisation was thus complete. The racemic substance melted at 135° (from acetone). The iodomethylate prepared therefrom melted at 232° (from water).

Preparation and Properties of Bis-(demethyl)-sinomenyliden. Sinomenine hydrochloride (10gr.) is dissolved in 100 c.c. 2N hydrochloric acid, and heated on the steam bath for 2 hours. The base is set free with

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(1) *J. prakt. Chem.*, **101** (1921), 30.

ammonia and extracted with chloroform. The substance is easily crystalliable. M.p. >312°. Yield ca. 10%.⑴

For the properties of bis-[demethyl]-sinomenylinen. see Table 4.

Anal. Found : C=71.90, 71.43 ; H=6.95, 6.86 ; N=5.04%. Calc. for $(C_{18}H_{21}NO_3)_2=598$: C=72.24 ; H=7.02 ; N=4.68%.

Methoxyls. Found : C=10.07, 10.08%. Calc. for two (one for each sinomenine molecule) 10.36%.

Mol. wt. Found (in glacial acetic acid) : 622.

Sp. rotatory power. 0.9694 gr. substance was dissolved into 25 c.c. 1% hydrochloric acid. l=1 dm., $\alpha=+13.01$, $[\alpha]^{17}_{D}=+335.52$

Methiodide: Very fine needles from water. M.p. 285° (?). Found : I=27.2% Calc. : I=28.78%.

Dioxim: M.p. >315° from chloroform. Found: N=8.66% Calc. for dioxim: N=8.91%.

Semicarbazone: M.p. >300°, prepared in the oridinary way. Found: N=7.29%. Calc. for disemicarbazone : N=14.96%.

Reduction of Sinomenine with Nascent Hydrogen. Sinomenine hydrochloride (1gr.) was dissolved in 30 c.c. 4% hydrochloric acid and added with 5gr. granular zinc. The mixture is cooled with water, and added with 10% hydrochloric acid from time to time (50 c.c. in total). Extracted in ordinary way and recrystallised from methyl alcohol, the reaction mixture gave 0.15gr. hydrosinomenine (m.p. 196° ; mixed melting point with that obtained by palladium-hydrogen reduction was 197°).

The mixture of sinomenine hydrochloride (4.5 gr.) zinc amalgam (ca. 10 gr.) and hydrochloric acid (1 : 1, ca 50 c.c.) was left overnight in a cool place. The filtrate gave no precipitate on the addition of water, but about 2.4 gr. hydro-sinomenine were isolated from it (m. p. 192°).

Hydrosinomenine, morphine and codein were not reduced in the above treatment. The reduction mixture of codeinone gave much precipitate with water, but it was not further studied.

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(1) A better yield will be achieved when sinomenine hydrate is decomposed by ammonia (see Part XII).

SOME NOTES ON THE THEORY OF ELECTRO-OSMOSIS. PART I.

By Sakuji KOMAGATA.

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1. Introduction. The phenomenon of electro-osmosis was, at first, discovered by Reuss, Russian scientist, on 1808. Since then, many authorities have been in research on this subject. The phenomenon takes place in the following familiar experiment: the bath is separated by a membrane (for examples, porcelain, texture and glass powder etc.) as shown in Fig. 1. The electrodes are inserted in each chamber and the electromotive-force is applied between them. Then, the liquid flows out through capillaries of membrane under the applied electric force, the level of one chamber being raised up over that of the other.

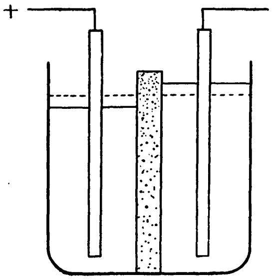

Fig. 1.

The mechanism for this phenomenon is considered to be due to the electric double layers existed on the surface of capillary wall. This theory was chiefly treated by Helmholtz, Lamb, Smoluchowski and others, and the very simplified following equation was dedused:

$$W=\frac{\zeta VDA}{4\pi\mu L}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where W is the quantity of liquid flowed out per unit time; A, the area of capillary; L, the length of capillary; ζ, the potential of double layers; V, the applied electric field; D, the dielectric constant of liquid; μ, the coefficient of viscosity of liquid.

But, we can also treat the theory of electro-osmosis in far more details under some assumptions. The purpose of this paper is to present one of these methodes carried out, as follows.

2. Electrical Condition in Capillary. Generally, at the surface of separation of two different materials, the ionic balance differs from that in the inner part of them. One kind of ion, positive or negative, accumulates there over the another kind of ion, according to the electrical properties of these materials.

The electrical condition in capillary is an interesting problem on the physical point of view. In our problem, the variation in configuration of electric charges takes place only in the capillary, because the solution in capillary are far more ionized than the materials of capillary wall.

For the convenience to the mathematical treatment, here we use the cylindrical coordinates (r, θ, z), z-axis being coincided with the axis of capillary as shown in Fig. 2. To neglect the effect of its terminals, the capillary is of infinite length for both directions of z.

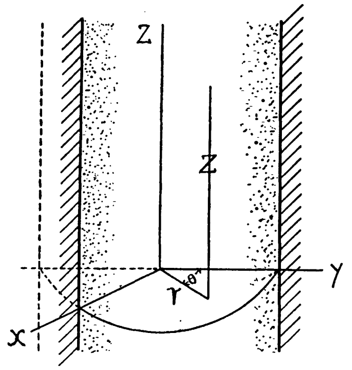

Fig. 2.

Let φ, be the potential;
ρ, the electric charge;
T, the absolute temperature;
C, the concentration;
D, the dielectric constant of liquid;
R, the radius of capillary;
k, Boltzmann's constant;
F, Faraday's constant.

The following two relations are established in this case:

(a) Equation of Poisson.

$$\Delta\varphi=-\frac{4\pi}{D}\rho \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

(b) Maxwell-Baltzmann's distribution law. For the sake of simplicity, we take up the special case of monovalent ion as follows. That is,

$$\rho=F(C_+-C_-) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

$$=FC_0\left(e^{-\frac{\varphi F}{kT}}-e^{\frac{\varphi F}{kT}}\right)$$

$$=-FC_0\sinh\frac{\varphi F}{kT} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4)$$

where C_0 is the concentration for $\varphi=0$.

For the small quantity of $\left(\frac{\varphi F}{kT}\right)$, we can neglect the higher power of $\left(\frac{\varphi F}{kT}\right)$ and obtain the simplified equation:

$$\rho=\frac{2C_0F^2}{kT}\varphi\,, \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (5)$$

From (2) and (5),

$$\Delta\varphi=\frac{\partial^2\varphi}{\partial r^2}+\frac{1}{r}\,\frac{\partial\varphi}{\partial r}=\frac{8\pi F^2C_0}{DkT}\,\varphi=\varkappa^2\varphi\ , \qquad\ldots\ldots\ldots\ldots\ (6)$$

where $$\varkappa=\sqrt{\frac{8\pi F^2C_0}{kDT}}\ ,\ \text{say}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (7)$$

Also from (5) and (7),

$$\rho=\frac{D}{4\pi}\,\varkappa^2\varphi\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (8)$$

The solution of (6) is given by;

$$\varphi=C_1J_0(i\varkappa r)+C_2Y_0(i\varkappa r)\ ,\ \ldots\ldots\ldots\ldots\ldots\ldots\ (9)$$

where C_1 and C_2 are the integration constants to be determined from the boundary conditions; J_0 and Y_0 are Bessel functions of zeroth order of first and second kind respectively.

For $r=0$, φ does not become infinite. That is, $C_2=0$.

At the surface of separation (capillary wall) $r=R$, we have

$$\begin{cases} & \varphi=\varphi_0\ ,\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (10)\\ \text{and} & \dfrac{\partial\varphi}{\partial r}=-\dfrac{4\pi}{D}\,\eta_0\ ,\ \ldots\ldots\ldots\ldots\ldots\ (11)\end{cases}$$

where η_0 is the surface density of charge at the separation.

From (10), $$C_1=\frac{\varphi_0}{J_0(i\kappa R)}\ .\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (12)$$

or, from (11), $$\left[\frac{\partial\varphi}{\partial r}\right]_{r=R}=-C_1i\varkappa J_1(i\varkappa R)=-\frac{4\pi}{D}\,\eta_0\ ,$$

$$C_1=\frac{4\pi N_0}{Di\varkappa J_1(i\varkappa R)}\ .\ \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (13)$$

But, from equation (8), the total charge in capillary per unit length is given by

$$2\pi\int_0^R\rho.r\,dr=2\pi\,\frac{D}{4\pi}\,\varkappa^2C_1\int_0^R rJ_0(i\varkappa r)dr$$

$$=-\frac{2\pi R D i\varkappa J_1(i\varkappa R)C_1}{4\pi}$$

$$=-2\pi R\eta_0\ , \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

This is, the total charge in capillary is equal to the total surface charge at the surface of capillary wall in amount but with opposite sign. This is the condition which satisfies our problems.

The distribution of potential is:

$$\varphi=\varphi_0\frac{J_0(i\varkappa r)}{J_0(i\varkappa R)} \quad \text{[from (12),]} \quad \ldots\ldots\ldots\ldots \quad (15)$$

$$=\frac{4\pi\eta_0 J_0(i\kappa r)}{Di\varkappa J_1(i\varkappa R)} \quad \text{[from (13),]} \quad \ldots\ldots\ldots\ldots \quad (16)$$

and

$$\left.\begin{aligned}[\varphi]_{r=o}=\varphi^*&=\frac{\varphi_0}{J_0(i\varkappa R)}\\ &=\frac{4\pi\eta_0}{Di\varkappa J_1(i\varkappa R)}\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (17)$$

and

$$[\varphi]_{r=R}=\varphi_0=\frac{4\pi\eta_0 J_0(i\varkappa r)}{Di\varkappa J_1(i\varkappa R)} \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

The distribution of charge is:

$$\rho=\frac{D\varkappa^2\varphi_0 J_0(i\varkappa r)}{4\pi J_0(i\varkappa R)} \quad \text{[from (12),]} \quad \ldots\ldots\ldots\ldots \quad (19)$$

$$=\frac{\varkappa\eta_0 J_0(i\varkappa r)}{iJ_1(i\varkappa R)} \quad \text{[from (13),]} \quad \ldots\ldots\ldots\ldots \quad (20)$$

and

$$\left.\begin{aligned}[\rho]_{r=o}=\rho^*&=\frac{D\varkappa^2\varphi_0}{4\pi J_0(i\varkappa R)}\\ &=\frac{\varkappa\eta_0}{iJ_1(i\varkappa R)}\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (21)$$

and

$$[\rho]_{r=R}=\frac{D\varkappa^2\varphi_0}{4\pi}=\frac{\varkappa\eta_0 J_0(i\varkappa R)}{iJ_1(i\varkappa R)} \quad \ldots\ldots\ldots\ldots \quad (22)$$

The distribution of charges is shown in Fig. 3.

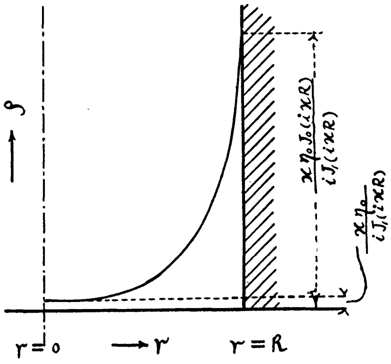

Fig. 3.

