BULLETIN OF THE
CHEMICAL SOCIETY OF JAPAN

ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. X. THE MECHANISMS OF THE PROMOTION AND POISONING OF THE CATALYTIC ACTION.*

By Koshiro ISHIMURA.

Received July 26th, 1934. Published January 28th, 1935.

The Mechanism of the Promotion. It has been suggested in a previous paper[1] that the co-existence of Al_2O_3 and SiO_2 is essential to the catalytic action of Japanese acid earth on naphthalene and all other metallic oxides are unnecessary for it. There has been, however, always present in the reaction system another component not to be overlooked, i.e. water. The earth heated at 500° still contains a few per cent. of water.[2] Isobe[3] observed that it retains a small amount of water even after heated at 1000° for six hours.

The earth dried at 300° rapidly adsorbs water vapour. A small fraction of this adsorbed water is held very firmly by the earth and cannot be set free at 120° even after the constant weight of the earth is obtained. This tenaciously held water has been called "retained water" by the present author[4] in order to distinguish it from adsorbed or added water. The molecules of the retained water may highly probably be those directly held by the bare surface of the earth. The catalytic activity of the earth is greatly promoted when it carries the retained water as described in details in the preceding paper. Therefore, it is very probable that the catalysis in question is performed by the three component catalyst consisting of Al_2O_3, SiO_2, and water; the molecules of naphthalene are activated when they are adsorbed on the catalytically active centres of these three components.

When the earth is heated at 300° some of these active centres lose molecules of water and consequently become inactive. They will, however, recover their ability if water molecules are put in their original positions, and this recovery of the catalytic activity is accomplished by the retained

* An epitomized translation of the original published in Vol. 29 of the Reports of the Tokyo Imperial Industrial Research Laboratory.

(1) Inoue and Ishimura, This Bulletin, **9** (1934), 431.

(2) Ishimura, This Bulletin, **9** (1934), 522.

(3) Isobe, *J. Chem. Soc. Japan*, **51** (1930), 761.

(4) Ishimura, *loc. cit.*

water, giving rise to the observed promotion of the activity. The promotion would be therefore necessarily accompanied by the increase in the water content of the earth. On the contrary, if the promotion is caused by the increase in the surface area due to the prolonged exposure to water vapour in the same manner as many metals are activated by the adsorption of gases,[5] the promotive power would be a function of the time of adsorption or of the total amount of adsorbed water but not of the amount of retained water. The experimental results however contradict with the latter view. When water is adsorbed in the absence of air the adsorption proceeds much more rapidly and the ratios of retained water to the total amounts adsorbed are much greater than in the case of the adsorption in the open air. By comparing the promotive powers of the samples thus prepared with those given in Table 2 in Part IX of this series,[6] one comes at once to the conclusion that the promotive power is a function of the amount of retained water but not of the total amount adsorbed nor of the time of adsorption. Moreover, when the moist earth is dried at 120° under highly reduced pressure the amount of the retained water is diminished with the decrease in the promotive power.

Thus it is most probable that the existence of water is indispensable for the promotion of the catalytic activity.[7]

As always stated,[8] the retained water can be replaced by other neutral substances containing oxygen in their molecules such as alcohols, acetone, and ether. So, generally speaking, the catalytic action on naphthalene is effected by the three component catalyst consisting of Al_2O_3, SiO_2, and one of these substances mentioned above.

The Mechanism of the Poisoning. The poisons in this catalytic action can be classified into two distinct types: strong poisons such as ammonia, amine, nitrile, and amyl nitrite, and weak poisons such as hydrogen chloride and acetic acid. The mechanism of poisoning will be discussed separately about each type.

Though poisoning by ammonia is very drastic, its action is not fatal to the active centres. The catalytic activity will be restored completely if the adsorbed poison is all expelled. It is very difficult however to liberate the total ammonia retained. The complete liberation was attained only when

(5) It is believed that molecules of gas diffusing through metal actually enter into metal lattice, distending it, breaking it, and thus activating the surface of the metal. Piper, *Trans. Faraday Soc.*, **24** (1933), 540.

(6) Ishimura, This Bulletin, **9** (1934), 523.

(7) It goes without saying that the promotion is not a mere annealing effect.

(8) Ishimura, *loc. cit.*

the poisoned earth was heated at 500° for two hours under the reduced pressure of 4 mm. The activity of the earth thus freed from the retained ammonia was compared with that of the original sample with the same heat treatment and there could be seen no difference between them.

The earth with the sufficient amount of the poison to cover the whole surface does not recover its activity by adsorbing water or alcohol. When, however, its surface is only partly covered by the poison and there is left an ample room to retain these oxygen-containing neutral substances, then the activity is increased to a marked degree by the adsorption of these substances. It seems therefore that the strong poisons are adsorbed selectively and strongly on the active centres, rendering them inactive for the catalysis.

This is not the case with the weak poisons such as hydrogen chloride and acetic acid. Though they are in themselves poisons their selection of the location of adsorption would be different; they are adsorbed first and retained to the very last on the inactive parts of the surface. Their poisoning effects are not therefore manifested unless their retained amounts are relatively large, and even if all the active centres are covered by them they may be liberated easily in the course of reaction, hence the weakness of their poisoning actions.

The amount of naphthalene adsorbed by the acid earth with the various retained substances are plotted against time as shown in Fig. 1.

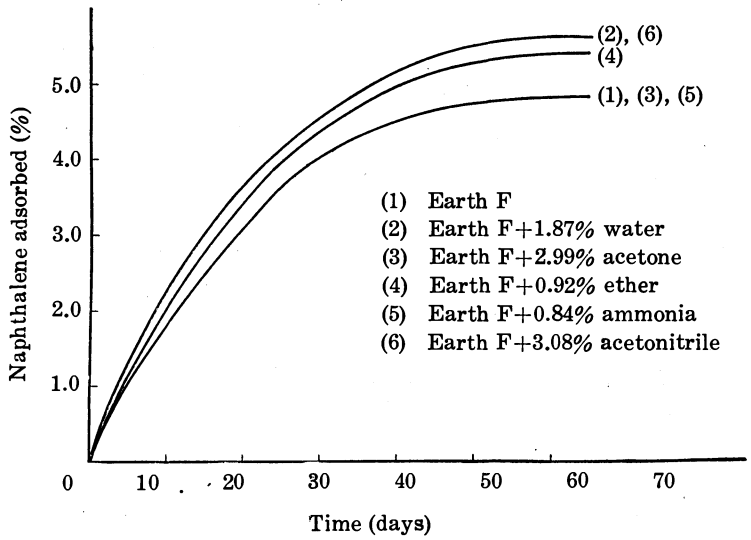


Fig. 1.

The adsorption experiment was carried out in the same manner as described in the previous paper.[9] Fig. 1 shows that the total amount adsorbed is not influenced appreciably by the retained substance, whether it is a promoter or a poison. Therefore the rôle of poisons does not consist in the prevention of the adsorption of naphthalene. They only render the catalytically active parts inactive before there occurs the adsorption of naphthalene. In other words, the adsorption of naphthalene is converted from the "chemical" into the "physical" by the poisons.

The Surface Area of the Acid Earth. The surface area per gram of the acid earth was calculated from the specific gravity and diameter of the particles of the earth. Kobayashi[10] measured the specific gravities of the dried earths and gave the values 2.7—2.9, while Isobe[11] 2.67—2.70. Recently Yamamoto[12] determined them again and found 2.4~2.5. The value 2.7 was taken in the present calculation. The diameter of the particles of the dried earth is presumed to be less than 10^{-5} cm. from the observation of X-ray patterns.[13] Isobe[14] determined it from the apparent and true specific gravities and the number of cracks on the surface of the earth observed by a microscope and found the value 2.35×10^{-5} cm., while Kobayashi[15] gave $3.3\sim6.2\times10^{-5}$ cm. by counting the number of particles suspended in water using an ultramicroscope and measuring the weight after evaporating up the water. The value 2×10^{-5} cm. was here adopted.

Let us assume that each particle is cubic in form with the sides of 2×10^{-5} cm. in length, then the surface area of one particle is 2.4×10^{-9} sq. cm. Since the specific gravity is 2.7, the number of particles contained in 2.7 g. is $(1/2^3)\times10^{15}=1.25\times10^{14}$, hence the number of particles per gram is 4.63×10^{13}. The total surface area per gram is therefore 1.11×10^{5} sq. cm. $\fallingdotseq$ 10 sq. m. This represents about one tenth of the surface area[16] of active charcoal.

As stated in the previous paper, when 0.49 millimol of ammonia is retained by one gram earth, the activity of the earth is entirely lost. Further experiment showed that by 0.15 millimol of ammonia retained by one gram earth the activity was decreased by 77 per cent. Adopting a

(9) Ishimura, This Bulletin, **9** (1934), 498.
(10) Kobayashi, "Japanese acid earth," 2nd Ed. (1927).
(11) Isobe, *Sci. Pap. Inst. Phys. Chem. Research (Japan)*, **5** (1926), 175.
(12) Yamamoto, *Waseda Appl. Chem. Soc. Bull.*, No. **17** (1932), 2.
(13) Kameyama and Oka, *J. Soc. Chem. Ind. Japan*, **33** (1930), 307.
(14) *Loc. cit.*
(15) *Loc. cit.*
(16) Cude and Hullet, *J. Am. Chem. Soc.*, **42** (1920), 398; Lamb and Coolidge, *ibid.*, **42** (1920), 1168.

value of 6.06×10^{23} for the Avogadro constant and 1.6×10^{-8} cm. for a molecular diameter of ammonia, we obtain an area of 1.71×10^{4} sq. cm. to be covered by 0.15 millimol of ammonia on the assumption of a packed monomolecular layer. Therefore, the total area of the active centres per gram earth is 2.22×10^{4} sq. cm. or about 20 per cent. of the total surface area. This represents the greatest value possible, since the adsorption of ammonia is not necessarily quite selective and moreover the liberation of ammonia from the active centres may occur in the course of the reaction.

A simple calculation shows that the amount of water to cover the whole surface of the earth by a monomolecular layer would be about 2.5 per cent. of the weight of the dry earth, if the effective diameter of water molecule on the adsorption layer is 3.5×10^{-8} cm.[17]

The author expresses his sincere gratitude to Dr. Inoue for his interest taken in and criticism made on this work.

The Tokyo Imperial Industrial Research Laboratory,
Hatagaya, Tokyo.

(17) This is not known accurately and must depend upon the orientation of molecules. It may be less than the above-mentioned value since it is probable that molecules on the adsorption layer are more closely packed than in liquid state.

ON THE ABSORPTION OF HYDROGEN CHLORIDE INTO VARIOUS ORGANIC LIQUIDS AND CALCULATION OF THE HEAT OF ABSORPTION. I.

By Senzo HAMAI.

Received September 14th, 1934. Published January 28th, 1935.

On account of the great interest in solubility in general, and especially in the possible relations between various physical and chemical properties of solutes as well as of solvents and solubilities, numerous investigations have been carried out. However, there is not yet a theory which enables us to account for all types of solubility dada, although there is a definite trend

as to what direction we should look for. Hildebrand gives an excellent discussion in his book "Solubility" and he states in his introductory remark, "The solubility of one substance in another depends fundamentally upon the ease with which the two molecular species are able to mix, and if the two species display a certain hostility towards mixing, not only will saturation be attained at smaller concentration, but in the unsaturated solution the tendency to mutual segregation will give rise to a partial separation or adsorption of one species at the surface, with a consequent lowering of surface tension. It is likely also to give rise to an expansion and absorption of heat upon mixing, phenomena not ordinarily connected with solubility". Thus the investigation of solubility is not only highly practical, but also very fascinating and interesting from a theoretical standpoint. With this view, the present author has undertaken the investigation on some aspects of solubility of gases in various organic solvents.

In order to systematize various solubility data several attempts have hitherto been done to find general laws which govern the solubility. We have a great deal of evidences that polarity of substances involved has much to do with the solubility. Still another criterion which has been taken into account is the relations between the solubilities and the internal pressures of substances, as measured by $-T\frac{\alpha}{\beta}$ which was proposed by Dupré :[1][2]

$$T\left(\frac{\partial P}{\partial T}\right)_V = -T\frac{\alpha}{\beta}, \qquad (1)$$

where α is the coefficient of expansion, β the coefficient of compressibility, and the term $T\left(\frac{\partial P}{\partial T}\right)_V$ appears in the thermodynamic equation of state, namely

$$P+\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V. \qquad (2)$$

The purpose of the present investigation is to see whether the solubility of a relatively polar gas in various non-polar liquids can be correlated with the various chemical and physical properties of these non-polar liquids.

(1) Dupré, *Ann. chim. phys.*, **2** (1864), 201.

(2) For fuller discussion of internal pressure, see "Solubility" by Hildebrand, Chem. Catalogue Co.

As a polar gas hydrogen chloride[2a][3] is chosen, and as non-polar liquids carbon tetrachloride, ethylene chloride, ethylene bromide, and 1,1,2,2-tetrachlorethane are selected.

Experimental Procedure. The method for measuring the absorption of hydrogen chloride into these liquids consists in finding the volume of hydrogen chloride absorbed by a given amount of these liquids. The measuring apparatus of hydrogen chloride is a U-shaped gas burette which is filled with mercury, and calibrated to 0.5 c.c., and can be read to 0.1 c.c., and at the same time the pressure of hydrogen chloride plus the vapour pressure of the liquid used, which has absorbed hydrogen chloride also can be read so that the amount of hydrogen chloride absorbed at various pressures can be obtained. The U-shaped gas burette is provided with water jacket. During a run there is practically no variation of temperature, so that the water in the jacket is stopped from flowing. The absorption vessel is about 80 c.c. in capacity and connected to the gas generating system through a capillary tube and also to an ordinary mercury manometer with a stopcock to cut it off from the absorption chamber during the absorption experiment. The vessel is also connected to the graduated liquid reservoir at the top from which a given amount of liquid is introduced into the absorption vessel after the vessel has been evacuated. The whole absorption vessel is immersed in the thermostat with constancy of $\pm 0.1°$. Between the gas burette and the absorption chamber a vessel of 335 c.c. capacity is inserted as a gas reservoir which is also immersed into the thermostat in order to make the gas to acquire the same temperature as the liquid before entering the absorption vessel. Furthermore, in order to saturate the liquid with hydrogen chloride thoroughly, the whole absorption apparatus is shaken by tapping from time to time until there occurs no more absorption. One to one and a half hours are usually sufficient to establish the equilibrium. Thus from the volume change in

(2a) Debye, "Polar Molecules," Chem. Catalogue Co.; F. I. G. Raulins, *Z. Physik*, **50** (1928), 440; J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford Press; L. Pauling, *J. Am. Chem. Soc.*, **54** (1932), 988.

(2b) L. Pauling, "The Nature of The Chemical Bond. IV," *J. Am. Chem. Soc.*, **54** (1932), 3570.

(2c) L. Pauling and J. Sherman, *J. Chem. Phys.*, **1** (1933), 606.

(3) Recent development in the quantum mechanics seems to show that as far as the valence in HCl is concerned it may be regarded perhaps more non-polar in nature, although it is more or less accepted as a polar gas from the dielectric measurement and the direct measurement of the electric moment by the molecular ray method. Zahn, *Phys. Rev.*, **24** (1924), 400; Estermann and Fraser, *J. Chem. Phys.*, **1** (1933), 390.

the gas burette, the initial and final pressures, and the volume of the system, the volume (ΔV) of hydrogen chloride actually absorbed into the liquid is calculated.

The Materials Used. Hydrogen chloride was prepared by dropping concentrated hydrochloric acid into pure concentrated sulphuric acid, passing the gas through two sulphuric acid bubblers, and condensing twice with liquid nitrogen. Only the middle portion of it was used after passing it finally through a calcium chloride tube before it was allowed to enter into the burette and reservoir.

1,1,2,2-Tetrachlorethane (Kahlbaum's product, b.p. 143.5—144°) was distilled twice. The another sample of 1,1,2,2-tetrachlorethane was kindly supplied by Dr. Fukagawa of the Institute of Physical and Chemical Research, Tokyo, to whom the author wishes to express his best thanks.

Carbon tetrachloride (Kahlbaum's product, b.p. 76.0°), ethylene chloride (Takeda's product, b.p. 83.0°), and ethylene bromide (Takeda's product, b.p. 129.0°) were all distilled twice.

Results. For all of these organic liquids, the volume of hydrogen chloride absorbed was plotted against respective pressures at which the system finally reached an equilibrium, one of examples, of 1,1,2,2-tetrachlorethane being shown in Fig. 1, so that we can get the volume of the gas to be absorbed at the total pressure of 760 mm. by either extrapolation or interpolation as the case may be, and this is converted to mol fraction: $N'_{HCl} = n_{HCl}/(n_{HCl}+n_{liquid})$. This corresponds to the solubility of hydrogen chloride at the total pressure of 1 atmosphere expressed in mol fraction. To find the value of the solubility of hydrogen chloride, i.e. N_{HCl}, when P_{HCl} equals 1 atmosphere, Henry's law in the following form was used:

$$N_{HCl} = N'_{HCl} \times \frac{760}{P_{HCl}} .$$

In order to find P_{HCl}, Raoult's law was assumed to hold and the values of the vapour pressures of the organic liquids were obtained from the International Critical Table and those not given directly was calculated by the equation:

$$\log_{10} P_{mm.} = \frac{0.05223}{T} \times A + B . \qquad (4)$$

In the case of 1,1,2,2-tetrachlorethane the data for the above expression could be obtained only for the range 26—145°, so that strictly speaking the

vapour pressure calculation could not be correct, but, for the temperatures 15°, 20°, and 25°, calculation may not be so much far from the true values even if we assume it holds for 15°, 20°, and 25°C.

Tables 1–4 show the results of the absorption experiments for 20 c.c. of respective liquids at 15°, 20°, and 25°C. In Table 5, N, $\log N$, and $\frac{1}{T}\times 10^{-3}$ for 15°, 20°, and 25° for each liquid are listed, and $\log N$ plotted against $\frac{1}{T}\times 10^{-3}$ as shown in Figs. 2–4. The heat of absorption ΔH can be calculated by

$$\frac{d\log N}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H}{2.303\times R}\,. \qquad (5)$$

ΔH for each liquid is also listed in Table 5.

Table 1. Absorption of Hydrogen Chloride into 1,1,2,2-Tetrachlorethane at 25°, 20°, and 15°C., per 20.0 c.c. of $C_2H_2Cl_4$.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	739.0	112.55	0.0239	2.39
2	396.0	59.38	0.0128	1.28
3	493.5	74.90	0.0161	1.61
4	614.5	94.18	0.0201	2.01
5	541.0	83.41	0.0178	1.78
6	442.0	68.04	0.0146	1.46
		20°C.		
7	731.5	122.05	0.0258	2.58
8	390.0	65.29	0.0140	1.40
9	582.0	99.27	0.0211	2.11
10	631.5	108.21	0.0229	2.29
11	680.0	114.97	0.0243	2.43
12	621.5	106.25	0.0225	2.25
		15°C.		
13	663.5	124.30	0.0261	2.61
14	384.5	72.81	0.0155	1.55
15	722.5	133.84	0.0281	2.81
16	573.5	109.81	0.0231	2.31

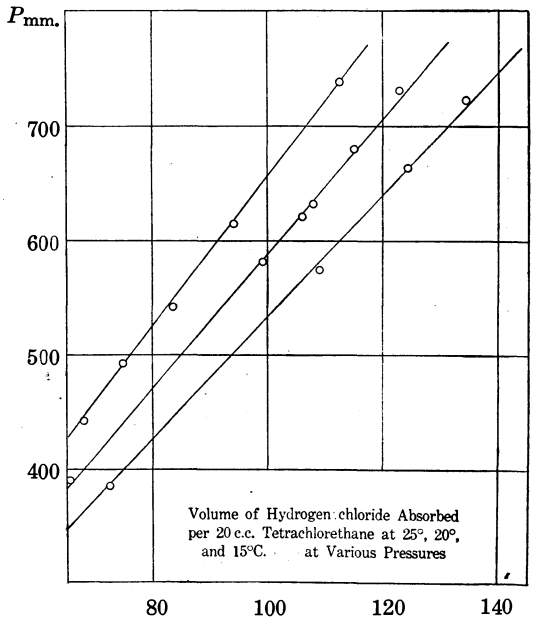


Fig. 1.

Table 2. Absorption of Hydrogen Chloride into Carbon Tetrachloride at 25°, 20°, and 15°C., per 20.0 c.c. of CCl_4.

Exp. No.	Pressure Pmm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	631.5	40.90	0.00817	0.817
2	779.5	60.42	0.01200	1.200
3	433.5	18.28	0.00367	0.367
4	531.5	31.09	0.00622	0.622
5	680.5	47.89	0.00955	0.955
6	580.0	37.86	0.00757	0.757
		20°C.		
7	770.5	70.25	0.01380	1.380
8	425.0	28.33	0.00563	0.563
9	521.0	41.83	0.00829	0.829
10	572.0	44.22	0.00876	0.876
		15°C.		
11	614.0	59.89	0.01170	1.170
12	420.5	31.10	0.00613	0.613
13	515.5	47.24	0.00928	0.928
14	664.0	64.99	0.01270	1.270

Table 3. Absorption of Hydrogen Chloride into Ethylene Chloride at 25°, 20°, and 15°C., per 20.0 c.c. $C_2H_4Cl_2$.

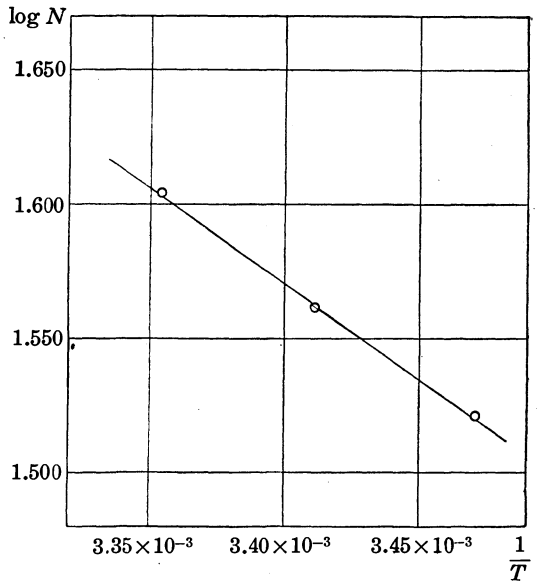
Exp. No.	Pressure Pmm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	680.0	183.09	0.0291	2.91
2	467.5	123.49	0.0198	1.98
3	500.0	133.20	0.0213	2.13
4	584.0	158.00	0.0252	2.52
		20°C.		
5	526.5	163.19	0.0258	2.58
6	526.5	163.19	0.0258	2.58
7	540.0	164.64	0.0261	2.61
8	600.0	192.45	0.0303	3.03
9	731.5	223.49	0.0350	3.50
10	520.5	159.48	0.0253	2.53
		15°C.		
11	533.5	189.89	0.0298	2.98
12	342.5	118.80	0.0188	1.88
13	550.0	191.22	0.0300	3.00
14	422.0	145.20	0.0229	2.29

Table 4. Absorption of Hydrogen Chloride into Ethylene Bromide at 25°, 20°, and 15°C., per 20.0 c.c. $C_2H_4Br_2$.

Exp. No.	Pressure Pmm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mol fraction N	Mol per cent.
		25°C.		
1	672.0	155.08	0.0269	2.69
2	507.0	117.81	0.0206	2.06
3	368.5	87.16	0.0153	1.53
4	601.0	138.96	0.0242	2.42
5	279.0	66.40	0.0117	1.17
		20°C.		
6	362.0	94.28	0.0165	1.65
7	453.5	119.11	0.0207	2.07
8	679.5	179.78	0.0309	3.09
9	496.0	129.53	0.0225	2.25
		15°C.		
10	672.0	189.96	0.0325	3.25
11	354.0	103.72	0.0180	1.80
12	531.0	154.62	0.0266	2.66
13	719.0	204.37	0.0348	3.48

Table 5.

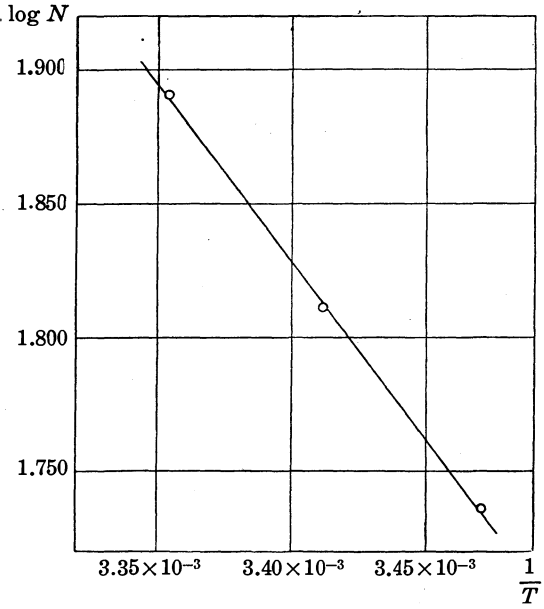
Substance	N(HCl)	log N	$1/T\times10^3$
		15°C.	
$C_2H_2Cl_4$	0.03006	1.52201	3.471
CCl_4	0.01826	1.73850	3.471
$C_2H_4Cl_2$	0.04377	1.35882	3.471
$C_2H_4Br_2$	0.03754	1.42551	3.471
		20°C.	
$C_2H_2Cl_4$	0.02744	1.56162	3.411
CCl_4	0.01550	1.80967	3.411
$C_2H_4Cl_2$	0.03993	1.39870	3.411
$C_2H_4Br_2$	0.03441	1.46332	3.411
		25°C.	
$C_2H_2Cl_4$	0.02481	1.60537	3.354
CCl_4	0.01277	1.89381	3.354
$C_2H_4Cl_2$	0.03576	1.44660	3.354
$C_2H_4Br_2$	0.03116	1.50640	3.354
Heat of Absorption, ΔH/mol in cal.			
$C_2H_2Cl_4$	3300		
CCl_4	6100		
$C_2H_4Cl_2$	3500		
$C_2H_4Br_2$	3200		



($\log N - \frac{1}{T}$ Curve)

Variation of the Absorption of Hydrogen Chloride in Tetrachlorethane with Respect to Temperature.

Fig. 2.



($\log N - \frac{1}{T}$ Curve)

Variation of the Absorption of Hydrogen Chloride in Carbon Tetrachloride with Respect to Temperature.

Fig. 3.

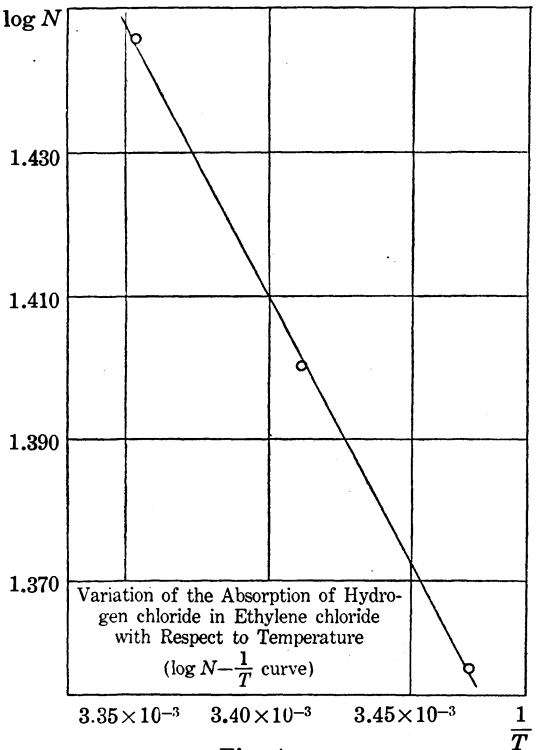
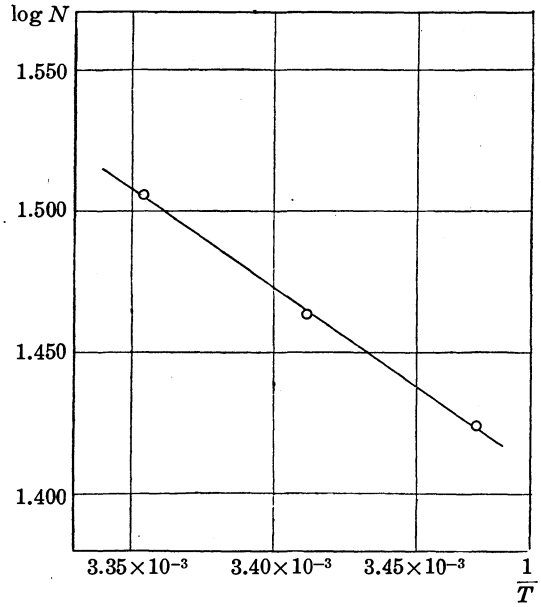


Fig. 4.



($\log N - \frac{1}{T}$ Curve)

Variation of the Absorption of Hydrogen Chloride in Ethylene Bromide with Respect to Temperature.

Fig. 5.

Discussion of Results. (a) Polarity in Connection with Solubility. Whether certain liquids into which a gas is absorbed are polar or non-polar, is very significant to the determination of the solubility of that gas. There are quite convincing evidences for the effects of polarity on solubility. Usually polar gases are more soluble in polar liquids than in non-polar liquids, and non-polar gases more soluble in non-polar liquids than in polar liquids. In other words, the degree of polarity plays a very important rôle. The dielectric constant usually can be regarded as the most direct evidence of polarity and the magnitude of it may be quite conveniently considered as a measure of degree of polarity. According to Van Vleck,[2a] "A molecule may be defined as polar if it has a permanent electrical moment, i.e. an electrical moment which is on the time average different from zero even in the absence of external fields. A molecule without such a permanent moment is termed non-polar". Then polarity of a substance can be estimated from the electric moment of the molecule in question. Besides these, other factors in the molecule such as chemical structure play important parts, that is to say, polarity is influenced by certain groups or radicals such as $-NH_2$, $-OH$, $-NO_2$, $=CO$, etc. These groups substituted in the molecule usually contribute much to the polarity of the substance in question, and the symmetry in the molecule seems to play a very significant rôle in almost every possible case such as the degree of the polarity as we find in the case of CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, $C_2H_4Cl_2$, $C_2H_2Cl_4$, etc., among which CCl_4 is considered to be the most symmetrical and hence the least polar.

Distinction between the polarity of the substances and that of the bond should be carefully noted especially in connection with solubility. The atomic volume is also considered to be an effective factor for determining the polarity, those elements having higher atomic volumes give higher polarity, and the element having the smallest atomic volume of all known elements—carbon—gives the least polar compounds. There are still some other factors which contribute much to the determination of polarity.[4] Besides, the polar character of a substance is also dependent on the so-called polar environment, as G. N. Lewis says, "ranging from the extremely polar to the extremely non-polar.....Great as the difference is between the typical polar and non-polar substance we may show how a single molecule may, according to its environment, pass from th extreme polar to the extreme non-polar form not per saltum, but by im-

(4) For fuller discussion on polarity, see the following: Debye, "Polar Molecules"; G. N. Lewis, "Valence and the Structure of Atoms and Molecules"*; *J. Am. Chem. Soc.*, **35** (1913), 1448; *J. Am. Chem. Soc.*, **38** (1916), 762*; J. H. Hildebrand, "Solubility"; Van Vleck, "The Theory of Electric and Magnetic Susceptibilities".

perceptible gradations, as soon as we admit that an electron may be the common property of two atomic shells."[4]* At any rate, the dielectric constant does give a rough measure of the polarity of the molecule with some exceptions. Therefore, it has been attempted to see any possible correlation between the solubility of hydrogen chloride in the mentioned organic solvents, and the polarity as measured by the dielectric constant, molecular symmetry, electric moment, Eötvös's constant, and the polarity with the effects of substituents. These are tabulated in Table 6. The results indicate that the solubility is in the order of increasing values of dielectric constants in the series of chlorine derivatives of hydrocarbon, i.e. hydrogen chloride being the most soluble in ethylene chloride with the highest dielectric constant 10.8 at 20°, next in tetrachlorethane with 8.2, and the least in carbon tetrachloride with 2.24; the same could be said with regards to the electric moment. In these cases, however, ethylene bromide does not seem to be accounted in the same categories. With respect to Eötvös's constants, and the molar volumes of the solvents we can hardly find any regularity.

Table 6.

Substance	D.C. 20°	$\mu\times10^{18}$	Mol. vol. c.c.	Eötvös's const.		Solubility (20°) mol fraction
				Calc.	Obs.	
1,1,2,2-Tetrachlorethane	8.2	1.6	105.30	2.26	—	0.02744
Carbon tetrachloride	2.24	0	97.10	2.20	2.10	0.01550
Ethylene chloride	10.8	1.8	78.90	2.15	—	0.03993
Ethylene bromide	6.3	1.4	86.20	2.19	2.17	0.03441
Hydrogen chloride		1.03				

Table 7.

$\mu\times10^{18}$ HCl	Solvent	Authors
1.286 1.273 } 1.3 1.32	Benzene CCl_4 Cyclohexane	F. Fairbrother[5a]
1.02 0.97 1.26	Ethylene bromide Ethylene chloride Benzene	F. Fairbrother[5a]
1.034 1.18 1.48 2.15	Gaseous[5b] ,, ,, ,,	Zahn Braunmühl Frivold and Hassel Falkenhangen

The electric moment of hydrogen chloride in various non-polar solvents has been reported by Fred Fairbrother.[5a] (Table 7)

Change in the effective electric moment of hydrogen chloride was found not influenced by solvents. From these we can say that, when the solvent molecules are as

(5a) F. Fairbrother, *J. Chem. Soc.*, **1932**, 43; *ibid.*, **1933**, 1541; Hassel and Uhl, *Z. physik. Chem.*, [B], **8** (1930), 187.