From the fact mentioned in (14), we can replace this configuration by the effective condenser. This is the so-called condenser-like-configuration of electrical double layers. Let a and b the radii of inner and outer concentric cylinders respectively, then the capacity per unit length is given by $\frac{D}{2\log\left(\frac{b}{a}\right)}$. Therefore, putting δ the distance between two concentric cylinders, we have

$$\frac{D}{2\log\left(\frac{b}{a}\right)}=\frac{D}{2\log\frac{R}{R-\delta}}=q\ ,\ \text{say}\ \ldots\ldots\ldots\ldots \tag{24}$$

Therefore, we have $\delta=R\left(1-e^{-\frac{D}{2q}}\right)$, ... (25)

where

$$q=\frac{2\pi\int\rho r dr}{\varphi_0-\varphi^*}=\frac{RD\varkappa\{-iJ_1(i\varkappa R)\}}{2\{J_0(i\varkappa R)-1\}}\ \ldots\ldots\ldots\ldots \tag{26}$$

Actually, in some cases, one part of ions in capillary are adsorbed on the capillary wall by the specific adsorption, as shown in Fig. 4. Then the distributions of potential and charge are far more complicate than that discussed above.[1] But, here we will not enter into these subjects further.

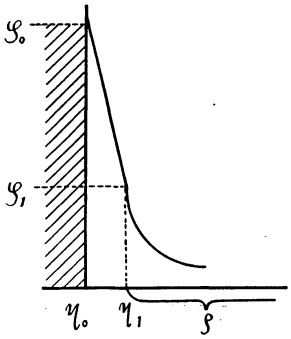

Fig. 4.

And, for the mixture of polivalent ions, the equations become complicate, but the just similar considerations are also to be carried out.

3. Electro-osmotic Flow in Capillary.

Let us consider the steady motion of liquid through capillary under applied electric force.

Let us take the coordinates the same used in Section 2, and also

v, be the velocity of flow;
p, the pressure;

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[1] Cf. O. Stern, *Z. Elektrochem.*, **30** (1923), 508.

d, the density;
μ, the coefficient of viscosity;
ν, the kinematic coefficient of viscosity $(=\mu/d)$;
E, the applied electric field intensity.

For a considerable small capillary, it is questionable whether μ, ν and D are given by their normal values or not. Although this problem is important, it is not yet been made clear now.

The lines of flow in this case are all parallel to the z-axis:

$$v_x=v_y=0 \ .$$

As the liquid is considered to be imcompressible, we have also

$$\frac{\partial v_z}{\partial z}=\frac{\partial v}{\partial z}=0,$$

that is, v is the function of x and y, but not of z.

The electric charges are set in motion under the applied electric force toward the electrode of opposite sign. And the liquid element is, too, acted by the force due to the resultant volume charges which are contained in it. Here, we assume that the distribution of charges in this case is the same as that discussed in section 2 and that the body force acting on the liquid element is equal to that on the resultant volume charges in it. Then, the body force is given by:

$$K=EF(C_+-C_-)=\rho E=\rho^* J_0(i\varkappa r)E=K_0J_0(i\varkappa r) \ , \ \ldots\ldots \quad (27)$$

where

$$K_0=E\rho^*=\frac{\varkappa E\eta_0}{iJ_1(i\varkappa R)} \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

Resulting from these considerations, the following equation of hydrodynamics for viscous liquid is applicable:

$$K-\frac{1}{d}\operatorname{grad} p+\nu\Delta v=0 \ , \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

or

$$K_0J_0(i\varkappa r)-\frac{1}{d}\frac{\partial p}{\partial z}+\nu\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right)=0 \ . \ \ldots \quad (30)$$

Differentiating (30) with z, we have

$$\frac{\partial^2 p}{\partial z^2}=0 \ ,$$

therefore

$$\frac{\partial p}{\partial z}=a \ . \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

where a is the integration constant.

Inserting (31) into (30) and integrating with r twice, then we have

$$v=\frac{a}{4\mu}r^2-\frac{K_0}{\chi^2\nu}J_0(i\chi r)+A\log r+B \;.\;\dots\dots\dots \quad (32)$$

where A and B are the integration constants. The boundary conditions are:

(i) v is not infinite at $r=0$; $A=0$. (33)

(ii) The liquid is not in motion on the surface of capillary wall;

$$[v]_{r=R}=0 \;.$$

So

$$B=\frac{K_0 J_0(i\chi R)}{\chi^2\nu}-\frac{a}{4\mu}R^2 \;.\;\dots\dots\dots\dots\dots \quad (34)$$

Therefore,

$$v=\frac{1}{4}\frac{a}{\mu}(r^2-R^2)+\frac{K_0}{\nu\chi^2}[J_0(i\chi R)-J_0(i\chi r)] \;.\;\dots\dots \quad (35)$$

Now, let the length of capillary be L ($L \gg R$) and the pressures at two ends be p_1 and p_2 respectively, then

$$\frac{\partial p}{\partial z}=a=-\frac{(p_1-p_2)}{L} \;.\;\dots\dots\dots\dots\dots\dots \quad (36)$$

So

$$v=\frac{(p_1-p_2)}{4\mu L}(R^2-r^2)+\frac{K_0}{\nu\chi^2}[J_0(i\chi R)-J_0(i\chi r)] \;.\;\dots\dots \quad (37)$$

If the pressure difference between two ends of capillary be very small compared with the body force acting on the liquid, then we can neglect the first term in (37):

$$v'=\frac{K_0}{\nu\chi^2}[J_0(i\chi R)-J_0(i\chi r)] \;,\;\dots\dots \quad (38)$$

which is shown in Fig. 5.

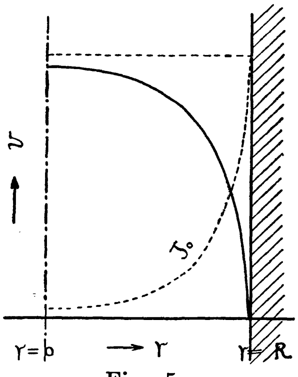

Fig. 5.

The quantity of liquid flowed out through capillary per unit time is

$$W=2\pi\int_0^R vr\,dr$$

$$=\frac{\pi(p_1-p_2)}{8\mu L}R^4+\frac{2\pi K_0}{\nu\chi^2}\left[\frac{R^2}{2}J_0(i\chi R)+\frac{iRJ_1(i\chi R)}{\chi}\right]\dots \quad (39)$$

Also, if we neglect the first term, we obtain

$$W' = \frac{\pi R^2 K_0}{\nu \varkappa^2} \left[J_0(i\varkappa R) + \frac{2iJ_1(i\varkappa R)}{\varkappa R} \right] . \quad \cdots\cdots\cdots \quad (40)$$

If we can balance the hydrostatic force and the electric force,

$$W = 0 ,$$

or

$$\frac{p_1 - p_2}{L} = \frac{P}{L} = -\frac{8\mu K_0}{\nu \varkappa^2 R^2} \left[J_0(i\varkappa R) + \frac{2iJ_1(i\varkappa R)}{\varkappa R} \right] . \quad \cdots\cdots \quad (41)$$

The electric charges are transfered by the flow of liquid. This amount per unit time is given by the equation:

$$\begin{aligned} Q &= 2\pi \int_0^R \rho v r \, dr \\ &= 2\pi \int_0^R r\rho^* J_0(i\varkappa r) \left[\frac{a}{4\mu} (r^2 - R^2) + \frac{K_0}{\nu \varkappa^2} \Big(J_0(i\varkappa R) - J_0(i\varkappa r) \Big) \right] dr \\ &= \frac{\pi \rho^* a R^2}{\mu \varkappa^2} J_2(i\varkappa R) + \frac{\pi \rho^* K_0 R^2}{\nu \varkappa^4} \left\{ \Big[J_0 i\varkappa R \,) \Big]^2 - 2 \left(\frac{\varkappa}{R} \right) \Big[J_0(i\varkappa R) J_1(i\varkappa R) \Big] \right. \\ &\qquad \left. + \Big[J_1(i\varkappa R) \Big]^2 \right\} \quad \cdots\cdots\cdots\cdots \quad (42) \end{aligned}$$

When $a = 0$, the first term in (42) vanishes as in the equation (38) and (40).

4. Electric Current through Capillary. In the present section, we consider the electric current through capillary. From Section 2, we can obtain the values of the charges:

$$\rho_+ = FC_0 e^{-\frac{\varphi F}{kT}} \quad \cdots\cdots\cdots\cdots \quad (43)$$

$$\doteqdot FC_0 \left\{ 1 - \frac{\varphi F}{kT} \right\} = FC_0 \left\{ 1 - \frac{\rho^*}{2FC_0} J_0(i\varkappa r) \right\} \quad \cdots\cdots \quad (44)$$

$$\rho_- = FC_0 e^{-\frac{\varphi F}{kT}} \quad \cdots\cdots\cdots\cdots \quad (45)$$

$$\doteqdot FC_0 \left\{ 1 + \frac{\varphi F}{kT} \right\} = FC_0 \left\{ 1 + \frac{\rho^*}{2FC_0} J_0(i\varkappa r) \right\} \quad \cdots\cdots \quad (46)$$

The electric current (I) required is given by the equation:

$$i = E(\rho_+ m_+ + \rho_- m_-) , \quad \cdots\cdots\cdots\cdots \quad (47)$$

and
$$I=2\pi\int_0^R ir\,dr \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (48)$$

where m_+ and m_- are the mobilities of ions. The electro-osmotic flow takes place in capillary as has treated in Section 3. For example, let the electro-osmotic flow be directed from the positive electrode to the negative, then, the negative charges are prevented their motion by the flow, and contrary to it, the positive charges are promoted their motion. Therefore, the mobility is smaller for negative ions and greater for positive ones than the normal values, and moreover differs from place to place as velosity does. But, as far as this flow is very small, this deviation is also small. In general, the mobility will be smaller in such a small capillary than in a normal free state.

But assuming here m_+ and m_- to be their normal values, then we have from (44), (46), (47) and (48),

$$i=EFC_0\left[\left\{1-\left(\frac{\rho^*}{2FC_0}\right)J_0(i\kappa r)\right\}m_+ +\left\{1+\left(\frac{\rho^*}{2FC_0}\right)J_0(i\kappa r)\right\}m_-\right]. \quad (49)$$

and

$$I=2\pi EFC_0\int_0^R\left[(m_+ +m_-)r-(m_+ -m_-)\left(\frac{\rho^*}{2FC_0}\right)rJ_0(i\kappa r)\right]dr$$

$$=EFC_0\pi R^2(m_+ +m_-)\left\{1+\left(\frac{m_+ -m_-}{m_+ +m_-}\right)\left(\frac{\rho^*}{2FC_0}\right)\left(\frac{iJ_1(i\kappa R)}{\kappa R}\right)\right\}. \quad (50)$$

The first term, $EFC_0\pi R^2$ $(m_+ + m_-)$, is the current established in the large vessel. Therefore, the current differs in the capillary by the amount equal to the second term.

Summary

(1) Under some assumptions, the distributions of potential and electric charge in capillary are given by the equations (15)—(22) . . . . (Section 2.)

(2) The quantity of liquid flowed out electro-osmotically W' is given by the equation (40), and $W'/\pi R^2$ is expressed by the function of radius R. The relation between permeability of membrane and electro-osmotic transfer has already been pointed out(1) to be different from that given by the Helmholtz's equation in which $W'/\pi R^2$ is constant for any R, although it is only considered to be caused from the "free-osmosis"—that is, equivalent to the first term in right hand member of equation (39). . . . . (Section 3.)

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(1) A. Strickler and J. H. Mathews, *J. Am. Chem. Soc.*, **44** (1922), 1647.

(3) The current in capillary differs from that in the large vessel, because of its non-uniform distribution of electric charge. This is given by the equation (50). And, the relation between so-called surface conduction and ζ-potential seems to be slight, as D.R. Briggs(1) has stated. (Section 4.)

The writer wishes to express his hearty thanks to Prof. Setoh for his kind advice.

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(1) D. R. Briggs, "Colloid Symposium Monograph", **4** (1928), 41.

STUDIES ON MERCAPTALS OF SUGARS. III. ISO-BUTYL MERCAPTALS OF SUGARS.⁽²⁾

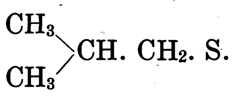
By Yoshisuke UYEDA.