(5b) Zahn, *Phys. Rev.*, **24** (1924), 400; H. J. Braunmühl, *Physik. Z.*, **28** (1927), 141; O. E. Frivold and O. Hassel, *ibid.*, **24** (1923), 82; H. Falkenhangen, *ibid.*, **23** (1922), 87.

polar as those of the solute or more polar as in the solution of ethylene bromide and ethylene chloride, the electric moment is much lessened; this can be accounted parallel with the approximate proportionality of the frequency shift with the electric moment of the molecules of the solvent in "Raman spectra of hydrogen chloride in non-ionizing solvents" which was recently reported by W. West and P. Arthor.[6] This in turn means, as they remarked, that a large part of the shift is due to dipole interaction between solvent and solute molecules. The existence of dipole interaction may indicate that hydrogen chloride has greater solubility in ethylene chloride than in any other and the solubility is roughly in the order of magnitude of the electric moment of the solvents; possibly it means more dipole interaction in ethylene chloride than in others, which in turn increases the solubility, and the fact that the electric moment of hydrogen chloride increases in such solvents as CCl_4 and benzene as given by Fairbrother is true and the account that it is due to the stretching of the molecule in solution is concordant with the fact that hydrogen chloride is less soluble in CCl_4 than in $C_2H_4Cl_2$ and $C_2H_2Cl_4$.

(b) **Internal Pressure in Connection with the Solubility.** Although there is controversy as to whether the internal pressure as measured in various different ways gives some correlation with solubility or not, it is very interesting to see the actual cases. Those data selected and given in "Solubility" by Hildebrand seem to give a very good criterion in the discussion of solubility, but W. Kunerth[7] has given some contradictory evidences to usefulness of the internal pressure from the study of the solubility of CO and N_2O in some twelve organic liquids. Before we go into the detailed discussion of our results in the light of the internal pressure it would be profitable to state what we mean by the internal pressure of the liquid. Accepting a definition given by Hildebrand internal pressure is the maximum negative pressure that a liquid could support if no nuclei of vapour were allowed to form. The internal pressure can be best estimated if the internal forces which operate in liquid could be known well. We therefore, must have definite knowledge, of their equation of state for liquid in question as already stated, and of $-T\frac{\alpha}{\beta}$ as a measure of internal pressure. Relative internal pressure could be estimated in various ways, for instances, from van der Waals's equation, coefficient of expansion, heat of vaporization, boiling points $\frac{5200+30t_b}{V}$, surface tension, and total surface energy.

(6) W. West and P. Arthor, *J. Chem. Phys.*, **2** (1934), 215.
(7) W. Kunerth, *Phys. Rev.*, **19** (1922), 512.

The values of the internal pressure are not quite concordant as the methods of calculation differ and it is very difficult to find what method we should most rely upon in correlation with solubility. Some of these values of the relative internal pressure from various methods are tabulated with our solubility data in Table 8. As far as the comparison in the table is concerned, we hesitate to draw any definite conclusion upon this point.

Table 8.

Subst.	$T\frac{\alpha}{\beta}$	Mathews[9]	Sutherland[9]	$E/V^{\frac{1}{3}}$[9]	$\frac{(n-1)L}{V}$	$(5200+30t_b)/V$	Van Laar's a	$\gamma/V^{\frac{1}{3}}$	$N(20°)$
CCl_4	3362[8] 3690	2660	490	14.3	308	77.06	496	5.78	0.01550
$C_2H_4Br_2$	4455[8] 4760	3900	710	17.2	422	105.23	549	8.7	0.03441
$C_2H_4Cl_2$	4153[8]	—	—	17.0	406	97.45	475	7.5	0.03993
$C_2H_2Cl_4$	—	—	—	15.58	368	90.72	555	7.71	0.02744

Table 9.

Bond	Bond energy in v.e.[2b][2c]
C — Cl	3.22[10]
C — Br	2.89[10]
C — H	4.34
C — C	3.6
Substance	**Total bond energy in v.e.[11]**
CCl_4	12.88
$C_2H_4Br_2$	26.74
$C_2H_4Cl_2$	27.40
$C_2H_2Cl_4$	25.16

With exception of $C_2H_4Br_2$, the solubilities of hydrogen chloride in these liquids lie in the order of their relative internal pressures.

After taking the polarity and the internal pressure into consideration of influencing factors of the solubility of hydrogen chloride gas in each case, we find that $C_2H_4Br_2$ comes out to be exceptional in these discussions, hence we must look for some additional causes. Not only the dielectric constant for determining the polarity of molecule, but also other properties of it should

(8) J. H. Hildebrand, *Phys. Rev.*, **34** (1929), 649,

(9) "Solubility" by J. H. Hildebrand.

(10) Average of values of the various authors are used:
A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56** (1934), 1099.

(11) "The observed energy of the molecule is equal to that calculated for an assumed distribution of bonds or differs from it in the direction corresponding to greater stability in accord with the quantum mechanical requirement that the actual energy for the normal state of any system is the lower limit for values of the energy integral calculated for any wave function". L. Pauling and J. Sherman, *J. Chem. Phys.*, **1** (1933), 607.

be taken into account. For instance, the kind of halogen substituted and chemical stability as estimated from the relative strength of bonds involved in the compound :

Total bond energy

$$C_2H_4Cl_2 > C_2H_4Br_2 > C_2H_2Cl_4 > CCl_4$$

Solubility

$$C_2H_4Cl_2 > C_2H_4Br_2 > C_2H_2Cl_4 > CCl_4$$

The solubility of hydrogen chloride lies in the order of the strength of bonds as estimated by total bond energy similarly calculated as L. Pauling has done by assuming the additivity of energy. The strength of bonds as indicated by the total bond energy can be interpreted that those with larger bond energy are more capable of standing against external disturbances such as stretching or compression of bonds in these compounds effected as the solute molecules dissolve into them; in other words, those solvents with higher bond energy are possibly more capable of holding more solute molecules.

Summary.

(1) Absorption of hydrogen chloride into CCl_4, $C_2H_4Cl_2$, $C_2H_2Cl_4$ (1,1, 2,2), and $C_2H_4Br_2$ at 15°, 20°, and 25°C. has been studied.

(2) The heats of absorption of hydrogen chloride into these solvents were calculated.

(3) The relations between the solubility and polarity of organic liquids involved, and also the internal pressure have been discussed.

(4) The solubilities of hydrogen chloride in these liquids have been found in the order of increasing bond energies of the liquids calculated similarly as Pauling has done, and a possible explanation of it has been suggested.

In conclusion, the author wishes to express the best thanks to Prof. S. Mitsukuri for his kind advices and suggestions in the course of this investigation, also thanks that a part of the expenses has been paid from the grant given to Prof. S. Mitsukuri by the Saito Gratitude Foundation.

Laboratory of Theoretical Chemistry,
Faculty of Science, Tohoku Imperial University,
Sendai, Japan.

ÜBER DIE MULTIKONDENSATION DER FUMAR- UND MALEINSÄURE MIT ÄTHYLENGLYKOL.

Von Yojiro TSUZUKI.

Eingegangen am 2. Oktober, 1934. Ausgegeben am 28. Januar, 1935.

Einleitung. Über die Reaktion der Fumar- und Maleinsäure mit Äthylenglykol (in Form der Derivate) liegen einige ältere Versuche vor. Schon vor 40 Jahren hat Vorländer durch die Einwirkung von Äthylenbromid auf das Silbersalz der Fumar- und Maleinsäure neutrale Äthylenester erhalten.(1) Diese Äthylenester gaben nicht übereinstimmende Werte von Molekulargewicht, aber er hat diesen Substanzen die dimere Molekularformel $(C_6H_6O_4)_2$ zugeschrieben nach Analogie von dem gleicherweise erhaltenen Bernsteinsäure-Äthylenester. Spärter haben Carothers und Arvin sehr hochpolymere (vermutlich) Reaktionsprodukte erhalten, wenn sie Fumarsäure- und Maleinsäure-diäthylester mit Äthylenglykol auf hoher Temperatur erhitzten, aber sie konnten nicht ihre Molekulargewichte bestimmen, weil diese Äthylenester ganz unlöslich in allen Lösungsmitteln waren.(2) Ausserdem haben Carothers und Arvin wie auch Vorländer mehrere Zahlenwerte der Elementaranalyse angegeben, die von der Theorie merklich abwichen.

Um die Kenntnisse über die Molekulargrösse sowie über die Zusammensetzung der Kondensationsprodukte von Fumar- und Maleinsäure mit Äthylenglykol zu gewinnen, habe ich die vorliegenden, präparativen Versuche ausgeführt, dabei habe ich auch für die Reaktionsweise noch ein Interesse genommen. Nach Carothers' Grundgedanken über „Polymerisation and Ring Formation"(3) müssen immer hochmolekulare Verbindungen von Kettenstruktur resultieren (mit Ausnahme von einigen Fällen d. Ringbildung); wenn zwei zwei- oder mehrfunktionelle Molekülarten miteinander reagieren; aber es ist dabei zu denken, dass der räumliche Bau der reagierenden Moleküle auf die Molekulargrösse (Kettenlänge) der resultierenden Substanzen oder auf ihre Ausbeute beeinflussen.

Reaktion. Es ist jedoch tatsächlich aufgefunden worden, dass es ziemlich schwer ist, die Reaktion dieser beiden Säuren mit Äthylenglykol unter ganz gleichen Bedingungen miteinander zu vergleichen. Die

(1) *Ann.*, **280** (1894), 167.
(2) *J. Am. Chem. Soc.*, **51** (1929), 2560.
(3) *J. Am. Chem. Soc.*, **51** (1929), 2548.

Ursache der Schwierigkeit ist darauf zurückzuführen, dass bei niedriger Temperatur Fumarsäure infolge ihres hohen Schmelzpunktes sowie ihrer Schwerlöslichkeit ungewöhnlich reaktionsträge ist, während sich Maleinsäure unter dem Einfluss der Temperatursteigerung leicht umwandelt.

Wenn man Maleinsäure mit Äthylenglykol über 130° erhitzt, so geht sie erheblich in Fumarsäure über. Dagegen, wenn man ein äquimolares Gemisch von Fumarsäure und Äthylenglykol—ein „ideales" System für Multikondensation(4)—erhitzt, tritt die Reaktion unter 150° nur langsam ein, da Fumarsäure ganz schwer in Lösung geht. Somit wurde versucht, unter Anwendung geeigneter Lösungsmitteln, wie Cyclohexanon, Dioxan bei möglichst niedriger Temperatur Fumarsäure-Ester zu gewinnen, aber dies bewies sich erfolglos. Die niedrigste Temperatur für Fumarsäure, bei welcher die Reaktion eintritt ist 135–140°, hierbei aber nur unter Anwendung überschüssiges Äthylenglykols, welches auch dabei als Lösungmittel wirkt. Wenn man ein äquimolares Gemisch von Fumarsäure und Äthylenglykol über 150° erhitzt, tritt die Reaktion langsam ein, indem sich Fumarsäure allmählich verflüssigt. Je länger die Reaktionsdauer und je höher die Reaktionstemperatur ist, umso mehr entstehen dabei hochmolekulare Kondensationsprodukte, wie man in dem experimentellen Teile sieht. Wenn man Zinkchlorid als Katalysator anwendet, so wird die Reaktion dadurch ziemlich beschleunigt, aber bei höherer Temperatur dagegen wirkt der Katalysator depolymerisierend.

Da Maleinsäure, wie oben erwähnt, bei höherer Temperatur leicht umgewandelt wird, wurde die Reaktion mit Äthylenglykol bei möglichst niedriger Temperatur ausgeführt. Erhitzt man Maleinsäure mit äquimolarer Menge Äthylenglykol einige Stunden bei 120–126°, kann man Kondensationsprodukte (verhältnismässig niedermolekulare) gewinnen, wenn auch mit einer geringen Ausbeute. Erhitzt man dieses Gemisch bei derselben Temperatur nur eine Stunde, so entstehen nur niedermolekulare, wasserlösliche Produkte, die von der unveränderten Maleinsäure nicht getrennt werden können. Steigert man die Temperatur auf 155–160°, so kann man mit nur einstündiger Reaktionsdauer einige Menge Kondensationsprodukte erhalten, wobei aber eine beträchtliche Umwandlung der Maleinsäure stattfindet. Erhitzt man noch längere Zeit, so beobachtet man, dass etwa ein Drittel der Säurenmenge im Produkte in Fumarsäure umgelagert werden. In Gegenwart von Zinkchlorid als Katalysator wird die Reaktion schon bei niedriger Temperatur (115–120°) ziemlich beschleunigt, aber die Umwandlungsgefährlichkeit wird vermehrt; bei 1-stündiger Reaktionsdauer ist die Umlagerung nicht

(4) Dieser Ausdruck, nach W. Chalmers, *J. Am. Chem. Soc.*, **56** (1934), 922.

merkwürdig, bei 3-stündiger aber beträchtlich (2/3), und bei hoher Temperatur wie 150–160° wird die Maleinsäure nur bei 1-stündiger Reaktionsdauer grösstenteils umgewandelt. Ebenfalls wie bei Fumarsäure, schreitet der Kondensationsprozess bei Maleinsäure je noch weiter, je nach der Grösse der Reaktionsdauer und der Temperatursteigerung.

Konstitution der Reaktionsprodukte. Die Moleküle der durch diese Reaktionen entstandenen Polyester sind, wie Carothers an anderen Beispielen gezeigt hat,[5] kettenförmig aufgebaut und tragen, wie ich bei dem sauren, polymeren Glutarsäure-Äthylenester deutlich bewiesen habe,[6] eine freie Carboxylgruppe an einem Ende ihrer langen Ketten. Die Molekulargrösse, die durch Titrierung der End-Carboxylgruppe ermittelt wird, stimmt ziemlich gut mit der ebullioskopischen überein. Daraus folgt, dass alle diese saueren Ester die Struktur $HO\text{-}[OC\text{-}CH = CH\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_n\text{-}H$ haben. Tatsächlich ist diese Schlussfolgerung auch durch die an der Verseifung der neutralisierten Ester erhaltenen Versuchsresultate bestätigt worden. Das heisst: das Verhältnis von *Neutralisationswert* zu *Verseifungswert*,[7] welches experimentell gefunden ist, stimmt ziemlich gut mit dem Verhältnis überein, welches aus der Molekulargrösse (die durch die Endgruppen-Bestimmung unter Annahme der obenerwähnten Kettenstruktur ermittelt wird) in folgender Weise berechnet wird. Zwischen diesen Quantitäten bestehen selbstverständlich die folgenden, numerischen Beziehungen:

$$M = nC_6H_6O_4 + H_2O = n \times 142 + 18\,,$$
$$\gamma_{ber.} = 2n - 1\,.$$

Hier bedeutet M Molekulargrösse, n Multikondensationsgrad, $\gamma_{ber.}$ berechnetes Verhältnis von Neutralisationswert zu Verseifungswert.

Das wirklich aufgefundene Verhältnis $\gamma_{gef.}$ bzw. Multikondensationsgrad n ist nicht eine ganze Zahl. Dies ist aber ein natürliches Ergebnis; denn beim Multikondensationsprozess geht die Reaktion schrittweise vor, wie Chalmers kürzlich über den Mechanismus theoretisch diskutiert hat.[8] Daher ist das entstandene Reaktionsprodukt immer ein

(5) W. H. Carothers und J. A. Arvin, *J. Am. Chem. Soc.*, **51** (1929), 2560; und spätere zahlreiche Mitteilungen, Literatur-Verzeichnis: F. J. van Natta, J. W. Hill, und W. H. Carothers, *J. Am. Chem. Soc.*, **56** (1934), 455.

(6) Y. Tsuzuki, Dieses Bulletin **8** (1933), 313.

(7) *Neutralisationswert* = c.c. der für die Endcarboxylgruppen-Titrierung von Einheits-Gew. Ester gebrauchten N/10-KOH Lösung. *Verseifungswert* = c.c. der für die Verseifung der soeben neutralisierten Esters gebrauchten N/10-KOH Lösung.

(8) *J. Am. Chem. Soc.*, **56** (1934), 921.

Gemisch von verschiedenen Gliedern der polymer-homologen[9] Reihe. Folglich stellt die oben geschilderte Grösse M, n bzw. $\gamma_{ber.}$ der mittlere Wert eines solchen Gemisches dar.

Es ist eine mühevolle Aufgabe, aus diesem Gemisch eine einheitliche Substanz, nämlich ein einziges Glied der polymer-homologen Reihe zu isolieren. Ich habe daher verzichtet, dieses Gemisch zu fraktionieren, sondern habe mich bemüht, die unveränderte Säure und Glykol zu entfernen, wobei sehr niedrige Glieder auch beseitigt worden sind.

Eigenschaften der Reaktionsprodukte. Über die Eigenschaften dieser Polyester wird zusammenfassend im folgenden dargelegt. Bei der Fumarsäureester reihen sich ihre Durchschnitts-Molekulargrössen zwischen 700 und 1300 an. Niedermolekulare Produkte bilden schmierige, weisse Masse, aber Hochmolekulare weisses Pulver. Sie schmelzen im allgemeinen unscharf, das Schmelzpunktsintervall ist ungefähr 2–10°. Ihre Schmelzpunkte liegen zwischen 50° und 95°. Aus der Schmelze der Hochmolekularen kann man seidenglänzende Fäden ausziehen. Sie lösen sich leicht in Chloroform, Essigester, Aceton, aber schwer in Äther, kaltem Alkohol und in Wasser. Seine Löslichkeit verringert sich beim Bewahren. Die Polyester aus Maleinsäure sind meist farbloses Syrup mit Ausnahme von dem, welcher eine beträchtliche Menge Fumarsäure-Komponent enthält. Ihre durchschnittlichen Molekülgrössen liegen zwischen 450 und 900. Sie sind leicht löslich in Chloroform, und Aceton, besonders leicht in Essigester, aber schwer in kaltem Alkohol, Äther und in Wasser.

Über die Zusammensetzung der Maleinsäure-Ester sei bemerkt, dass der Kohlenstoff-Wert in einigen Fällen (meist d. hohen Reaktionstemperaturen) etwas zu niedrig ausfällt, wenn auch nicht so merklich wie bei den älteren Versuchen.[10] Vielleicht finden sich hier etwa komplizierte Verhältnisse infolge der ungesättigten Kohlenstoff-Bindung.[11]

Räumlicher Bau der Moleküle und Kondensationsvorgänge. Zum Schluss sei kurz über den räumlichen Bau der reagierenden Moleküle, den

(9) Dieser Ausdruck, etwa im Sinne von H. Staudinger, *Z. angew. Chem.*, **42** (1929), 69; vgl. „Die hochmolekularen organischen Verbindungen—Kautschuk und Cellulose," Berlin, 1932, S. 4.

(10) D. Vorländer, *Ann.*, **280** (1894), 167; W. H. Carothers und J. A. Arvin, *J. Am. Chem. Soc.*, **51** (1929), 2560.

(11) Anlagerung von Luftsauerstoff ist hier zu vermuten. Es muss aber durch weitere Versuche bestätigt werden. Über die Anlagerungsfähigkeit des Maleinsäureanhydrids. Siehe z. B. O. Diels u. K. Alder, *Ann.*, **460** (1927), 98; R. Kuhn u. Th. Wagner-Jauregg, *Ber.*, **63 B** (1930), 2662.

Multikondensationsgrad der Produkte und eine Ausbeute erwähnt. Vergleicht man miteinander die Kondensationsreaktionen dieser beiden Säuren mit Äthylenglykol ohne Berücksichtigung der Maleinsäure-Umwandlung, so sieht man aus dem experimentellen Teil entweder bei hoher Temperatur oder bei langer Reaktionsdauer kein grosser Unterschied in der mittleren Molekulargrösse zwischen beiden Reaktionsprodukten, aber man bemerkt eine grössere Ausbeute bei der Fumarsäure als bei der Maleinsäure. In dem Falle, wo die Reaktion bei höherer Temperatur in Gegenwart von Zinkchlorid ausgeführt wird (Umwandlung der Maleinsäure beträchtlich!), wird bei der Maleinsäure ein etwas kleinere Wert der mittleren Molekulargrösse des Reaktionsproduktes gefunden, wenn auch die beiden Ausbeuten beinahe gleich sind.

Überblickt man über die obigen Resultate mit Erwägung des Umstandes, dass im Gegensatz zu Maleinsäure Fumarsäure ganz allmählich in Lösung geht, so könnte man schliessen, dass bei der Fumarsäure eine grössere Neigung zur Bildung der hochmolekularen Kondensationsprodukte beobachtet wird. Der Unterschied ist, glaube ich, entscheidend, wenn auch nie merklich gross ist. Dieses Ergebnis (dass der Unterschied gering ist) ist mir unerwartet, weil, obwohl über eine etwas verschiedene Reaktion, eine solche Beobachtung schon durch Wagner-Jauregg[12] angestellt worden ist, dass Stilben mit Maleinsäure-Anhydrid zu hochmolekularen „Heteropolymerisaten" vereinigt, während die cis-Form, das Iso-Stilben ein solches Polymerisat nur in schlechter Ausbeute ergibt.[13] Um das vorliegende Resultat zu verstehen, dürfte man sich so vorstellen, dass Äthylenglykol selbst eine weitergehende Multikondensation auch bei der Reaktion mit Maleinsäure verursacht habe, indem es in einer etwa trans-Figur,[14] einer zur Kettenbildung

(12) *Ber.*, **63 B** (1930), 3213.

(13) Als diesbezügliche Versuche (über die Konfiguration der Moleküle und die Reaktion) sind auch die Arbeiten von G. Vavon und Mitarbeitern zu nennen, die über die Kinetik der Veresterung von stereoisomeren, einwertigen *o*-Cyclanolen sowie über die der Verseifung ihrer Ester ausgeführt wurden, die ergaben, dass in verschiedenen Fällen die cis-Verbindungen immer langsamer reagieren als die trans-Formen. Zusammenfassend: *Bull. soc. chim.*, [4], **49** (1931), 937.

(14) Dies ist durch Versuche von verschiedenen Seiten bewiesen worden. Durch die bekannten Versuchen von J. Böesekensche Schule nach „Borsäuremethode" (*Ber.*, **46** (1913), 2612; *Rec. trav. chim.*, **40** (1921), 553) sowie nach „Acetonmethode" (Chr. van Loon, Thèse Delft, 1919; J. Böeseken und P. H. Hermans, *Rec. trav. chim.*, **40** (1921), 525; P. H. Hermans, *Z. physik. Chem.*, **113** (1924), 337.), und auch durch das Studium von B. Englund (*J. prak. Chem.*, **122** (1929), 121.) über den Einfluss der Polyoxyverbindungen auf die Löslichkeit der Arsonessigsäure ist so zu schliessen, dass die Hydroxylgruppen in Äthylenglykol eine zur Ringbildung ungünstige Lagerung d. h. die trans-Stellung oder eine ihr ähnliche einnehmen. Ferner aus den Ergebnissen der Dipolforschung lässt sich eine derartige Lagerung der Hydroxylgruppen als wahrscheinlich ableiten. C. T. Zahn, *Physik. Z.*, **33** (1932), 525.

begünstigten Lagerung an der Reaktion teilgenommen hat. Jedoch auf diese Multikondensationsvorgänge mögen neben dem räumliche Bau der beteiligenden Moleküle noch weitere massgebende Einflusse wie z.B. elektrolytische Dissoziation der Säure vorhanden sein.[15] Trotzdem wäre es von grossem Interesse, die Reaktion zwischen dem Diol, welcher als cis-förmig deutlich bewiesen ist, wie z. B. cis 1.2-Cyclopentandiol,[16] und der zweibasischen Säure von cis-Form zu untersuchen,[17] aber da dieser Diol schwer zugänglich ist, ist es mir leider jetzt unmöglich, diese Reaktion weiter zu untersuchen.

Beschreibung der Versuche.

A. Reaktion zwischen Fumarsäure und Äthylenglykol.

Versuch 1. Ein Gemisch von 2.32 g. feingepulverter Fumarsäure (0.02 Mol) und 1.36 g. Äthylenglykol (0.022 Mol) wurde 90 Minuten auf 160–170° erhitzt. Reaktion trat allmählich ein; am Ende blieb etwas Fumarsäure noch ungelöst. Das Reaktionsprodukt wurde mit Wasser einige Male gewaschen. Die ausgeschiedene, weisse Masse wurde in Chloroform aufgenommen, das dabei ungelöste Pulver (hauptsächlich unveränderte Fumarsäure) abfiltriert. Die klare Chloroformlösung wurde mit Wasser gewaschen, mit Na_2SO_4 getrocknet, eingedampft und mit Äther gefällt. Etwas schmierige, weisse Masse. Es wurde bei 70° und dann in Vakuum getrocknet. Schmilzt unscharf bei 68–73°. Ausbeute 1.39 g., d. h. 41% d. Theorie.

Neutralisation: Die Substanz wird in 15 c.c. Aceton gelöst und mit N/50-KOH neutralisiert (Phenolphthalein als Indikator). 0.1068 g. Subst. verbrauchten 6.50 c.c. Kalilauge. Neutralisationsäquivalent 821. Multikondensationsgrad $n=5.65$.

Verseifung: Die soeben neutralisierte Lösung wird mit 15 c.c. N/5-KOH versetzt. Nach 24-stdg. Stehen wird die Lösung zur Ergänzung der Verseifung 15–20 Minuten auf dem Wasserbad erwärmt, und das überschüssige Kali mit N/10-H_2SO_4 zurücktitriert. 17.00 c.c. N/10-H_2SO_4 wurden verbraucht. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 10.00$, $\gamma_{ber.} = 10.30$.

Elementaranalyse: 0.2065 g. Subst. (60 Min. unter 20 mm. Druck, bei 77° getr.) gaben 0.3717 g. CO_2 und 0.0824 g. H_2O. Gefunden: C, 49.09; H, 4.47. Berechnet für $HO-(C_6H_8O_4)_{5.65}-H$ (820.3): C, 49.59; H, 4.41%.

Ebullioskopie: in Aceton. 0.4414 g. Subst. in 15–25.2 c.c. Lösung. $\Delta t=0.053$–0.076°. Mol.-Gew. 730–850.

---

(15) Über den Einfluss der elektrolytischen Dissoziation der Säure auf die Veresterungsgeschwindigkeit vgl. M. Conrad und C. Brücker, *Z. physik. Chem.*, **7** (1891), 290; H. Goldschmidt, *Ber.*, **29** (1896), 2210; A. Michael, *Ber.*, **42** (1909), 326; ferner A. Kailan, *Z. physik. Chem.*, **87** (1914), 619.

(16) Chr van Loon, Thèse Delft, 1919: J. Böeseken, *Rec. trav. chim.*, **40** (1921), 553. (nach „Borsäuremethode"); P. H. Hermans, *Z. physik. Chem.*, **113** (1924), 337 (nach „Acetonmethode"). vgl. B. Englund, *J. prak. Chem.*, **122** (1929), 121; **129** (1931), 1.

(17) Dabei ist es zu erwarten, dass die Multikondensation nicht so weiter schreiten werde.

Versuch 2. 1 Mol Fumarsäure+1.05 Mol Äthylenglykol. Reaktionsdauer 4 Stunden. Reaktionstemperatur 170–180°. Produkt weisses Pulver. Beim Erhitzen erweicht es bei 80° und schmilzt hauptsächlich bei 95–97°. Ausbeute 68% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 1043. Multikondensationsgrad $n=7.21$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 13.13$, $\gamma_{ber.} = 13.42$.

Elementaranalyse: Gefunden: C, 50.07; H, 4.60. Berechnet für HO-$(C_6H_6O_4)_{7.21}$-H(1043): C, 49.81; H, 4.38%.

Ebullioskopie: in Aceton. Mol.-Gew. 1020–1260.

Versuch 3. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol. Reaktionsdauer 3.5 Stunden. Reaktionstemperatur 155–160°. Produkt schwachgelbliches weisses Pulver. Schmelzpunkt 74–76°. Ausbeute 52% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 954. Multikondensationsgrad $n=6.59$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.50$, $\gamma_{ber.} = 12.18$.

Elementaranalyse: Gefunden: C, 48.86; H, 4.68. Berechnet für HO-$(C_6H_6O_4)_{6.59}$-H(954): C, 49.73; H, 4.39%.

Ebullioskopie: in Aceton. Mol.-Gew. 920–970.

Versuch 4. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol. 2 Stunden auf 140–150°, dann 7 Stunden auf 160–165° erhitzt. Produkt gelblichweisses Pulver. Schmelzpunkt 92–95°. Ausbeute 67% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 1212. Multikondensationsgrad $n=8.41$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 15.15$, $\gamma_{ber.} = 15.81$.

Elementaranalyse: Gefunden: C, 49.83; H, 4.52. Berechnet für HO-$(C_6H_6O_4)_{8.41}$-H(1212.6): C, 49.77; H, 4.35%.

Ebullioskopie: in Aceton. Mol.-Gew. 1220–1480.

Versuch 5. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol+0.5 Mol $ZnCl_2$. Reaktionsdauer 60 Minuten. Reaktionstemperatur 150–160°.

Die Reaktion wurde durch $ZnCl_2$ beschleunigt: schon nach 30 Minuten-Erhitzen wurde Fumarsäure nahezu in Lösung gebracht. Die Reaktionsmasse war in der Hitze eine klare Schmelze, in der Kälte eine harte undurchsichtige Masse. Dies wurde mit Wasser einigemal gewaschen, in $CHCl_3$ aufgenommen, wobei unveränderte Fumarsäure ungelöst blieb. Die $CHCl_3$-Lösung wurde mehrmals mit Wasser geschüttelt, wodurch $ZnCl_2$ völlig entfernt wurde, mit Na_2SO_4 getrocknet und verdampft.

Der Rückstand bildet eine schmierige weisse Masse von unscharfem Schmelzpunkt 50–60°. Ausbeute 35% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 685. Multikondensationsgrad $n=4.70$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 8.10$, $\gamma_{ber.} = 8.40$.

Elementaranalyse: Gefunden: C, 48.12, 48.29; H, 4.73, 4.70. Berechnet für HO-$(C_6H_6O_4)_{4.70}$-H(685.6): C, 49.35; H, 4.44%.

Versuch 6. 1 Mol Fumarsäure+1.1 Mol Äthylenglykol+0.5 Mol $ZnCl_2$. Beim Erhitzen dieses Gemisches 90 Minuten auf 165–170° wurde ein harziges, etwas gefärbtes Reaktionsprodukt (Molekulargewicht ca. 650) erhalten mit einer Ausbeute 24% d. Theorie.

Aus den Versuchen 5 und 6 sieht man auch eine degenerierende Wirkung von $ZnCl_2$ bei hoher Temperatur.

Versuch 7. 3.48 g. Fumarsäure (0.03 Mol) und *überschüssiges* Äthylenglykol (0.062 Mol) wurden mit 2.57 g. geschmolzenem Zinkchlorid 60 Minuten auf 135–140°

erhitzt. Am Ende war Fumarsäure nahezu in Lösung. Das flüssige Reaktionsgemisch wurde in Wasser gegossen, die ausgeschiedene, weisse Masse mit Wasser verrieben, und dann wie bei Versuch 5 bearbeitet. Produkt eine weisse schmierige Masse vom Schmelzpunkt 54–57°. Ausbeute 0.62 g.

Neutralisation und Verseifung: Neutralisationsäquivalent 998. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.95$.

Ebullioskopie: in Aceton, Mol.-Gew. 608–680.

Elementaranalyse: Gefunden: C, 48.82; H, 4.82%.

Wenn man diesen sauren Ester einbasisch annimmt, so wird der Multikondensationsgrad (n) als 6.90 berechnet. Daraus folgt: $\gamma_{ber.} = 12.80$. Diese Abweichungen von den experimentellen Ergebnissen zeigen, dass ein Gemenge von neutralem und saurem Polyester von dem Molekulargewicht ca. 650 vorliegt. Wählt man zu dem Mengeverhältnis der beiden Ester 1:2, so treffen die berechneten Werte ($\gamma_{ber.} = 12.00$, C=49.37, H=4.56%) mit den gefundenen zusammen.

B. Reaktion zwischen Maleinsäure und Äthylenglykol.

Versuch 1. Ein Gemisch von 6.96 g. Maleinsäure (0.06 Mol) und 3.72 g. Äthylenglykol (0.06 Mol) wurde mit 2.25 g. geschmolzenem Zinkchlorid 55 Minuten auf 115–120° erhitzt. Das klare Reaktionsprodukt wurde in Wasser gegossen, die ausgeschiedene, halbfeste Masse zweimal mit Wasser verrieben, wodurch die unveränderten Ausgangsstoffe sowie $ZnCl_2$ grösstenteils entfernt wurden, und der Rückstand in Essigester aufgenommen. Die Essigesterlösung wurde mit Wasser zweimal gewaschen, mit Na_2SO_4 getrocknet und verdampft. Der Rückstand bildet ein farbloses, zähes Syrup. Ausbeute 1.04 g., d. h. 12% d. Theorie.

Neutralisation: 0.0542 g. Subst. in 5 c.c. Acetonlösung verbrauchten 5.55 c.c. N/50-KOH. Neutralisationsäquivalent 488. Multikondensationsgrad $n=3.31$.

Verseifung: Die oben neutralisierte Lösung verbrauchte zur Verseifung 3.10 c.c. N/5-KOH. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 5.58$, $\gamma_{ber.} = 5.62$.

Elementaranalyse: 0.1079 g. Subst (30 Min. in Vakuum bei 77°, über P_2O_5 getr.) gaben 0.1950 g. CO_2 und 0.0436 g. H_2O. Gefunden: C, 49.28; H, 4.52. Berechnet für $HO-(C_6H_6O_4)_{3.31}-H$ (488.2): C, 48.80; H, 4.52%.

Ebullioskopie: 0.1503 g. Subst. in 17–23 c.c. Aceton. $\Delta t = 0.030–0.037°$. Mol.-Gew. 480–530.

Fumarsäure-Gehalt: Die Menge der durch Umwandlung entstandenen Fumarsäure in den Polyestern aus Maleinsäure wurde nach zwei Methoden abgeschätzt: die ein Methode a) stammt von D. Vorländer,[18] der zeigte, dass sich die beiden genannten Säuren in den Kristallwasser-Gehalt des gut kristallisierbaren Bariumsalzes voneinander unterscheiden, damit kann man die Fumarsäuremenge abschätzen durch Bestimmung des Ba-Gehaltes von dem durch Verseifung erhaltenen Bariumsalz-Gemisch; die andere b) ist eine nach Hahn-Haarmann,[19] deren Prinzip auf die direkte Wägung des für Fumarsäure charakteristischen, schwerlöslichen Merkuro-Salzes beruht.