Received October 3, 1929. Published November 28, 1929.

Normal butyl⁽³⁾ and normal propyl mercaptals⁽⁴⁾ of sugars have been studied by the present author and were reported in this journal.

This paper is the outline of the results of the studies of iso-butyl mercaptals of various sugars.

Experimental.—Mercaptals are prepared by the same method as described in the previous paper.⁽³⁾ The condensation is carried out by using conc. HCl (sp. gr. 1.20), as proposed by Fischer.⁽⁵⁾ The crude products are purified by the crystallization from dilute alcohol. The new mercaptals of sugars obtained have the following chemical constitution, which are determined by the analysis; here R representing



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big> CH.\ CH_2.\ S.$$

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(2) Read before the annual meeting of the Chemical Society of Japan, April 7, 1929.

(3) This Bulletin, **1** (1926), 179.

(4) This Bulletin, **1** (1926), 181.

(5) Fischer, *Ber.*, **27** (1894), 673.

Table 1.

		Sulphur⁽¹⁾	
		Calc. %	Found %
Glucose-iso-butyl mercaptal	$C_6H_{12}O_5\ (R)_2$	18.71	18.44
Galactose ,,	$C_6H_{12}O_5\ (R)_2$	18.71	18.67
Mannose ,,	$C_6H_{12}O_5\ (R)_2$	18.71	18.50
Rhamnose ,,	$CH_3.\ C_5H_9O_4\ (R)_2$	19.63	19.08
Arabinose ,,	$C_5H_{10}O_4\ (R)_2$	20.51	20.34
Maltose ,,	$C_{12}H_{22}O_9\ (R)_4$	19.21	19.20
Sucrose ,,	$C_{12}H_{22}O_9\ (R)_4$	19.21	19.13

The physical constants of these mercaptals are shown in the following table.

Table 2.

	M. p.	Sp. rotation
Glucose-iso-butyl mercaptal	130°	$[\alpha]_D^{14^\circ} = +40.0$
Galactose ,,	129°	$[\alpha]_D^{13^\circ} = +41.2$
Mannose ,,	111°	,, $= +16.4$
Rhamnose ,,	112°	,, $= +14.0$
Arabinose ,,	123°	$[\alpha]_D^{14^\circ} = +20.0$
Maltose ,,	140°	$[\alpha]_D^{12^\circ} = +13.2$
Sucrose ,,	138°	$[\alpha]_D^{14^\circ} = +\ 9.6$

Summary.—Iso-butyl mercaptals of three hexoses, one methyl pentose, one pentose and two dioses are crystallized out as new compounds.

Other sugars, e. g. lactose, fructose, xylose are tried but ended in negative results.

The author is much indebted to Mr. Masao Hiraoka for his kind assistance.

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(1) The sulphur is determined by using Parr bomb.

REDUCTION OF TRIMETHYL STANNYL HYDROXIDE IN LIQUID AMMONIA.

By Taichi HARADA.

Received October 19, 1929. Published November 28, 1929.

The alkali metals are very strong reducing agents. Fittig and Wurtz have applied this principle in the synthesis of various hydrocarbons at ordinary temperatures in ethereal solutions ; however, the rate of reaction is very slow, It has been recognized that the alkali metals, such as sodium and potassium, in liquid ammonia solution react as strong and convenient reducing agents for various organic compounds and possess the advantage that the reduction may be carried out at as low a temperature as 33.5° C. Therefore, in such a solution, the stability of the resulting substance is relatively great. The reactions involved are in many cases instanteneous and quantitative.

Metallic sodium is extremely soluble in liquid ammonia in which the following reactions probably take place :(1)

$$\begin{array}{l} Na+NH_3 \rightleftarrows [NaNH_3^+ + e^-] \rightleftarrows Na+e^- +NH_3 \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad NaNH_2+H^+ +e^- \rightarrow NaNH_2+\tfrac{1}{2}H_2 \end{array}$$

It is interesting to note that the characteristic blue color reaction is present even with a minute trace of sodium in the solution. In the above reaction, the formation of $NaNH_2$ and H_2 is very slow in comparison with others.

The reactions of alkali metals on organic compounds in liquid ammonia were first investigated by Moissan.(2) Since then it has been extensively developed by Lebeau(3), Lebeau and Picon(4), Kraus(5), Kraus and his students(6),

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(1) Kraus *J. Am. Chem. Soc.*, **30** (1908), 1323.

(2) *Compt. rend.*, **127** (1898), 911 ; **136**, (1903), 1217.

(3) Lebeau, ibid., **140** (1905), 1042, 1264.

(4) Lebeau and Picon, ibid., **157** (1913), 137,223 ; **158** (1914), 1514 ; **159** (1914), 70 ; **173** (1921), 84 ; Picon, ibid., **175** (1922), 1213 ; Picon, *Bull. soc. chim.*, **35** (1924), 979.

(5) Kraus, *J. Am. Chem. Soc.*, **35** (1913), 1732.

(6) Kraus and Greer, *J. Am. Chem. Soc.*, **44** (1922), 2629 ; Kraus and White, ibid., **45** (1923), 768 ; Kraus and Kawamura, ibid., **45** (1923), 2756 ; Kraus and Sessions, ibid., **47** (1925), 2361 ; Kraus and Bullard, ibid., **48** (1926), 2131 ; Kraus and Rosen, ibid., **47** (1925), 2739 ; Kraus and Foster, ibid., **49** (1927), 457 ; Kraus and Neal, ibid., **51** (1929), 2403.

Chablay(1), Dains, Vaughan and Janney(2), Clifford(3), White(4), and White and his students(5). Other workers will be found elsewhere. X denotes an electro-negative radical or element and R an electro-positive radical or element. Since various salts, acids and bases assume a state of more or less electrical dissociation in liquid ammonia (a condition which does not necessarily require the actual solution of these materials), they may be represented according to the following general equation:

$$RX \rightleftharpoons R^+ + X^-$$

The reactions between organic compounds and alkali metals in liquid ammonia are extremely varied and quite complex. This is shown by Professors Kraus and White, and with their students, on a large number of experiments with various organic compounds. It has been stated that organic compounds containing strong electro-negative radicals or elements are, in general, reduced to the radical or elements of the radical, forming salts with the reducing metals, depending upon the nature of the radical in question and various other substances present. For instance, an alkyl or aryl radical is relatively strongly electro-positive and weakly electro-negative and univalent. Since the sodium salt of these groups is very unstable in liquid ammonia, it hydrolyzes (ammonolyzes) to form its hydrocarbon and amines(6). In such an electro-negative radical, the electron is relatively loosely attached to the radical and therefore tends to combine with a more strongly electro-negative radical or element; while in the case of $(C_6H_5)_3CK$(7) or $(CH_3)_3SnNa$(8) the electron is relatively strongly or moderately strongly attached to the radical since they are not ammonolyzed in liquid ammonia solution. However the latter hydrolyzes in the presence of ammonium chloride to form trimethyl stannane, $(CH_3)_3SnH$(9).

The general reactions may be represented as follows:

$$\text{I} \qquad R^+ + X^- + Na^+ + e^- \rightleftharpoons R + Na^+X^-$$

$$\text{II} \qquad R^+ + X^- + 2Na^+ + 2e^- \rightleftharpoons R^-Na^+ + Na^+X^-$$

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(1) *Compt. rend.*, **140** (1905), 1262; **154** (1912), 364; **156** (1913), 1020; *Ann. Chim.*, **9.** I, (1914), 469.

(2) *J. Am. Chem. Soc.*, **40** (1918), 936.

(3) ibid., **41** (1919), 1051.

(4) ibid., **45** (1923), 779.

(5) White and Knight, ibid., **45** (1923), 1781; White, Morrison and Anderson, ibid., **46** (1924), 961; Wooster, **50**, (1928), 1388.

(6) White, *J. Am. Chem. Soc.*, **45** (1923), 779.

(7) Kraus and Rosen, *J. Am. Chem. Soc.*, **47** (1925), 2739.

(8) Kraus and Sessions, ibid., **47** (1925), 2361.

(9) Kraus and Greer, ibid., **44** (1922), 2629.

A couple of years ago, the author prepared trimethyl stannyl free radical(1) by the reduction of trimethyl stannyl hydroxide as one of the materials for the preparation or the reduction products of the so-called "Metallo Organic Oxonium Salt," $[(CH_3)_3\,Sn]_2\,O(CH_3)_3\,SnX$, with metallic sodium in liquid ammonia. The present paper will describe its method of preparation in some detail.

Apparatus. The reaction tube A is immersed in a Dewer tube B containing commercial liquid ammonia as shown in the accompanying figure.

Dewer tube B has a capacity of about 700 c.c. It is 45 cm. long, and 5.5 cm. in diameter. Ammonia dried by sodium is introduced into the reaction tube through the inlet tube C. The side tube D permits the introduction of air, oxygen or nitrogen gas, at will. The reaction tube is connected through the pinchcock F with the mercury manometer H, in which the pressure can be varied at G, as desired. The reaction tube also has a side tube J, with rubber stopper K, through which small pieces of alkali metal can be introduced into the reaction tube. The tube L with stop cock M is connected with the side tube E of the reaction tube, and by this means, ammonia and other accompanying gases can be drawn out from the manometer outlet and can be collected over the water in the burette W which is filled with water from the vessel P by suction through the stop cock O.

Preparation of Trimethyl Stannyl Iodide. Trimethyltin iodide was prepared by treating sodium-tin or sodium-tin-zinc alloy with methyl iodide.(2)

The alloys were treated over night with methyl iodide at room temperature and then heated on a water bath and finally in an oil bath at 120°C. The products then were separated by means of fractional distillation.

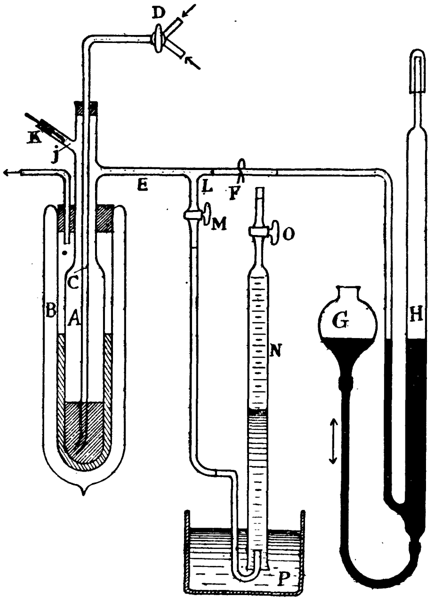

Fig. 1.

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(1) This Bulletin, **2** (1927), 107.

(2) Tetramethyl tin by Cahours, *Ann.*, **111** (1859), 236 and Ladenburg, *Ann. Suppl.*, **8** (1870), 74.

Zn%	Na%	Sn%	Alloy	CH_3I	$(CH_3)_3SnI$	$(CH_3)_4Sn$
2	14	C.P. 84	128	97	trace	22.8
-	7	C.P. 93	45	35	5	-
0.5	7	Comm. 92.5	115	90	41	2
-	14	Comm. 86	92	70	trace	16

The results indicate that the amount of sodium in the alloy is a controlling factor in regard to the production of $(CH_3)_3SnI$ or $(CH_3)_4Sn$, whereas zinc is more in the nature of a catalyzer of the reaction. This material also may be obtained by treating tetramethyl tin with iodine in a bath of ice water according to the following reaction equation:

$$(CH_3)_4Sn + I_2 = (CH_3)_3SnI + CH_3I$$

Trimethyl Stannyl Hydroxide. This compound was prepared by treating trimethyltin iodide with concentrated sodium hydroxide in alcoholic solution and distilled.

$$(CH_3)_3SnI + NaOH = (CH_3)_3SnOH + NaI$$

When the alcoholic solution is evaporated under suitable conditions it gives colorless crystals. On heating, it sublimes in a white, snow-like form. It can be recrystallized out from strong alcoholic solution as large colorless crystals. It melts and sublimes at 118°C.