---

(18) *Ann.*, **280** (1894), 167.

(19) A. Hahn und W. Haarmann, *Z. Biol.*, **87** (1928), 107; *ibid.*, **89** (1929), 159. vgl. A. Ölander, *Z. physik. Chem.*, [A], **144** (1929), 49; H. Meyer, „Nachweis und Bestimmung der org. Verbindungen," Berlin, 1933, S. 141.

a) *nach Bariummethode.* Die Bereitung des Ba-Salzes habe ich folgenderweise ausgeführt: der Polyester wird durch halbstündiges Erwärmen mit N/5-KOH verseift, überschüssiges Kali mit N/10-HCl neutralisiert, und mit einer berechneten Menge 1 N-$BaCl_2$ versetzt; beim Verdampfen der Lösung scheidet das Ba-Salz als schöne Kristallen aus. 0.0956 g. Ba-Salz (lufttrocken) gaben 0.0815 g. $BaSO_4$. Gefunden: Ba, 50.3. Berechnet für $C_4H_2O_4Ba+H_2O$ (Maleinat): Ba, 50.93, für $C_4H_2O_4Ba+3H_2O$ (Fumarat): 44.91%. Daraus Fumarsäure: ca. 10% d. Gesamtsäure.

b) *nach Merkurosalzmethode:* Der Polyester wird wie bei a) verseift, das überschüssige Kali mit N/5-HNO_3 neutralisiert, und dazu Fällungsreagenz hinzugefügt. Der Niederschlag wird nach 1-tägigem Stehen durch Glasfilter filtriert, gewaschen, und bei 70° getrocknet. 0.1658 g. Ester gaben 0.0534 g. Merkuro-Fumarat. Daraus Fumarsäure-Gehalt des Polyesters: 9.7%. (entsprechend 12.2% d. Gesamtsäure.)

Versuch 2. 1 Mol Maleinsäure + 1 Mol Äthylenglykol. Reaktionsdauer 4 Stunden. Reaktionstemperatur 120–126°. Produkt schwach braungefärbtes Harz. Ausbeute 14% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 510. Multikondensationsgrad $n=3.46$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 5.90$, $\gamma_{ber.} = 5.92$.

Elementaranalyse: Gefunden: C, 48.78; H, 4.75. Berechnet für HO–$(C_6H_6O_4)_{3.46}$–H (509.5): C, 48.89; H, 4.51%.

Ebullioskopie: in Aceton. Mol.-Gew. 450–560.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 50.7%. Fumarsäure: ca. 5% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Gefunden: Fumarsäure-Gehalt im Ester 5.6% (entsprechend 7.1% d. Gesamtsäure.)

Versuch 3. 1 Mol Maleinsäure+1.1 Mol Äthylenglykol. Reaktionsdauer 60 Minuten. Reaktionstemperatur 155–160°. Produkt farbloses Harz. Ausbeute 18.5% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 457. Multikondensationsgrad $n=3.09$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 5.14$, $\gamma_{ber.} = 5.18$.

Elementaranalyse: Gefunden: C, 48.78; H, 4.60. Berechnet für HO–$(C_6H_6O_4)_{3.09}$–H (457.0): C, 48.69; H, 4.53%.

Ebullioskopie: in Aceton. Mol.-Gew. 500–560.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 48.0%. Fumarsäure: ca 45% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Gefunden: Fumarsäure-Gehalt im Ester 16.3% (entsprechend 20.8% d. Gesamtsäure.)

Versuch 4. 1 Mol Maleinsäure+1 Mol Äthylenglykol+0.5 Mol $ZnCl_2$. Reaktionsdauer 3 Stunden. Reaktionstemperatur 115–120°. Das entstandene, weisse, zähe Harz wurde zweimal mit Wasser verrieben, in Essigester aufgenommen, mit Wasser mehrmals gewaschen, mit Na_2SO_4 getrocknet, und mit Äther gefällt. Farbloses Harz. Ausbeute 24% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 659. Multikondensationsgrad $n=4.51$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 7.92$, $\gamma_{ber.} = 8.02$.

Elementaranalyse: Gefunden: C, 48.43; H, 4.68. Berechnet für HO–$(C_6H_6O_4)_{4.51}$–H (659.0): C, 49.30; H, 4.45%.

Ebullioskopie: in Aceton. Mol.-Gew. 590–660.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 46.0%. Fumarsäure: ca. 80% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Fumarsäure-Gehalt im Ester 53.9%. (entsprechend 67.8% d. Gesamtsäure.)

Im folgenden werden die Versuche beschrieben, die unter gleichen Bedingungen bei Fumarsäure ausgeführt wurden, wenn auch solche Bedingungen für Maleinsäure allzu heftig sind.

Versuch 5. 1 Mol Maleinsäure+1.1 Mol Äthylenglykol. Reaktionsdauer 90 Minuten. Reaktionstemperatur 160–170°. (Vergleich mit Fumarsäure-Versuch 1.) Die entstandene, klare Schmelze wurde in Wasser verrieben, das ausgeschiedene, farblose Öl in $CHCl_3$ gelöst. Die Lösung wurde mit Wasser zweimal gewaschen, mit Na_2SO_4 geklärt und verdampft. Farbloses Harz. Ausbeute 31% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 891. Multikondensationsgrad $n=6.15$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.24$, $\gamma_{ber.} = 11.30$.

Elementaranalyse: Gefunden: C, 48.73; H, 4.52. Berechnet für HO–$(C_6H_6O_4)_{6.15}$–H (891.6): C, 49.66; H, 4.40%.

Ebullioskopie: in Aceton. Mol.-Gew. 830–910.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 49.8%. Fumarsäure: ca. 20% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Gefunden: Fumarsäure-Gehalt im Ester 23.1% (entsprechend 28.9% d. Gesamtsäure.)

Versuch 6. 1 Mol Maleinsäure+1 Mol Äthylenglykol+0.5 Mol Zinkchlorid. Reaktionsdauer 60 Minuten. Reaktionstemperatur 150–160°. (Vergleich mit Fumarsäure-Versuch 5.) Das entstandene, schwachgelbliche, ziemlich feste Reaktionsprodukt wurde mit Wasser gut gewaschen. Der $CHCl_3$-Extrakt wurde mit Wasser geschüttelt, mit Na_2SO_4 geklärt, und verdampft; dieser Reinigungsprozess nochmal wiederholt. Schmierige, weisse Masse. Schmilzt hauptsächlich bei 52–55°. Ausbeute 34% d. Theorie.

Neutralisation und Verseifung: Neutralisationsäquivalent 562. Multikondensationsgrad $n=3.84$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 6.54$, $\gamma_{ber.} = 6.68$.

Elementaranalyse: Gefunden: C, 48.30; H, 4.73. Berechnet für HO–$(C_6H_6O_4)_{3.84}$–H (563.5): C, 49.06, 49.06; H, 4.48%.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 45.8%. Fumarsäure: ca. 85% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Fumarsäure-Gehalt im Ester 56.8%. (entsprechend 71.7% d. Gesamtsäure.)

Versuch 7. Beim Erhitzen von 3.48 g. Maleinsäure (0.03 Mol) und 2.05 g. Äthylenglykol (0.033 Mol) 3.5 Stdn. auf 155–160° wurden 2.22 g. schwachgelbes, zähes Harz gewonnen. (Extraktionsmittel $CHCl_3$) Ausbeute 51% d. Theorie. (Vergleich mit Fumarsäure-Versuch 3.)

Neutralisation und Verseifung: Neutralisationsäquivalent 919. Multikondensationsgrad $n=6.34$. Verseifungswert/Neutralisationswert $\gamma_{gef.} = 11.39$, $\gamma_{ber.} = 11.68$.

Elementaranalyse: Gefunden: C, 47.87, 47.92, 48.19; H, 4.43, 4.53, 4.47. Berechnet für HO–$(C_6H_6O_4)_{6.34}$–H (918.6): C, 49.69; H, 4.39%.

Ebullioskopie: in Aceton. Mol.-Gew. 694–746.

Fumarsäure-Gehalt: a) *nach Bariummethode.* Gefunden: Ba, 48.8%. Fumarsäure: ca. 35% d. Gesamtsäure. b) *nach Merkurosalzmethode.* Fumarsäure-Gehalt im Ester 27.6% (entsprechend 34.5% d. Gesamtsäure.)

Chemisches Laboratorium,
Musashi Hochschule,
Tokio-Nakaarai.

A SPECTROGRAPHIC METHOD FOR THE STUDY OF UNSTABLE COMPOUNDS IN EQUILIBRIUM.

By Ryutaro TSUCHIDA.

Received October 20th, 1934. Published January 28th, 1935.

Introduction. As early as 1921 Professor Y. Shibata established a spectroscopic method for the detection of the formation of complex salts in dilute solution.[1] This method consists in preparing a set of solutions, in which initial concentrations of the components of the molecular compound have simple ratio to each other, and comparing the absorption spectra of these solutions. The ratio of initial concentrations of the components in the solution, which gives the strongest end absorption, shows the ratio of combination of the components to form the molecular compound. Four years later P. Job[2] also proposed a similar method.

The present paper deals with a quantitative extension of Prof. Shibata's method in finding composition of unstable compounds and at the same time proposes a general method for the study of chemical equilibrium, determining the equilibrium constant, concentration of unstable compounds, as well as extinction coefficients of the compounds whose spectra are not obtainable without superposition of those of other substances.

The Method. (1) Two substances, A and B, react with each other in dilute solution to form an unstable compound whose composition is unknown.

$$mA + nB \rightleftarrows A_mB_n .$$

$$K = \frac{[A_m B_n]}{[A]^m [B]^n} , \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where m and n are unknown.

Let the initial concentrations of A and B be a and b respectively, and the concentration of the compound (C) x.

$$K = \frac{x}{(a-mx)^m (b-nx)^n} . \quad \cdots\cdots\cdots\cdots (1')$$

Also let the extinction coefficients of A, B and A_mB_n for a wave-length λ_1 be ε_1^A, ε_1^B and ε_1^C respectively, then

(1) Y. Shibata, T. Inoue, and Y. Nakatsuka, *J. Chem. Soc. Japan*, **42** (1921), 983; *Japanese J. Chem.*, **1**, (1922), 1; *Chem. Abst.*, **16** (1922), 2075.

(2) P. Job, *Compt. rend.*, **180** (1925), 928; **182** (1926), 1622; *Ann. chim.*, **9** (1928), 143.

$$E_1 = \Sigma\varepsilon c = \varepsilon_1^A(a-mx)+\varepsilon_1^B(b-nx)+\varepsilon_1^C x\ , \quad \cdots\cdots\cdots \quad (2)$$

where E_1 is measurable absorption of the equilibrium mixture, representing $\Sigma\varepsilon c$ in

$$I = I_0 \times 10^{-\Sigma\varepsilon cd}\ .$$

Therefore

$$x = \frac{E_1-\varepsilon_1^A a-\varepsilon_1^B b}{\varepsilon_1^C-m\varepsilon_1^A-n\varepsilon_1^B}\ . \quad \cdots\cdots\cdots\cdots \quad (3)$$

For another wave-length λ_2 and for the same solution,

$$x = \frac{E_2-\varepsilon_2^A a-\varepsilon_2^B b}{\varepsilon_2^C-m\varepsilon_2^A-n\varepsilon_1^B}\ . \quad \cdots\cdots\cdots\cdots \quad (3')$$

From (3) and (3′)

$$(E_2-\varepsilon_2^A a-\varepsilon_2^B b)\varepsilon_1^C-(E_1-\varepsilon_1^A a-\varepsilon_1^B b)\varepsilon_2^C+\left\{(E_1-\varepsilon_1^A a-\varepsilon_1^B b)\varepsilon_2^A-(E_2-\varepsilon_2^A a-\varepsilon_2^B b)\varepsilon_1^A\right\}m$$

$$+\left\{(E_1-\varepsilon_1^A a-\varepsilon_1^B b)\varepsilon_2^B-(E_2-\varepsilon_2^A a-\varepsilon_2^B b)\varepsilon_1^B\right\}n = 0\ . \quad \cdots\cdots\cdots \quad (4)$$

As ε_1^A, ε_2^A, ε_1^B and ε_2^B may be obtained by measurements of spectra of A and B, all the terms in brackets are known or measurable values and the equation (4) may be expressed as

$$\left.\begin{aligned} & p\varepsilon_1^C-q\varepsilon_2^C+rm+sn = 0\ , \\ \text{where}\quad & p = E_2-\varepsilon_2^A a-\varepsilon_2^B b\ , \\ & q = E_1-\varepsilon_1^A a-\varepsilon_1^B b\ , \\ & r = q\varepsilon_2^A-p\varepsilon_1^A\ , \\ \text{and}\quad & s = q\varepsilon_2^B-p\varepsilon_1^B\ . \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots \quad (4')$$

For various combinations of a and b, the following set of equations are obtained:

$$\left.\begin{aligned} & p_1\varepsilon_1^C-q_1\varepsilon_2^C+r_1m+s_1n = 0 \\ & p_2\varepsilon_1^C-q_2\varepsilon_2^C+r_2m+s_2n = 0 \\ & \cdots\cdots\cdots\cdots \\ & \cdots\cdots\cdots\cdots \\ & p_N\varepsilon_1^C-q_N\varepsilon_2^C+r_Nm+s_Nn = 0 \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots \quad (5)$$

By the method of least squares, $\frac{\varepsilon_1^C}{n}$, $\frac{\varepsilon_2^C}{n}$ and $\frac{m}{n}$ may be determined. Being usually small integers, m and n may easily be found from the ratio of m to n, e.g., for $\frac{m}{n} = 0.67$, $m = 2$ and $n = 3$, etc. Consequently ε_1^C and ε_2^C are found. Repeating the above process for various wave-lengths, extinction coefficients and the absorption curve of the unstable compound are obtained.

Substituting these values of ε_1^C, ε_2^C, m, n, etc. in (3), (3′), etc., we can find the concentrations of the compound, from which the equilibrium constant K is calculated.

It is, however, difficult to find the ratio of m to n, if the absorption coefficients of component substances are very small compared with those of the compound. In such cases m and n may conveniently be determined by a spectrographic method similar to the original works of Prof. Y. Shibata.

(2) If both the components, A and B, give no appreciable absorption in spectral regions in which the compound shows absorption, the following method is adopted.

The method consists in preparing a series of mixed solutions, in which initial concentrations of A and B vary to have simple ratio to each other, keeping their sum constant, and measuring the absorption of these solutions. Then the ratio of the initial concentrations of the mixed solution, which gives the highest absorption for the molecular compound, is the ratio of combination, because the maximum concentration for the compound is attained when the ratio of the initial concentrations of the components is exactly the ratio of combination to form the compound. This fact can be proved simply as follows.

From
$$\frac{x}{(a-mx)^m(b-nx)^n} = K,$$

and
$$a + b = \text{constant},$$

$$\frac{dx}{da} = \frac{K(a-mx)^{m-1}(b-nx)^{n-1}(mb-na)}{1+K\{m^2(a-mx)^{m-1}(b-nx)^n + n^2(a-mx)^m(b-nx)^{n-1}\}}.$$

The condition for the maximum value of x is given by

$$\frac{dx}{da} = 0, \quad \text{i.e.} \quad \frac{a}{b} = \frac{m}{n}.$$

Prof. Y. Shibata applied this principle only to end absorption in ultraviolet region. It is, however, clear that this principle can be applied to any absorption bands.

(3) If the absorption of one of the components overlaps the absorption of the compound, i.e., the other component only gives no appreciable absorption in spectral parts in which the compound shows absorption bands, it is difficult to find the highest concentration of the compound directly from comparison of a set of absorption curves prepared as in the previous case (2).

Suppose two cases (I and I′) of different initial concentrations, a and a' for A component and b and b' for B component, and let the concentrations of the compound C be x and x' respectively,

$$\frac{x}{(a-mx)^m(b-nx)^n} = \frac{x'}{(a'-mx')^m(b'-nx')^n} .$$

Also let extinction coefficients of B and C at wave-lengths λ_1 and λ_2 be ε_1^B, ε_2^B, ε_1^C and ε_2^C, the component A giving no appreciable absorption at these wave-lengths. The absorption for these cases (I and I′) is represented in Fig. 1.

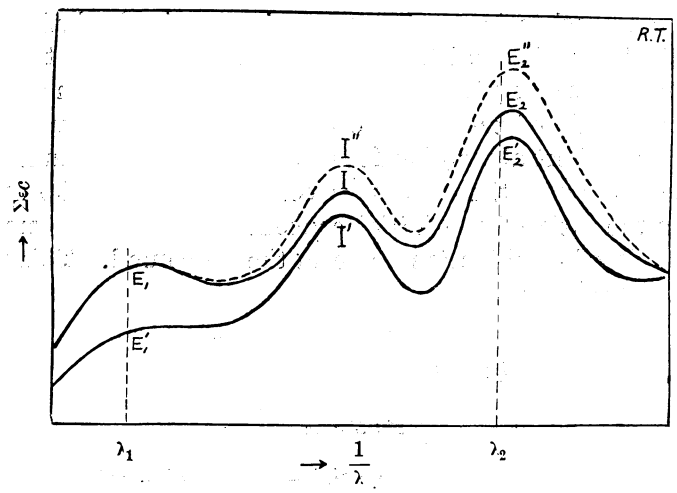


Fig. 1.

At λ_1 and λ_2

$$E_1 = \varepsilon_1^B(b-nx)+\varepsilon_1^C x . \qquad E_2 = \varepsilon_2^B(b-nx)+\varepsilon_2^C x .$$

$$E_1' = \varepsilon_1^B(b'-nx')+\varepsilon_1^C x'. \qquad E_2' = \varepsilon_2^B(b'-nx')+\varepsilon_2^C x'.$$

The difference of $\Sigma\varepsilon c$ at λ_1

$$a_1 = E_1-E_1' = \varepsilon_1^B\{(b-nx)-(b'-nx')\}+\varepsilon_1^C(x-x') .$$

The concentration of B corresponding to this absorption difference $\delta = (b-nx)-(b'-nx')+\frac{\varepsilon_1^C}{\varepsilon_1^B}(x-x')$. The absorption which should be given by this quantity of B is added throughout the curve I'. The curve thus drawn is shown as I'' in Fig. 1.

Then the addition to I' at λ_2

$$\alpha_2 = \varepsilon_2^B\left\{(b-nx)-(b'-nx')\right\}\frac{\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}(x-x') \ .$$

$$\therefore \quad E_2'' = E_2'+\alpha_2 = \varepsilon_2^B(b-nx)+\varepsilon_2^Cx'+\frac{\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}(x-x') \ ,$$

therefore

$$E_2''-E_2 = \frac{\varepsilon_1^B\varepsilon_2^C-\varepsilon_1^C\varepsilon_2^B}{\varepsilon_1^B}(x'-x)$$

$$E_2''-E_2 \propto x'-x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

The difference between the curves I and I'' is proportional to the difference of concentrations of C.

This principle affords the means of comparing concentrations of the compound in equilibrium with other substances. Absorption is measured with a series of mixed solutions, in which initial concentrations vary, keeping the sum constant. To the curves of $\Sigma\varepsilon c$, calculated absorption of B is added to make total absorption in all cases the same at one wave-length, and then the heights of the curves at another wave-length are compared. Then the height-differences are proportional to the concentration-differences for the compound in question. The solution corresponding to the highest curve at the wave-length of comparison is of the highest concentration in C and the ratio of the initial concentrations for this solution gives the ratio of combination of A and B to form C. The equalization and comparison may theoretically be executed at any wave-lengths, but, for practical purpose, it is convenient to choose some particular wave-lengths. In order to facilitate the comparison, i.e., to make the difference $E_2''-E_2$ larger, the wave-lengths should be chosen so that the proportionality constant in the relation (6) may attain the highest possible absolute value. This condition may be fulfiled when

1) ε_1^B and ε_2^C are as large as possible, and ε_1^C and ε_2^B are as small as possible, or 2) vice versa.

In practice, therefore, the wave-lengths of absorption bands are preferably adopted as the points of equalization and comparison. An example of this method is given hereunder.

The Example: The Complex Salt Formation between Potassium Iodide and Iodine. This reaction has been investigated by many authors in various directions, the existence of complex compounds being proved by researches on freezing point depression,[3] solubility,[4] diffusion,[5] conductivity,[6] vapour pressure,[7] adsorption,[8] partition of iodine between two solvents,[9] as well as absorption spectra.[10]

The compositions of these complex compounds are known, but the experiment was carried out as if they were unknown. It is simply because the example is given for the purpose of showing the general procedure of this method.

The equilibrium constant was determined by several authors by measuring vapour pressure,[11] conductivity,[12] partition of iodine in different solvents[13] or solubility.[14]

Of these methods, those which deal with vapour pressure, solubility or partition can be applied only for special cases and are not suitable for general use in studying equilibrium. Compared with these methods, the conductivity method is of more general application, but is apt to suffer a

(3) M. Le Blanc and A. A. Noyes, *Z. physik. Chem.*, **6** (1890), 401; E. Paterno and A. Peratoner, *Gazz. chim. ital.*, **21** (1891), 110; S. R. Ray, *J. Ind. Chem. Soc.*, **9** (1932), 268.

(4) A.A. Noyes and J. Seidersticker, *Z. physik. Chem.*, **27** (1899), 360; *J. Am. Chem. Soc.*, **21** (1899), 217; A. P. Laurie, *Pr. Edinb. Soc.*, **29** (1909), 304; *Z. physik. Chem.*, **67** (1909), 627.

(5) G. Edgar and St. H. Diggs, *J. Am. Chem. Soc.*, **38** (1916), 256.

(6) M. Le Blanc and A. A. Noyes, *Z. physik. Chem.*, **6** (1890), 401; P. Lami, *Boll. chim. farm.*, **47** (1908), 425; W. Ridel, Dissert. Halle a.S. 1913; H. Bruns, *Z. Physik*, **34** (1925), 751; E. Thönnessen, *Z. Physik*, **41** (1927), 810; M. Hlasko, *Roczniki chemji*, **6** (1927), 228; W. Birkenstock, *Z. physik. Chem.*, [A], **138** (1928), 432; F. Nies, *Z. physik. Chem.*, [A], **138** (1928), 447.

(7) G. Jones and B. B. Kaplan, *J. Am. Chem. Soc.*, **50** (1928), 1845.

(8) N. Schilow and L. Lepin, *Z. physik. Chem.*, **94** (1920), 57.

(9) A. A. Jakowkin, *Z. physik. Chem.*, **13** (1894), 539; *ibid.*, **20** (1896), 19; H. M. Dawson, *J. Chem. Soc.*, **93** (1908), 1308; R. G. van Name and W. G. Brown, *Am. J. Sc.*, **44** (1917), 106; G. A. Linhart, *J. Am. Chem. Soc.*, **40** (1918), 158; J. N. Pearce and W. G. Eversole, *J. Phys. Chem.*, **28** (1924), 245.

(10) Y. Shibata, T. Inoue, and Y. Nakatsuka, *loc. cit.*; Ch. K. Tinkler, *J. Chem. Soc.*, **91** (1907), 996; *ibid.*, **93** (1908), 1611; P. Job, *Compt. rend.*, **182** (1926), 1622.

(11) G. Jones and B. B. Kaplan, *loc. cit.*

(12) G. Jones and M. L. Hartmann, *J. Am. Chem. Soc.*, **37** (1915), 250.

(13) H. M. Dawson, *J. Chem. Soc.*, **79** (1901), 224; *ibid.*, **81** (1902), 1090; *ibid.*, **93** (1908), 1310; Ch. Winter, *Z. physik. Chem.*, [B], **3** (1929), 303; A. A. Jakowkin, *loc. cit.*; R. G. van Name and W. G. Brown, *loc. cit.*; E. W. Washburn and E. K. Strachan, *J. Am. Chem. Soc.*, **35** (1913), 692; J. N. Pearce and W. G. Eversole, *loc. cit.*; R. Abegg and W. Maitland, *Z. anorg. Chem.*, **49** (1906), 351.

(14) G. Jones and B. B. Kapland, *loc. cit.*; Ch. Winter, *loc. cit.*

great deal from the error caused by the slightest contamination of impurities. On the contrary, the spectrographic method here proposed is more direct than those which consist in measuring partition, vapour pressure, etc. and moreover it is safer than the conductivity method so long as the characteristic absorption bands are the object of the measurement. The spectroscopic method proposed by P. Job,[15] deals only with absorption limit and is not adequate for quantitative calculation of equilibrium constant, etc.

Absorption of mixed solutions of potassium iodide and iodine was photographed with a Spekker photometer and a Hilger spectrograph. Special precaution was taken to avoid photochemical reactions making the time of exposure as short as possible and changing solutions frequently. As the concentration is very small throughout the experiment and total ionization and complete hydration may reasonably be assumed, there is no need of considering change of absorption due to these effects. The absorption of these solutions is shown in Fig. 2 (I, II, III, IV, V and VI) together with the absorption of potassium iodide (A) and iodine (B).

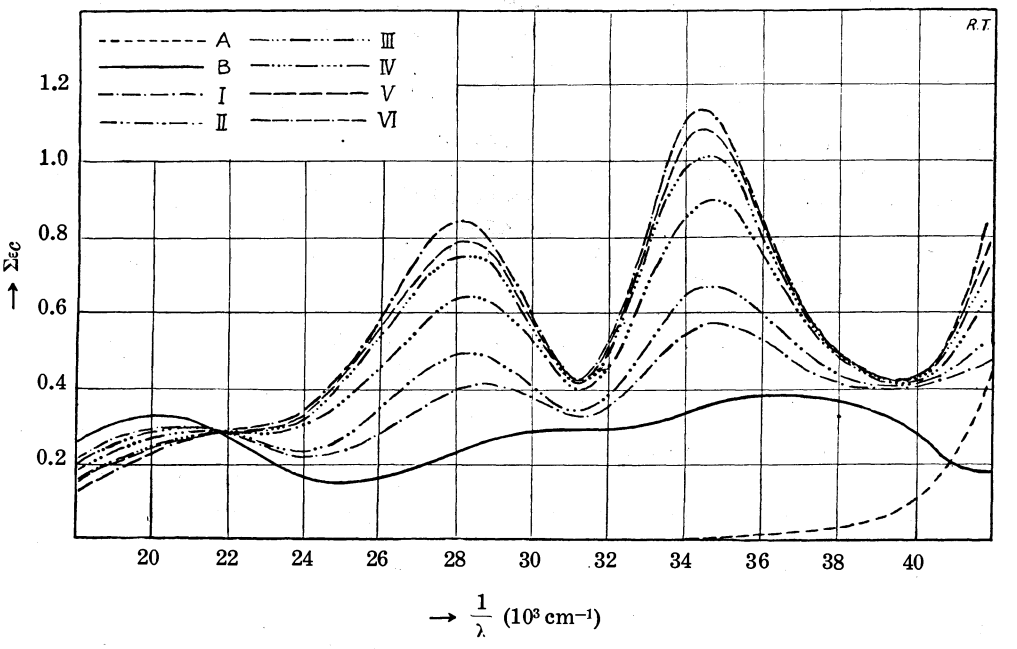


Fig. 2.

(15) *Loc. cit.*

The absorption is shown by plotting $\Sigma\varepsilon c$ against wave-number. The initial concentration of potassium iodide a and iodine b, together with E at wave numbers, 20×10^3, 28×10^3, and 34.5×10^3, are given in Table 1.

Table 1. (cf. Fig. 2)

Curve	$a:b$	$a(10^{-5}$mol/l.)	$b(10^{-5}$mol/l.)	d(cm.)	E		
					20×10^3	28×10^3	34.5×10^3
A		100.0	0.0	20			
B		0.0	10.8	1	0.34	0.24	0.36
I	1 : 2	5.0	10.8	1	0.30	0.40	0.57
II	2 : 2	10.0	10.8	1	0.29	0.49	0.67
III	3 : 2	15.0	10.8	1	0.27	0.64	0.89
IV	4 : 2	20.0	10.8	1	0.24	0.75	1.02
V	5 : 2	25.0	10.8	1	0.24	0.79	1.08
VI	6 : 2	30.0	10.8	1	0.22	0.85	1.13

Fig. 2 and Table 1 plainly show that the maximum at 20×10^3 belongs to iodine and the other two maxima at 28×10^3 and 34.5×10^2 to the compound between potassium iodide and iodine. At 22×10^3 all the solutions have the same absorption. It shows that iodine and the compound have the same extinction coefficient at this wave-length. It is also obvious from the curve A that potassium iodide gives no appreciable absorption at the points of absorption maxima of either iodine or the compound. This is exactly the case corresponding to (3) on p. 30.

In order to find m and n empirically, absorption of another series of solutions was measured, varying initial concentrations of potassium iodide and iodine, and at the same time keeping the sum constant. The absorption is shown in Fig. 3.

In Fig. 3 the curves XI, XII, and XIII show the highest absorption in spectral regions of absorption bands of the compound, but it is also clear that these solutions contain more iodine than the rest of the solutions.

E_1 at wave number 20×10^3 is measured. The differences of E_1's are shown in Table 3 as α_1 and δ is the corresponding quantity of iodine. α_2 shows the addition at wave number 34.5×10^3. Then E_2 at the same wave number plus α_2 gives E_2''.

Fig. 4 shows the curves after the graphical addition. Differences of these curves are theoretically proportional to the differences of concentrations of the molecular compound as we have shown above in the relation (6). We can, therefore, plainly see from these curves that the molar ratio of

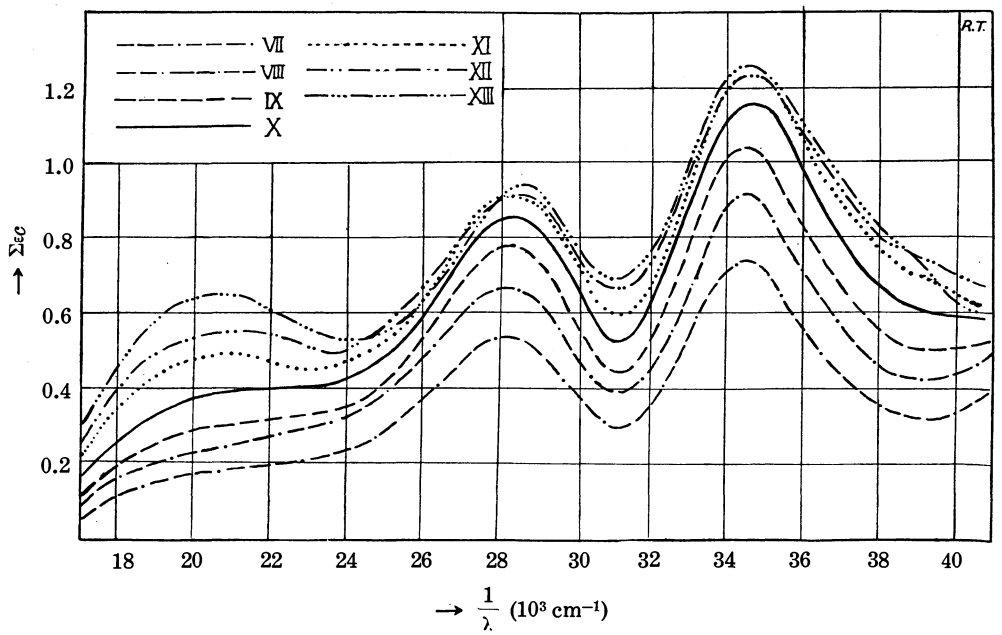


Fig. 3.

Table 2. (cf. Fig. 3)

Curve	$a:b$	a(10^{-5}mol/l.)	b(10^{-5}mol/l.)	d(cm.)	E		
					20×10^3	28×10^3	34.5×10^3
VII	3 : 1	22.5	7.5	1	0.18	0.54	0.74
VIII	2 : 1	20.0	10.0	1	0.22	0.66	0.90
IX	3 : 2	18.0	12.0	1	0.29	0.77	1.04
X	1 : 1	15.0	15.0	1	0.37	0.84	1.14
XI	2 : 3	12.0	18.0	1	0.48	0.90	1.23
XII	1 : 2	10.0	20.0	1	0.55	0.90	1.23
XIII	1 : 3	7.5	22.5	1	0.64	0.91	1.25

Table 3. (Fig. 3 and Fig. 4)

Curve	E_1 / 20×10^3	E_2 / 34.5×10^3	α_1	δ(10^{-5}mol/l.)	α_2	E_2''
VII	0.18	0.74	0.46	14.6	0.47	1.21
VIII	0.22	0.90	0.42	13.3	0.43	1.33
IX	0.29	1.04	0.35	11.1	0.36	1.40
X	0.37	1.14	0.27	8.6	0.28	1.42
XI	0.48	1.23	0.16	5.1	0.16	1.39
XII	0.55	1.23	0.09	2.9	0.09	1.33
XIII	0.64	1.25	0.00	0.0	0.00	1.25

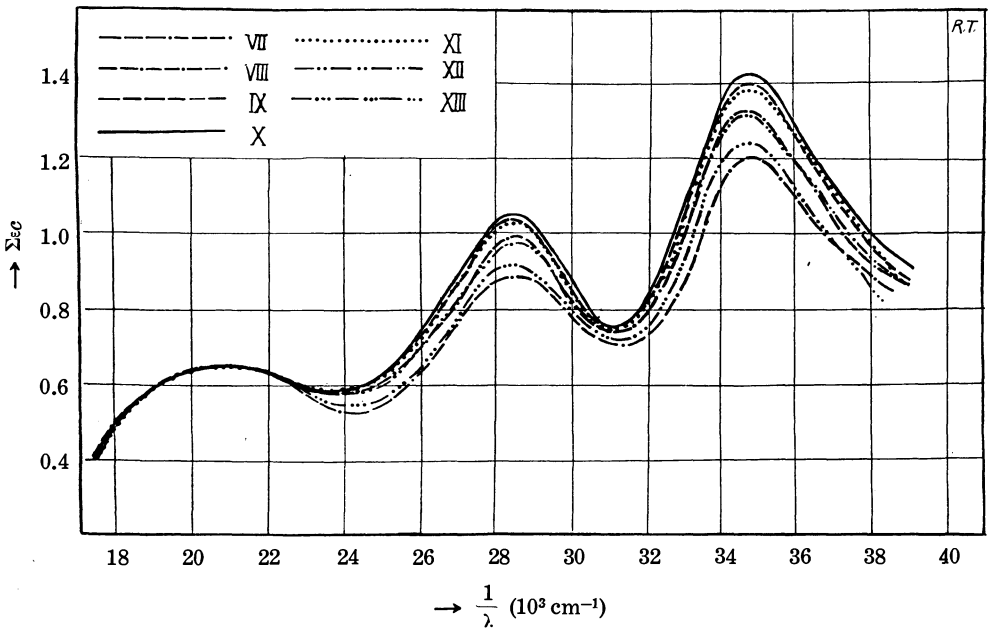


Fig. 4.

combination between potassium iodide and iodine, in our case, is one to one, as the curve X gives the highest absorption at wave numbers 28×10^3 and 34.5×10^3, which correspond to the absorption bands of the molecular compound. Thus m and n are found to be 1 and 1, the formula for the molecular compound being, therefore, KI_3.

We can calculate extinction coefficients for the compound KI_3, substituting m, n and experimental spectrographic data as below in the equations (1′), (3) and (3′).

$m=1$ $\varepsilon_1^B=0.22\times10^4$ extinction coeff. of iodine at 28×10^3

$n=1$ $\varepsilon_2^B=0.32\times10^4$,, ,, ,, at 34.5×10^3

The extinction coefficients of the potassium triiodide at wave numbers 28×10^3 and 34.5×10^3 were found to be 1.20×10^4 and 1.58×10^4 respectively.

Substituting these values in the equations (3) and (3′),

i.e., $x=\dfrac{p}{15800-3200}$ and $x=\dfrac{q}{12000-2200}$,

concentrations of potassium triiodide in each case in Fig. 2 and Fig. 3 were calculated. These values of x are shown in Table 4 together with the equilibrium constant calculated for them.

Table 4.

Curve	a (10^{-5}mol/l.)	b (10^{-5}mol/l.)	E_1	E_2	p	q	$\frac{p}{12600}$	$\frac{q}{9800}$	x (10^{-5}mol/l.)	K (10^3)
I	5.0	10 8	0.40	0.57	0.22	0.16	1.8	1.6	1.7	5.7
II	10.0	10.8	0.49	0.67	0.32	0.25	2.6	2.7	2.7	4.6
III	15.0	10.8	0.64	0.89	0.54	0.40	4.3	4.1	4.2	5.9
IV	20.0	10.8	0.75	1.02	0.67	0.51	5.3	5.2	5.3	6.5
V	25.0	10·8	0.79	1.08	0.73	0.55	5.7	5.6	5.7	5.8
VI	30.0	10.8	0.85	1.13	0.78	0.61	6.3	6.2	6.3	5.6
VII	22.5	7.5	0.54	0.74	0.50	0.37	4.0	3.8	3.9	5.8
VIII	20.0	10,0	0.66	0.90	0.58	0.44	4.6	4.5	4.6	5.5
IX	18.0	12.0	0.77	1.04	0.63	0.50	5.0	5.1	5.1	5.7
X	15.0	15.0	0.84	1.14	0.65	0.52	5.1	5.3	5.2	5.4
XI	12.0	18.0	0.90	1.23	0.63	0.50	5.0	5.0	5.0	5.5
XII	10.0	20.0	0.90	1.23	0.57	0.45	4.5	4.5	4.5	5.3
XIII	7.5	22.5	0.91	1.25	0.52	0.41	4.1	4.3	4.3	6.7

The mean value of the equilibrium constant between 23° to 25° is 5.6×10^3. The deviation in the equilibrium constant is supposed to be caused by the flactuation of temperature, as the experiment was carried out at room temperature.

Subtracting the calculated absorption of iodine and potassium iodide from the curve VI which has the mean value of K, the absorption for potassium triiodide is worked out. (Fig. 5)

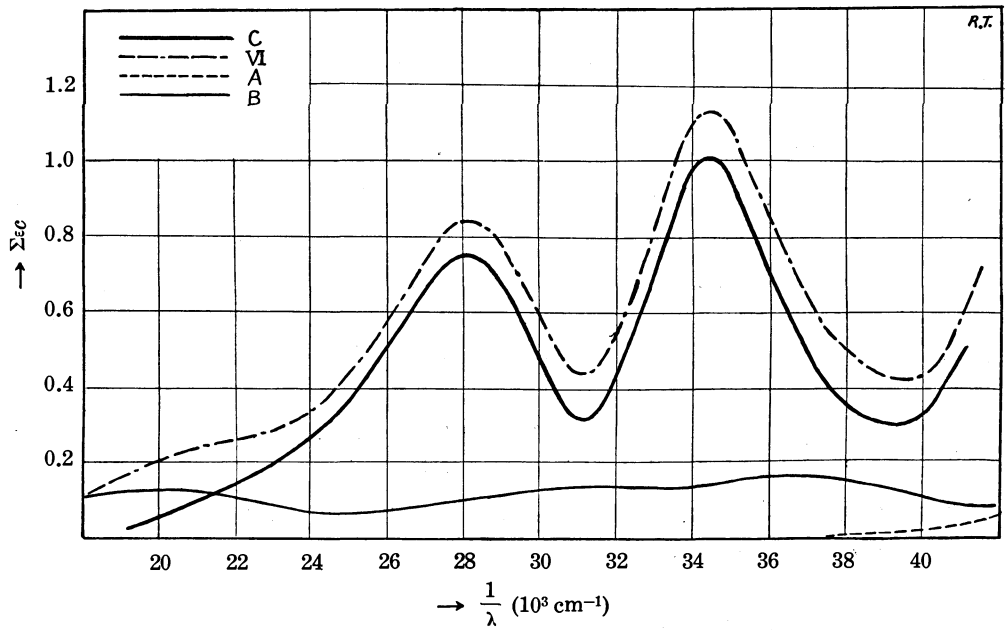


Fig. 5.

The absorption has two maxima at 360 mμ and 290 mμ and minima at 320 mμ and 250 mμ. The extinction coefficients at the maxima are 1.20×10^4 and 1.58×10^4.

An experimental evidence for the relation (6) is given in Fig. 6 in which E_2'' in Table 3 is plotted against x in Table 4.

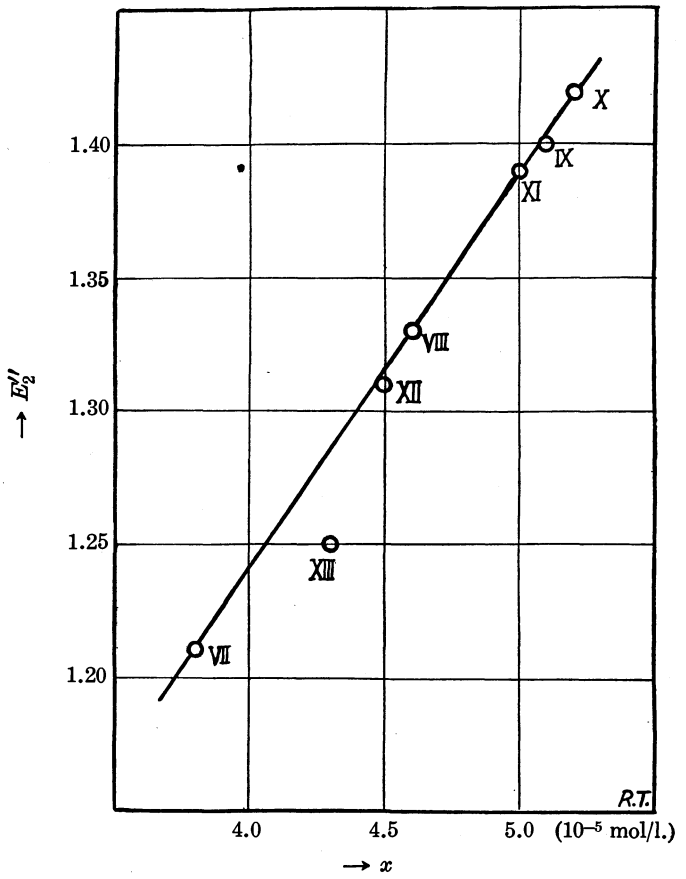


Fig. 6.

Fig. 6 shows that E_2'' is a linear function of x, i.e., the difference of E_2'' is proportional to the difference of concentrations of the compound. The tangent of this line is 15×10^3, and the calculated value of $\frac{\varepsilon_1^B \varepsilon_2^C - \varepsilon_1^C \varepsilon_2^B}{\varepsilon_1^B}$ is 14.8×10^3. ($\frac{\varepsilon_2^B}{\varepsilon_1^B} = 1.1$ from Fig. 2, $\varepsilon_2^C = 15.8 \times 10^3$ as given above and $\varepsilon_1^C = \frac{0.06}{6.3 \times 10^{-5}} = 0.95 \times 10^3$ from Fig. 5 and Table 4.)

As it is clear from the calculation, the relation (6) holds not only for absorption, but also for other physical properties, such as refraction, optical rotation, etc. We may, therefore, take various combinations of physical properties, e.g., absorption at λ_1 and optical rotation at λ_2. This method can be applied not only to the study of molecular compounds as in this example but also can be widely applied to general study of chemical reactions in liquid and in gaseous state.

The examples for these applications will follow.

The author wishes to express his thanks to Prof. Y. Shibata and Mr. C. F. Goodeve for their kind interest in this work.

The Sir William Ramsay Laboratory,
University College, London.

THE ISOTOPIC FRACTIONATION OF WATER BY DISTILLATION.

By Masao HARADA and Toshizo TITANI.

Received October 29th, 1934. Published January 28th, 1935.

In the course of purifying water by distillation, we found always some small difference in density between the first and last portions of the distillate. In order to ascertain whether this difference in density is due to the isotopic fractionation of water or to some impurities dissolved therein, we carried out a fractional distillation of a considerable amount of water and measured the densities of its most and least volatile fractions respectively.

The method employed was as follows: The distilling flask was made of glass and fitted with a glass still of Hempel type, 3.5 cm. wide and 17 cm. long, which was filled with glass beads having 4 to 5 mm. diameter up to 6 to 7 cm. height. During the distillation a continuous flow of air free from carbon dioxide was sent through the still column. The distillation was carried out in three stages; namely, in the first stage, a given volume of water was equally divided into the distillate (D_1) and the residue (R_1); in the second stage, both the distillate (D_1) and the residue (R_1) from the first stage were again equally divided by distillation into

the distillate and the residue respectively. We may designate the distillate obtained by the second distillation from the first distillate (D_1) D_2 and at the same time the residue obtained by distilling the residue (R_1) in the first stage may be designated R_2; then in the third stage, both D_2 and R_2 were again divided equally by distillation into the distillate and the residue respectively and the distillate (D_3) obtained from D_2 and the residue (R_3) remained after distilling R_2 were saved for the comparison of their respective densities.

The two fractions thus obtained were at first carefully purified in the same way as described in the preceding paper,[1] the purity being checked by measuring the electrolytic conductivity. Then their densities were compared with that of normal water by a sensitive quartz bouyancy balance. The most volatile part (D_3) which was the last portion of the distillate saved was found to be lighter than ordinary water by 2.5 parts per million (p.p.m.) and the residue (R_3) saved for the density measurement showed an increase in density by 3.8 p.p.m. The difference between these two parts was 6.3 p.p.m. which might be due to the isotopic fractionation of water, if no impurity was occluded during the process of the purification.

Hall and Jones[2] called attention to the fact that a considerable isotopic fractionation occurred during the distillation of highly enriched heavy water under the atmospheric pressure. Our result shows that it is also important to take into consideration the above fact even in the distillation of ordinary water under the atmospheric pressure.

The Shiomi Institute of
Physical and Chemical Research
and
Chemical Laboratory of the Osaka
Imperial University

---

(1) M. Harada and T. Titani, this Bulletin, **9** (1934), 457.
(2) N. F. Hall and T. O. Jones, *J. Am. Chem. Soc.*, **56** (1934), 749.

THE ISOTOPIC FRACTIONATION OF WATER DUE TO EVAPORATION AND DISTILLATION.

By Toshizo TITANI and Masao HARADA.

Received October 29th, 1934. Published January 28th, 1935.

It has been shown by several investigators[1] that the isotopic fractionation of water occurs either by a slow evaporation or by a distillation especially under a reduced pressure. From this point of view we have examined two samples of water. The first sample was prepared from the mother liquor of the salt which was separated from sea-water by its slow evaporation being exposed to wind and sun. The mother liquor of the salt thus prepared is a brown syrup liquid and contains above all a considerable amount of magnesium chloride in solution which contributes to its bitter taste. Hence it is called "Nigari" (nigai = bitter) in Japanese. The sample water was prepared by distilling the "Nigari" to dryness. The second sample of water was obtained, according to the suggestion of Professor Ikeda, from the molasses of the cane sugar which was prepared by a vacuum distillation of the sap-juice of sugar canes. The molasses was burned in a flow of air and the water formed was twice passed over heated copper oxide for the purification.

The density of the both samples of water, after being carefully purified in the same way as before,[2] was compared with that of the ordinary water by the use of a quartz bouyancy balance. The water from "Nigari" was found, as a result of two determinations, to be heavier than the normal water by 5.4 parts per million. And the increase in density of the water from the cane sugar molasses was found, as a mean of three independent determinations, to be 2.8 parts per million. The increase in the density should be mainly due to the evaporation in the former case and to the distillation in the latter. However, it seems possible that very hygroscopic substances such as magnesium chloride dissolved in

(1) E. W. Washburn, E. R. Smith, and M. Frandsen, *J. Chem. Phys.*, **1** (1933), 288; *Bur. Standards J. Research*, **11** (1933), 453; E. W. Washburn and E. R. Smith, *J. Chem. Phys.*, **1** (1933), 426; *Bur. Standards J. Research*, **12** (1934), 305; *Science*, **79** (1934), 188; G. N. Lewis and R. E. Cornish, *J. Am. Chem. Soc.*, **55** (1933), 2616; G. N. Lewis and R. T. Macdonald, *J. Am. Chem. Soc.*, **55** (1933), 3502; E. S. Gilfillan, Jr., *J. Am. Chem. Soc.*, **56** (1934), 406; R. J. Clark and F. L. Warren, *Nature*, **134** (1934), 29; T. Tucholski, *Nature*, **134** (1934), 29, Cf. also the preceding article.

(2) M. Harada and T. Titani, this Bulletin, **9** (1934), 457.

"Nigari" plays a certain rôle in the former case. Moreover, the sap-juice of certain plants were found to be slightly heavier than the ordinary water.[3] Such a possibility can not be overlooked in the case of the sugar cane. These points will be interesting for further investigations.[4]

Chemical Laboratory of the Osaka Imperial University
and
The Shiomi Institute of Physical and Chemical Research

---

(3) E. W. Washburn and E. R. Smith, *loc. cit.*

(4) At the end of our experiment a comprehensive research by Messrs. Emeléus, James, King, Pearson, Purcell, and Briscoe (*J. Chem. Soc.*, **1934**, 1207) has been published. These authors have found that the water from the combustion of sucrose was heavier than the normal water by 8.61 p.p.m. This result is very interesting in connection with our present observation.

AN EXPERIMENTAL METHOD OF STUDYING SUBSTITUTION AND DECOMPOSITION REACTIONS BY MEANS OF PHOTOELECTRIC CELL. I. ABSORPTION OF LIGHT OF WAVE LENGTHS 3650 Å AND 4360 Å BY VAPOURS OF VARIOUS HALOGEN DERIVATIVES OF ETHANE.

By Senzo HAMAI.

Received September 14th, 1934. Published February 28th, 1935.

In a previous paper,[1] the author gave a suggestion as to usefulness of the phenomena of light absorption as applied to the investigation of certain chemical reactions especially where the reactions are rather slow and also an ordinary method of following the reaction fails. However, the idea requires rather an expensive apparatus[2] of infra-red analysis which, in an ordinary laboratory, can not be easily available. In order to overcome such a difficult situation, naturally we consider an alternative plan which may be used equally as well for the purpose.

Use of a photoelectric cell[3] is rather numerous, but, in the fields of chemical reactions, it is more or less limited and very scanty; for this reason it would be profitable to publish a few details of experimental apparatus and method to show its applicability.

The principle involved is rather well known. According to the law of Lambert, there exists the relation:

$$I = I_0 e^{-\beta d}, \qquad (1)$$

where I is transmitted light intensity, I_0 initial light intensity, β the specific light absorption coefficient, and d the thickness of the medium, but this can be transformed into:

$$I = I_0 e^{-\alpha c d} \quad \text{for} \quad \beta = \alpha c, \qquad (2)$$

where α is the absorption coefficient and c concentration of the medium in mol. This is a special case of Lambert's law known as the law of Beer.

(1) S. Hamai, this Bulletin, **9** (1934), 542.
(2) P. C. Cross and F. Daniels, *J. Chem. Physics*, **1** (1933), 48.
(3) N. R. Campbell and D. Ritchie, "Photoelectric Cells."

Since the laws of Lambert and Beer are valid only for monochromatic light, β and α vary with λ; furthermore, the law of Lambert presupposes only the homogeneity of the layer, whereas for the latter, because of its inclusion of the concentration of the medium, the independence of optical properties on the concentration has been assumed. Therefore in Beer's law we find several deviations as already recorded by various authors, but they do not very seriously interfere with our present purpose. By this relation, we can follow the reaction in which change of the reactants can be detected with a given λ which is absorbed by one of the constituents of the system; the amount of absorption of light directly gives the amount of substance present with known α of that substance, and with a given thickness of the medium. Batley,[4] using the light absorption with known extinction coefficient as a means of following the reaction of iodine with ethyl alcohol, investigated it spectroscopically.

The experimental apparatus and some of the experimental data will be described here in order to show the method is applicable for the purpose.

Experimental Apparatus. As shown in the diagram, the apparatus consists of a light source, colour filters,[5] absorption tube quartz-plated on both ends and inserted in a dark box, and the photoelectric cell with its recording instruments—amplifying circuit[6] of the photo-current and galvanometer.

Experimental Procedure. In the first place, the whole apparatus is set so that there is no current flowing in the galvanometer when there is no light falling on the photoelectric cell. In order that the perfect balance of the circuit is to be obtained, it is necessary to have as much similar vacuum tubes (UX 201 A) as possible; but ordinarily the characteristics of the vacuum tubes are not identical, hence we must balance the bridge by adjusting R_2. When the light from the mercury lamp is allowed to fall on the photoelectric cell, there is a steady deflection of the galvanometer depending on the photo-current which is amplified by the above bridge circuit. After the zero position in the galvanometer is obtained, to the evacuated absorption tube, the gases or vapours which are to be experimented upon, are introduced; and then the light from the mercury lamp filtered by the above combination of filters[5] are passed by opening the shutter S, and then the steady deflection of the galvanometer is read. And

(4) Batley, *Trans. Faraday Soc.*, **24** (1928), 438.
(5) (a) Wratten light filters, Eastman Kodak CO.
(b) M. Ritchie and R. G. W. Norrish, *Proc. Roy. Soc.*, **140** (1933), 99.
(6) Hughes and Dubridge, " Photoelectric Phenomena " ; see also (3).

also the deflection caused by the light through the empty tube before and after the experiment, is recorded so that we can see whether any change occurred during a run. The amount of deflection with or without gases or vapours will give the amount of the absorbing materials.

The following materials at 0° and room temperature were investigated, in the case of hydrogen chloride at various pressures, and all for wave lengths 4360 Å and 3650 Å.

(1) $C_2H_4Cl_2$ [1:2], b.p. 83°C.
(2) $C_2H_4Br_2$ [1:2], b.p. 129°C. } Takeda's products.
(3) $C_2H_3Cl_3$ [1:1:2], b.p. 113.6–114°C., Eastman's product.
(4) $C_2H_2Cl_4$ [1:1:2:2], b.p. 145°C., Kahlbaum's product.
(5) C_2HCl_5, b.p. 158.5–159.6°C., Eastman's product.
(6) C_2Cl_6, m.p. 183°C., Kahlbaum's product.
(7) HCl.
(8) Cl_2.

(1), (2), (3), (4), and (5) were all twice distilled and C_2HCl_5 was again distilled under reduced pressure.

Hydrogen chloride was prepared by dropping concentrated hydrochloric acid into concentrated sulphuric acid, washed twice through concentrated sulphuric acid, and then condensed twice with liquid nitrogen; only the middle portions were used after passing through a calcium chloride tube.

In every case, excepting (8), after the substance was exposed to the light, 3650 and 4360 Å, the vapour or gas was condensed out with liquid nitrogen and mixed with KI solution (0.1 N) in order to see whether any decomposition had occurred. None seemed to show even a trace of decomposition by having absorbed these light waves. (For corrosive gas—chlorine which has only been used in the qualitative experiment—it is expected to be investigated more thoroughly by this method; for measuring the pressure a click gage which has been described by Smith and Taylor[7] is used.)

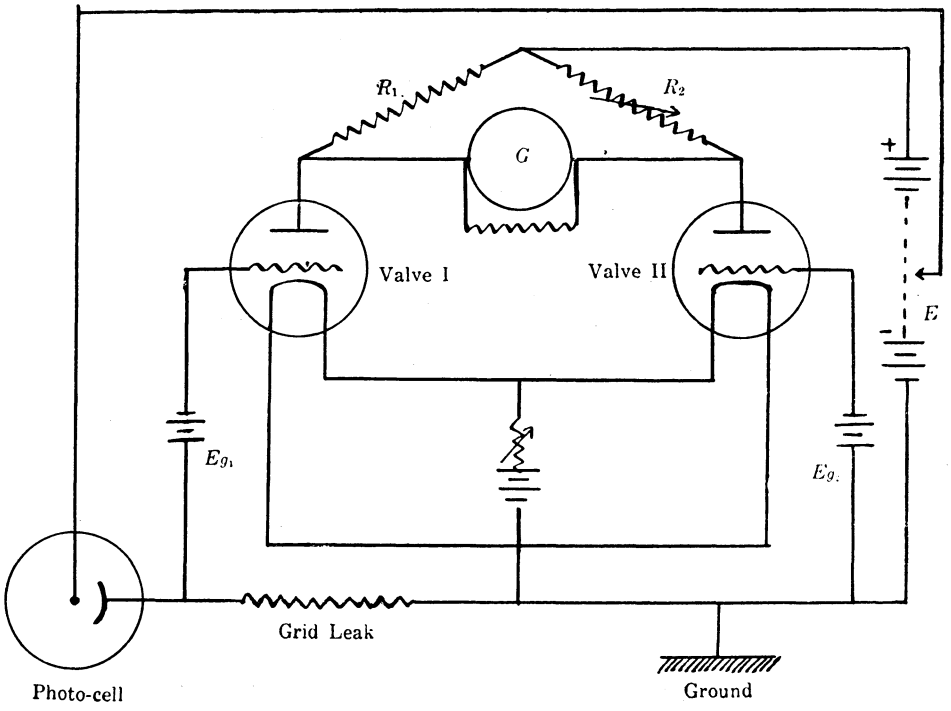
The results of these preliminary absorption experiments of above mentioned substances (including the qualitative data for chlorine) are tabulated in Tables 1–8. As shown in the tables, all of these materials except chlorine are transparent to 3650 and 4350 Å. The absorption experiments for the reaction system involving chlorine and various halogen derivatives of hydrocarbons are now under way; we hope we be able to report on these soon.

(Sample of quinine hydrochloride which has been used in the filter solutions was given generously to us by Prof. S. Fujise of the Bio-chemistry

(7) D. F. Smith and N. W. Taylor, *J. Am. Chem. Soc.*, **46** (1924), 1393.

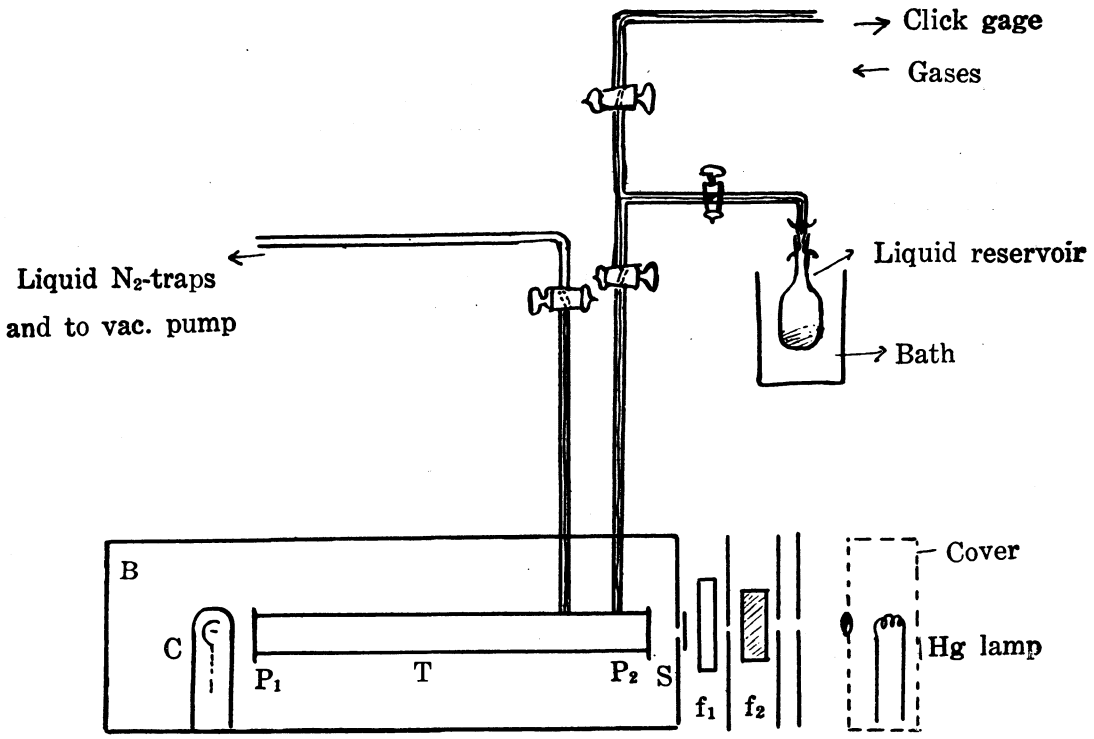
Institute of this University, to whom the author desires to thank for his kindness. Also the writer expresses very cordially his gratitude to Assist. Prof. T. Tonomura who kindly supplied a "one-stage-amplifying apparatus" used for the click gage, and to Assist. Prof. M. Arii of the Inorganic Chemistry Institute, who kindly gave $Cu(SO_4)(NH_4)_2SO_4$ used for the filter solutions.)

As shown in the case of the chlorine absorption, the present apparatus is very convenient, because only chlorine absorbs these waves and all other halogen derivatives have been found to be perfectly transparent to these waves, so that the reaction in which chlorine is substituted in these halogen derivatives of ethane as already published[1] where the amount of chlorine decreases as the reaction proceeds with no change in pressure, and where an ordinary method of following the reaction is powerless, can possibly be studied. Also for a certain decomposition reaction such as $C_2H_4I_2 \rightarrow C_2H_4 + I_2$ may easily be studied owing to the very effective absorption of these light waves, suitably selected, by halogens in general.



Valve I, II: UX 201 A

Fig. 1.



B.....Dark box
C.....Photo-cell (cesium)
T.....Absorption tube
P_1, P_2...Quartz plates
f_1, ...Wratten filter 18 A
f_2 .....Filter cell (quartz-plated) 3 cm. 6% $CuSO_4$ solution
S.....Shutter

Filters: For $\lambda = 3650$ Å, f_1 = Wratten filter 18A, f_2 = 3 cm. layer 6% $CuSO_4$ solution.
For $\lambda = 4360$ Å, without f_1, f_2 = 3 cm. $CuSO_4$ (6%) solution + 3 cm. 2/3% quinine hydrochloride + 3 cm. 1% $Cu(SO_4)(NH_4)_2SO_4$.

Fig. 2.

Table 1. Trichlorethane ($C_2H_3Cl_3$).

(1) $\lambda = 3650$ Å

Deflection			Pressure	
Vacuum	With vapour			$R_1 = 5377\ \Omega$
	Room temp.	0°C.		$R_2 = 2810\ \Omega$
cm.	cm.	cm.	mm.	$i_{Hg} = 2.0$ amp.
2.70	2.70	2.70	7.5	
2.70	2.70	2.70	7.5	$i_f = 0.26$
2.70	2.70	2.70	7.5	

(2) $\lambda = 3650$ Å

Vac.	18°C.	
cm.	cm.	$R_1 = 5377\ \Omega$
18.7	18.7	$R_2 = 4837\ \Omega$
18.7	18.7	$i_{Hg} = 2.20$ amp.
18.7	18.7	$i_f = 0.26$

(3) $\lambda = 3650$ Å

Vac.	17°C.	(The reservoir in ice bath)
cm.	cm.	$R_1 = 5377\ \Omega$
8.5	8.5	$R_2 = 4677\ \Omega$
8.5	8.5	$i_{Hg} = 2.0$ amp.
8.5	8.5	$i_f = 0.26$

(4) $\lambda = 4360$ Å

Vac.	17°C.	
cm.	cm.	$R_1 = 5377\ \Omega$
7.5	7.5	$R_2 = 4597\ \Omega$
7.5	7.5	$i_{Hg} = 2.0$-2.1amp.
7.5	7.5	$i_f = 0.26$

(i_{Hg} = the current intensity of the mercury lamp)

Table 2.

Ethylene chloride ($C_2H_4Cl_2$).

(1) $\lambda = 4360$ Å

Deflection		Pressure	
Vac.	With vapour 0°C.		$R_1 = 5377\ \Omega$
			$R_2 = 4597\ \Omega$
cm.	cm.	mm.	
17.6	17.6	23.47	$i_f = 0.26$ amp.
17.6	17.6	,,	
17.6	17.6	,,	$i_{Hg} = 2.0$

(2) $\lambda = 3650$ Å

Vac.	With vapour 0°C.	Pressure	
			$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 4416\ \Omega$
8.5	8.5	23.47	
8.5	8.5	,,	$i_f = 0.26$ amp.
8.5	8.5	,,	$i_{Hg} = 1.85$—1.90

(3) $\lambda = 3650$ Å

Vac.	With vapour 18°C.	Pressure	
			$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 4357\ \Omega$
3.6	3.6	57.97	
3.6	3.6	,,	$i_f = 0.26$ amp.
3.6	3.6	,,	
3.6	3.6	,,	$i_{Hg} = 1.90$

(4) $\lambda = 4360$ Å

Vac.	With vapour 18°C.	Pressure	
			$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 4357\ \Omega$
3.6	3.6	57.97	
3.6	3.6	,,	$i_f = 0.26$ amp.
3.6	3.6	,,	$i_{Hg} = 2.25$—2.3

Table 3.

Pentachlorethane (C_2HCl_5).

(1) $\lambda = 3650$ Å

Deflection		Pressure	
Vac.	With vapour 20°C.		$R_1 = 5377\ \Omega$
			$R_2 = 4357\ \Omega$
cm.	cm.	mm.	
3.3	3.3	6.97	$i_f = 0.26$ amp.
3.3	3.3	,,	
3.3	3.3	,,	$i_{Hg} = 2.00$

(2) $\lambda = 4360$ Å

Vac.	With vapour 20°C.	Pressure	
			$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 4357\ \Omega$
2.3	2.3	6.97	$i_f = 0.26$ amp.
2.3	2.3	,,	
2.3	2.3	,,	$i_{Hg} = 2.00$

(3) $\lambda = 4360$ Å

Vac.	With vapour 20°C.	Pressure	
			$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 4967\ \Omega$
8.5	8.5	6.97	$i_f = 0.28$ amp.
8.5	8.5	,,	
8.5	8.5	,,	$i_{Hg} = 2.10$

Table 4.

Tetrachlorethane ($C_2H_2Cl_4$).

(1) $\lambda = 4360$ Å

Deflection		Pressure	
Vac.	With vapour 18°C.		$R_1 = 5377\ \Omega$
			$R_2 = 4820\ \Omega$
cm.	cm.	mm.	
4.3	4.3	35.0	$i_f = 0.28$ amp.
4.3	4.3	,,	
4.3	4.3	,,	$i_{Hg} = 2.10$

(2) $\lambda = 3650$ Å

Vac.	With vapour 16.5°C.	Pressure	
			$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 4930\ \Omega$
7.1	7.1	20.0	$i_f = 0.26$ amp.
7.1	7.1	,,	
7.1	7.1	,,	$i_{Hg} = 2.08$—2.15

Table 5.
Hydrogen chloride (HCl).

(1) $\lambda = 3650$ Å			
Deflection		Pressure	$R_1 = 5377\ \Omega$
Vac.	With gas 18°C.		$R_2 = 4410\ \Omega$
cm.	cm.	mm.	
6.2	—	0.0	
	6.2	37.0	$i_f = 0.26$ amp.
	6.2	79.0	
	6.2	238.0	
	6.2	421.5	
	6.2	760.0	$i_{Hg} = 2.02$
6.2	—	0.0	
(2) $\lambda = 4360$ Å			
Vac.	With gas 18°C.	Pressure	$R_1 = 5377\ \Omega$
cm.	cm.	mm.	
2.8	—	0.0	$R_2 = 4160\ \Omega$
	2.8	9.5	
	2.8	61.0	
	2.8	408.0	$i_f = 0.26$ amp.
	2.8	423.0	
	2.8	765.5	$i_{Hg} = 2.04$
2.8	—	0.0	

Table 6.
Hexachlorethane (C_2Cl_6).