Trimethyl Stannyl free Radical. One molecular proportion of trimethyltin hydroxide was dissolved in liquid ammonia by passing a stream of ammonia through the clear solution and then one atomic proportion of small pieces of sodium was added slowly. Sodium reacted readily with the hydroxide without an evolution of gas along with the addition of sodium, and a white precipitate was formed and settled in the bottom of the reaction tube. When the total amount of sodium had been added to the solution, the ammonia was evaporated at room temperature and the resulting product was treated with alcohol and washed with an excess of water until free from sodium hydroxide. The yield was quantitative. The trimethyltin free radical thus obtained may be separated as a heavy, oily liquid by a separatory funnel through filter paper with anhydrous sodium sulphate in an atmosphere of nitrogen. It melts at 23°C. and boils at 181°C. and is not appreciably soluble in water.

Anal. Subst.=0.5241gr.; SnO_2=0.4840gr. Found: Sn=72.60%. Calc. for $(CH_3)_3Sn$: Sn=72.46%.

The compound was entirely identical with which obtained from trimethyltin halide with sodium in liquid ammonia by Kraus and Sessions(1).

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(1) Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2361.

The free radical possesses strong reducing power. It reduces silver nitrate in solution into metallic silver instantly.

$$(CH_3)_3Sn + Ag^+ + NO_3^- \rightleftharpoons Ag + (CH_3)_3Sn^+NO_3^-$$

Kraus and Sessions show the molecular weight of the radical in benzene at boiling point, at lower concentration, to be monomolecular; and at higher concentration to be dimolecular in form. However even at low concentration at its freezing point it is completely polymerized to the stannoethane(1):

$$2(CH_3)_3Sn \overset{\text{benzene}}{\rightleftarrows} [(CH_3)_3Sn]_2$$

when trimethyltin free group is treated with one atomic proportion of sodium in the solution it forms the corresponding sodium salt:

$$(CH_3)_3Sn + Na^+ + e^- \rightleftharpoons (CH_3)_3Sn^-Na^+$$

which is soluble and a light yellow color in liquid ammonia. According to Kraus and Sessions it is a good conductor in the solution. When an equivalent trimethyltin iodide was added to the resulting trimethyltin sodium the free group again settled to the bottom of the tube. In concluding, trimethyltin hydroxide is a fairly strong base since it ionizes to form $(CH_3)_3Sn^+$ and OH^- in liquid ammonia solution. The positive ion group $(CH_3)_3Sn^+$ is reduced by the electron into the neutral $(CH_3)_3Sn$ which is insoluble in the solution. However, along with the addition of an excess of sodium, the group dissolves in the solution again, for the group becomes electrically charged, due to the electron, forming the salt of $(CH_3)_3SnNa$.

Summary.

(1) General method of reduction of compounds in liquid ammonia by alkali metals and apparatus were described.

(2) Trimethyl stannyl iodide from methyl iodide and sodium-tin alloy and from which trimethyl stannyl hydroxide was prepared.

(3) Trimethyl stannyl free radical was prepared by the reduction of trimethyl stannyl hydroxide with metallic sodium in liquid ammonia solution.

Takamine Laboratory, Inc.,
Clifton, N. J., U. S. A.

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(1) Kraus and Bullard, *J. Am. Chem. Soc.*, **48** (1926), 2131.

SINOMENINE AND DISINOMENINE. PART XII. ON SINOMENINE HYDRATE.

By Kakuji GOTO and Hideo SUDZUKI.

Received September 21, 1929. Published December 28, 1929.

In the last report, the formation of the bis-(demethyl)-sinomenyliden from sinomenine by the agency of a hot dilute hydrochloric acid and the treatment of ammonia was reported. In this paper, the mechanism of this transformation will be dealt with in a more detailed way.

When sinomenine was heated on a steam bath with dilute hydrochloric acid and the base was set free with sodium carbonate, no formation of the bis-(demethyl)-sinomenyliden was noticed, but a new substance of m.p. 139° was obtained in a yield more than 80%. If this new substance was dissolved in 1% hydrochloric acid, and was added with an equal quantity of ammonia (d=0.9), and left standing overnight, then bis-(demethyl)-sinomenyliden was obtained in a yield about 40%. This showed clearly that the hot dilute hydrochloric acid could only effect the transformation of sinomenine into the substance of m.p. 139° and that the concentrated ammonia could then convert the latter into bis-(demethyl)-sinomenyliden.

The elemental analysis proved that the substance of m.p. 139° was nothing but the sinomenine added with one molecule of water, which could not be removed by drying at 100° over P_2O_5 in vacuum. The water forms, thus, an integral part of the molecule. And the new substance is, therefore, called sinomenine hydrate. The properties of this new substance are compared with those of sinomenine in the following table.

Table 1.

	Sinomenine	Sinomenine hydrate
Yield	—	80%
Crystal form	prisms or hairy needles	prisms
Mol. formula	$C_{19}H_{23}NO_4$	$C_{19}H_{25}NO$
M.p.	159° (or 182°)	139° (or 160°)
Solubility in methyl alc.	33% (hot)	3.3% (hot)
$[\alpha]_D$	−73.9°	+40.8°

Table 1. (*Continued.*)

	Sinomenine	Sinomenine hydrate
Methoxyls	two	two
M.p. of oxim	264° (monoxim)	231° (dioxim)
D.p. of ICH_3	255°	264°
$FeCl_3$ reaction	very strong	strong in alc.
Diazo-reaction	+ in 2,000,000th dilution	+ in 2,000,000th dilution
$K_3Fe(CN)_6$-reaction	+ in 500,000th dilution	+ in 500,000th dilution
Formaline-H_2SO_4	yellow, green, blue	yellow, bordeau-red

As regards the position taken by the added water, C_7 is selected for OH and C_8 for H, from the following four reasons.

(1) Sinomenine hydrate dissolves in caustic alkali almost colourless. This shows the original double linking of sinomenine, which was conjugated to the ketone group, is quite saturated.

(2) In contrary to sinomenine, sinomenine hydrate does not give a bimolecular substance, when reduced with Na-amalgam, but gives the monomolecular substance given in (3). This shows also that the original double linking was quite lost.

(3) By reduction with $Pd+H_2$, sinomenine hydrate loses one methoxyl group, and gives two isomeric substances of the molecular formula $C_{18}H_{23}NO_3$.

(4) By the action of semicarbazide or hydroxylamine, sinomenine hydrate loses one methyl group and gives a disemicarbazone or a dioxime.

These behaviours of sinomenine hydrate are best explained by the constitutional formula (II), although it involves some remarkable features, which are not usual in the hitherto well-known facts, viz. the astonishing stability of this semi-acetal against acidic agents, and the easy hydrolysableness by the amino-radical of ammonia, semicarbazide and hydroxylamine, which remain to be explained by the future study.

When sinomenine hydrate was reduced with $Pd+H_2$, it gives two isomeric demethoxysinomenine hydrates, which are characterised by the properties given in the Table 2.

Table 2.

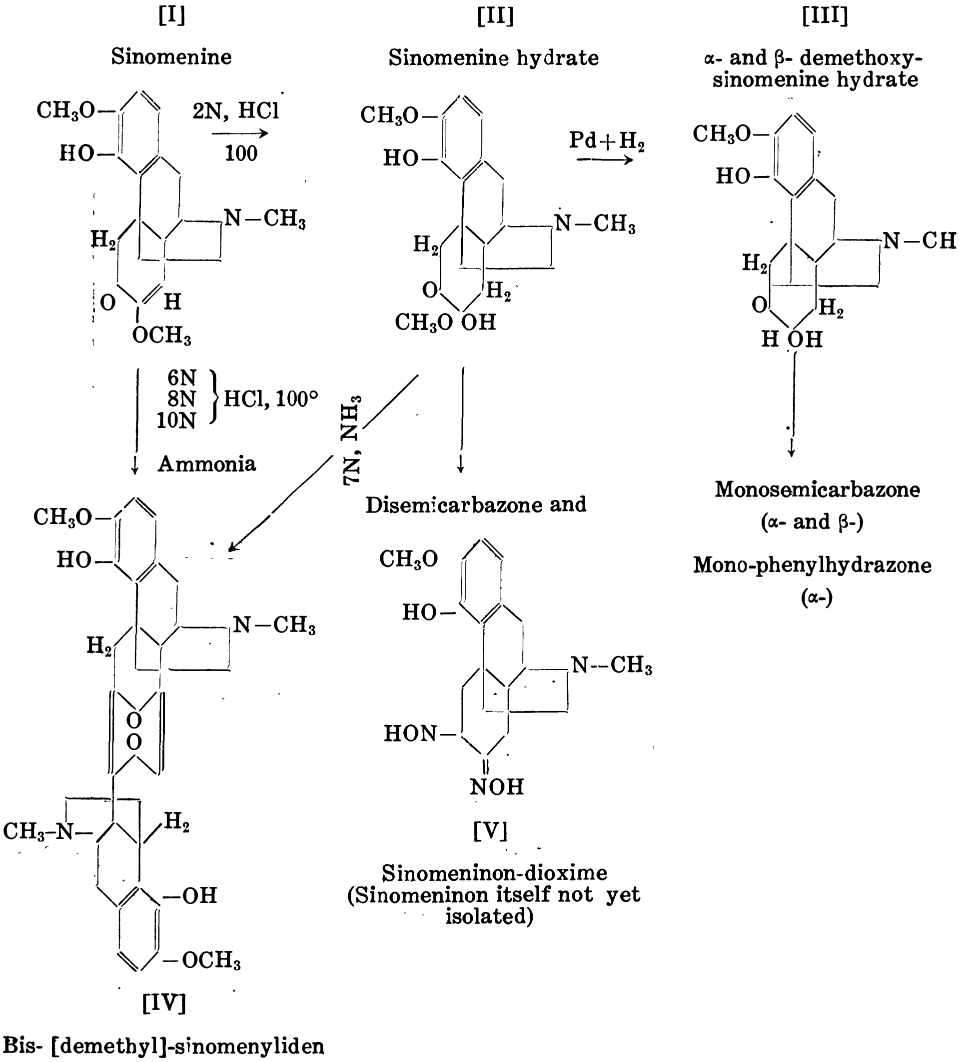
	α-Demethoxy-sinomenine hydrate	β-Demethoxy-sinomenine hydrate
Yield	45%	12.5%
Crystal form	stout prisms	hairy needles
M.p.	129°	65° (softens) 104° (melts)
Solubility in methyl alcohol	10% (hot)	3.3% (hot)
$[\alpha]_D$	+64.8°	+95.2°
Methoxyl	one	one
M.p. of oxim	170° (monoxim)	syrupy
D.p. of ICH_3	276°	289°
$FeCl_3$-reaction	+ in alcohol	+ in alcohol
Diazo-reaction	+ in 2,000,000th dilution	+ in 2,000,000th dilution
$K_3Fe(CN)_6$-reaction	+ in 500,000th dilution	+ in 500,000th dilution
Formaline-H_2SO_4	green, blue	green, blue

The reason, why these two isomeric substances are formed from sinomenine hydrate is not yet fully accounted for. The sinomenine hydrate may be an intimate mixture of two isomerides, which can only be separated by hydrogenation. This point needs further study.

The relation between sinomenine, sinomenine hydrate, α- and β-demethoxy-sinomenine hydrates, and bis-demethyl sinomenyliden are given in Table 3.

By simple heating of sinomenine hydrate, and α- and β-demethoxy-sinomenine hydrate for itself between 145°-155° for 10 minutes did not regain the sinomenine, nor gave demethoxy-sinomenine. Acetolysis of these three substances at 180° for 8 hours did not also give diacetyl-sinomenol resp. 3-methoxy-4, 6-diacetoxy-phenanthrene. The added water seems, therefore, to hinder the aromatisation of the nucleus.