(1) $\lambda = 3650$ Å			
Deflection		Pressure	$R_1 = 5377\ \Omega$
Vac.	With vapour 16°C.		$R_2 = 4336\ \Omega$
cm.	cm.	mm.	
4.5	4.5	0.15	$i_f = 0.26$ amp.
4.5	4.5	,,	
4.5	4.5	,,	$i_{Hg} = 2.20$
(2) $\lambda = 4360$ Å			
Vac.	With vapour 18°C.		$R_1 = 5377\ \Omega$
cm.	cm.		$R_2 = 4746\ \Omega$
9.0	9.0		
9.0	9.0		$i_f = 0.28$ amp.
9.0	9.0		$i_{Hg} = 2.1$

Table 7.
Ethylene bromide ($C_2H_4Br_2$).

(1) $\lambda = 3650$ Å			
Deflection		Pressure	$R_1 = 5377\ \Omega$
Vac.	With vapour 17.5°C.		$R_2 = 3506\ \Omega$
cm.	cm.	mm.	
2.1	2.1	10.0	$i_f = 0.26$ amp.
2.1	2.1	,,	
2.1	2.1	,,	$i_{Hg} = 2.1$
(2) $\lambda = 4360$ Å			
Vac.	With vapour 17°C.	Pressure	$R_1 = 5377\ \Omega$
cm.	cm.	mm.	$R_2 = 5416\ \Omega$
5.4	5.4	10.0	
5.4	5.4	,,	$i_f = 0.28$ amp.
5.4	5.4	,,	$i_{Hg} = 1.93$

Table 8. Chlorine (Cl_2).

(1) $\lambda = 3650$ Å		
Deflection	Pressure	At 18°C.
cm.	mm.	$R_1 = 5377\ \Omega$
15.0	0.0	$R_2 = 4957\ \Omega$
15.0	0.0	$i_f = 0.28$ amp.
15.0	0.0	$i_{Hg} = 2.1$
0.0	255.97	(Complete absorption)
(2) Chlorine is pumped out gradually		
Deflection	log I/I_0	mol/liter*
cm.		
8.0	0.2730	9.4×10^{-5}
11.5	0.11539	4.0 ,,
12.0	0.08691	3.0 ,,
12.4	0.08267	2.9 ,,
13.4	0.04899	1.7 ,,
14.0	0.02996	1.0 ,,
14.5	0.01572	5.4×10^{-6}
15.0	—	0.0

*Calculated from $I = I_0\times10^{-\alpha cd}$, where, $d = 100$ cm., $\alpha = 29$[8] at 18°C.

(8) G. E. Gibson and N. S. Baylis, *Phys. Rev.*, **44** (1933), 188–192.

Summary.

(1) An experimental technique, by which the halogen substitution reaction can be studied by using a photoelectric cell, is described. This may well also be applied to studying decomposition reaction where substances involved are susceptible to absorption of the light waves suitably selected.

(2) Absorption of light by the various organic vapours, hydrogen chloride, and chlorine has been studied by this apparatus, and it has been found that all except chlorine are transparent to 3650 and 4350 Å from the mercury lamp as a light source.

In closing, the author desires to thank Prof. S. Mitsukuri and his colleagues of this laboratory for the kind advices and suggestions rendered during the course of this investigation; furthermore, the author is very grateful that a part of expenses has been covered by the grant given to Prof. S. Mitsukuri by the Saito Gratitude Foundation.

The Laboratory of Theoretical Chemistry, Faculty of Science,
Tôhoku Imperial University, Sendai.

RECHERCHES SUR LA CONCENTRATION DES IONS D'HYDROGÈNE CONTENUS DANS LES SOLUTIONS AQUEUSES DES AMMINES-COBALTIQUES COMPLEXES ET SUR LEURS SPECTRES D'ABSORPTION[1]. I.

Par **Taku UÉMURA** et **Hidéo SUÉDA.**

Reçu le 29 octobre 1934. Publié le 28 février 1935.

Une question intéressante de chimie minérale consiste à préciser la stabilité des sels métalliques complexes mis sous forme de solutions aqueuses. Il existe déjà un certain nombre de publications, mais il y a peu de mémoires[2] pour les complexes cobaltiques qui ont une importance

(1) Exposé fait lors de la 56e Séance annuelle de la Société chimique du Japon, le 6 avril 1934, à Osaka (Japon).

(2) Nous connaissons seulement que plusieurs complexes en solution ammoniacale ont été électriquement mesurés, mais n'ont pas reproduit les résultats expérimentaux en acide et en neutre obtenus par A. B. Lamb et A. T. Larden (*J. Am. Chem. Soc.*, **42** (1920), 2024). Récemment, R. Schwarz et K. Tede (*Ber.*, **60 B** (1927), 63) n'ont écrit que sur la décomposition photochimique.

de premier ordre. Cela vient peut-être de ce qu'il est difficile de mesurer directement par des procédés électriques le degré de concentration des ions $Co^{\cdots}$ et que la réaction qui se produit dans la solution est très compliquée.

Lorsque les ammines-cobaltiques complexes se décomposent en solution aqueuse, la concentration des ions d'hydrogène (pH) des solutions varie sans cesse en précipitant le cobalt hydroxyde. En conséquence, le changement de valeur du pH est un facteur important au point de vue du mécanisme de cette décomposition. Il faut d'abord tenir compte de l'influence réciproque qui s'exerce entre les complexes et la variation du pH ; P. Job[3] a déjà montré que le sel roséo se change en oxyhydrile par l'addition de l'alcali. Si on admet l'existence de cette réaction, il est naturel qu'il se produise un spectre d'absorption différent quand on fait varier la valeur du pH d'une solution des sels complexes. Nous avons donc mis les corps complexes en des solutions où leur pH est différent, et dessiné les courbes d'absorption.

En utilisant des ammines-complexes déjà connus, on a observé le changement de ces courbes suivant les différents pH, cherché la production d'un composé différent dans la solution, en examinant les variations des courbes, et on les a comparées pour étudier la constitution chimique des complexes cobaltiques. Ces recherches ont porté systématiquement sur la série des complexes ci-dessous nommés.

Corps étudiés et procédé expérimental. Nous avons préparé, comme échantillons pour les recherches, une dizaine d'ammines-cobaltiques complexes dont voici la liste :

(1) $[Co(NH_3)_6]Cl_3$
(2) $[Co(NH_3)_5(H_2O)]Cl_3$
(3) $[Co(NH_3)_5Cl]Cl_2$
(4) $[Co(NH_3)_5OH]Cl_2$
(5) $[Co(NH_3)_4(H_2O)_2]Cl_3$
(6) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
(7) $[Co(NH_3)_4(H_2O)OH]Cl_2$
(8) $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$
(9) $[Co(NH_3)_4(H_2O)Cl]SO_4$
(10) $[Co(NH_3)_4(H_2O)OH]SO_4$
(11) $[Co_2(NH_3)_8(OH)_2]Cl_4$
(12) $[Co_2(NH_3)_8(OH)_2](SO_4)_2$

Les solutions aqueuses de concentration fixe[4] ont été préparées au moyen des sels ci-dessus nommés, et nous avons mesuré électriquement leur degré de concentration des ions d'hydrogène en nous servant de l'électrode d'antimoine[5] dont nous avons étudié, et déterminé les coefficients

(3) P. Job, *Compt. rend.*, **174** (1922), 613.

(4) Puisque la solution du chlorure lutéo a un pouvoir absorbant très pauvre, nous avons préparé sa solution à 1/200 mol, tandis que les autres solutions sont généralement de 1/500 ou de 1/2500 mol.

(5) Ce bulletin, **8** (1933), 1.

d'extinction au moyen du spectrographe en quartz des Français Jobin et Yvon. Nous avons pris comme source lumineuse une lampe à mercure en quartz et avons relevé la variation de Colog I/I_0 entre 230 mμ et 450 mμ de longueur d'onde sur une plaque photographique " extra rapide " Lumière (marque française). Après avoir préparé ces solutions, on a compté 5 ou 10 minutes en moyenne comme temps de pose photographique, c'est-à-dire qu'on a pu obtenir une photographie d'absorption un quart d'heure après la préparation des échantillons. La rapide mesure du *p*H par l'électrode d'antimoine a été parallèlement calculée tout de suite après la prise de la photographie. On a exactement trouvé des points de densité égale sur la plaque photographique au moyen de l'équidensimètre Georges et Bayle construit par Jobin et Yvon, et on a obtenu des coefficients d'extinction très justes.

Relation entre le coefficient d'extinction et la longueur d'onde des solutions des sels complexes. (1) $[Co(NH_3)_6]Cl_3$, *Chlorure lutéo cobaltique.* Après avoir terminé la synthèse du sel d'après les indications de l'ouvrage écrit par Biltz[6], nous avons mesuré la valeur du *p*H par des méthodes diverses. Les valeurs du *p*H de la solution aqueuse du sel à 1/200 mol ont été modifiées par l'acide chlorhydrique ou par une solution aqueuse de soude caustique, qui ont été tous les deux préparés à l'état de concentration fixe. Le *p*H a été potentiométriquement mesuré au moyen de l'électrode à hydrogène, mais les sels complexes mis en solution ont été influencés par le pouvoir réductif de l'hydrogène et par le noir de platine sur l'électrode. Donc, nous n'avons pas réussi à obtenir des valeurs exactes. Et de plus, en examinant l'état mousseux de l'hydrogène en présence du noir de platine, les expériences ont été faites sur de larges espaces de temps, et on n'a pas obtenu de bons résultats, ce qui prouve que l'électrode à hydrogène ne peut pas être employée pour mesurer les *p*H des solutions aqueuses concernant les sels complexes.

Pour rendre bien visibles les tranformations opérées dans les solutions aqueuses des sels complexes par l'hydrogène et le noir de platine, nous avons mesuré la conductibilité électrique au moyen de la méthode de Kohlrausch, et on a noté sa variation dans le cas du passage de l'hydrogène et dans celui où ce passage n'a pas lieu.

(A) Absence de courant d'hydrogène. La conductibilité spécifique (κ) a été mesurée le plus tôt possible après la préparation du sel lutéo cobaltique (3 minutes). (1/200 mol à la température 25°C.)

(6) H. Biltz et W. Biltz, " Uebungsbeispiele aus der unorganischen Experimentalchemie ", (1920), 3e et 4e édition, 168.

$$\kappa_{t=0} = 2.2 \times 10^{-3}$$

on n'a pas remarqué de changement après 1 à 2 heures, mais il s'en est produit un 17 heures après ;

$$\kappa_{t=17} = 2.1 \times 10^{-3}$$

(B) Passage de l'hydrogène au voisinage de l'électrode au noir de platine.

$$\kappa_{t=0} = 2.2 \times 10^{-3}, \quad \kappa_{t=2} = 2.2 \times 10^{-3}, \quad \kappa_{t=3} = 2.1 \times 10^{-3},$$
$$\kappa_{t=4} = 2.0 \times 10^{-3}, \quad \kappa_{t=5} = 2.0 \times 10^{-3}.$$

Comme les résultats indiqués nous ont montré que les solutions des sels complexes ont été définitivement influencées par leur contact avec l'hydrogène et le noir de platine, nous avons été obligés d'examiner la nature de l'électrode d'antimoine pour l'appliquer à nos solutions des complexes métalliques et obtenu des données exactes avec succès.

Tableau 1.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_6]Cl_3$ à même concentration (1/200 mol), pour des pH divers (cuve 50 mm.).

pH / mμ	1.1	2.0	2.9	4.1	5.1	6.7	8.1	9.6	10.9	11.3	11.5	11.9	12.3
250	...	...	1.00	...	0.80	0.90	0.90	0.90	...	...	...	...	...
251	...	1.00	0.90	1.00	0.70	0.70	0.80	0.80	...	...	...	...	...
252	...	0.80	0.70	0.90	0.60	0.50	0.70	0.70	...	...	...	...	...
253	1.00	0.70	0.60	0.70	0.50	...	0.60	...	1.00	...	...	...	...
254	...	...	0.50	0.60	0.45	0.40	0.50	0.60	0.90	...	...	...	...
255	0.90	...	0.45	0.50	...	...	...	0.50	...	...	...	...	...
257	0.80	...	0.40	0.40	...	0.35	0.35	0.40	...	...	...	...	...
259	0.60	0.45	0.35	0.35	0.25	0.30	0.30	0.35	0.60	1.00 (258)	...	...	...
260	0.50	0.40	0.30 (261)	0.30	...	...	0.25 (261)	0.30 (261)	...	0.90 (261)	...	...	...
262	0.45	0.35	0.25 (263)	0.20 (263)	0.20	0.25	...	0.25	0.50	0.80	...	...	...
265	0.30 (264)	0.25	...	...	0.15 (266)	0.20 (264)	0.20 (264)	0.20	0.35	0.60 (266)	1.00	...	...
268	0.20	0.20	0.15 (267)	0.10 (267)	...	0.15	...	0.15	0.30 (267)	...	0.90	1.00	...
270	...	...	...	...	0.10	...	0.10 (269)	...	0.25	0.50	...	...	...

Tableau 1. (*suite*)

mμ \ pH	1.1	2.0	2.9	4.1	5.1	6.7	8.1	9.6	10.9	11.3	11.5	11.9	12.3
272	0.15	0.15	...	...	...	0.10	...	...	0.20 (273)	0.45 (273)	0.80	0.90	...
275	...	...	0.10 (274)	...	...	...	...	0.10	...	0.40	0.70 (276)	0.80 (274)	1.00 (274)
277	...	...	0.10 (278)	...	...	...	...	...	...	0.35	0.60 (279)	0.70 (278)	0.90
280	...	...	...	...	...	...	...	...	...	0.30	. .	0.60 (279)	0.80
283	...	...	...	. .	...	...	...	0.10	...	...	...	0.50 (282)	0.70
286	...	0.15	0.15 (287)	0.10 (285)	0.10	0.10	0.10	0.15	...	...	0.50	0.45	0.60
292	0.15 (294)	0.20 (291)	0.20 (294)	0.15 (290)	0.15	0.15 (290)	0.20	0.20 (293)	...	...	...	...	0.50 (291)
297	...	0.25 (295)	0.25	0.20 (295)	0.20	0.20 (296)	0.25 (296)	0.25	0.20 (298)	0.30 (296)	0.50 (298)	...	...
300	0.20	0.30 (299)	0.30	0.25	0.25	0.25 (301)	0.30 (299)	0.30 (301)	...	0.35	...	...	...
302	...	0.35	0.35 (303)	0.30 (303)	0.30 (303)	0.30 (304)	0.35	...	0.25	...	...	0.45	0.50
305	0.25	0.40 (306)	...	0.35	...	0.35 (306)	0.40	0.35 (304)	0.30	0.45 (304)	0.60 (304)	0.50 (306)	...
308	0.35 (307)	0.45 (309)	0.45	0.40	0.40	...	...	0.40 (307)	0.35	0.50	0.70	0.60 (307)	0.60
310	0.40	...	...	...	...	0.40	...	0.45	0.40	...	...	0.70 (311)	...
312	...	0.50	0.50 (313)	0.45	...	0.45 (313)	0.45	...	0.45 (311)	0.60	...	...	...
314	...	...	...	0.50	...	...	0.50	...	0.50	...	...	...	0.70
316	0.45	...	0.60 (317)	...	...	0.50 (317)	...	0.50 (317)	...	0.70	0.80	...	...
319	0.50	0.60 (318)	0.70 (320)	0.60 (320)	0.50	...	0.60 (318)	0.60 (318)	0.60	...	...	0.80 (320)	0.80
322	0.60 (324)	0.70	0.80 (324)	0.70 (323)	0.70	0.60	...	0.70	0.70 (324)	0.80	0.90 (323)	0.90 (324)	0.90 (323)
326	0.70 (327)	0.80	...	0.80 (327)	0.90	0.80 (327)	0.70 (325)	0.80 (325)	...	0.90	1.00 (327)	1.00 (328)	1.00
330	0.80	0.90	0.90	0.90	1.00 (331)	1.00 (331)	0.80 (331)	0.90	0.80	...	...	...	...

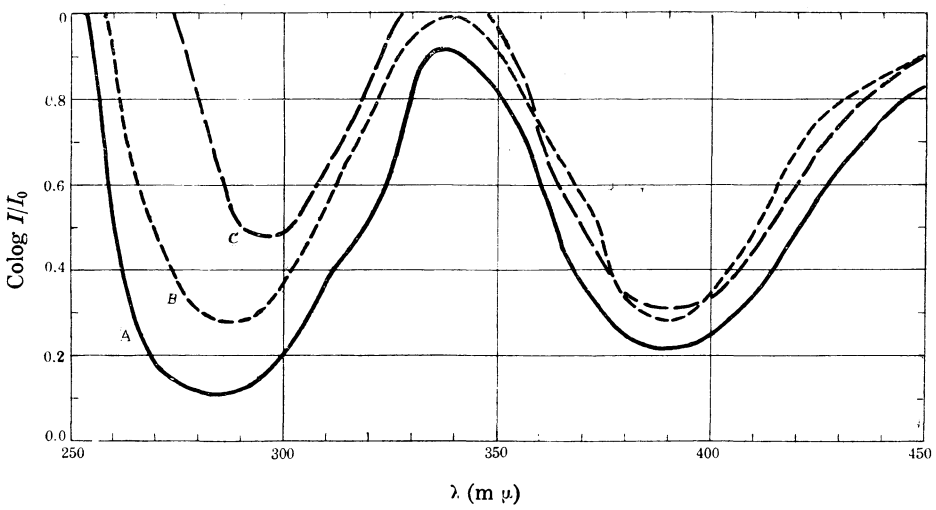
Tableau 1. *(suite)*

mμ \ pH	1.1	2.0	2.9	4.1	5.1	6.7	8.1	9.6	10.9	11.3	11.5	11.9	12.3
333	0.90	1.00 (332)	1.00	...	...	1.00 (334)	0.90 (331)	...	0.90	...	...	...	...
341	0.90	...	...	...	1.00 (340)	0.90	...	...	...	...	...	...	...
344	...	1.00 (343)	1.00	...	0.90 (343)	...	...	0.90	0.90	...	...	...	...
350	0.80 (351)	0.90 (351)	...	...	0.80	0.80 (349)	0.90	0.80 (351)	0.80 (349)	...	...	1.00	1.00 (348)
353	...	...	...	0.90 (352)	...	0.70	...	...	...	0.90 (352)	1.00 (354)	...	0.90
356	0.70	0.80	0.80	0.80 (355)	0.70	0.60	0.80	0.70 (355)	0.70 (355)	0.80	...	...	...
358	...	...	...	0.70	0.60	...	...	0.60	...	...	0.90	0.90	0.80
360	0.60	0.70	0.70 (359)	...	...	...	0.70	...	0.60	...	0.80 (361)	0.80	0.70
362	0.50 (363)	0.60 (364)	0.60 (363)	0.60	0.50	0.50	0.60	0.50	0.50	0.70	0.70 (364)	0.70	0.60 (363)
366	0.45	...	0.50	0.50	0.45	0.45	0.45 (367)	0.45 (365)	0.40	0.60 (368)	...	0.60 (365)	...
370	0.40 (368)	0.50 (369)	...	0.45 (369)	...	0.40	0.40 (371)	0.40 (371)	0.35	...	0.60	0.50 (371)	0.50 (369)
373	0.35 (372)	0.45 (372)	0.45	0.40 (372)	0.40	...	...	...	0.30	...	0.50 (374)	0.40 (374)	0.45
375	0.30	0.40	0.40 (376)	...	0.35	0.35	...	0 35 (374)	...	0.40 (376)	0.45	0.35 (376)	0.40 (376)
379	0.25 (378)	0.35	0.35 (378)	0.35 (377)	0.30	0.30	0.35 (377)	0.30	0.25 (377)	...	0.40 (377)	0.30 (378)	0.35
380	...	0.25 (382)	0.30	0.30	0.25	0.25	0.30	...	...	...	0.35	...	...
390	...	0.30 (387)	0.25	0.25 (388)	...	...	...	...	...	...	...	...	...
395	...	...	0.30	...	0.25	...	0.30 (394)	...	...	...	...	...	...
400	0.25	0.35	0.35 (402)	0.35 (402)	0.30 (399)	0.25 (399)	0.35	0.30	0.25	0.35	0.35	0.30 (403)	0.35 (403)
415	0.30 (406)	0.40 (406)	0.40 (404)	...	0.35	0.30	...	...	0.35 (406)	0.40	0.45	0.35 (404)	0.40 (406)
408	...	...	0.45 (407)	0.40 (407)	...	...	0.40	0.35	0.40	...	0.50	0.40 (407)	...

Tableau 1. (*fin*)

mμ \ *p*H	1.1	2.0	2.9	4.1	5.1	6.7	8.1	9.6	10.9	11.3	11.5	11.9	12.3
410	0.35	0.45 (412)	...	0.45 (411)	...	0.35 (411)	...	...	...	...	...	0.45 (411)	0.45
414	...	...	0.50	...	0.40 (413)	0.40 (415)	...	0.40	0.45	0.45	0.60	0.50 (415)	0.50 (415)
418	0.45 (419)	...	...	0.50	0.45 (416)	0.45 (417)	0.45	0.45	...	0.60 (416)	0.70	0.60	...
420	0.50	0.50	...	...	0.50	...	...	0.50	0.50 (421)	0.70	...	...	0.60
422	...	...	0.60 (423)	...	0.60	0.50 (424)	0.50	0.60 (423)	...	...	0.80 (424)	0.70 (423)	...
427	0.60 (426)	0.60 (426)	...	0.60	...	0.60 (429)	...	...	0.60	...	...	0.80 (428)	0.70
432	...	...	...	...	0.70 (430)	...	0.60	...	...	0.80	...	...	...
436	0.70	0.70 (437)	0.70 (435)	...	...	...	...	0.70 (435)	0.70	...	...	...	0.80
440	...	...	0.80	0.70	...	...	0.70	...	...	...	0.90 (441)	...	...
443	...	...	...	0.80 (444)	...	0.70 (444)	0.80	...	0.80 (442)	...	...	...	...
446	0.80 (445)	0.80	0.90	...	0.80	0.80 (445)	...	...	...	...	...	...	...
450	...	...	...	0.90 (451)	...	...	...	0.80 (449)	...	0.90	1.00	0.90 (449)	0.90
455	0.90	0.90	...	...	0.90 (454)	0.90	0.90 (456)	0.90	0.90	...	...	...	...
460	...	1.00	1.00	...	1.00 (459)	...	...	...	1.00 (462)	...	...	1.00	...
470	1.00	...	...	...	...	...	1.00 (468)	1.00 (465)	...	1.00 (464)	...	...	1.00 (473)

Pour les données indiquées dans le tableau 1, nous avons pris trois *p*H (1.1 ; 11.3 : 12.3) des solutions du lutéo pour désigner les courbes de relation entre l'absorption (Colog I/I_0) et la longueur d'onde (fig. 1). La figure 1 montre que le pouvoir absorbant augmente quand la valeur du *p*H s'accroît et que l'extrémité de la courbe d'absorption change vers des longueurs d'onde plus élevées.



$[Co(NH_3)_6]Cl_3$ (1/200 mol)
A : pH = 1.1 B : pH = 11.3 C : pH = 12.3

Fig. 1.

Comme on le voit dans le tableau 1, on a fait varier la valeur du pH du complexe lutéo entre 1.1 et 11.3, et l'influence de ces limites ne produit à peu près aucun effet sur les courbes d'absorption. C'est pourquoi nous avons éliminé de notre dessin les courbes n'indiquant aucun changement. Dans la solution du grand pH 12, il s'est produit un précipité colloïdal, peu de temps après la mesure de la concentration des ions d'hydrogène, et le déplacement de l'extrémité de la courbe du pH de haute valeur est probablement le résultat de ce phénomène. Il semble donc que le chlorure lutéo cobaltique mis sous forme de solutions aqueuses n'a pas été influencé par le pH jusqu'à ce qu'il se transformât en précitité.

(2) $[Co(NH_3)_5(H_2O)]Cl_3$, *Chlorure d'aquopentammine cobaltique* (*sel roséo*) ; (3) $[Co(NH_3)_5Cl]Cl_2$, *Chlorure de chloropentammine cobaltique* (*sel purpuréo*) ; (4) $[Co(NH_3)_5OH]Cl_2 \cdot H_2O$, *Chlorure hydroxopentammine cobaltique*. Les trois sels ci-dessus nommés ont été synthétiquement formés d'après les méthodes présentées dans le livre de Biltz ou dans les autres travaux faits par les différents chimistes[7].

Tous les échantillons étudiés avaient la concentration de 1/500 mol et les valeurs de leur pH ont subi des variations sous l'action de l'acide chlorhydrique ou de la solution de soude caustique des concentrations connues.

(7) H. Biltz et W. Biltz, *loc. cit.*; A. Benrath, *Z. anorg. Chem.*, **177** (1929), 288; W. D. Harkins, R. E. Hall et W. A. Roberts, *J. Am. Chem. Soc.*, **38** (1916), 2646; A. Werner, *Ber.*, **40** (1907), 4106.

Leurs coefficients d'extinction ont été déterminés par la même méthode appliquée au sel précédent. Les trois tableaux suivants montrent la relation qui existe entre la longueur d'onde et l'absorption.

Tableau 2.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_5(H_2O)]Cl_3$ à même concentration (1/500 mol), pour des *p*H divers (cuve 50 mm.).

mμ \ *p*H	1.4	2.5	3.0	4.5	6.8	7.1	7.5	7.9	8.0	8.4	8.9	10.2	11.7
255	1.00	1.00	0.90	...	0.90	...	...	...	...	...	...	...	...
257	0.80	...	0.70	...	0.70	...	...	...	...	...	...	...	...
260	0.50	0.60	0.50	0.90	0.50	...	...	...	...	...	...	...	...
263	0.40	...	0.35	0.60	0.40	0.50	...	...	...	...	...	...	...
265	0 35	0.35	...	...	...	...	...	...	...	...	...	...	...
267	0.30	0.30	...	0.50	...	0.35	0.90	...	...	...	...	...	...
272	...	0.25	...	...	...	...	0.70	...	...	...	...	...	...
274	0.25	0.20 (275)	0.15 (275)	...	...	0.25 (275)	0.60	1.00	...	...	...	...	...
277	...	...	...	0.30	...	...	0.50 (278)	0.80	...	...	...	...	...
280	...	...	...	0.20 (281)	0.15	0.20 (279)	0.45	0.60	...	...	...	...	...
286	...	...	...	...	...	...	0.40	0.45	0.90	...	1.00	...	1.00
290	...	...	...	...	...	...	...	0.35	0.70 (289)	0.90 (291)	0.80 (291)	0.70	...
295	...	...	...	...	...	...	0.30	0.30	0.50	0.70	0.55	...	0.70
297	...	...	...	...	...	...	...	...	0.45	...	...	0.50	...
300	...	...	...	...	...	...	...	...	0.40	0.50	0.45 (299)	0.45	...
304	...	...	...	...	...	...	...	...	...	0.45	0.35	...	0.45
309	...	0.15	...	0.20 (308)	0.15 (308)	...	...	...	...	...	...	...	...
313	...	...	0.15	0.25 (312)	0.20 (314)	0.25 (314)	0.30 (312)	...	...	...	...	...	...
320	...	0.25	...	0.30	...	0.30	0.35 (319)	0.30	...	...	...	...	...
324	0.25	...	...	0.35 (325)	0.25	...	0.40	...	0.40	0.40	0.30 (325)	0.45	...
326	...	...	0.25	...	...	...	...	0.35	...	...	...	...	...
334	0.30	..	...	0.40	...	...	0.50 (333)	0.40	0.45	0.45 (335)	0.35 (333)	...	0.45

Tableau 2. (*fin*)

mμ \ pH	1.4	2.5	3.0	4.5	6.8	7.1	7.5	7.9	8.0	8.4	8.9	10.2	11.7
338	...	...	...	...	...	...	...	0.45	...	...	0.45 (337)	...	0.50
341	...	...	...	...	...	...	...	...	...	0.50 (342)	...	0.50	...
346	...	...	...	...	...	...	...	...	...	...	0.50	...	0.60
354	...	...	...	...	...	...	...	...	...	0.60 (355)	...	0.60	...
366	0.25	0.30	...	0.40	...	0.35	0.45 (367)	0.40	...	...	...	...	...
376	0.20	0.25 (375)	0 15	0.35 (375)	...	0.25	0.40 (375)	0.35	0.45 (377)	...	...	...	...
380	...	0.20 (379)	...	0.30 (381)	0.15	...	0.35 (381)	...	...	0.60 (381)	...	...	0.60 (379)
383	...	...	...	...	...	...	...	...	...	...	0.60 (384)	0.60 (382)	...
392	...	...	...	...	...	...	...	0.30	...	0.50 (393)	...	0.50	
397	...	...	...	...	...	...	...	...	...	0.45	0.50 (396)	...	0.45 (398)
400	...	...	...	...	...	...	...	...	0.35	0.40	...	...	...
404	...	...	...	...	...	...	...	...	...	...	0.45	0.45 (405)	...
407	...	...	...	...	0.15 (406)	...	...	...	0.30 (408)	0.35	0.40	...	...
410	...	...	0.15	...	...	0.25	...	...	0.25	...	0.35	...	...
414	...	...	...	0.20	...	...	0.35 (415)	...	...	...	...	0.40 (413)	...
420	...	0.20 (421)	...	...	0.20	...	0.40	...	...	...	...	...	...
425	0.20	...	...	...	...	...	...	...	...	...	...	...	...
434	...	0.25	...	...	...	...	0.45 (433)	...	0.30 (435)	...	0.35	...	...
437	...	...	...	...	...	0.35	...	0.30	...	0.35	...	...	...
440	...	...	...	0.35	...	...	...	0 35	0.35	...	...	...	...
445	...	...	...	...	...	...	0.50	...	...	0.40	0.40	0.40 (444)	...
454	...	...	...	...	...	...	...	...	...	0.45	0.45	...	...
456	...	...	...	...	...	0.40	...	...	...	...	...	...	0.45
460	...	...	...	...	...	...	...	...	...	...	0.50	0.50	...

Tableau 3.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_5Cl]Cl_2$ à même concentration (1/500 mol), pour des pH divers (cuve 50 mm.).

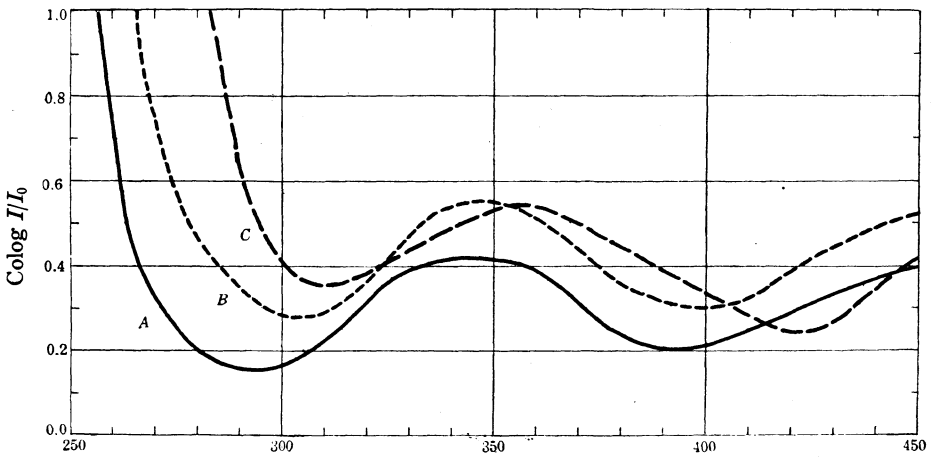
mμ \ pH	1.5	2.3	3.7	5.0	6.4	7.0	8.0	9.3	10.8
306	0.90	...	0.90	1.00	...	0.90	...	1.00	...
307	0.80	0.90	0.80	...	0.90	0.80	1.00	...	0.80
308	...	0.80	...	0.90	0.80	...	...	0.80	0.60
313	0.50	0.60	0.60	0.60	0.60	...	...	0.60	0.50
315	0.45	0.45	0.45	...	0.50	0.45	...	...	0.45
320	0.35	...	0.40	...	0.40	0.40	0.45	...	...
322	...	0.35	...	0.35	0.35	0.35	...	...	...
337	...	0.35	...	...	0.35 (336)	...	...	0.40	0.45
340	0.35	0.40	0.40	0.40 (339)	0.40	...	...	0.45	...
343	...	...	...	0.45	...	0.40 (342)	0.40	...	0.50 (342)
345	...	0.45 (346)	0.45	...	0.45	...	0.45 (347)	0.50 (347)	...
352	0.45 (353)	0.50	0.50 (353)	0.50	0.50	...	0.50 (353)	...	0.60 (351)
378	0.45	...	...	0.50	0.50 (379)	0.45	0.50 (377)	...	0.60
380	0.40 (379)	0.45 (381)	0.45	0.45 (381)	0.45	0.40	...	...	...
383	0.35	...	...	...	0.40	...	0.45 (382)	0.50 (382)	...
386	0.30	...	...	0.40	0.35	0.35	...	...	...
389	...	0.40 (388)	0.40 (390)	...	...	...	0.40 (388)	0.45	0.50
395	...	...	0.30	0.35 (396)	0.30 (394)	0.30	...	...	0.45 (396)
398	...	0.30	0.25	...	...	...	...	0.35	...
400	0.25	...	...	0.30	...	...	...	...	...
405	...	0.25	...	...	...	...	0.30	...	0.40
417	...	...	...	...	...	...	...	0.30 (416)	0.30
431	0.25	...	0.25	...	0.30 (430)	...	...	...	...
433	...	0.25	...	...	...	0.30	...	...	...
437	0.30	0.30	...	0.30	...	...	...	...	...
442	...	...	...	...	0.35	0.35	0.30 (443)	...	...
457	0.35	...	0.35 (458)	...	...	...	...	0.30 (456)	0.35 (458)

Tableau 4.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_5OH]Cl_2$ à même concentration (1/500 mol), pour des pH divers (cuve 50 mm.).

Colog I/I_0	pH = 1.1				pH = 7.3				pH = 8.0			
1.00	254				282				293			
0.90	256				284				299			
0.80	258				286				303			
0.70	...				289				308			
0.60	...				290				312	350	375	
0.50	263				294	352	371				387	
0.45	264				297	339	380	477			395	466
0.40	266	337	366		302	329	390	454			402	452
0.35	267	332	371	435			399	447			404	434
0.30	268	324	374	434			403	444				
0.25	270	318	381	422								

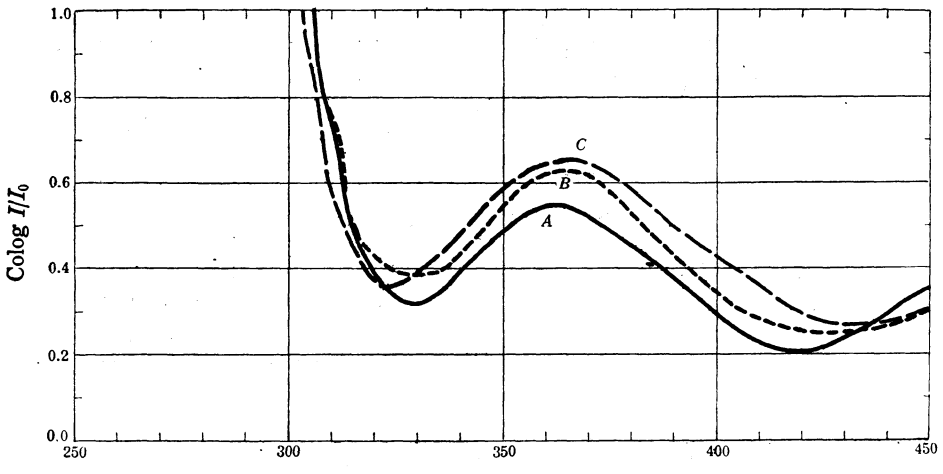
La figure 2 montre que la solution aqueuse du chlorure roséo n'éprouve pas de grands changements d'absorption quand les valeurs du pH varient de 1.4 à 6.8, tandis que des valeurs plus rapprochées du pH telles que 7.1 et 8.0 amènent des variations dans les bandes d'absorption. Cependant, le chlorure purpuréo ne présente qu'une légère différence d'absorption quand les valeurs du pH varient dans une plus grande mesure, par exemple de 2.3 à 10.8 (fig. 3).



$[Co(NH_3)_5(H_2O)]Cl_3$ (1/500 mol)

A: pH = 7.1 B: pH = 7.5 C: pH = 8.0

Fig. 2.



$[Co(NH_6)_5Cl]Cl_2$ (1/500 mol)
A: pH = 2.3 B: pH = 9.3 C: pH = 10.8
Fig. 3.

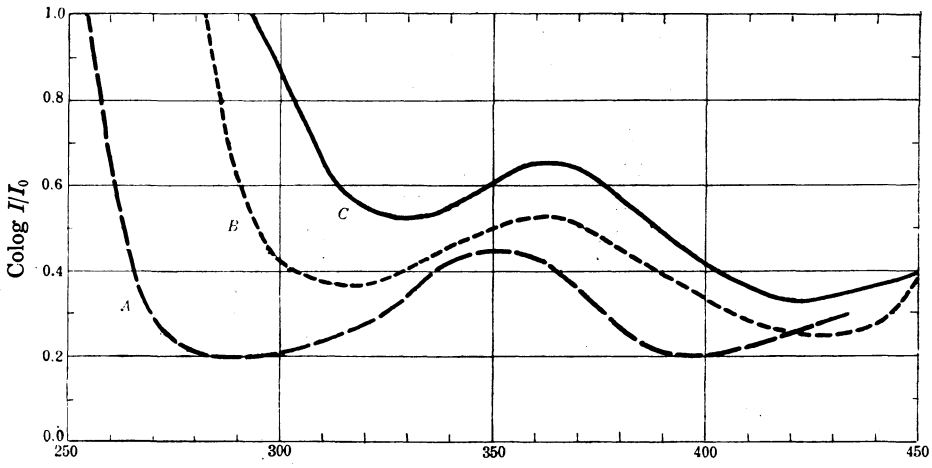
Ces deux sels se différencient très nettement à l'extrémité des courbes d'absorption des longueurs d'onde plus basses dans les solutions acides et neutres.

Le roséo a une molécule d'eau dans le radical complexe, tandis que le purpuréo y présente un radical acide Cl; c'est peut-être là une des causes des différences que l'on remarque dans les courbes de ces deux composés.

Quant à la vitesse de réaction qui se produit entre ces deux complexes à savoir $[Co(NH_3)_5Cl]Cl_2$ et $[Co(NH_3)_5(H_2O)]Cl_3$, et que l'on obtient par la mesure de l'électroconductibilité, la réaction monomoléculaire a été précisée par Lamb et Marden[8] qui ont trouvé la constante de réaction $K=0.6\times10^{-4}$. Mais, ce résultat ne s'accorde pas avec celui du Prof. Y. Shibata[9]. Puisque le chlorure roséo solide se change en purpuréo, il faut l'employer rapidement après la préparation du corps.

On peut facilement trouver une analogie remarquable entre les courbes des sels $[Co(NH_3)_5OH]Cl_2$ (fig. 4) et $[Co(NH_3)_5(H_2O)]Cl_3$ (fig. 2); c'est-à-dire, les courbes A de la figure 2 et A de la figure 4; les courbes C de la figure 2 et B de la figure 4. La solution aqueuse du sel roséo n'éprouve pas de changement quand elle est acide, mais il semble que la molécule d'eau dans son radical complexe soit facilement remplacée par OH en solution alcaline.

(8) A. B. Lamb et J. W. Marden, *J. Am. Chem. Soc.*, **33** (1911), 1873.
(9) Y. Shibata, *J. Ccll. Sci. Imp. Univ. Tokyo*, **37** (1915), Art. 2.



$[Co(NH_3)_5OH]Cl_2$ (1/500 mol)

A : pH = 1.1 B : pH = 7.3 C : pH = 8.0

Fig. 4.

Le sel $[Co(NH_3)_5OH]Cl_2$ est dissous dans l'eau en donnant la valeur du pH 8.0, et il faut ajouter l'acide chlorhydrique possédant la concentration convenable pour obtenir les solutions du pH 1.1 ou 7.3. Comme nous avons constaté une analogie de courbes entre la solution du $[Co(NH_3)_5OH]Cl_2$ additionnée par HCl (fig. 4—courbe A) et celle du $[Co(NH_3)_5(H_2O)]Cl_3$ (fig. 2 —courbe A), la réaction $[Co(NH_3)_5OH]Cl_2 \xrightarrow{pH<7} [Co(NH_3)_5(H_2O)]Cl_3$ est possible ; et, de plus, nous pouvons nettement conclure au changement du sel roséo en solution alcaline, à savoir, $[Co(NH_3)_5(H_2O)]Cl_3 \xrightarrow{pH>7} (Co(NH_3)_5OH]Cl_2$. Ces remarques ont déjà été faites par Werner[10] qui se basait lui-même sur l'opinion de Pfeiffer[11] ; et Job[12] a indirectement tiré une conclusion par une méthode de titration potentiométrique en employant $Ba(OH)_2$, et enfin, nous sommes arrivés à des résultats spectrochimiques décisifs.

Il est, cependant, difficile de porter un jugement définitif sur la réaction du sel purpuréo $[Co(NH_3)_5Cl]Cl_2 \rightarrow [CO(NH_3)_5OH]Cl_2$ par l'addition de l'alcali, parce que en comparant les figures 3 et 4, on remarque que les deux complexes $[Co(NH_3)_5Cl]Cl_2$ et $[Co(NH_3)_5OH]Cl_2$ ont une absorption qui a un centre de 360 mμ de longueur d'onde.

(10) A. Werner, *Ber.*, **40** (1907), 4098.
(11) P. Pfeiffer, *Ber.*, **39** (1906), 1864.
(12) P. Job, *loc. cit.*

(5) $[Co(NH_3)_4(H_2O)_2]Cl_3$, *Chlorure de diaquotétrammine cobaltique.* D'après la méthode préparation présentée par Jörgensen[13], on a obtenu le complexe de diaquotétrammine, et en faisant varier la valeur du *p*H des solutions, on a cherché la relation entre le coefficient d'extinction et la longueur d'onde avec une concentration de 1/500 mol. Nos résultats montrent que les variations du *p*H au-dessus de 7 n'exercent aucune influence sur les courbes d'absorption, mais que le centre d'absorption passe vers des longueurs d'onde plus élevées, et que le pouvoir absorbant augmente. Par l'addition de l'alcali au sel de diaquotétrammine, Job[14] a déjà indirectement remarqué la production du corps $[Co(NH_3)_4(OH)_2]Cl$.

Tableau 5.

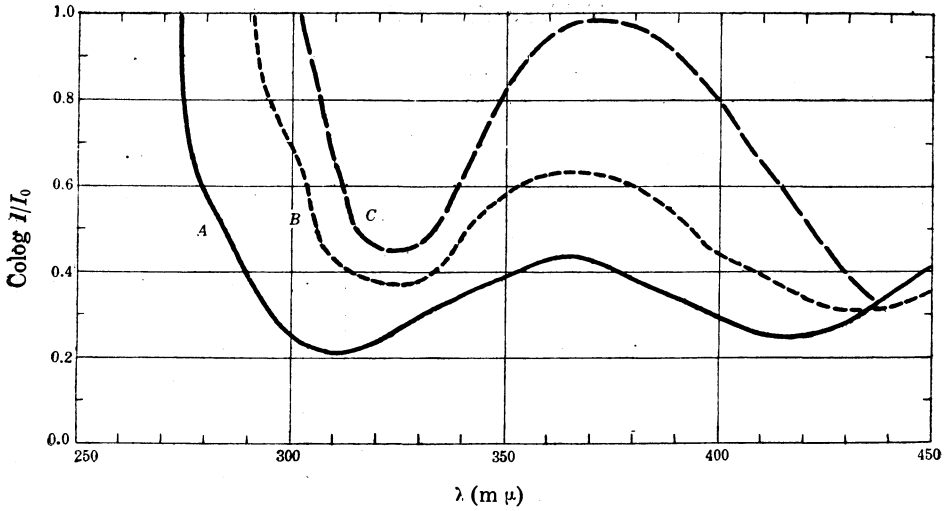
Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_4(H_2O)_2]Cl_3$ à même concentration (1/500 mol), pour des *p*H divers (cuve 50 mm.).

mμ \ *p*H	1.7	2.9	4.4	5.0	6.1	6.6	6.7	7.1	8.8	10.9
270	0.70	1.00	...	...	0.70	0.90	...	...	...	...
274	...	0.80	...	...	...	0.70	1.00	0.90	...	...
276	0.45	0.60	...	...	0.50	...	0.70	...	...	...
278	...	0.50	0.90	...	0.45	0.45	0.60	...	...	...
281	...	...	...	0.60	...	...	...	...	...	...
283	...	...	...	0.50	0.35	...	...	0.60	...	...
286	...	0.40	0.70	0.45	0.30	0.40	0.50	0.50	...	...
		(287)	(285)	(287)	(287)					
289	0.25	0.35	0.60	0.40	...	0.35	0.40	0.45	1.00	...
	(288)		(288)				(290)	(290)	(291)	
294	0.20	...	0.50	0.35	0.25	0.30	...	0.40	0.80	...
	(295)		(295)	(295)	(293)			(293)		
297	...	0.25	0.40	...	0.20	0.25	0.30	0.35	...	...
					(296)	(296)				
302	...	...	...	...	...	0.20	...	0.30	...	1.00
308	...	...	0.30	...	...	...	...	...	0.45	0.70
										(309)
314	...	...	...	...	...	0.20	...	...	0.40	0.50
										(315)
320	...	0.25	0.30	0.30	0.20	...	...	...	...	...
			(321)							

(13) S. M. Jörgensen, *Z. anorg. Chem.*, **2** (1892), 294.
(14) P. Job, *loc. cit.*

Tableau 5. (*fin*)

mμ \ *pH*	1.7	2.9	4.4	5.0	6.1	6.6	6.7	7.1	8.8	10.9
324	0.25 (323)	...	0.35 (323)	...	...	...	0.25	0.30	...	...
331	0.30 (330)	0.30 (332)	...	...	0.25 (330)	...	0.30 (332)	...	...	...
334	...	...	...	0.35 (335)	0.30	0.35 (335)	...	0.35	0.40	0.50
337	0.35	0.35	...	...	...	...	...	...	0.45 (338)	0.60 (338)
341	0.40 (342)	...	0.40	0.40 (340)	0.35 (342)	0.40 (340)	0.35 (342)	0.45	0.50 (340)	...
347	...	...	0.45 (346)	0.45 (348)	...	0.50	...	...	...	0.80 (348)
354	...	...	...	...	...	...	0.40	0.50	0.60 (353)	0.90 (355)
372	0.45	0.40	...	...	...	0.45 (371)	...	0.40	...	...
376	0.40 (375)	0.35 (377)	0.45	0.40 (375)	0.35	0.40 (377)	0.40	...	...	...
379	0.35	...	0.40 (378)	...	0.30	...	...	0.35 (378)	0.60	...
382	0.30	0.30	0.35	...	...	...	0.35 (383)	...	...	...
388	0.25	...	0.30 (387)	...	0.25	...	...	...	...	...
391	...	...	0.20 (392)	0.30	...	...	...	0.30 (390)	...	0.90 (390)
398	...	0.25	...	0.25	...	...	0.30	0.25 (399)	0.45 (397)	...
420	...	...	...	...	...	...	...	...	0.35 (419)	0.60
430	0.25	...	...	...	...	...	...	...	...	0.50
435	...	0.25	...	...	...	0.25 (436)	0.30	0.30 (436)	...	...
440	...	...	0.25	0.25	...	...	0.35	...	...	0.45
445	0.35 (444)	0.35	...	...	...	...	...	...	...	...
450	0.40	...	...	...	0.35	0.30 (451)	...	...	0.30	...



$[Co(NH_3)_4(H_2O)_2]Cl_3$ (1/500 mol)
A : pH = 6.7 B : pH = 8.8 C : pH = 10.9
Fig. 5.

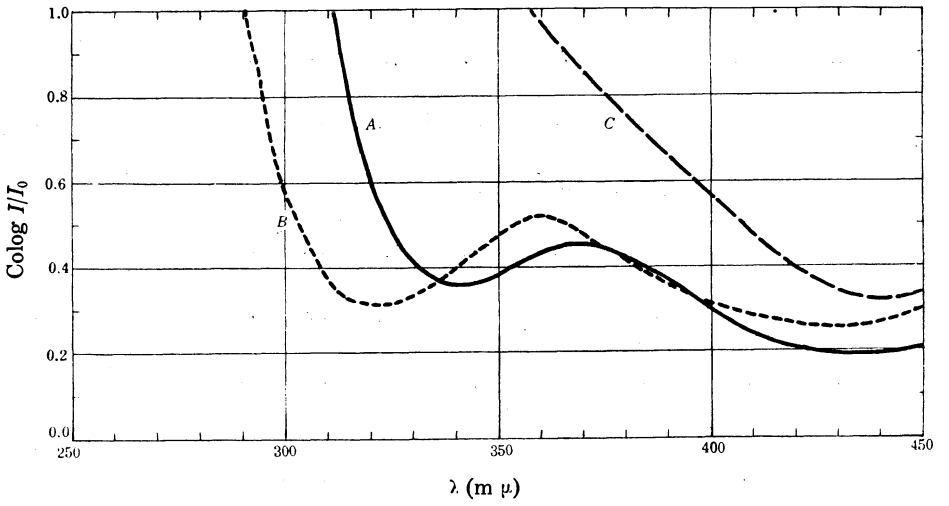
Tableau 6.
Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_4(H_2O)Cl]Cl_2$ à même concentration (1/500 mol) pour des pH divers (cuve 50 mm.).

mμ \ pH	2.0	2.9	4.6	6.4	6.9	7.0	7.0	7.4	7.4	7.4	7.6
293	...	...	...	...	...	...	0.80	0.90	...	...	...
303	...	...	...	...	...	0.80	0.50	0.50	1.00 (302)	0.90 (304)	...
313	1.00	...	1.00	...	0.90	0.50	...	0.35 (312)	0.70 (314)	0.60	...
317	0.90	0.90	0.90 (318)	0.90 (318)	0.70	0.45 (316)	0.40 (316)	...	0.60 (318)	0.50 (318)	...
319	0.80	0.80	0.80 (318)	0.80	0.60 (320)	0.40 (320)	...	...	...	...	...
321	0.70	0.70 (320)	0.60	0.70	0.60 (320)	...	...	...	...	...	...
325	0.50 (326)	0.50 (326)	0.50	0.50	0.45 (326)	...	...	...	...	...	...
330	...	0.45	0.40	0.40 (329)	0.40 (331)	...	...	...	...	...	...
333	...	0.40	...	0.35 (332)	...	...	...	0.35 (334)	...	...	...
340	...	...	...	...	...	...	0.40	0.40	...	...	...

Tableau 6. (*fin*)

mμ \ *p*H	2.0	2.9	4.6	6.4	6.9	7.0	7.0	7.4	7.4	7.4	7.6
345	...	0.40	0.35 (346)	...	...	...	...	...	...	0.50 (344)	...
348	0.35	...	...	...	...	...	...	0.45	...	...	...
350	...	...	0.40	0.35	...	0.40 (349)	...	...	...	...	...
353	...	0.45	...	...	0.40	0.45 (354)	0.45 (354)	...	...	0.60	...
358	...	...	...	0.40	...	...	...	...	0.60 (357)	...	1.00 (357)
361	0.45	0.50	0.45 (360)	...	...	...	0.50	...	...	...	...
374	0.45	0.50	...	...	...	0.45 (373)	0.50	...	...	0.80 (375)	...
376	...	...	...	...	...	...	0.45 (377)	0.45	...	...	...
380	...	...	0.45 (379)	0.40	...	...	...	0.40 (381)	...	...	...
385	...	...	...	0.35	0.40 (384)	...	...	...	...	0.70 (387)	0.60
390	...	...	...	0.30	...	...	0.35	0.35	...	...	...
396	0.35	0.40	...	...	0.35 (397)	0.35	...	...	0.40	...	...
400	...	0.35 (401)	0.35	0.20 (399)	0.30 (399)	...	...	...	...	0.60 (399)	...
405	...	...	...	0.10	0.25 (406)	...	...	0.30	...	...	...
408	0.25	...	0.30	...	...	...	...	...	0.35	0.50	...
412	0.20 (413)	...	...	...	...	...	...	...	...	0.45	...
419	...	...	...	...	...	...	0.30	...	...	0.40 (418)	0.45 (417)
428	...	...	...	...	...	...	...	...	...	0.35	...
450	...	...	0.25	...	...	0.35 (455)	0.35 (448	0.30	...	0.35 (453)	...
460	0.20 (462)	0.30	...	...	...	...	0.40 (459)	...	...	...	0.45 (465)
470	...	...	0.30 (465)	...	0.25 (475)	...	...	0.35 (473)	0.35 (467)	0.40 (471)	...
480	0.25	0.35	0.35	...	...	...	...	...	...	...	0.50

(6) $[Co(NH_3)_4(H_2O)Cl]Cl_2$, *Chlorure de chlorotétrammoniohydrine cobaltique.* Nous avons obtenu le sel $[Co(NH_3)_4(H_2O)Cl]Cl_2$ en appliquant la méthode de Jörgensen[15], et étudié la relation qui existe entre la longueur d'onde et le coefficient d'extinction, surtout au voisinage du *p*H 7.0, avec la concentration de 1/500 mol. Ce complexe est cependant bien différent des autres. On peut facilement l'observer dans la figure 6 ; c'est-à-dire que la fin de l'absorption passe vers des longueurs d'onde plus basses quand le *p*H des solutions grandit.



$[Co(NH_3)_4(H_2O)Cl]Cl_2$ (1/500 mol)
A : *p*H = 6.9 B : *p*H = 7.4 C : *p*H = 7.6

Fig. 6.

Le complexe $[Co(NH_3)_4(H_2O)Cl]Cl_2$ ne subit pas l'influence de l'addition d'alcali quand la valeur du *p*H est voisine de 7.4, et que le *p*H n'augmente pas dans ce cas. Cependant lorsque le *p*H atteint 7.6, la forme de la courbe d'absorption (fig. 6—courbe C) change considérablement, et la précipitation se produit un instant après qu'on a evalué la mesure du *p*H.

Les deux courbes B, dans les figures 6 et 5, ont des formes semblables ; c'est que le radical Cl du sel $[Co(NH_3)_4(H_2O)Cl]Cl_2$, comme la molécule d'eau du $[Co(NH_3)_4(H_2O)_2]Cl_3$, est influencé dans le noyau complexe par l'alcali vers la valeur du *p*H 7.4. La précipitation du composé $[Co(NH_3)_4(H_2O)Cl]Cl_2$ se produit au-dessus du *p*H 7.6 tandis que celle du $[Co(NH_3)_4(H_2O)]Cl_3$ ne peut pas être obtenue même au *p*H 11. Cette différence vient peut-être de

(15) S. M. Jörgensen, *J. prakt. Chem.*, [2], **42** (1890), 211.

l'effet que l'alcali produit sur le radicale Cl ou H_2O, c'est-à-dire que le radical Cl est plus influencé que la molécule H_2O.

(7) $[Co(NH_3)_4(H_2O)OH]Cl_2$, *Chlorure de hydroxotétrammoniohydrine cobaltique*; (11) $[Co_2(NH_3)_8(OH)_2]Cl_4$, *Chlorure de dioloctammine dicobaltique.* Le premier sel ci-dessus indiqué a été préparé d'après la méthode de Dubsky[16] et le second d'après celle de Werner[17]. Nous avons étudié le spectre d'absorption avec les solutions acides et alcalines. La concentration de ces deux sels est respectivement 1/1000 mol et 1/2000 mol pour que la solution contienne le même nombre d'atomes de cobalt.

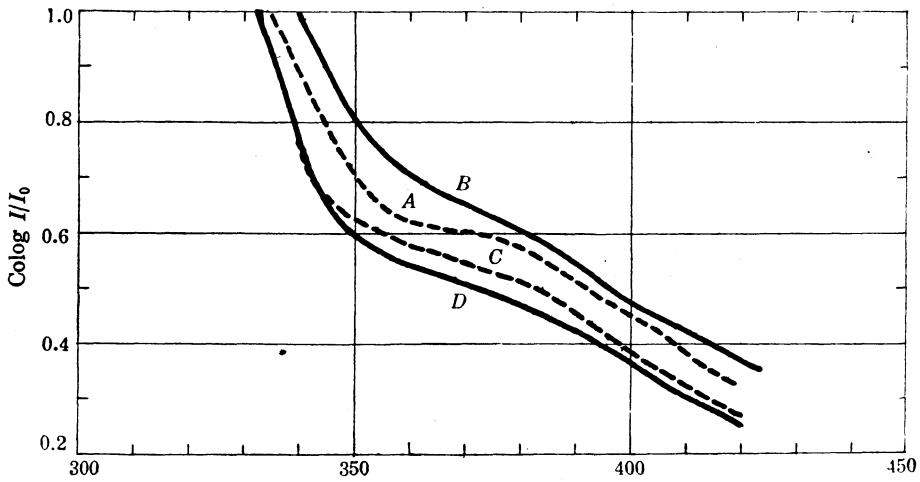
Tableau 7.
Absorption (Colog I/I_0) des solutions, pour des pH divers
(cuve 50 mm.)

	$[Co(NH_3)_4(H_2O)OH]Cl_2$ (1/1000 mol)				$[Co_2(NH_3)_8(OH)_2]Cl_4$ (1/2000 mol)			
Colog I/I_0	pH = 1.7		pH = 7.9		pH = 1.8		pH = 8.2	
1.00	334		340		333		332	
0.90	339		346		336		336	
0.80	345		350		338		339	
0.70	350		361		341		341	
0.60	(360)	377	383		356		349	
0.50		392	396		334		371	
0.45		405	405		391		382	
0.40		409	415		398		395	
0.35		415	424	466	405		402	
0.30					415	481	410	
0.25					423	476	420	475

Les courbes de la figure 7 sont à peu près analogues les unes et les autres et la variation de la valeur du pH n'apparaît pas dans les courbes d'absorption; ce qui diffère des autres cas généraux. C'est une des caractéristiques des solutions des complexes polynucléaires[18], et il semble que le sel $[Co(NH_3)_4(H_2O)OH]Cl_2$ prenne la forme $[Co_2(NH_3)_8(OH)_2]Cl_4$ en solution. Les courbes présentées par les complexes $[Co(NH_3)_4(H_2O)_2]Cl_3$ et $[Co(NH_3)_4(H_2O)Cl]Cl_2$, dans les figures 5 et 6, ne montrent pas en solutions alcalines la caractéristique que nous venons de signaler, cela vient, peut-on dire, de ce que ces deux composés ne se trouvent pas, en leur solution aqueuse, sous la forme polynucléaire comme le corps $[Co(NH_3)_4(H_2O)OH]Cl_2$. Mais, Werner[19] a décrit comment il obtenait le sel $[Co(NH_3)_4(H_2O)OH]Cl_2$ en préparant le diaquotétrammine cobaltique alcalin par l'ammoniaque et

(16) J. Dubsky, *J. prakt. Chem.*, [2], **90** (1914), 98.
(17) A. Werner. *Ber.*, **40** (1907), 4820.
(18) Je toucherai ce sujet encore une fois dans notre mémoire suivant.
(19) A. Werner, *Ber.*, **40** (1907), 4114.

en précipitant le sel obtenu par l'alcool. Cependant d'après nos résultats spectrochimiques, nous n'arrivons pas à bien comprendre les resultats obtenus par Werner, et nous supposons plutôt qu'il y a transformation du sel diaquotétrammine en $[Co(NH_3)_4(OH)_2]Cl$ et non en $[Co(NH_3)_4(H_2O)]Cl_2$, ce que Job en a déjà prouvé. En tout cas, nous signalerons ce point plus tard, après avoir obtenu le sel complexe $[Co(en)_2(OH)_2]Cl$.



$[Co(NH_3)_4(H_2O)OH]Cl_2$ (1/1000 mol)
A: pH = 1.7 B: pH = 7.9
$[Co_2(NH_3)_8(OH)_2]Cl_4$ (1/2000 mol)
C: pH = 1.8 D: pH = 8.2

Fig. 7.

(8) $[Co(NH_3)_4(H_2O)]_2(SO_4)_3$, *Sulfate de diaquotétrammine cobaltique*; (9) $[Co(NH_3)_4(H_2O)Cl]SO_4$, *Sulfate de chlorotétrammoniohydrine cobaltique*; (10) $[Co(NH_3)_4(H_2O)OH]SO_4$, *Sulfate de hydroxotétrammoniohydrine cobaltique*; (12) $[Co_2(NH_3)_8(OH)_2](SO_4)_2$, *Sulfate de dioloctammine dicobaltique.* Nous avons eu l'intention d'examiner de nouveau les résultats obtenus par les chlorures avec les sulfates correspondants. On a appliqué les méthodes de Jörgensen ou de Dubsky[20] pour préparer les trois premiers corps. Le quatrième sel $[Co_2(NH_3)_8(OH)_2](SO_4)_2 \cdot 2H_2O$ a été aussi obtenu par l'indication de Werner[21], mais comme il est peu soluble dans l'eau, sa photographie

(20) S. M. Jörgensen, *Z. anorg. Chem.*, **2** (1892), 297; J. Dubsky, *J. prakt. Chem.*, [2], **90** (1914), 103; S. M. Jörgensen., *J. prakt. Chem.*, [2], **42** (1890), 212; *Z. anorg. Chem.*, **16** (1898), 184,

(21) A. Werner, *Ber.*, **40** (1907), 4440.

d'absorption n'a pu être prise. Les solutions des trois premiers complexes ont été mesurées d'après leurs coefficients d'absorption pour en tirer leurs relations entre les longueurs d'onde et les *p*H.

Tableau 8.

Absorption (Colog I/I_0) des solutions, pour des *p*H divers (cuve 50 mm.).

$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$

Colog I/I_0	*p*H = 6.5 (1/500 mol)				*p*H = 8.1 (1/1000 mol)	
1.00	277				311	
0.90	280				316	
0.80	284				320	
0.70	287				325	
0.60	291				328	
0.50	295				332	
0.45	297	340	367		366	
0.40	303	332	373	477	392	
0.35	308	325	382	469	399	
0.30			391	456	407	
0.25			399	431	421	475

$[Co(NH_3)_4(H_2O)Cl]SO_4$

Colog I/I_0	*p*H = 6.6 (1/500 mol)				*p*H = 7.7 (1/500 mol)
1.00	309				...
0.90	310				326
0.80	311				331
0.70	314				335
0.60	317				339
0.50	320				348
0.45	322				364
0.40	324	357	378		380
0.35	329	343	391		390
0.30			...		398
0.25			405	458	
0.20			419	450	

$[Co(NH_3)_4(H_2O)OH]SO_4$

Colog I/I_0	*p*H = 1.3 (1/500 mol)				*p*H = 8.1 (1/1000 mol)	
1.00	288				297	
0.90	292				304	
0.80	295				308	
0.70	298				313	
0.60	303				315	
0.50	308				320	
0.45	311				325	
0.40	313	342	367		328	
0.35			380	470	332	360
0.30			391	450		379
0.25			399	426		398

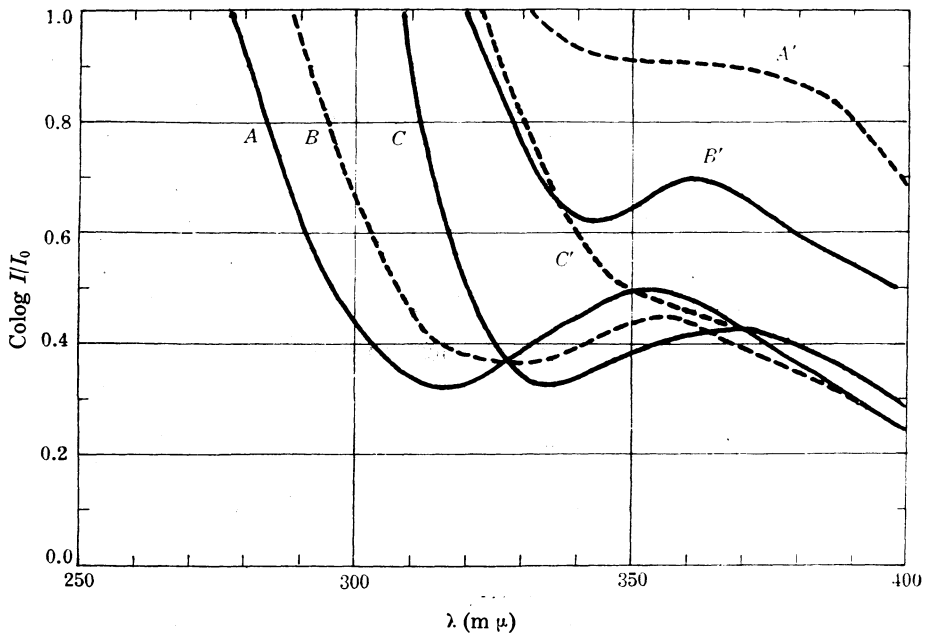
Dans le tableau 8, les deux corps, $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ et $[Co(NH_3)_4(H_2O)OH]SO_4$, en solution aqueuse ont été présentés avec la concentration 1/1000 mol au *p*H 8.1.

En supposant que toutes les solutions obéissent à la loi de Beer, nous avons calculé tous nos résultats à la même concentration 1/500 mol, tels qu'ils apparaissent dans la figure 8.

On voit, dans cette figure 8, que le sel $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ présente une grande différence entre la courbe du *p*H 6.5 et celle du *p*H 8.1. Il semble que cette dernière courbe A′ soit variée de celle de A, en passant par la courbe B′ du corps $[Co(NH_3)_4(H_2O)OH]SO_4$, en remplaçant une molécule d'eau dans le premier corps par le radical OH, ce qui diffère du cas du chlorure.

En faisant dissoudre le sel $[Co(NH_3)_4(H_2O)OH]SO_4$ solide dans l'eau, on

obtient une solution du pH 8.1 (courbe B′) et en ajoutant une quantité convenable de HCl à cette solution, le pH passe à 1.3 (courbe B), et cette courbe se place entre celle de A et celle de C. C'est peut-être le composé $[Co(NH_3)_4(H_2O)OH]SO_4$ qui change en solution les mélanges $[Co(NH_3)_4(H_2O)Cl]SO_4$ et $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$. La solution alcaline ($p$H = 7.7) du sel $[Co(NH_3)_4(H_2O)Cl]SO_4$ montre que la courbe C′ est bien différente de la courbe B′ du $[Co(NH_3)_4(H_2O)OH]SO_4$ d'après leur position de la bande d'absorption. On ne peut donc pas admettre l'existence du $[Co(NH_3)_4(H_2O)OH]SO_4$ dans la solution aqueuse, pas plus que dans le cas du chlorure.



$[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ (1/500 mol)
A: pH = 6.5 A′: pH = 8.1

$[Co(NH_3)_4(H_2O)OH]SO_4$ (1/500 mol)
B: pH = 1.3 B′: pH = 8.1

$[Co(NH_3)_4(H_2O)Cl]SO_4$ (1/500 mol)
C: pH = 6.6 C′: pH = 7.7

Fig. 8.

Lorsque deux molécules d'eau se trouvent dans le radical complexe, le chlorure $[Co(NH_3)_4(H_2O)_2]Cl_3$ (fig. 5) voit seulement augmenter son pouvoir absorbant en solution alcaline, mais ne se transforme pas en sel

$[Co(NH_3)_4(H_2O)OH]Cl_2$ en solution. Cependant, ici, on voit la transformation du sulfate $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ en $[Co(NH_3)_4(H_2O)OH]SO_4$ en solution alcaline, et cela vient manifestment de ce que le radical complexe est influencé par l'ion négatif hors de ce radical. Cette différence entre le chlorure et le sulfate peut permettre au chlorure d'opérer la réaction $[Co(NH_3)_4(H_2O)_2]Cl_3 \rightleftarrows [Co(NH_3)_4(OH)_2] + 2HCl$, et au sulfate celle $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \rightleftarrows 2[Co(NH_3)_4(H_2O)OH]SO_4 + H_2SO_4$.