Table 3.



Experimental.

Preparation of Sinomenine Hydrate. Sinomenine hydrochloride (10 gr.) s heated with 2N hydrochlcior acid (100 c.c.) on a steam-bath for two hours. After cooling, the base is precipitated with sodium carbonate, and extracted with chloroform in the ordinary way. The residue of chloroform is recrystallised from methyl alcohol. Prisms, isolated or collected in rosettes, m.p. 139°; yield over 80%. 4N, 6N, 8N, and 10N hydrochloric acid may be used in this hydration, but with different amount of the yield. Sulphuric acid (10%) can also effect this transformation, but the yield is far behind that obtained with hydrochloric acid.

The m.p. of this substance is raised slowly by repeated recrystallisation, but the above figure is commonly met with when measured soon after the isolation.

Anal. Found: C=65.74, 66.07; H=7.57, 7.37; N=3.91%. Calc. for $C_{19}H_{25}NO_5$: C=65.70; H=7.20; N=4.03%.

Mol. wt. Found (in glacial acetic acid): 289. Calc. for $C_{19}H_{25}NO_5$: 347.

Specific rotatory power. $[\alpha]_D^{26}=+40.8$ (0.9862 gr. subst. into 25 c.c. CCl_3H sol. l=2 dm.; $\alpha=+1.°61$).

Methoxyls. Found: 17.32, 16.82, 16.65, 16.24%, Calc. for two methoxyls: 17.86%.

Methiodide: dec. p. 264°. Found: I=27.18%. Calc. I=25.96%).

Disemicarbazone: prepared in the ordinary way, but not crystallisable. Purified by dissolving in a little methyl alcohol and precipitating with water, m.p. 191° (dec.)

Anal. Found: N=21.41, 20.71%. Calc. for $C_{20}H_{27}N_7O_5$: N=22.02%.

Methoxyls. Found: 6.36%. Calc. for one methoxyl: 6.96%.

Dioxim. Purified by dissolving in acetone and adding methyl alcohol to the residue of the acetone, m.p. 231° (dec.) Yield: 80%.

Anal. Found: N=11.35%. Calc. for $C_{19}H_{27}N_3O_5$: N=11.14%.

Methoxyls. Found: 8.85%. Calc. for one methoxyl: 8.22%.

Reduction of Sinomenine Hydrate by Na-amalgam. This reduction was carried out in the same way as was given in the last report.(1) The amalgam was very quickly consumed. Yield: 40%; m.p. 128°; admixture with α-demethoxy-sinomenine hydrate given below did not lower the m.p.

Methoxyl. Found: 9.72%. Calc. for one methoxyl in $C_{18}H_{23}NO_4$: 9.72%.

Preparation of α- and β-Demethoxy-sinomenine Hydrates. Sinomenine hydrate (10 gr.) was dissolved in 1% hydrochloric acid (100 c.c.), added with $PdCl_2$ (0.1 gr. in 50 c.c. H_2O) and gummi arabicum (0.1 gr. in 50 c.c.) and shaken in a hydrogen atmosphere. The absorption of hydrogen went on rather slowly. $PdCl_2$ and gummi arabicum were therefore added from time to time. After three or four hours, when 80% of the calculated quantity of the hydrogen was absorbed, the base was isolated in a usual way, and recrystallised from methyl alcohol. α- Compound crystallised out first in

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

stout prisms. The syrupy residue was again reduced in the above way and from this fraction, β- compound was chiefly obtained. Average yield: α- compound 45% ; and β- compound 20%.

α- Demethoxy-sinomenine Hydrate. General properties were given in the Table 2. The melting point is raised slowly on keeping.

Anal. Crystal methyl alcohol. Found: 9.39%. Calc. for $C_{18}H_{23}NO_4$: $CH_3OH=9.64\%$. Found: $C=68.50$, 68.62; $H=6.99$, 7.32; $N=4.19\%$. Calc. for $C_{18}H_{23}NO_4$; $C=68.13$; $H=7.25$; $N=4.41\%$.

Methoxyl. Found: 9.53, 9.99%. Calc. for one methoxyl: 9.77%.

Mol. wt. Found (in glacial acetic acid): 343. Calc. for $C_{18}H_{23}NO_4$: 317.

Sp. rotatory power. 0.9799 gr. subst. was dissolved into 25 c.c. chloroform solution. $\alpha=+2.54°$; d=1 dm. $[\alpha]_D^{26°}=+64.8°$.

Oxim: prisms of m.p. 170° (dec.) Yield almost quantitative.

Anal. Found: $N=8.25\%$. Calc. for $C_{18}H_{24}N_2O_4$: $N=8.43\%$.

Methoxyl. Found: 9.12%. Calc. for one methoxyl: 9.33%.

Semicarbazone: m.p. 191° (dec.) ($N=14.70\%$. Calc. for $C_{18}H_{26}N_4O_4$: $N=14.97\%$).

Phenyl-hydrazone: hygroscopic, m.p. 140° (softening at 123°) ($N=10.31\%$. Calc. for $C_{24}H_{29}N_3O_3$: $N=10.31\%$).

Methiodide: m.p. 274~276° (dec.). Yield almost quantivative. ($I=27.11\%$. Calc.: $I=27.65\%$).

β- Demethoxy-sinomenine Hydrate. See the Table 2 for general properties.

Anal. Crystal methyl alcohol. Found: $CH_3OH=9.24\%$. Calc.: 9.64%. Found: $C=68.56$; $H=7.22$; $N=4.35$. Calc. for $C_{18}H_{23}NO_4$: $C=68.13$; $H=7.25$; $N=4.41\%$.

Methoxyl. Found: 9.96%. Calc. for one methoxyl: 9.77%.

Mol. wt. Found (in glacial acetic acid): 346.5,

Sp. rotatory power: 0.3466 gr. subst. was dissolved into 10 c.c. chloroform solution. $\alpha=+3.30$; d=1 dm. $[\alpha]_D^{26°}=+95.2°$.

Methiodide: m.p. 280° (dec.) ($I=28.82\%$. Calc: $I=27.65\%$).

Semicarbazone: m.p. 206° (dec.) ($N=15.14\%$. Calc. for monosemicarbazone $C_{19}H_{26}N_4O_4$: $N=14.97\%$).

Oxim: not crystallisable, in contrary to the α-compound.

Preparation of Bis-(demethyl)-sinomenilyden from Sinomenine Hydrate. Sinomenine hydrate (1 gr.) was dissolved in 1% HCl (10 c.c.) and, after the addition of conc. ammonia (10 c.c.; d=0.9), left standing overnight. The precipitate was recrystallised from alcohol. Yield: 40%. m.p. >312°.

With sinomenine and dihydrosinomenine, only the original substances were recovered over 80% yield by this treatment.

By the way the crystallisable part isolated from the reduction product of the bis-demethyl-sinomenyliden by Pd + H_2, seems to be nothing but the unchanged starting material.

Anal. Found: C = 72.07; H = 6.94%. Calc. for unchanged bis-demethyl-sinomenilyden $(C_{18}H_{21}NO_3)_2$: C = 72.24; H = 7.02%.

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Kitasato Institute, Tokyo.

THE VISCOSITY OF VAPOURS OF ORGANIC COMPOUNDS. PART I.

By **Toshizo TITANI.**

Received October 22, 1929. Published December 28, 1929.

The viscosity of several organic liquids were already measured by the writer at temperatures extending over their boiling points.⁽¹⁾ The present work concerns with the viscosity of organic compounds in gaseous state. The object is not only to supply reliable data in respective states of aggregation, but also to compute the diameters of molecules from these observations. The temperature coefficient of viscosity which is specially important in this case has been determined with great care.

Theory of the Method. One of the most prevalent principle to determine the viscosity of gases and vapours is that of transpiration. This principle was used by Pedersen,⁽²⁾ Rappenecker⁽³⁾ and Rankine⁽⁴⁾ in their well-known works. On the same principle is based also the viscosimeter devised by the writer, the principal part of which is diagramatically illustrated in Fig. 1. The fine glass capillary tubes, each having internal diameter of about 0.194 mm. and length of 39.5 cm. respectively, are connected below by a wider U-tube. The upper end of each capillary tube is fused on to a wider uniform glass tube bent to the vertical position parallel to the capillaries. The inner diameters of both wider limbs are almost equal with each other, being about 1.86 mm. Two marks, M_1 and M_2,

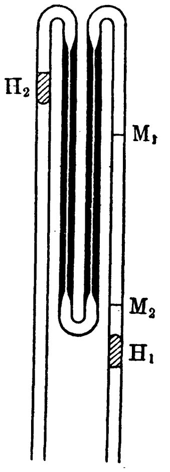

Fig. 1.

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(1) This Bulletin, **2** (1927), 95; ibid., 161; ibid., 196; ibid., 225; **4** (1929), 68.

(2) Pedersen, *Phys. Rev.*, **25** (1907), 225.

(3) Rappenecker, *Z. physik. Chem.*, **72** (1910), 695.

(4) Rankine, *Proc. Roy. Soc. London*, [A], **83** (1910), 265.

are etched on the right limb a distance of about 27 cm. apart, containing about 0.73 c.c. between them.

A short mercury-column is placed in each wider limb respectively, its length being chosen as equal as possible. The space between these two columns is filled with the gas to be examined. If we connect the right limb of the viscosimeter to a constant pressure source slightly higher than one atmosphere and let the left one open to air, the equilibrium is broken, the right mercury-column H_1 being pushed up driving the gas above it through the capillaries, so that the left column H_2 is pushed down; and vice versa. The times required by the right column to pass through the two marks are successively recorded, t_1 denoting the upward and t_2 the downward. From each of these two recorded times, the viscosity η of the gas may be calculated by the following formulae.

$$\frac{\eta}{k}=\frac{P^2-p^2}{P}\cdot t_1 \;\ldots\ldots\ldots\ldots\; \text{up} \;\ldots\ldots\ldots\ldots\; (1)$$

$$\frac{\eta}{k}=\frac{P^2-p^2}{p}\cdot t_2 \;\ldots\ldots\ldots\ldots\; \text{down} \;\ldots\ldots\ldots\ldots\; (2)$$

$$k=\frac{\pi g r^4}{16\, l v} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\; (3)$$

Corrections for slipping and kinetic energy were found to be within the limit of the experimental error. The apparatus constant k expressed by equation (3) contains the radius r and length l of the capillaries and the volume v between the two marks. By P and p are expressed respectively the effective driving pressures at the inlet and the outlet of the capillary U-tube. These effective pressures P and p may differ from the pressure outside of the mercury-columns minus their lengths, because the moving mercury-columns have some resistance, mainly due to capillarity at their end-surfaces and also probably due to their friction against the walls of the tubes. Elimination of this complicated resistance is one of the most difficult but important matters in this type of viscosimeter. Though an allowance was made by Pedersen only for the friction of the mercury-column against the wall, this was neglected by Rankine who took only an account for the resistance due to capillarity. On the other hand both sorts of resistances were completely neglected by Rappenecker in his works with Pedersen's viscosimeter. This unknown resistance of mercury-columns has been eliminated by the writer in the following way.

Substituting for the true effective pressures P and p in equations (1) and (2) the apparent pressures P' and p' which are equal to the outer pressure minus the lengths of the mercury-columns but not their resistance, we obtain apparent viscosities η' instead of the true one η by equations (4) and (5).

$$\left(\frac{\eta'}{k}\right)_1=\frac{P'^2-p'^2}{P'}t_1 \;\ldots\ldots\ldots\ldots\; \text{up} \;\ldots\ldots\ldots\ldots\; (4)$$

$$\left(\frac{\eta'}{k}\right)_2=\frac{P'^2-p'^2}{p'}t_2 \;\ldots\ldots\ldots\ldots\; \text{down} \;\ldots\ldots\ldots\ldots\; (5)$$

The apparent viscosities so calculated are no more independent of the driving pressure but decrease as the latter increases. It was found by the writer experimentally that the reciprocal of the apparent viscosity $\frac{k}{\eta'}$ is a linear function of the reciprocal of the apparent driving pressure $\left(\frac{1}{P'-p'}\right)$.

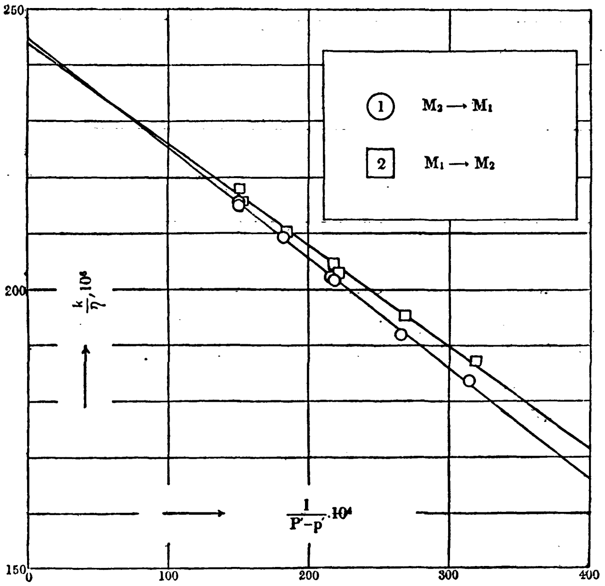

Fig. 2.

This is illustrated in Fig. 2, in which the former is plotted as ordinate and the latter as abscissa, each straight line corresponding to the case of pushing up or down. This relation may be seen more clearly in the following example.

Table 1. Air at 20°C.

Length of the mercury-columns: right=26.5 mm., left=26.7 mm.

(1) The case of pushing up.

P'	p'	t_1 sec.	$\frac{1}{P'-p'}$	$(k/\eta')_1\cdot 10^6$ Obs.	$(k/\eta')_1\cdot 10^6$ Calc.
—	—	0	0	—	244.8
803.2	736.3	36.2	0.01495	215.4	215.3
803.7	736.9	36.3	1497	215.1	215.2
791.6	736.6	45.0	1818	209.3	208.9
783.1	736.5	54.7	2146	202.1	202.4
782.9	737.1	55.8	2183	201.6	201.7
774.4	736.7	70.9	2653	191.7	192.4
768.5	736.6	87.2	3135	183.6	182.9

(2) The case of pushing down.

P'	p'	t_2 sec.	$\frac{1}{P'-p'}$	$(k/\eta')_2\cdot 10^6$ Obs.	$(k/\eta')_2\cdot 10^6$ Calc.
—	—	0	0	—	243.8
803.0	736.5	33.0	0.01504	218.0	216.5
803.5	737.1	33.4	1506	215.6	216.5
791.4	736.8	42.0	1832	210.2	210.6
782.9	736.7	51.3	2165	204.6	204.6
782.7	737.3	52.6	2203	203.1	203.9
774.2	736.9	67.0	2681	195.1	195.2
768.3	736.8	83.1	3175	187.1	186.3

The values in the last columns were calculated by the following equations,

$$(1)\quad (k/\eta')_1\cdot 10^6=244.8-1975\frac{1}{P'-p'}\ \cdots\cdots\cdots\ \text{up.}$$

$$(2)\quad (k/\eta')_2\cdot 10^6=243.8-1812\frac{1}{P'-p'}\ \cdots\cdots\cdots\ \text{down.}$$

or expressed in general form:

$$(k/\eta')_1 \cdot 10^6 = \frac{1}{a_1} - \frac{b_1}{P'-p'} \quad \text{........... up ....} \quad (6)$$

$$(k/\eta')_2 \cdot 10^6 = \frac{1}{a_2} - \frac{b_2}{P'-p'} \quad \text{...........down ....} \quad (7)$$

The first terms in the right hand side express the limiting values of apparent fluidity k/η' when the driving pressure becomes infinite, where all sorts of resistances of mercury-columns can safely be neglected, so that these limiting values give the true relative fluidity k/η. As exactly equal values for $\frac{1}{a_1}$ and $\frac{1}{a_2}$ could not be obtained practically, the mean of the two graphically extrapolated values from the observations under various driving pressures was taken as the final result.

$$k/\eta \cdot 10^6 = \frac{\frac{1}{a_1} + \frac{1}{a_2}}{2} \quad \text{.........................} \quad (8)$$

For example in the above case of air we have:

$$k/\eta \cdot 10^6 = \frac{244{\cdot}8 + 243{\cdot}8}{2} = 244.3\,.$$

Although this way of computation was first obtained solely experimentally, it can be shown that exactly the same result is deduced theoretically under some plausible assumptions.

If we assume the resistances of the right and left mercury-columns being expressed by Δ and $\Delta+\delta$ respectively, it will easily be seen from Fig. 1 that, in the case of pushing up, the true effective pressures P and p are related with apparent pressures P' and p' by the following equations.

$$P = P' - \Delta\,, \qquad p = p' + \Delta + \delta\,. \quad \text{.................} \quad (9)$$

Substituting these relations for P' and p' in eq. (4), we have

$$(\eta'/k)_1 = t_1 \frac{P'^2 - p'^2}{P'} = t_1 \frac{(P+\Delta)^2 - (p-\Delta-\delta)^2}{P+\Delta}$$

$$= t_1 \frac{P^2 - p^2}{P} \cdot \frac{\left(1 + \dfrac{2P\Delta + 2p\Delta + 2p\,\delta}{P^2 - p^2}\right)}{1 + \dfrac{\Delta}{P}} \quad \text{.............} \quad (10)$$

This is the exact solution, but it contains not only the unknown value Δ but also that of δ. Now we assume that the resistances of both columns are equal, i.e. δ is zero. This assumption seems very plausible if we take the following facts into consideration. First of all, the capillarity of both columns may be acknowledged to be equal with each other. Because the diameters of both mercury limbs are practically the same, as they are made of one long uniform tube by cutting it in the middle; and also a little difference in the section may have little influence, since the curvature of the meniscus of a moving mercury becomes larger in the smaller diameter and vice versa. In the second place it was found by the preliminary research that a fairly large difference in lengths of columns has no effect on the resultant resistance, so that the resistance due to friction is considered to be of second order compared with that due to capillarity. Thus, putting $\delta=0$ in eq. (10) and considering that the first factor in the right hand side is equal to η/k, it becomes

$$(\eta'/k)_1=(\eta/k)\frac{1}{1+\dfrac{\Delta}{P}}\left(1+\frac{2\Delta}{P-p}\right). \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

Substituting for P and p in this equation the relations (9) and reverting both sides of the equation thus obtained, we have

$$(k/\eta')_1=\frac{k}{\eta}\cdot\left(1+\frac{\Delta}{P}\right)\cdot\left(1-\frac{2\Delta}{P'-p'}\right). \quad \ldots\ldots \text{ up } \ldots\ldots \quad (12)$$

In exactly the same way, in the case of pushing down we have

$$(k/\eta')_2=\frac{k}{\eta}\cdot\left(1-\frac{\Delta}{p}\right)\cdot\left(1-\frac{2\Delta}{P'-p'}\right). \quad \ldots\ldots \text{ down } \ldots\ldots \quad (13)$$

These two equations are nothing but eqs. (6) and (7), if we assume the second factors $\left(1+\frac{\Delta}{P}\right)$ and $\left(1-\frac{\Delta}{p}\right)$ are constant within the range of pressures applied. Comparing above eqs. (12) and (13) with (6) and (7) respectively, it follows:

$$\frac{\dfrac{1}{a_1}+\dfrac{1}{a_2}}{2}\cdot 10^{-6}=\frac{\dfrac{k}{\eta}\left(1+\dfrac{\Delta}{P}\right)+\dfrac{k}{\eta}\left(1-\dfrac{\Delta}{p}\right)}{2}\fallingdotseq k/\eta\,, \quad \ldots\ldots \quad (14)$$

and

$$b_1=\frac{2\Delta}{a_1}\,, \qquad b_2=\frac{2\Delta}{a_2}\,. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (15)$$

Eq. (14) corresponds to formula (8) and the column-resistance Δ can be computed by eq. (15). This value was found to be about 4 mm. Hg, this being of quite reasonable order as compared with ordinary capillary depression.

Description of the Apparatus. The general view of the apparatus used is shown in Fig. 3. The viscosimeter V is supported by a rubber stopper S in a vapour jacket F and heated to a constant temperature by the vapour of the boiling liquid L. The vapour jacket is surrounded by a wider glass cylinder not shown in the figure, the cylinder being partially covered by cotton wool and asbestos paper. The heating liquid is introduced through a bent tube I and heated by a spiral of nichrom wire E. Some mercury is placed on the rubber stopper to prevent the liquid touching it. The upper end of the jacket is fused on to a Liebig's condenser K, the upper end of which being connected to a big air reservoir, a pump and a manometer. By means of them the pressure in the jacket can be regulated to keep the vapour at desired temperature. A thermometer T is hanged from the top of the viscosimeter and serves also as a plumb line.

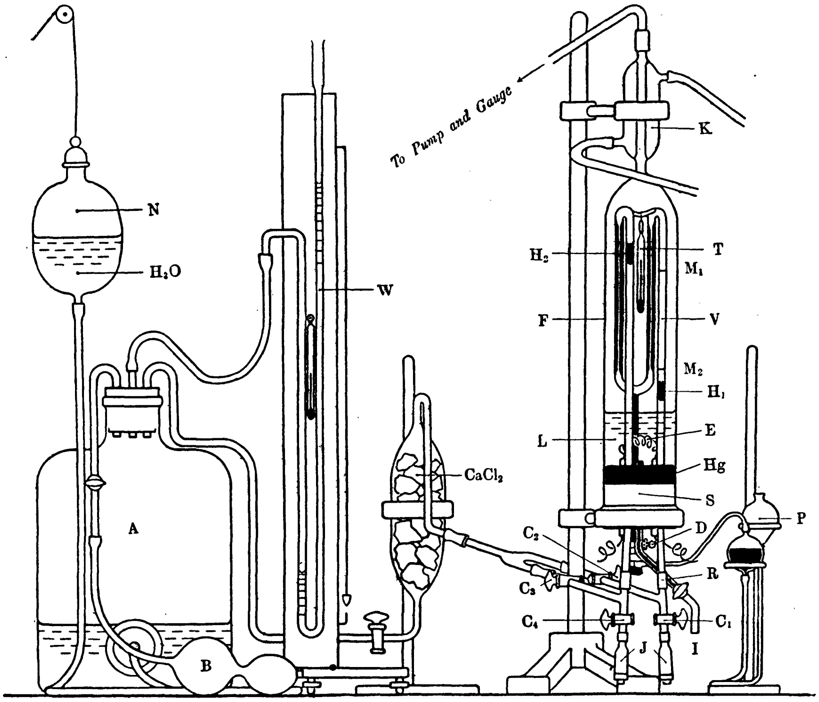

Fig. 3.

The capillaries of the viscosimeter are bent behind so as to spare the space as possible. A vertical central limb shown black in the figure passes through the stopper and is connected through a two way tap D to a small mercury pot. This tube was introduced for the purpose of cleaning and filling of the viscosimeter by means of a mercury reservoir P. Both limbs containing the indicating mercury-columns also pass through the stopper and their lower end are connected by means of rubber stoppers R to a commutating devise. It consists of a pair of T-shaped tubes, each of which being provided with two stop-cocks C_1, C_2 or C_3, C_4. By means of this devise either limb can be turned to the driving pressure at C_2 or C_3, or to air at C_1 or C_4. Two $CaCl_2$-tubes J are placed at the openings to air. A compressed air from the reservoir A is dried by passing it through a $CaCl_2$-tower, whence being lead through a wide Y-shaped tube to the commutating taps C_2 and C_3. The pressure in the reservoir A is controlled by means of a water vessel N and a hand-bellows B and is measured on the water manometer W. The reservoir is packed round with cotton wool and put in a wooden box.