Résumé.

(1) Nous avons constaté que la concentration des ions d'hydrogène de la solution du lutéo ne peut pas être mesurée par l'électrode à hydrogène.

(2) Les sels qui n'ont pas de molécule d'eau de constitution comme les lutéo et purpuréo ne sont pas grandement influencés par la variation du *p*H.

(3) Aucun des complexes hydrines étudiés ne subit de grands changements dans ses courbes d'absorption quand sa solution est acide, c'est-à-dire lorsque son *p*H est inférieur à 7.

(4) Il semble que les molécules d'eau de constitution soient remplacées par le radical oxhydryle en solution alcaline quand le *p*H est supérieur à 7 et que l'oxyhydrile se change en sel hydrine lorsque le *p*H est inférieur à 7.

(5) La bande d'absorption du sel oxyhydrile se présente sur une longueur d'onde plus élevée que celle du complexe hydrine, et son pouvoir absorbant est aussi plus considérable.

(6) Le chlorure et le sulfate de $[Co(NH_3)_4(H_2O)_2]$ subissent des transformations différentes sous l'influence des changements du *p*H.

Nous tenons à exprimer nos sincères remerciements à la Société "Téjima Kogyô-Shikindan" pour l'aide bienveillante qu'elle a apportée aux présentes recherches.

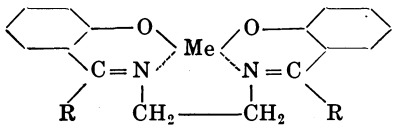
Laboratoire de Chimie minérale, Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku).

ÜBER EINIGE EISENVERBINDUNGEN MIT NEBENVALENZRINGEN.*

Von Tokuichi TSUMAKI.

Eingegangen am 3. Dezember, 1934. Ausgegeben am 28. Februar, 1935.

In einer Mitteilung von P. Pfeiffer, E. Breith, E. Lübbe und mir ist eine Untersuchung über die polycyclischen Nebenvalenzringverbindungen der nachstehenden allgemeinen Formel beschrieben[1].

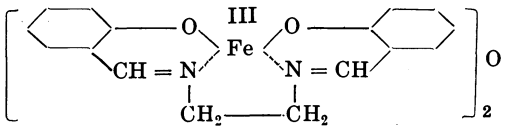


Die Verbindungen dieser Art entstehen entweder durch Einwirkung von Äthylendiamin auf die Metallsalze der *o*-Oxyaldehyde und *o*-Oxyketone oder aus den freien Oxyaldehyden und Oxyketonen mit Äthylendiamin und gewöhnlichen Metallsalzen.

Als Metalle, die die Stelle von Zentralatomen der Komplexen einnehmen, benutzten wir Mn, Fe, Co, Ni, Cu, Zn, Mg und Cd.

Vor allem interessierten mich die Verbindungen des Eisens wegen ihrer nahen Beziehung zu dem Blutfarbstoffe. In vorliegender Mitteilung berichte ich über die experimentellen Resultate meiner weiteren Untersuchungen über die *Eisen*-komplexverbindungen verschiedener Arten.

Bei der Einwirkung von Ferrosulfat auf Salicylaldehyd und Äthylendiamin erhielten wir, wie schon mitgeteilt, eine Komplexverbindung des 3-wertigen Eisens, d.h. Salicylaldehyd-äthylendiimin-ferrioxyd (1), welches in braunen Prismen krystallisiert.



(1)

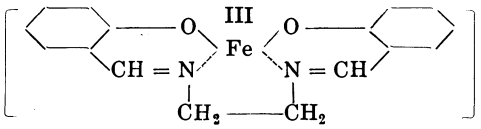
Die Verbindung hat Ähnlichkeit mit *Hämatin* in ihrer Konstitution und zwar in dem Bindungszustand des Eisens, welches die Stelle des

* Übersetzung einer Mitteilung, die in *J. Chem. Soc. Japan*, **55** (1934), 1245, auf Japanisch beschrieben.

(1) *Ann.*, **503** (1933), 84–130.

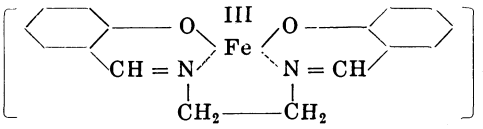
Zentralatoms des Komplexes einnimmt, und folglich in ihren Eigenschaften. Während man aber Hämatin als Hydroxyd eines Eisenkomplexes $(C_{34}H_{32}O_4N_4Fe)OH$ betrachtet, ist die Verbindung ein *Oxyd*.

Mit Säuren geht das Oxyd in Salze der allgemeinen Formel $(C_{16}H_{14}O_2N_2Fe)X$ über, von denen wir das Acetat, Benzoat, *d*-Campher-β-sulfonat und das mandelsaure Salz, vor allem aber aus dem Campher-sulfonat durch doppelten Umsatz mit Chlorammonium das *Chlorid* $(C_{16}H_{14}O_2N_2Fe)Cl$ (2) dargestellt haben. Das Chlorid ist dem *Hämin* an die Seite zu stellen.



(2)

Nun habe ich Ferrosulfat auf Salicylaldehyd und Äthylendiamin *in Pyridin* wirken lassen, um das Oxyd zu erhalten. Da habe ich im Gegensatz zu meiner Erwartung statt brauner Krystalle des Oxyds schwarzviolette Krystalle erhalten. Die Krystalle sind wenig löslich in Wasser mit rotvioletter Farbe, während das Oxyd in Wasser ganz unlöslich ist. Das Eisenatom in der Verbindung ist 3-wertig. Bei der Bildung dieser Verbindung findet also durch den Luftsauerstoff auch eine Oxydation des 2-wertigen Eisens zum 3-wertigen statt. Nach der Analyse und den Eigenschaften ist wahrscheinlich die Verbindung Salicylaldehyd-äthylendiimin-ferrihydroxyd mit 1/4 Mol. Pyridin (3), welches selbst bei 130° nicht abgegeben wird.



(3)

Löst man die Verbindung in heissem Pyridin und gibt man Alkohol und Äther dazu, so erhält man das Oxyd als braune Krystalle. Das Hydroxyd geht also in Pyridinlösung leicht in das Oxyd über. Nicht nur durch Pyridin sondern auch durch andere basische Substanzen z. B. Ammoniak, Natriumhydroxyd und Natriumbicarbonat wird das Hydroxyd in wässriger Lösung leicht in das Oxyd übergeführt.

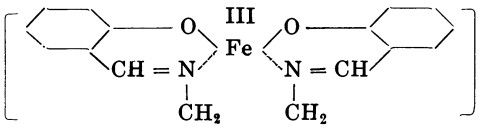
Löst man das Hydroxyd oder das Oxyd in verdünnter Schwefelsäure oder Essigsäure, so erhält man eine dunkelviolette Lösung wegen der Bildung von einem komplexen Sulfat oder Acetat[2]. Beim Zusatz von ver-

(2) *Ann.*, **503** (1933), 121.

dünnter Schwefelsäure tritt bald Entfärbung ein, weil das komplexe Sulfat weiter durch die Schwefelsäure zerfällt. Suspendiert man die Krystalle des Oxyds in Wasser und leitet man in die Lösung Kohlendioxydgas ein, so färbt sich die Lösung allmählich rotviolett wegen des Übergehens des Oxyds ins Hydroxyd.

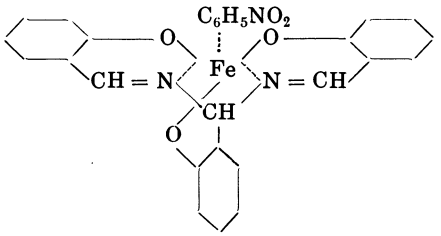
Die Ursache, dass das komplexe *Hydroxyd* bei der Einwirkung von Ferrosulfat auf Salicylaldehyd und Äthylendiamin in *Pyridin*-lösung dargestellt wurden, erblicke ich darin, dass die Pyridinlösung infolge der Schwefelsäure, welche durch Umsatzreaktion aus Ferrosulfat entstand, schwach sauer reagierte.

Um das Hydroxyd einmal umzukrystallisieren, löst man es in heissem Aceton, gibt dazu mit Kohlendioxyd gesättigtes Wasser und leitet Kohlendioxydgas ein. So erhält man violettbraune Krystalle des Salicylaldehyd-äthylendiimin-ferrihydroxyds, das 2 Mol. Wasser enthält, welche bei 140° nicht abgegeben werden (4).



(4)

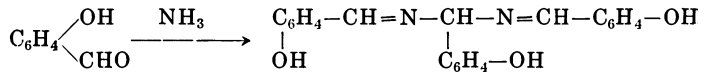
Lässt man nun auf eine Mischung von Salicylaldehyd und 25-proz. Ammoniak bei Wasserbadtemperatur Ferrosulfat einwirken, so erhält man uneinheitliche Krystalle, aus denen ich, wie weiter unten im experimentellen Teil angegeben, durch Behandlung mit Pyridin und Nitrobenzol fast schwarze Krystalle des Trisalicylaldehyd-diimin-eisens, welches 1 Mol. Nitrobenzol enthält (5), isolieren konnte.



(5)

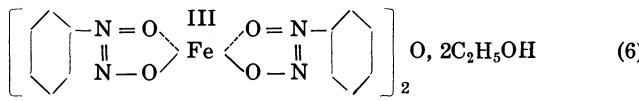
Die Verbindung enthält ein 3-wertiges Eisenatom; bei der Bildung der Verbindung findet also auch eine Oxydation des 2-wertigen Eisens zum 3-wertigen statt. Beim Erhitzen der Verbindung auf 150° wird 1 Mol. Nitrobenzol abgegeben; der Erhitzungsrückstand ist auch schwarzes Pulver.

Für die Entstehung des Trisalicylaldehyd-diimin-eisens aus Salicylaldehyd, Ammoniak und Ferrosalz findet man die einfache Erklärung in der Tatsache, dass die aromatischen Aldehyde mit Ammoniak die Hydrobenzamid-derivate bilden. Salicylaldehyd bildet also mit Ammoniak Hydrosalicylamid; das Trisalicylaldehyd-diimin-eisen ist das komplexe Eisensalz des Hydrosalicylamids[3].



Hydrosalicylamid.

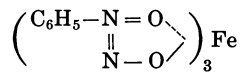
Weiter habe ich eine Reaktion zwischen Kupferron und Ferrosulfat in wässriger Lösung versucht. Bei der Mischung der beiden Verbindungen erhält man sofort einen rotbraunen Niederschlag, der in Chloroform gelöst und mit Alkohol und Wasser ausgefällt wird. So erhält man dunkelbraunrote Krystalle des Phenylnitrosohydroxylamin-ferrioxyds, welches 2 Mol. Äthylalkohol enthält (6). Die Verbindung gibt beim Erhitzen auf 110° leicht 2 Mol. Äthylalkohol ab und das alkoholfreie Oxyd zersetzt sich auch dabei gleichzeitig.



(6)

Die Verbindung eignet sich aber nicht zu weiteren Umsatzreaktionen.

Aus dem oben-erhaltenen Filtrat, aus dem die Krystalle des Phenylnitrosohydroxylamin-ferrioxyds gesondert wurden, habe ich nach Stehenlassen rotbraune Krystalle des schon bekannten Phenylnitrosohydroxylamin-eisens (7) erhalten[4].



(7)

Bei den Darstellungen der oben-angegebenen Verbindungen habe ich in allen Fällen als Ausgangsmaterial Ferrosulfat gebraucht und das Eisen in den erhaltenen Substanzen ist immer 3-wertig. Bei der Bildung der

(3) Vgl. Ettling, *Ann.*, **35**, 261; Delépine, Rivals, *Bull. soc. chim.*, (3) **21**, 943. Durch Fällung einer alkoholischen, mit Ammoniak versetzten Lösung von Hydrosalicylamid mit Ferrichlorid, dem vorher Ammoniak und Weinsäure zugesetzt sind, erhielt Ettling das Eisensalz des Salicylaldehydimids.

(4) O. Baudisch, *Chem. Zeit.*, **33** (1909), 1298; E. Bamberger und O. Baudisch, *Ber.*, **42** (1909), 3568.

Verbindungen findet also, weil sie an der Luft behandelt werden, eine Oxydation durch den Luftsauerstoff statt. Bei diesen Reaktionen erhalten wir 2 Typen der komplexen Ferri-verbindungen, d. h. $(>)_3Fe$ und $(>Fe<)_2O$. Die Hydroxyd-form $(>Fe<)OH$ wird auch erhalten, welche in alkalischer Lösung unbeständig ist und in die Oxyd-form $(>Fe<)_2O$ leicht übergeht.

Während man Hämatin als Hydroxyd eines Eisenkomplexes betrachtet und die Oxyd-form nicht bekannt ist, werden bei unseren einfachen komplexen Verbindungen 2 Formen, Hydroxyd-form und beständige Oxyd-form, erhalten. Es gibt natürlich in der Konstitution einen grossen Unterschied zwischen unseren Komplexsalzen und den Verbindungen der Blutfarbstoff-reihe, nämlich das Eisenatom in unseren Komplexsalzen knüpft sich an die 2 Stickstoffatome und 2 Sauerstoffatome, während das Eisen im Blutfarbstoffe an die 4 Stickstoffatome gebunden ist. Es ist aber merkwürdig, dass der Bindungszustand des Eisens, welches als das Zentralatom des Komplexes 2 Hauptvalenzen und 2 Nebenvalenzen hat, in beiden Verbindungsreihen ganz gleich ist und dass bei unseren Komplexverbindungen das hämin-artige Chlorid und das hämatin-artige Oxyd bzw. Hydroxyd erhalten wurden.

Beschreibung der Versuche.

(1) *Salicylaldehyd-äthylendiimin-ferrihydroxyd* $+2H_2O$. Ein Gemisch von 6 g. Salicylaldehyd und einer Lösung von 6 g. Ferrosulfat in 30 c.c. Wasser wird mit einer Lösung von 2 g. 50-proz. Äthylendiamin in 8 g. Pyridin verrührt. So erhält man eine schwarzbraune Lösung. Aus der Lösung scheiden sich allmählich schwarzviolette Krystalle aus, die abfiltriert und im Vakuum-exsikkator über konz. Schwefelsäure getrocknet werden. Ausbeute 5 g.

Die Krystalle sind löslich in verdünnter Schwefelsäure mit dunkelvioletter Farbe, die bald in Folge von Zersetzung verschwindet. Die Lösung gibt mit Rhodankalium eine blutrote Färbung. Das Eisenatom in dieser Verbindung ist 3-wertig. Die Analyse der bei 130° getrockneten Substanz stimmt auf die Formel $C_{16}H_{14}O_2N_2Fe\text{-}OH \cdot 1/4C_5H_5N$ (Salicylaldehyd-äthylendiimin-ferrihydroxyd+1/4 Pyridin). (Gefunden: N, 8.58, 8.82; Fe, 15.47. Berechnet für $C_{16}H_{14}O_2N_2Fe\text{-}OH \cdot 1/4C_5H_5N$: N, 8.79; Fe, 15.57%.)

Man löst die Verbindung in heissem Pyridin, filtriert und gibt zum Filtrat viel Alkohol und Äther hinzu. Nach Stehenlassen erhält man braune Krystalle, die abfiltriert, mit Alkohol gewaschen und im Vakuum über konzentrierter Schwefelsäure getrocknet werden.

Beim Erhitzen der Verbindung auf 130° trat kein Gewichtsverlust ein.

Die erhaltene Substanz war nicht das Hydroxyd, sondern Salicylaldehydäthylendiimin-ferrioxyd. Das Hydroxyd geht also in Pyridinlösung leicht in das Oxyd über. (Gefunden: N, 8.65; Fe, 16.78. Berechnet für $(C_{16}H_{14}O_2N_2Fe)_2O$: N, 8.49; Fe, 16.92%).

Die Krystalle des Hydroxyds sind löslich in Äthylalkohol, Chloroform, Pyridin und heissem Nitrobenzol, sehr wenig löslich in Benzol und fast unlöslich in Äther. Die Krystalle sind wenig löslich in Wasser mit rotvioletter Farbe. Gibt man zu dieser wässrigen Lösung eine basische Substanz, z. B. Natronlauge, Ammoniak, Pyridin oder Natriumbicarbonat, so verschwindet augenblicklich die rotviolette Farbe und fällt das Oxyd als gelbbrauner Niederschlag aus. Gibt man zu der Lösung verdünnte Schwefelsäure oder Essigsäure, so erhält man eine dunkelviolette Lösung wegen der Bildung von einem komplexen Sulfat oder Acetat. Bei Zusatz von verdünnter Schwefelsäure tritt bald Entfärbung ein, weil das komplexe Sulfat weiter durch die Schwefelsäure zersetzt wird.

Das Oxyd ist unlöslich in Wasser. Suspendiert man die Krystalle des Oxyds in Wasser und leitet man in die Lösung Kohlendioxydgas ein, so färbt sich die Lösung allmählich rotviolett, indem das Oxyd ins Hydroxyd übergeht.

Um das Hydroxyd einmal umzukrystallisieren löst man es in heissem Aceton, filtriert schnell die Lösung ab, gibt zum Filtrat viel mit Kohlendioxyd gesättigtes Wasser und leitet Kohlendioxydgas ein. Man filtriert die entstandenen Krystalle ab, die mit dem mit Kohlendioxyd gesättigten Wasser gewaschen und im Vakuum über konzentrierter Schwefelsäure getrocknet werden. Violettbraune Krystalle.

Beim Erhitzen der Verbindung auf 140° trat kein Gewichtsverlust ein.

Bei der Zersetzung der Verbindung mit Schwefelsäure, entsteht kein Kohlendioxyd; die Verbindung ist nicht das Carbonat. Rhodankalium färbt die Lösung blutrot; das Eisenatom in der Verbindung ist 3-wertig. Zersetzt man die Substanz mit rauchender Salpetersäure und gibt dazu Bariumchloridlösung, so erhält man keinen Niederschlag des Bariumsulfats; die Substanz enthält also kein Sulfat.

Die Verbindung zeigt die oben-beschriebenen Eigenschaften des Hydroxyds und nicht des Oxyds. Sie ist pyridinfrei. (Gefunden: N, 7.66, 7.70; Fe, 14.94, 14.92. Berechnet für $C_{16}H_{14}O_2N_2Fe\text{-}OH\cdot 2H_2O$: N, 7.47; Fe, 14.89%.)

(2) *Trisalicylaldehyd-diimin-eisen* + $C_6H_5NO_2$. Man erwärmt 4.9 g. Salicylaldehyd mit 13.6 g. 25-proz. Ammoniak und 200 c.c. Alkohol auf

dem Wasserbad und fügt eine Lösung von 5.6 g. Ferrosulfat in 100 c.c. Wasser hinzu. Es scheidet sich sofort ein rotbrauner Niederschlag aus, der nach dem Erwärmen auf dem Wasserbad abgesaugt und auf Ton an der Luft getrocknet wird. Man erwärmt den Niederschlag mit Pyridin und filtriert die dabei hinterbleibende mikrokrystalline schwarze Substanz ab. Aus dem Filtrat erhält man nach Zusatz von viel Alkohol, nach einigem Stehenlassen, auch etwas von derselben schwarzen Substanz. Die Substanz wird aus heissem Nitrobenzol umkrystallisiert, mit Alkohol gewaschen und im Vakuum über Chlorcalcium getrocknet. Fast schwarze Krystalle (Blättchen). Ausbeute 3 g.

Die Krystalle sind löslich in heissem Nitrobenzol mit schwarzbrauner Farbe, wenig löslich in Äthylalkohol, Chloroform und Pyridin und unlöslich in Äther. In Eisessig sind sie löslich; nach einigem Stehen aber zersetzt sich die Substanz.

Beim Erwärmen der Verbindung mit verdünnter Schwefelsäure zersetzt sie sich; die Lösung riecht nach Salicylaldehyd und Nitrobenzol. Die Lösung gibt mit Rhodankalium eine blutrote Färbung. Es ist also das Eisenatom in dieser Verbindung dreiwertig. Beim Erwärmen der Lösung nach dem Zusatz von Natronlauge riecht sie nach Ammoniak. Die Verbindung enthält 1 Mol. Nitrobenzol. (0.1003 g. Subst. gab bei 150° einen Gewichtsverlust von 0.0231 g. Gefunden: $C_6H_5NO_2$, 23.03. Berechnet für $C_{21}H_{15}O_3N_2Fe \cdot C_6H_5NO_2$: $C_6H_5NO_2$, 23.57%. Gefunden: N, 8.55, 8.53; Fe, 10.92. Berechnet für $C_{21}H_{15}O_3N_2Fe \cdot C_6H_5NO_2$: N, 8.05; Fe, 10.70%).

Der Erhitzungsrückstand (Nitrobenzolfreies Salz) ist auch schwarzes Pulver. Die Analyse stimmt gut auf die Formel des Trisalicyladehyddiimin-eisen-komplexsalzes (Gefunden: N, 7.06; Fe, 14.23. Berechnet für $C_{21}H_{15}O_3N_2Fe$: N, 7.02; Fe, 14.00%.)

(3) *Phenylnitrosohydroxylamin-ferrioxyd* + $2C_2H_5OH$. Man gibt zu eine Lösung von 10 g. Ferrosulfat in 100 c.c. Wasser eine Lösung von 10 g. Kupferron in 400 c.c. Wasser. So erhält man sofort einen braunroten Niederschlag, der abgesaugt und auf Ton an der Luft getrocknet wird. Man löst das erhaltene braune Pulver in wenig Chloroform, filtriert und gibt zum Filtrat Alkohol und Wasser. Es scheiden sich dann allmählich dunkelbraunrote Krystalle aus, die abfiltriert, zweimal aus Chloroform-Alkohol umkrystallisiert (in heissem Chloroform gelöst, mit Alkohol ausgefällt), mit Alkohol und dann Äther gewaschen und auf Ton an der Luft getrocknet werden. Glänzende dunkelbraune Krystalle. Ausbeute 1.2 g.

Die Krystalle sind leicht löslich in Chloroform, löslich in Pyridin, weniger löslich in Benzol und Eisessig, sehr wenig löslich in Äther und unlöslich in Äthylalkohol, Petroleumbenzin und Wasser. Beim Erhitzen

der Verbindung auf 110° ist keine Gewichtskonstanz zu erzielen; die Substanz zersetzt sich.

Die Analyse stimmt gut auf die Formel des Phenylnitrosohydroxylamin-ferrioxyds mit 2 Mol. Äthylalkohol. (Gefunden: C, 44.09, 43.82; H, 3.97, 4.18; N, 14.77, 14.71; Fe, 14.43, 14.52. Berechnet für $C_{24}H_{20}O_9N_8Fe \cdot 2C_2H_5OH$: C, 43.75; H, 4,20; N, 14.59; Fe, 14.54%.)

Bei der Zersetzung durch Erhitzen auf 110° gaben die Krystalle leicht den Krystall-alkohol ab, der in kaltes Wasser geleitet und durch Jodoformreaktion nachgewiesen wurde.

(4) *Phenylnitrosohydroxylamin-eisen.* Aus dem oben-erhaltenen Filtrat, das Chloroform, Alkohol und Wasser enthält, scheiden sich nach dem Stehen nach einigen Tagen glänzende rotbraune Tafeln aus, die zweimal aus heissem Alkohol umkrystallisiert und auf Ton an der Luft getrocknet werden. Ausbeute 1.5 g. Die Krystalle sind leicht löslich in Chloroform, Pyridin, Benzol und Äther, löslich in Eisessig, wenig löslich in Äthylalkohol und Petroleumbenzin und unlöslich in Wasser. (Gefunden: C, 45.80, 45.68; H, 3.60, 3.61; N, 17.61, 17.70; Fe, 12.06. Berechnet für $(C_6H_5O_2N_2)_3Fe$: C, 46.25; H, 3.24; N, 18.00; Fe, 11.96%.)

Man pulverisiert 1.5 g. von oben erhaltenem Phenylnitrosohydroxylamin-ferrioxyd und löst das Pulver in wenig heissem Eisessig. So erhält man eine weinrote Lösung. Wenn man die Lösung einige Minuten stehen lässt, verschwindet die Farbe der Lösung infolge der Zersetzung. Deshalb ist es nötig, sofort zu der Lösung viel Wasser zu geben, um die Zersetzung der entstandenen Substanz zu vermeiden. So erhält man einen braunen flockigen Niederschlag. Nach einigem Tage filtriert man den Niederschlag ab und löst ihn in wenig heissem Alkohol. Man filtriert die alkoholische Lösung ab, und zum Filtrat gibt man wenig Wasser und lässt die Lösung stehen. Man erhält rotbraune Tafeln, die noch einmal aus verdünntem Alkohol umkrystallisiert und im Vakuum-exsikkator über Chlorcalcium getrocknet werden. Ausbeute 0.65 g. Die Eigenschaften der Krystalle stimmen mit den bekannten Eigenschaften des Phenylnitrosohydroxylamineisens überein. (Gefunden: C, 45.84, 46.16; H, 3.64, 3.56; N, 17.86, 17.79; Fe, 12.31. Berechnet für $(C_6H_5O_2N_2)_3Fe$: C, 46.25; H, 3.24; N, 18.00; Fe, 11.96%.)

Osaka-Hochschule, Osaka.

ORGANIC SALTS CONTAINING IRON AND CALCIUM.

By Taichi HARADA.

Received December 22nd, 1934. Published February 28th, 1935.

Some years ago the author prepared the complex salts of organic compounds containing heavy metals, such as $[(CH_3)_3Sn]_2O(CH_3)_3SnX.\ H_2O$,[1] $[(CH_3)Sn]_2O{\cdot}HX.\ H_2O$,[1] and $X(CH_3)_3NCH_2CH_2SAg.AgX$.[2] At present, however, these compounds are not important from the physiological point of view. Present investigation on the preparation of the complex salts of organic compounds containing iron and calcium has been undertaken chiefly from the physiological as well as pharmaceutical ground.

Iron and calcium, especially the latter, are very important in regard to our daily life. The deficiencies of these elements cause various diseases such as anemia on one hand, and tetany, rickets, and others, on the other. The absorption of these elements by intestinal tract depends upon their solubility.[3] Among the organic compounds ferric citrate and calcium lactate are more easily absorbed through the intestinal mucosa than other iron and calcium compounds. However, these compounds are not like the inorganic compounds, they do not cause an acidosis or alkali deficit of the blood. It is presumed that the organic radicals are burned up in the body. On the other hand an inorganic compound, for example calcium chloride, causes acidosis by selective excretion but not selective absorption, according to the following reaction :

$$\underset{\text{(in the intestine)}}{CaCl_2} + 2NaHCO_3 = \underset{\text{(into the faces)}}{CaCO_3} + \underset{\text{(absorbed)}}{2NaCl} + H_2O + CO_2 .$$

Of course the equation affords the end result of the reaction involved in the body. That is, the part of the bicarbonate in the body is replaced by an equivalent amount of the chloride, indicated as NaCl in the equation, which is absorbed consequently causing alkali deficit.

Reaction between Ferric Citrate and Calcium Lactate. It appears that when one molecular proportion of calcium lactate is treated with one molecular proportion of ferric citrate in a solution, a salt-like compound is formed according to the following reaction :

$$Fe(C_6H_5O_7) + Ca(C_3H_5O_3)_2 + H_2O = Fe(C_6H_5O_7)Ca(OH)C_3H_5O_3 + C_3H_6O_3 .$$

The compound formed is very easily soluble in water compared with iron

(1) T. Harada, this Bulletin, **2** (1927), 105.
(2) This Bulletin, **4** (1929), 171 ; *ibid.*, **6** (1931), 25.
(3) H. S. Mitchell and L. Schmidt, *J. Biol. Chem.*, **70** (1926), 471 ; H. S. Mitchell and N. Vaughn, *ibid.*, **75** (1927), 123 ; A. M. Hjört, *ibid.*, **65** (1925), 783 ; E. H. Masson, *ibid.*, **47** (1921), 3.

citrate or calcium lactate. It has no definite melting nor decomposition point.

Experimental Part.

When calcium lactate (5 g.) was treated with iron citrate (5 g.) which was previously dissolved into about 20 c.c. of water by aid of heat, the colour of iron citrate was affected. The solution was filtered through filter paper, cooled down to about 50°C., then the compound formed was precipitated with four times by volume of 95% alcohol at about 50°C. Then the alcoholic solution was decanted.

The precipitated compound was a gummy greenish mass. For its purification the above process was repeated. Finally the gummy mass or its thick syrup was dried, or still better, scaled on a glass plate under 60°C. The yield was about 6 g. The salt thus prepared, when dried at 100°C. in open air, usually contains from 8 to 9 per cent. of water. The presence of water as the hydrate is suspected, It is a bright, shining, greenish substance and has no definite melting nor decomposition point. However, it slowly decomposes at above 150°C.

The aqueous solution of the above substance is slightly acidic. It was believed to be a definite compound of a type of a salt according to the following analytical results, and hence the reaction equation was formulated as described above.

When the substance was heated at above 100°C. in open dry air it probably changed into a lactone form. Thus:

$$Fe(C_6H_5O_7)Ca(OH)C_3H_5O_3 = Fe(C_6H_5O_7)CaC_3H_4O_3 + H_2O\,.$$

In regard to the definite structure of this compound, the author hopes to report later after further study on its physical properties has been made. (Found: Fe, 15.48, 15.24; Ca, 10.25 (Kramer-Tisdall), 10.59; lactic acid, 27.12 (Clausen), 24.95. Calc. for $FeCaC_9H_9O_{10}$: Fe, 14.98; Ca, 10.75; lactic acid, 24.14%.)

Summary.

One molecular proportion of calcium lactate appears to react with one molecular proportion of ferric citrate in aqueous solution, producing a salt-like substance having the formula, $FeCaC_9H_{11}O_{11}$, according to the following reaction:

$$Fe(C_6H_5O_7) + Ca(C_3H_5O_3)_2 + H_2O = Fe(C_6H_5O_7)Ca(OH)C_3H_5O_3 + C_3H_6O_3\,.$$

Yokohama, Kanagawa.

RECHERCHES SUR LA CONCENTRATION DES IONS D'HYDROGÈNE CONTENUS DANS LES SOLUTIONS AQUEUSES DES AMMINES-COBALTIQUES COMPLEXES ET SUR LEURS SPECTRES D'ABSORPTION.[1]

II.

Par Taku UÉMURA et Hidéo SUÉDA.

Reçu le 29 octobre 1934. Publié le 28 mars 1935.

Nous avons déjà publié les résultats de nos recherches sur l'hexammines, les pentammines et les tétrammines, résultats qui ont fait l'objet de notre précédent mémoire,[2] et maintenant nous allons étudier les sels triammines et quelques complexes polynucléaires ayant quelques relations avec ces triammines.

Les procédés expérimentaux que nous avons indiqués dans notre première publication[2] ont été également appliqués pour les sels ci-dessous nommés, à savoir :

(1) $[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis et trans)
(2) $[Co_2(NH_3)_6(OH)_3]Cl_3$
(3) $[Co(Co(NH_3)_4(OH)_2)_3]Cl_6$
(4) $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (bleu, gris et noir)
(5) $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$
(6) $[Co(NH_3)_3(H_2O)_2Cl]SO_4$ (violet et bleu-gris)
(7) $[Co(NH_3)_3(H_2O)Cl_2]SO_4H$

Relation entre le coefficient d'extinction et la longueur d'onde des solutions des sels complexes. (1) $[Co(NH_3)_3(H_2O)_3]Cl_3$, *Chlorure de triammoniotrihydrine cobaltique* (cis et trans). Le type cis de ce composé se formait d'après la méthode indiquée par Werner,[3] et son isomère trans par Matsuno.[4] Avec les deux corps obtenus, nous avons étudié la relation qui existe entre la longueur d'onde et le spectre d'absorption en faisant varier la valeur du *p*H, et nos résultats sont marqués dans les deux tableaux 1 et 2.

---

(1) Exposé fait lors de la 56e Séance annuelle de la Société chimique de Japon, le 6 avril 1934, à Osaka (Japon).

(2) Ce bulletin, **10** (1935), 50.

(3) A. Werner, *Ber.*, **39** (1906), 2678.

(4) K. Matsuno, *J. Coll. Sci. Imp. Univ. Tokyo*, **41** (1921), Art. 10.

Tableau 1.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis) à même concentration (1/2500 mol), pour des pH divers (cuve 50 mm.)

mμ \ pH	1.8	2.7	7.0	7.2	7.6	7.7	7.9	8.2
266	1.00	...	...	1.00	...	...	...	...
267	...	0.90	1.00	0.90	...	...	...	...
268	0.90	0.80	...	...	1.00	...	...	...
269	0.80	0.70	0.90	...	...	...	...	...
270	0.70	...	0.80	0.80	0.90	...	...	...
273	0.60	...	0.70	...	0.80	...	...	...
274	...	0.50	...	0.60	0.70	...	...	...
					275)			
276	0.50	...	0.60	...	...	...	...	...
277	...	0.45	...	0.50	0.60	...	...	...
279	0.40	0.40	0.45	0.45	...	1.00	...	...
	(280)							
281	...	0.35	0.40	0.40	0.50	0.90	...	...
				(282)				
285	0.35	...	0.35	0.35	0.45	0.80	...	...
	(284)			(284)				
289	0.30	0.30	0.30	...	0.40	0.70	...	...
		(288)	(290)			(288)		
293	0.25	0.25	0.25	0.25	0.35	0.50	...	...
		(292)		(292)				
297	...	0.20	0.20	0.20	0.30	0.45	...	...
				(296)		(296)		
303	...	0.15	...	0.15	0.25	0.35	...	...
				(304)				
308	...	...	0.15	...	...	0.25	...	...
						(309)		
313	0.10	...	...	0.10	...	...	...	...
319	...	...	...	...	...	0.20	...	...
328	...	...	...	...	...	...	1.00	...
338	...	...	...	...	...	...	0.80	...
345	...	...	...	...	...	...	0.60	...
352	...	...	...	0.10	0.20	...	...	...
					(354)			
357	...	...	...	...	...	0.20	0.60	...
							(356)	

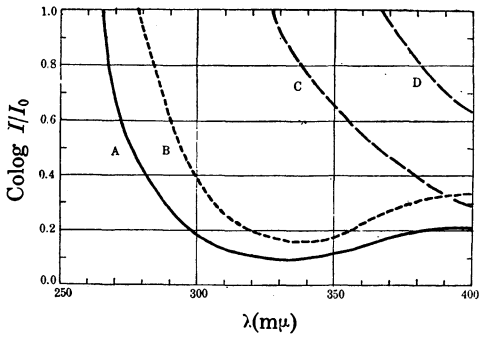
Tableau 1. (*fin*)

mμ \ *p*H	1.8	2.7	7.0	7.2	7.6	7.7	7.9	8.2
361	0.10	...	...	...	...	...	...	...
364	...	0.15	0.15 (365)	...	...	...	0.50 (363)	...
367	...	...	...	...	...	...	...	1.00
377	...	...	...	...	...	0.25	...	0.90
380	...	...	...	...	...	...	0.40	...
391	...	...	...	...	...	...	...	0.70
396	...	...	...	...	...	...	0.30	...
405	...	...	...	...	...	...	0.25	0.60
412	...	...	...	0.10	...	...	...	0.50 (414)
420	...	...	0.15 (421)	...	...	0.25	...	...
426	...	0.15	...	...	...	...	...	...
430	...	...	...	...	...	...	...	0.40
450	0.10	...	...	...	...	...	...	...