In this type of viscosimeter it is specially important that the mercury limbs should be quite clean, or the mercury-columns will stick and move with jerks. Standing over a night or more with freshly prepared concentrated chromic mixture was found very effective for this purpose. Great care was taken to prevent some dust particles or greasy matter entering into the viscosimeter during washing and drying.

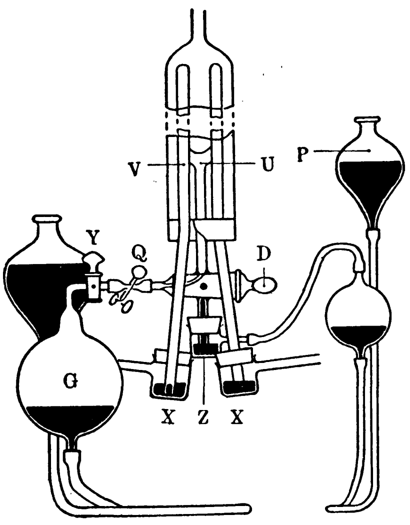

Fig. 4.

In order to fill the viscosimeter with the gas to be examined, the commutating devise is removed and the lower end of each mercury limb is dipped respectively in a pot (X in Fig. 4) containing some clean mercury. To the end of the central limb is also fixed a small mercury pot Z, to which a pressure is applied by means of a mercury reservoir P. The two way tap D is at first turned to its side tube, which is connected to the gas reservoir G of about 150 c.c. capacity. Keeping proper pressure in the reservoir and opening taps Q and Y, the gas is forced into the viscosimeter, the excess bubbling out through the mercury in the pots X, until all the air in the viscosimeter is completely expelled. Then the pinch-cock Q is closed and the pressure in the reservoir is somewhat lowered, after which Q is opened for a moment to suck up a small quantity of mercury from pots X. As soon as desired amounts are taken, the mercury pots are quickly removed, and the pinchcock Q is sufficiently opened to suck up the mercury columns at a suitable height. The two way tap D is then turned, so that the mercury in the pot Z is allowed to run up into the central limb just to the blanching point U. The viscosimeter is now ready for measurement. The length of mercury column can be calculated from the loss of the weight of the pot X by multiplying it with suitable coefficient obtained by the preliminary determination.

After each filling, the movability of mercury columns has been tested repeatedly during one hour, before the actual measurement begins. This preliminary tests are necessary to secure the steady state.

Experiment with Air. At first an experiment was done with dry air free from carbon dioxide, in order to test the method and to find the viscosimeter-constant. The results are shown in the following table.

Table 2.

t°C	$\frac{1}{a_1}$	b_1	$\frac{1}{a_2}$	b_2	$\frac{1}{a}$	(η/k)
20°	244.8	1975	243.8	1812	244.3	4093
40	234.5	1999	231.6	1830	233.0	4292
60	220.7	1806	219.8	1788	220.2	4541
80	211.0	1734	214.3	1902	212.6	4704
100	204.6	1719	202.9	1639	203.8	4907

The values $\frac{1}{a}$ in the sixth column are the means of the two limiting values $\frac{1}{a_1}$ and $\frac{1}{a_2}$, and those in the next column are the reciprocal of $\frac{1}{a}$ multiplied by 10^6. This is the true relative viscosity η/k, and can be expressed by the following Sutherland's formula:

$$\eta/k = 330.9\frac{T^{3/2}}{T+112.6}.$$

The viscosimeter-constant k is known from the calculated value of η/k at 23°C. and the known absolute value at the same temperature given by Millikan.

$$(\eta/k)_{23}=330.9\frac{(296.1)^{3/2}}{296.1+112\cdot6}=4125\ ,$$

$$\eta_{23}=1823\times10^{-7}\ \text{(Millikan)}\ ,$$

$$\therefore\ \ k=0.4419\times10^{-7}.$$

The relative values of viscosity η/k in Table 2 can now be expressed in absolute unit, which is shown in the following table.

Table 3.

Air $\eta=146.3\frac{T^{3/2}}{T+112.6}\cdot10^{-7}$

t°C	$\eta\cdot10^7$	
	Obs.	Calc.
0	—	1711
20	1809	1809
40	1897	1903
60	2007	1995
80	2079	2084
100	2169	2170

It will be seen that the above values agree well with values given by other observers.

Table 4.

Sutherland's Constant C of Air.

113 (Sutherland)	107 (Pedersen)
111 (Rayleigh)	119 (Rappenecker)
119 (Breitenbach)	113 (K. Schmitt)
116 (Rankine)	117 (Rankine & Smith)
124 (Fisher)	113 (Titani)

Table 5.

The Viscosity of Air at 0°C.

$\eta_0 \cdot 10^7$	Observers
1683	Graham (1846)
1678	v. Obermayer (1875)
1733	Breitenbach (1901)
1802*	Pedersen (1907)
1736	Zimmer (1912)
1726*	Kuenen and Visser (1913)
1724	Vogel (1914)
1724	Smith (1922)
1725	Klemenc and Remi (1923)
1711*	Ishida (1923)
1735*	Trautz and Weizel (1925)
1711	Titani (1929)

An advantage of the writer's method is that the viscosity of a gas available only in a small quantity can be measured at various temperatures with single filling. The viscosities of the following seventeen gases have been determined with this apparatus at several temperatures between 20° and 120°C:

Ethane, propane, *n*-butane, isobutane, ethylene, propylene, α-butylene, β-butylene, γ-butylene, isoamylene, acetylene, allylene, trimethylene, methyl-ether, methyl-chloride, methyl-bromide and sulphur-dioxide.

The results of the measurements will be reported in the second part of this paper.

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

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

By Tetsuya ISHIKAWA.

Received October 24, 1929. Published December 28, 1929.

The writer proposed(1) a viscosity formula for a chemically indifferent binary mixture of the form:

$$\eta=\eta_1+(\eta_2-\eta_1)\frac{k_2a_2z_m}{k_1a_1(1-z_m)+k_2a_2z}\,,$$

where η, a and k with the suffixes 1 and 2 signify the viscosities, the association degrees and the field constants of components 1 and 2 respectively; z_m is the molar fraction of component 2.

The formula was confirmed with satisfactory results and also proved to be applicable for the mixture in which molecular compounds are formed.(2) Thus, the deviation δ of the measured viscosity (η) from that calculated from the formula (η_0) is expressible in the following form:

$$\delta=\eta-\eta_0=C\cdot(1-z_m)^{\nu_1}z_m^{\nu_2}\,,$$

where ν_1 and ν_2 are the numbers of reactive molecules of each component to form a molecular compound and C is an empirical constant.

The field constant k which is a measure of molecular field of attraction was shown to be an important factor by which a liquid is particularized from other liquids.(3)

This paper is a further study on k for the mixture where one of its components suffers molecular dissociation.

If the associated molecules of one component, say, component 2 of a binary mixture dissociates in the solution, the values $\left(\frac{k_2a_2}{k_1a_1}\right)$ do not keep constant, since a_2 is a variable with concentration. Suppose the group of such points to lie on a straight line, the extrapolated values to $z_m=0$ and to $z_m=1$ are easily obtainable and are accurate at the same time.

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(1) This Bulletin, **4** (1929), 5.

(2) This Bulletin, **4** (1929), 25.

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

Now consider three binary mixtures composed of three liquids A, B and C, among which only C dissociates in the admixtures of A and of B. Then we have

$$\left(\frac{k_c a_c}{k_A a_A}\right)_{z_m\text{-}C=1} \quad \text{and} \quad \left(\frac{k_c a_c}{k_B a_B}\right)_{z_m\text{-}C=1}.$$

Taking the ratio of these two, we get $\left(\frac{k_B a_B}{k_A a_A}\right)$.

The writer's theory demands that this value must coincide with that directly obtained from the viscosity of the mixture of A and B, provided that they are chemically non-reactive with each other.

It would be interesting to know whether the extrapolated values thus obtained obey the proposition, and the following six cases will be adopted from the literature.

Calculations of the degree of molecular dissociation.

Since the field constant k is invariable, it is easily understood that the degree of molecular dissociation of one component, say, component 2 in the admixture of infinite quantity of the other, component 1 which is non-dissociated, can be estimated by the following method: By extrapolation we get

$$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=0} \quad \text{and} \quad \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=1},$$

in which $(a_2)_{z_m=1}$ denotes the association degree of component 2 in singly existence,

and $(a_2)_{z_m=0}$, the decreased association degree of component 2 dissolved in infinite quantity of component 1.

If we denote the degree of molecular dissociation at infinite dilution by α_∞,

$$\alpha_\infty = 1 - \frac{(a_2)_{z_m=0}}{(a_2)_{z_m=1}} = 1 - \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=0} \Big/ \left(\frac{k_2 a_2}{k_1 a_1}\right)_{z_m=1},$$

since $(a_1)_{z_m=0} = (a_1)_{z_m=1}$ by assumption.

Table 1.

$C_6H_5CH_3-C_6H_5CH_2\cdot C_7H_5O_2$ (Benzyl benzoate), 25°C.
(Kendall & Monroe).(1)

z_m-Ester	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.005520		
0.2367	0.01183	0.280	0.282
0.4261	2015	0.306	0.310
0.6502	3614	0.341	0.341
0.7890	5080	0.359	0.360
0.9002	6660	0.378	0.376
1.0000	8450		

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.250, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.390$$

and

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.250+(0.390-0.250)z_m\,.$$

Table 2.

$C_6H_6-C_6H_5CH_2\cdot C_7H_5O_2$ (Benzyl benzoate), 25°C.
(Kendall & Monroe)(2).

z_m-Ester	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.006044		
0.1886	0.01196	0.343	0.345
0.4124	2301	0.392	0.386
0.5832	3584	0.437	0.418
0.7827	5478	0.455	0.455
0.8952	6883	0.468	0.476
1.0000	8454		

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(1), (2) J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, **39** (1917), 1787.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.310\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.495$$

and

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.310+(0.495-0.310)z_m\,.$$

From the values

$$\left|\frac{(ka)\text{Ester}}{(ka)\text{C}_6\text{H}_5\text{CH}_3}\right|_{z_m\text{-Ester}=1} = 0.390 \quad \text{and} \quad \left|\frac{(ka)\text{Ester}}{(ka)\text{C}_6\text{H}_6}\right|_{z_m\text{-Ester}=1} = 0.495$$

we obtain, since $(a)\text{C}_6\text{H}_6=(a)\text{C}_6\text{H}_5\text{CH}_3=1$,

$$\frac{(ka)\text{C}_6\text{H}_5\text{CH}_3}{(ka)\text{C}_6\text{H}_6}=\frac{(k)\text{C}_6\text{H}_5\text{CH}_3}{(k)\text{C}_6\text{H}_6}=\frac{0.495}{0.390}=1.27\,.$$

Satisfactory coincidence is found between this value and $k=1.23$ obtained in the previous paper for the field-constant of $\text{C}_6\text{H}_5\text{CH}_3$. Also

$$\left|\frac{(ka)\text{Ester}}{(ka)\text{C}_6\text{H}_5\text{CH}_3}\right|_{z_m\text{-Ester}=0} = \frac{(ka')\text{Ester}}{(ka)\text{C}_6\text{H}_5\text{CH}_3}=0.250\,,$$

where (a') =the decreased association degree of the ester at zero concentration in $\text{C}_6\text{H}_5\text{CH}_3$.

$$\left|\frac{(ka)\text{Ester}}{(ka)\text{C}_6\text{H}_6}\right|_{z_m\text{-Ester}=0} = \frac{(ka'')\text{Ester}}{(ka)\text{C}_6\text{H}_5\text{CH}_3}=0.310\,,$$

where (a″) =the decreased association degree of the ester at zero concentration in C_6H_6.

From these two we get

$$\left(\frac{a''}{a'}\right)_{\text{Ester}} \cdot \frac{(k)\text{C}_6\text{H}_5\text{CH}_3}{(k)\text{C}_6\text{H}_6}=\frac{0.310}{0.250}=1.24\,.$$

This value is in good agreement with the above, so that $a'=a''$, i. e. benzyl benzoate dissociates in equal amount at zero concentration in $\text{C}_6\text{H}_5\text{CH}_3$ and in C_6H_6; the degree of the molecular dissociation,

$$\alpha_\infty=1-\frac{0.250}{0.390} \quad \text{or} \quad 1-\frac{0.310}{0.495}=0.36 \quad \text{or} \quad 0.37\,.$$

Table 3.

$C_6H_4(OCH_3)OH$ (Guaiacol)$-C_6H_6$, 30°C. (Puschin & Pinter).⁽¹⁾

z_m-C_6H_6	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.00	0.0445		
0.10	0.0340	3.34	3.64
0.20	0.0249	4.08	3.88
0.30	0.0197	4.13	4.12
0.40	0.0157	4.32	4.36
0.50	0.0129	4.38	4.60
0.60	0.0104	4.82	4.84
0.70	0.00873	5.04	5.08
0.80	742	5.36	5.32
0.90	641		
1.00	569		

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 3.40 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 5.80$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.} = 3.40 + (5.80-3.40)z_m \,.$$

Table 4.

$C_6H_4(OCH_3)OH$ (Guaiacol)$-C_6H_5CH_3$, 30°C. (Puschin & Pinter).⁽²⁾

z_m-$C_6H_5CH_3$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.00	0.0445		
0.10	0.0317	4.36	4.35
0.20	0.0247	4.08	4.50
0.30	0.0183	4.69	4.65
0.40	0.0150	4.54	4.80
0.50	0.0120	4.82	4.95
0.60	0.00981	5.08	5.10
0 70	815	5.39	5.25
0.80	700	5.39	5.40
0.90	599		
1.00	526		

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(1), (2) N. A. Puschin and T. Pinter, *Z. physik. Chem.*, Abt. A, **142** (1929), 211.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 4.20 \text{ and } \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 5.70\,.$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 4.20 + (5.70-4.20)z_m\,.$$

We obtain, from the values

$$\left.\frac{(ka)C_6H_6}{(ka)\text{Guaiacol}}\right|_{z_m\text{-}C_6H_6=0} = \left.\frac{(ka)C_6H_6}{(ka)\text{Guaiacol}}\right|_{z_m\text{-Guai.}=1} = 3.40$$

and

$$\left.\frac{(ka)C_6H_5CH_3}{(ka)\text{Guaiacol}}\right|_{z_m\text{-}C_6H_5CH_3=0} = \left.\frac{(ka)C_6H_5CH_3}{(ka)\text{Guaiacol}}\right|_{z_m\text{-Guai.}=1} = 4.20\,,$$

$$\frac{(ka)C_6H_5CH_3}{(ka)C_6H_6} = \frac{(k)C_6H_5CH_3}{(k)C_6H_6} = \frac{4.20}{3.40} = 1.24\,.$$

This is strictly concordant with the known value of field constant of $C_6H_5CH_3$.

$$a_\infty \text{ in } C_6H_6 = 1 - \frac{\frac{1}{5.80}}{\frac{1}{3.40}} = 1 - 0.586 = 0.41\,,$$

while $$a_\infty \text{ in } C_6H_5CH_3 = 1 - \frac{\frac{1}{5.70}}{\frac{1}{4.20}} = 1 - 0.737 = 0.26\,.$$

Table 5.

$C_2H_5OH-(C_2H_5)_2O$, 25°C. (Baker).(1)

z-$(C_2H_5)_2O$	z_m-$(C_2H_5)_2O$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.0000	0.01112		
0.2315	0.1577	0.007414	3.84	3.84
0.4743	0.3593	4782	4.48	4.48
0.5751	0.4569	4005	4.84	4.78
0.6448	0.5302	3590	5.02	5.02
0.7299	0.6269	3152	5.32	5.32
0.7837	0.6925	2897	5.73	5.53
0.8639	0.7978	2635	5.73	5.86
1.0000	1.0000	2260		

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(1) F. Baker, *J. Chem. Soc.*, **60** (1912), 1409.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 3.34\,, \qquad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 6.50$$

and
$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 3.34 + (6.50-3.34)z_m\,.$$

Table 6.

n-$C_3H_7OH-(C_2H_5)_2O$, 25°C. (Baker).(1)

z-$(C_2H_5)_2O$	z_m-$(C_2H_5)_2O$	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{obs.}}$	$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{calc.}}$
0.0000	0.0000	0.01971			
0.1193	0.0991	0.01404	4.39	0.228	0.228
0.2299	0.1949	0.01024	4.90	0.204	0.204
0.3492	0.3032	0.007528	5.32	0.188	0.188
0.4716	0.4198	5619	5.78	0.173	0.173
0.5989	0.5475	4274	6.33	0.158	0.158
0.7297	0.6864	3356	6.80	0.147	0.147
0.8622	0.8354	2717	7.30	0.137	0.137
1.0000	1.0000	2260			

Since $\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$ are not strictly linear, their reciprocals are taken.

$$\left(\frac{k_1a_1}{k_2a_2}\right)_{z_m=1} = 0.258 \quad \text{and} \quad \left(\frac{k_1a_1}{k_2a_2}\right)_{z_m=0} = 0.129\,.$$

$$\left(\frac{k_1a_1}{k_2a_2}\right)_{\text{calc.}} = 0.258 - (0.258-0.129)z_m\,.$$

The four values above obtained are rewritten as follows:

(i) $\left|\frac{(ka')_{\text{Ether}}}{(ka)_{C_2H_5OH}}\right|_{z_m\text{-}C_2H_5OH=1} = 3.34\,,$ where $(a')_{\text{Ether}}$ = the association degree of ether at zero concentration in ethyl alcohol.

(ii) $\left|\frac{(ka)_{\text{Ether}}}{(ka')_{C_2H_5OH}}\right|_{z_m\text{-Ether}=1} = 6.50\,,$ where $(a')_{C_2H_5OH}$ = the association degree of C_2H_5OH at zero concentration in ether.

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(1) Loc. cit.

(iii) $\left|\dfrac{(ka)_{C_3H_7OH}}{(ka'')_{Ether}}\right|_{z_m\text{-}C_3H_7OH=1} = 0.258$, where $(a'')_{Ether}$ = the association degree of ether at zero concentration in n-propyl alcohol.

(iv) $\left|\dfrac{(ka'')_{C_3H_7OH}}{(ka)_{Ether}}\right|_{z_m\text{-}Ether=1} = 0.129$, where $(a'')_{C_3H_7OH}$ = the association degree of n-C_3H_7OH at zero concentration in ether.

We have from the preceding papers

$$\frac{(ka)_{C_3H_7OH}}{(ka)_{C_2H_5OH}} = \frac{0.31 \times 1.31}{0.34 \times 1.37} = 0.87$$

While from (ii) and (iv) we get

$$\frac{(ka'')_{C_3H_7OH}}{(ka)_{C_2H_5OH}} = 6.50 \times 0.129 = 0.84\,,$$

which is fairly concordant with the above. Hence we may say that the molecular dissociation of these alcohols does not take place in ether solution.

Again from (i) and (iii) we get

$$\left(\frac{a'}{a''}\right)_{Ether} \frac{(ka)_{C_3H_7OH}}{(ka)_{C_2H_5OH}} = 3.34 \times 0.258\,.$$

$$\left(\frac{a'}{a''}\right)_{Ether} = \frac{3.34 \times 0.258}{0.87} = 0.99\,.$$

This tells that the decreased association degrees of ether at zero concentration in C_2H_5OH and in n-C_3H_7OH are the same, a_∞ having the value 0.50.

The two more examples, C_6H_5Cl-C_6H_5OH and C_6H_6-C_6H_5OH will be quoted.

Table 7.

C_6H_5Cl–C_6H_5OH, 20°C. (Bramley).(1)

z-C_6H_5OH	z_m-C_6H_5OH	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{obs.}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{calc.}$
0.0000	0.0000	0.00768		
0.0493	0.0584	0.00825	0.090	0.088
0.0978	0.1148	0.00888	0.091	0.094
0.2173	0.2493	0.01122	0.107	0.107
0.3043	0.3435	0.01374	0.116	0.117
0.3890	0.4324	0.01673	0.127	0.126
0.4990	0.5437	0.02218	0.138	0.137
0.5815	0.6243	0.02748	0.144	0.146
0.7141	0.7493	0.04070	0.158	0.158
0.8145	0.8400	0.05555	0.166	0.168
1.0000	1.0000	0.1104		

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(1) A. Bramley, *J. Chem. Soc,*, **109** (1916), 10.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.082 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.184\,.$$

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}} = 0.082 + (0.184-0.082)z_m\,.$$

$$\alpha_\infty \text{ of } C_6H_5OH=1-\frac{0.082}{0.184}=0.55\,.$$

H. Hirobe⁽¹⁾ studied the partition of phenol between water and chlorobenzene and concluded that if phenol in chlorobenzene solution is assumed to consist of two kind of molecules of monomol and trimol which are in the equilibrium:

$$3\ C_6H_5OH \rightleftarrows (C_6H_5OH)_3\,,$$

$$\frac{C_1^3}{C_3}=K\,,$$

where C_1 and C_3 are the numbers of mols of monomol and of trimol, the equilibrium is sufficiently explained, giving $\log K=\bar{1}.44$ at 30°C.

Now, put $C_1+C_3=1$ in order to find the fraction of respective molecules, then we get

$$C_1+\frac{C_1^3}{0.276}=1\,.$$

The solution of the equation is $C_1=0.51$. The coincidence of this and the above obtained value is satisfactory.

Table 8.

$C_6H_6-C_6H_5OH$, 20°C. (Bramley).⁽²⁾

z-C_6H_5OH	z_m-C_6H_5OH	η	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{obs.}}$	$\left(\frac{k_2a_2}{k_1a_1}\right)_{\text{calc.}}$
0.0000	0.0000	0.00629		
0.0604	0.0506	0.00683	0.098	0.094
0.0984	0.08305	0.00724	0.102	0.099
0.2001	0.1723	0.00865	0.111	0.111
0.3240	0.2877	0.01126	0.124	0.127
0.4209	0.3762	0.01401	0.133	0.139
0.5302	0.4836	0.01911	0.150	0.154
0.6365	0.5775	0.02642	0.175	0.168
0.7411	0.7037	0.03811	0.185	0.185
0.8320	0.8043	0.0535	0.202	0.200
1.0000	1.0000	0.1104		

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(1) H. Hirobe. *J. Coll. Sci., Imp. Univ. Tokyo,* **25** (1908), Art. 12, p. 35.

(2) A. Bramley, *J. Chem. Soc.* **109** (1916), 10.

$$\left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=0} = 0.087 \quad \text{and} \quad \left(\frac{k_2a_2}{k_1a_1}\right)_{z_m=1} = 0.227 .$$

$$\alpha_\infty \text{ of } C_6H_5OH = 1 - \frac{0.087}{0.227} = 0.62 .$$

K. Endo,⁽¹⁾ in his study on the partition of phenol between water and benzene, assumed that phenol in benzene takes similar molecular state as that in chlorobenzene as was discussed by Hirobe, and observed

$$\frac{C_3}{C_1^3} = K = 1.072 \ (25°\text{C.}) .$$

From this and $C_1 + C_3 = 1$,

we get $1.072\, C_1^3 + C_1 = 1$

Whence $C_1 = 0.67$,

which is in fair agreement with the value above obtained.

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(1) K. Endo, this Bulletin, **1** (1926), 25.