Tableau 2.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_3(H_2O)_3]Cl_3$ (trans) à même concentration (1/2500 mol), pour des *p*H divers (cuve 50 mm.)

Colog I/I_0	*p*H = 2.4	*p*H = 7.8	*p*H = 8.3		*p*H = 9.9		
1.00	287	284	283		287		
0.90	289	286	284		289		
0.80	292	288	285		291		
0.70	294	292	287		295		
0.60	298	294	289		298		
0.50	303	295	292		302		
0.45	306	298	295		307		
0.40	309	303	297		312		
0.35	313	308	301		320	353	378
0.30	316	313	306				398
0.25	319	318	313				411
0.20	326		319	354			
0.15	392			405			

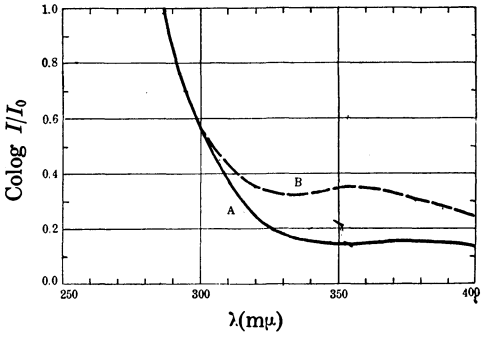


$[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis) (1/2500 mol)

A : pH = 2.7 B : pH = 7.7

C : pH = 7.9 D : pH = 8.2

Fig. 1.



$[Co(NH_3)_3(H_2O)_3]Cl_3$ (trans) (1/2500 mol)

A : pH = 2.4 B : pH = 9.9

Fig. 2.

Nous avons préparé la concentration de 1/2500 mol de ces deux complexes afin de pouvoir prendre la photographie d'absorption convenable.

Les deux figures 1 et 2 nous montrent que le type cis amène la fin des courbes d'absorption vers des longueurs d'onde plus élevées lorsque le pH augmente, surtout quand il atteint 7.9 ; tandis que l'isomère trans ne présente pas de grands changements dans le spectre d'absorption acide et alcaline.

(2) $[Co_2(NH_3)_6(OH)_3]Cl_3$, *Chlorure de triolhexammine dicobaltique* ; (3) $[Co(Co(NH_3)_4(OH)_2)_3]Cl_6$, *Chlorure de hexoldodécammine tétracobaltique.*

Tableau 3.

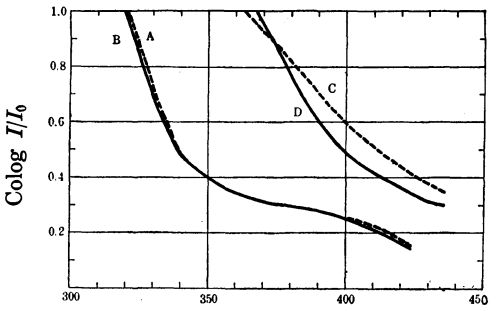
Absorption (Colog I/I_0) des solutions, pour des pH divers (cuve 50 mm.)

Colog I/I_0	$[Co_2(NH_3)_6(OH)_3]Cl_3$ (1/5000 mol)	
	pH = 2.2	pH = 8.0
1.00	321	320
0.90	325	323
0.80	328	326
0.70	331	330
0.60	334	334
0.50	340	339
0.45	343	343
0.40	351	350
0.35	359	358
0.30	377	375
0.25	405	400
0.20	418	410
0.15	424	424

Colog I/I_0	$[Co((OH)_2Co(NH_3)_4)_3]Cl_6$ (1/10000 mol)	
	pH = 2.3	pH = 8.2
1.00	363	366
0.90	374	372
0.80	383	380
0.70	392	383
0.60	399	390
0.50	...	398
0.45	417	403
0.40	425	410
0.35	436	422
0.30	...	433

D'après les indications de Birk,[5] les deux sels complexes se sont formés et ont la concentration 1/5000 mol du $[Co_2(NH_3)_6(OH)_3]Cl_3 \cdot H_2O$, et 1/10000 mol du $[Co(Co(NH_3)_4(OH)_2)_3]Cl_6$ pour étudier le spectre d'absorption en faisant varier la valeur du pH.

Les solutions aqueuses de ces sels sont faiblement alcalines, c'est-à-dire que le sel No. 2 présente un pH 8.0, et celui de No. 3 un pH 8.2; et les courbes d'absorption n'ont pas été influencées quand elles sont en solution acide. Ces résultats montrent une caractéristique des complexes polynucléaires que nous avons déjà signalée dans notre mémoire précédent, et qui les différencie grandement des autres cas généraux. Il semble que ces composés aient des radicaux OH de constitution qui n'ont pas été influencés par l'extérieur, comme pour les solutions acides.



$[Co_2(NH_3)_6(OH)_3]Cl_3$ (1/5000 mol)
A: pH = 2.2 B: pH = 8.0
$[Co(Co(NH_3)_4(OH)_2)_3]Cl_6$ (1/10000 mol)
C: pH = 2.3 D: pH = 8.2

Fig. 3.

(4) $[Co(NH_3)_3(H_2O)Cl_2]Cl$, *Chlorure de dichlorotriammoniohydrine cobaltique* (vert, gris et noir); (5) $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$, *Chlorure de chlorotriammoniodihydrine cobaltique.* Trois isomères du sel $[Co(NH_3)_3(H_2O)Cl_2]Cl$ se formaient suivant les indications de Jörgensen et Werner, et le sel $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$, d'après Werner.[6]

Tableau 4.

Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (vert) à même concentration 1/2500 mol pour des pH divers (cuve 50 mm.)

mμ \ pH	1.8	2.7	2.9	4.4	7.0	7.6	7.9	8.0	8.3
276	1.00	1.00	0.90	...	...	...	...	...	...
278	0.90	0.90	...	1.00	1.00	...	...	...	...
279	...	0.80	...	0.90	0.90	...	. .	...	...
280	0.80	0.70	0.70	...	0.80	1.00	...	...	...
283	0.70	...	...	0.70	...	...	...	. .	...

(5) Birk, *Z. anorg. Chem.*, **175** (1928), 411.
(6) S. M. Jörgensen, *Z. anorg. Chem.*, **14** (1897), 418; **17** (1898), 475. A. Werner, *Z. anorg. Chem.*, **15** (1897), 157.

Tableau 4. (*fin*)

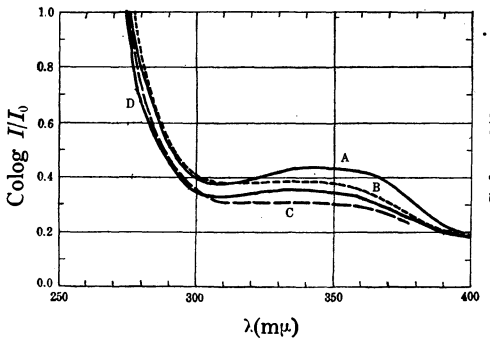
mμ \ *p*H	1.8	2.7	2.9	4.4	7.0	7.6	7.9	8.0	8.3
284	...	...	...	...	0.70	0.90	...	...	...
286	0.60	0.60	0.50	...	0.60	0.80	1.00	...	...
	(287)	(285)			(287)	(285)			
290	...	0.50	0.45	...	...	0.70	0.90	...	...
		(291)							
292	...	...	...	0.50	0.50	...	...	...	...
294	0.50	0.45	0.40	...	...	0.60	0.80	...	...
296	0.45	...	0.35	0.45	0.45	...	...	...	...
301	...	0.40	...	0.40	...	0.50	...	...	...
307	0.40	...	...	...	...	...	0.70	...	...
322	...	...	...	...	...	...	...	1.00	...
324	...	...	0.35	..	...	...	...	...	...
326	...	0.40	...	..	...	...	...	...	...
329	...	...	...	...	...	...	0.60	...	...
343	...	...	...	...	...	...	...	0.80	...
349	...	...	...	...	...	...	0.50	...	...
254	...	...	...	..	...	0.40	...	...	...
361	...	0.40	0.35	...	...	...	...	...	...
364	...	...	...	...	...	0.35	...	0.60	...
366	0.35	0.35	0.30	0.35	...	0.30	0.40	...	...
		(367)	(368)	(365)		(367)			
370	0.30	...	...	0.30	0.30	...	0.35	...	...
375	...	...	0.25	0.25	...	...	0.30	...	...
							(374)		
378	0.25	0.30	...	...	0.25	0.25	...	...	...
	(377)					(377)			
381	...	...	0.20	...	...	...	0.25	...	...
			(382)						
384	0.20	...	...	...	..	...	...	0.40	...
391	...	...	...	...	...	0.20	...	0.35	...
398	0.15	0.20	...	...	...	...	...	...	...
		(399)							
403	...	...	...	...	...	...	...	0.30	...
419	...	...	...	...	...	...	...	...	1.00
426	...	...	...	...	...	...	...	...	0.90
432	...	...	...	...	...	...	...	0.20	...
436	...	...	...	...	...	...	...	...	0.80
450	...	...	...	...	...	...	...	...	0.70

Tableau 5.
Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (gris et noir) à même concentration (1/2500 mol) pour des pH divers (cuve 50 mm.)

Colog I/I_0	Sel gris							Sel noir
	pH = 2.3				pH = 6.9			pH = 6.2
1.00	274				275			275
0.90	275				277			276
0.80	276				279			278
0.70	278				284			280
0.60	281				287			284
0.50	286				290			286
0.45	290				294			291
0.40	294	321	363		297	322	367	295
0.35			373				373	298
0.30			383				378	307
0.25			394	446			386	372
0.20							397	—

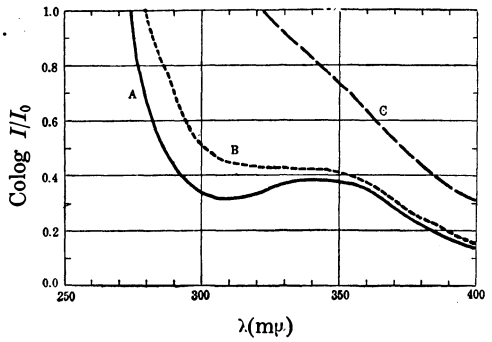
Tableau 6.
Absorption (Colog I/I_0) des solutions de $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ à même concentration (1/2500 mol) pour des pH divers (cuve 50 mm.)

Colog I/I_0	pH = 3.0			pH = 7.0			pH = 7.2		
1.00	...			274			277		
0.90	...			276			278		
0.80	275			277			280		
0.70	278			278			285		
0.60	285			280			286		
0.50	289			287			290		
0.45	292			290			293		
0.40	294	329	354	294			297		
0.35			360	297	332	344	304	332	350
0.30			373			366			365
0.25			378			376			378
0.20			385			390			397
0.15			396			420			421



$[Co(NH_3)_3(H_2O)Cl_2]Cl$ (1/2500 mol)
(gris) A : pH = 6.9
(vert) B : pH = 7.0
(noir) C : pH = 6.2
$[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ (1/2500 mol)
D : pH = 7.0

Fig. 4.



$[Co(NH_3)_3(H_2O)Cl_2]Cl$ (vert) (1/2500 mol)
A : pH = 2.9
B : pH = 7.6
C : pH = 8.0

Fig. 5.

Nous avons pris des solutions de même concentration 1/2500 mol pour ces quatre corps, et la figure 4 met en comparaison les courbes d'absorption de ces quatre composés.

Le sel vert de la figure 5, comme les autres, présente sa variation de fin des courbes d'absorption vers des longueurs d'onde plus grandes lorsque le pH augmente. La courbe C de la figure 5 ressemble par sa forme à la courbe C du sel $[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis) (fig. 1), et cela vient peut-être de ce que ces deux complexes se trouvent semblablement dans la solution alcaline. Il y a encore de l'analogie entre ces courbes et les courbes A et B (fig. 3) du sel $[Co_2(NH_3)_6(OH)_3]Cl_3$; entre la courbe D (fig. 1) du composé $[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis) et la courbe C (fig. 3) du sel $[Co(Co(NH_3)_4(OH)_2)_3]Cl_6$.

D'après toutes ces analogies de courbes, il semble qu'on puisse conclure que les complexes triammines cobaltiques se changent en $[Co_2(NH_3)_6(OH)_3]Cl_3$ ou en $[Co(Co(NH_3)_4(OH)_2)_3]Cl_6$ mis en solutions alcalines, question que plusieurs savants[7] ont déjà étudiée et pour laquelle ils ont obtenu des résultats identiques.

Puisque la figure 4 montre que les trois isomères des $[Co(NH_3)_3(H_2O)Cl_2]Cl$ et $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ présentent le même type à l'état de solution aqueuse, il n'y a presque pas de différence entre eux quand ils sont à l'état de solution, même si leurs couleurs varient lorsqu'ils sont à l'état solide.

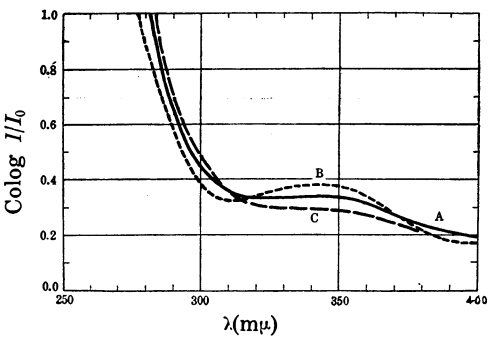
(7) J. Mayer, G. Dirska et F. Clemens, *Z. anorg. Chem.*, **139** (1924), 381.

Tableau 7.

Absorption (Colog I/I_0) des solutions à même concentration 1/2500 mol pour des pH divers (cuve 50 mm.)

Colog I/I_0	$[Co(NH_3)_3(H_2O)_2Cl]SO_4$					$[Co(NH_3)_3(H_2O)Cl_2]SO_4H$
	Sel violet pH = 2.4	Sel bleu-gris pH = 7.6				pH = 2.1
1.00	282	277				284
0.90	284	279				285
0.80	285	283				287
0.70	288	286				291
0.60	292	290				294
0.50	296	293				...
0.45	299	295				303
0.40	305	297				307
0.35	310	302	323	360		310
0.30	364			366		324
0.25	376			373		368
0.20	393			382	451	383

(6) $[Co(NH_3)_3(H_2O)_2Cl]SO_4$, *Sulfate de chlorotriammoniodihydrine cobaltique* (violet et bleu-gris); (7) $[Co(NH_3)_3(H_2O)Cl_2]SO_4H$, *Sulfate acide de dichlorotriammoniohydrine cobaltique.* Deux isomères du $[Co(NH_3)_3(H_2O)_2Cl]SO_4$ et de sel $[Co(NH_3)_3(H_2O)Cl_2]SO_4H$ ont été préparés d'après Werner[8] et étudiés d'après les relations qui existent entre la longueur d'onde et le Colog I/I_0 à l'état de solutions aqueuses de même concentration 1/2500 mol. Nous en avons dessiné la figure 6 en nous servant du tableau 7. En comparant cette figure 6 avec la figure 4, nous voyons que les résultats obtenus ont de grandes analogies entre eux. Parmi ces composés étudiés, puisque le sel



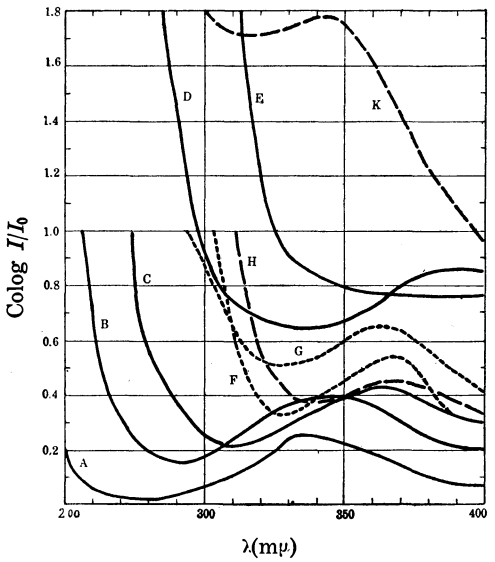
$[Co(NH_3)_3(H_2O)_2Cl]SO_4$ (1/2500 mol)
(violet) A : pH = 2.4
(bleu-gris) B : pH = 7.6
$[Co(NH_3)_3(H_2O)Cl_2]SO_4H$ (1/2500 mol)
C : pH = 2.1

Fig. 6.

(8) A. Werner, *Z. anorg. Chem.*, **15** (1897), 153, 156, 158.

$[Co(NH_3)_3(H_2O)_2Cl]X_2$ seul ne subit aucun changement dans sa couleur soit à l'état solide soit à l'état dissous, la courbe de la solution se présente donc comme celle du corps lui-même.[9]

Comparaison des courbes d'absorption des complexes étudiés. On peut comparer dans la figure 7 les courbes d'absorption des complexes contenus dans nos deux mémoires que nous avons tous calculés à un même degré de concentration 1/5000 mol et sur un *p*H stable. Les courbes A—E représentent des chlorures qui se différencient les uns des autres par une molécule d'eau.



A : $[Co(NH_3)_6]Cl_3$ *p*H = 6.7
B : $[Co(NH_3)_5(H_2O)]Cl_3$ *p*H = 7.1
C : $[Co(NH_3)_4(H_2O)_2]Cl_3$ *p*H = 6.7
D : $[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis) *p*H = 7.0
E : $[Co(NH_3)_3(H_2O)_3]Cl_3$ (trans) *p*H = 2.4
F : $[Co(NH_3)_5Cl]Cl_2$ *p*H = 7.0
G : $[Co(NH_3)_5OH]Cl_2$ *p*H = 8.0
H : $[Co(NH_3)_4(H_2O)Cl]Cl_2$ *p*H = 6.9
K : $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ *p*H = 7.2

Relation entre la longueur d'onde et Colog I/I_0 des chlorures des ammines-cobaltiques complexes (cuve 50 mm.)

Fig. 7.

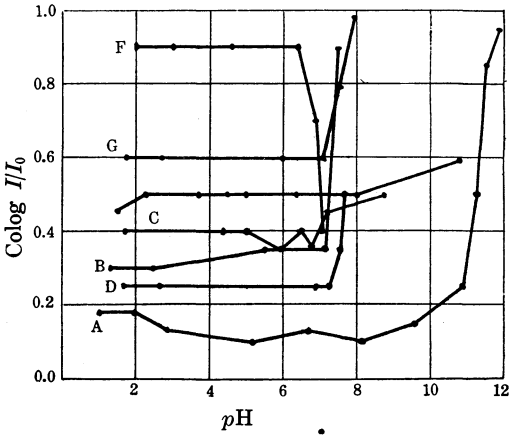
(9) Monsieur K. Matsuno, dans ses recherches sur le spectre d'absorption des complexes triammines cobaltiques (K. Matsuno, *loc. cit.*), a déjà publié qu'il a obtenu des résultats différents pour les deux complexes: $[Co(NH_3)_3(H_2O)Cl_2]Cl$ (vert) et $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$. Nos études sur le coefficient d'extinction de leurs solutions aqueuses cependant n'a pas réussi à trouver ces différences. Le sel vert se change tout de suite en bleu en le dissolvant, et après en rouge-violet. Les complexes bleu-gris et gris voient aussi leur couleur passer rapidement au rouge-violet. Le complexe $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ seul se dissout en rouge-violet, même couleur que le corps solide. Nous avons étudié toutes les solutions rouge-violettes, et avons obtenu des résultats semblables, on peut donc conclure avec certitude que ces complexes ont la même constitution chimique en solution aqueuse.

Leur fin des courbes d'absorption et leur bande d'absorption passent vers une longueur d'onde plus élevée quand le nombre des molécules d'eau dans le radical complexe augmente et accroît du même coup le pouvoir absorbant. Des influences semblables sont aussi observées en comparant entre eux ; les sels $[Co(NH_3)_5(H_2O)]Cl_3$ (B), $[Co(NH_3)_5Cl]Cl_2$ (F) et $[Co(NH_3)_5OH]Cl_2$ (G) ; ou $[Co(NH_3)_4(H_2O)_2]Cl_3$ (C) et $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (H) ; cela se produit lorsqu'on remplace la molécule H_2O dans le radical complexe par OH ou Cl. Cependant, en comparant les deux sels $[Co(NH_3)_5Cl]Cl_2$ (F) et $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (H), on remarque que le pouvoir absorbant du sel F est inférieur à celui de H, mais que la position de sa bande d'absorption sélective occupe une longueur d'onde plus élevée. Cela vient peut-être de ce que le radical Cl qui existe dans le radical complexe exerce une influence par suite de la substitution de NH_3 dans le composé F à une molécule d'eau. On n'a pas encore étudié la bande d'absorption du sel $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ (K) (centre : 340 mμ) correspondant à celle du sel $[Co(NH_3)_3(H_2O)_3]Cl_3$ (centre : 400 mμ). Il est nécessaire d'étudier d'abord plus attentivement le sel K dans son spectre d'absorption, sur une longueur d'onde plus grande pour pouvoir discuter la question en détail.

En tout cas, les résultats que Luther et Colmar[10] ont obtenus et les conclusions qu'ils ont tirées concernant les déplacements des absorptions des bandes visibles sont qualitativement identiques à ceux présentés par nos recherches de la région ultra-violette. Nos résultats, cependant, ne donnent pas la proportion qui existe entre le nombre de substitution et le déplacement des bandes comme dans la région visible.

Relation entre le coefficient d'extinction et la concentration des ions d'hydrogène des sels complexes. La figure 8 montre la relation qui existe entre le coefficient d'extinction (Colog I/I_0) et le pH pour des chlorures à une longueur d'onde donnée. La valeur du pH qui donne lieu à ce changement remarquable se trouve vers 7, pour tous les chlorures, excepté pour le lutéo. Cela explique comment le coefficient d'extinction ne varie guère lorsqu'on est en présence d'un acide, mais change rapidement là où l'acidité passe à l'alcalinité. L'accroissement du coefficient d'extinction pour le chlorure lutéo se présente seulement quand la valeur du pH est supérieure à 10. Cela est probablement dû uniquement à la présence des molécules NH_3 avec le métal dans le radical complexe du sel lutéo. Parmi les chlorures trouvés dans nos deux mémoires, le complexe lutéo est donc le plus stable en solution alcaline.

(10) R. Luther et A. Nikolopulos, *Z. physik. Chem.*, **82** (1913), 36 ; R. I. Colmar et E. W. Schwartz, *J. Am. Chem. Soc.*, **54** (1928), 3209.



A : $[Co(NH_3)_6]Cl_3$ $\lambda = 270$ mμ
B : $[Co(NH_3)_5(H_2O)]Cl_3$ $\lambda = 267$ mμ
C : $[Co(NH_3)_4(H_2O)_2]Cl_3$ $\lambda = 341$ mμ
D : $[Co(NH_3)_3(H_2O)_3]Cl_3$ (cis) $\lambda = 293$ mμ
E : $[Co(NH_3)_5Cl]Cl_2$ $\lambda = 352$ mμ
F : $[Co(NH_3)_4(H_2O)Cl]Cl_2$ $\lambda = 317$ mμ
G : $[Co(NH_3)_3(H_2O)_2Cl]Cl_2$ $\lambda = 286$ mμ

Relation entre Colog I/I_0 et pH des solutions aqueuses des chlorures des ammines-cobaltiques complexes.

Fig. 8.

Résumé.

(1) Les triammines cobaltiques étudiés ne se présentent presque pas de changements dans leurs d'absorption en solution quand le pH est inférieur à 7, c'est-à-dire ne subissent pas d'influence du fait de la variation du pH dans les limites ci-dessus nommées. (Cette conclusion peut aussi s'appliquer aux complexes précédemment étudiés dans notre premier mémoire.)

(2) En solution pour un pH supérieur à 7, les triammines étudiés, excepté le sel hydrine (trans), indépendamment de l'existence du radical Cl dans leurs noyaux complexes, paraissent se changer en complexes polynucléaires où les atomes centraux sont reliés par des " ponts " OH, c'est-à-dire se change en sels triols. (Cette conclusion n'a pas pu s'appliquer à notre mémoire précédent.)

(3) Nous avons admis que le complexe dichloro-cobaltique se transforme en cobalti-chlorotriammoniodihydrine en solution aqueuse.

(4) Les complexes polynucléaires publiés dans ce mémoire ne sont guère influencés par la variation du pH en solution aqueuse. Leur absorption est plus forte que celle du complexe ordinaire, et la bande d'absorption ne peut être appréciée dans la région ultra-violette.

(5) Nous avons comparé les courbes d'absorption et observé les relations qui existent entre les valeurs des différents pH et les coefficients d'extinction des solutions pour tous les sels complexes contenus dans nos deux mémoires.

En terminant ce mémoire, nous tenons à exprimer notre vive reconnaissance à la Société " Téjima Kogyô-Shikindan " qui a bien voulu se charger d'une partie des frais de nos recherches.

Laboratoire de Chimie minérale, Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku).

ZUR KINETIK DER REAKTION ZWISCHEN HALOGENSAUERSTOFFSÄURE UND HALOGENWASSERSTOFFSÄURE.

Von J. HIRADE.

Eingegangen am 17. Dezember, 1934. Ausgegeben am 28. März, 1935.

Einleitung. Unter allen möglichen Reaktionen zwischen Halogensauerstoffsäuren vom Typus HXO_3 und Halogenwasserstoffsäuren vom Typus HY finden sich gegenwärtig noch fünf Reaktionsarten vor, welche kinetisch entweder bisher noch nicht studiert sind oder im Lichte der Veränderlichkeit der Aktivitätskoeffizienten der reagierenden Ionen einer experimentellen Revision bedürfen. Es sind nämlich die Reaktionen zwischen Bromsäure und Salzsäure, Chlorsäure und Bromwasserstoffsäure, Jodsäure und Salzsäure und Chlorsäure und Salzsäure. In der vorliegenden Arbeit beschäftige ich mich mit den kinetischen Untersuchungen über die eben genannten Reaktionen, um den Mechanismus jedes studierten chemischen Vorganges klarzulegen und somit eine Übersicht betreffend die Kinetik der sämtlichen Reaktionsarten erhalten zu können.

Es ist seit Brönsted[1] eine schon allgemein anerkannte Folgerung, dass in einer konzentrierten, indifferenten Salzlösung als Lösungsmittel die Aktivitätskoeffizienten der anwesenden Ionen überhaupt unverändert bleiben und hier das alte Konzentrationsmassenwirkungsgesetz seine Gültigkeit besitzt. Mein Versuchsprinzip besteht nun darin, die kinetischen Messungen in diesem Spezialfall Brönsteds auszuführen. Verändert man nämlich in einem bestimmten Elektrolytüberschuss, der die Konstanz der Aktivitätskoeffizienten der vorhandenen Ionen bedingen soll, die von vornherein zweckmässigerweise klein gewählte Konzentration einer der reagierenden Ionenarten wie c_1 und c_2 und misst man die zugehörigen Werte der Anfangsgeschwindigkeiten h_1 und h_2, so wäre dafür die klassische van't

(1) Brönsted, *Z. physik. Chem.*, **102** (1922), 169; Brönsted u. Pedersen, *Z. physik. Chem.*, **103** (1923), 307.

Hoffsche Formel vollkommen gültig und daher würde sich die gesuchte Reaktionsordnung (n) in bezug auf diese Ionenart sogleich wie folgt berechnen:

$$n = \frac{\log h_1 - \log h_2}{\log c_1 - \log c_2}.$$

Die Ermittlung der Anfangsgeschwindigkeiten der in Betracht kommenden Reaktionen hat sich aber als leicht zugänglich erwiesen, indem einerseits unter geeigneten Bedingungen die Reaktionsfortschreitung meist auf eine bequem messbare Stärke reguliert werden konnte und anderseits die Reaktionsprodukte stets diejenigen Halogene oder Halogenderivate waren, die sich durch Abführen leicht vom Reaktionsgemisch abtrennen liessen. Es wurde nunmehr sehr zweckmässig gefunden, die Luftdurchleitungsmethode von Luther und Mac Dougall[2] auch hier anzuwenden, damit die dabei fortgeführten leichtflüchtigen Reaktionsprodukte in eine geeignete Abfangslösung abgeleitet und dort jodometrisch bestimmt werden könnten. Zugleich erwies es sich im allgemeinen auch möglich, durch die fortwährende Beseitigung der Reaktionsprodukte die fast stets vorhandene Reversibilität der Reaktion praktisch vollständig zu unterdrücken.

Die Versuchsapparatur wurde im grossen und ganzen nach Luther und Mac Dougall konstruiert und sei in Fig. 1 schematisch dargestellt.

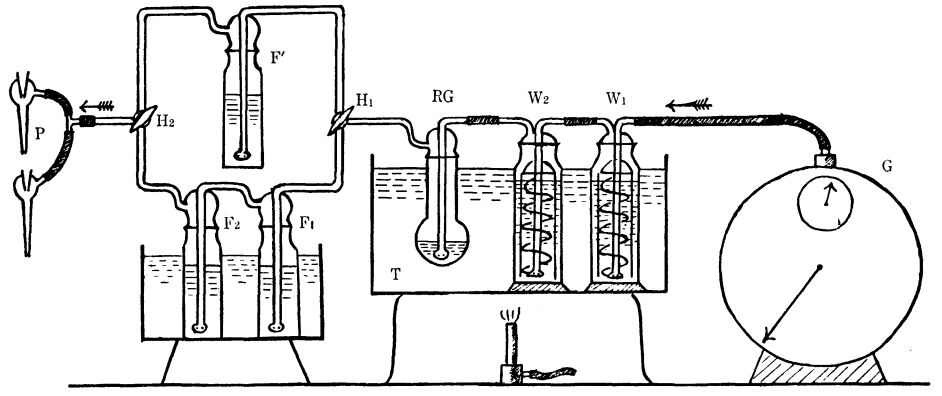


Fig. 1.

Sobald das Reaktionsgemisch im Reaktionsgefäss (RG) das Temperaturgleichgewicht erreicht hat, durchleitet man die event. vorher erwärmte Luft zuerst durch zwei Waschflaschen (W_1 und W_2), wodurch jene in genügendem Grade befeuchtet und erwärmt wird, und dann durch das Reaktionsgemisch. Während der ersten mehreren Minuten geschieht die

(2) Luther u. Mac Dougall, *Z. physik. Chem.*, **62** (1908), 199.

Durchlüftung, unter Vermeidung der KJ-Vorlagen (F_1 und F_2), durch die Thiosulfatvorlage (F'), um die vorher stagnierten Reaktionsprodukte solange auszutreiben, bis im Reaktionsgemisch ein pseudostationärer Zustand erreicht wird. Alsdann schaltet man den Luftstrom mittels der Dreiweghähne (H_1 und H_2) in die KJ-Vorlagen um und die abgeführten Gase werden dort abgefangen. Die durchgeleitete Luft beträgt gewöhnlich 3 bis 5 Liter pro Minute. Nach einer bestimmten Zeit (gewöhnlich 5 bis 20 Minuten) werden die beiden Abfangslösungen zusammen mit einer N/50 Thiosulfatlösung titriert. In F_2 ist von vornherein eine bestimmte kleine Menge Thiosulfat vorhanden, welches dazu genügt, das Abfangen der Reaktionsprodukte zu vervollständigen. Schliesslich erwies sich die Volumänderung des Reaktionsgemisches infolge der Abdunstung oder der Kondensation der Wasserdämpfe bei 30° bis 40° als ganz unbedeutend, und nur bei höheren Temperaturen (bei der Reaktion zwischen Jodsäure und Salzsäure z. B.) erschien eine besondere Rücksicht auf derartigen Einfluss nötig.

In den folgenden Abschnitten sollen die kinetischen Versuchsresultate über die mehreren von mir studierten Reaktionen kurz zusammengefasst erwähnt werden.

I. Die Reaktion zwischen Bromsäure und Salzsäure. Die kinetischen Untersuchungen bezüglich der $HBrO_3$-HCl-Reaktion wurden nach dem Brönstedschen Prinzip in 1 molarer $NaNO_3$-Lösung ausgeführt. In den Tabellen 1 bis 3 sind die Versuchsresultate zusammengestellt (Temp. 30°C.,

Tabelle 1.
Ordnung in bezug auf BrO_3'.

$(NaNO_3)$	(HCl)	$(KBrO_3)$	h	n
1.00	0.144	0.04	0.280	
1.00	0.144	0.02	0.140	1
1.00	0.144	0.01	0.070	

Tabelle 2.
Ordnung in bezug auf Cl'.

$(NaNO_3)$	$(KBrO_3)$	(H_2SO_4)	(KCl)	h	n
1.00	0.04	0.144	0.2	0.968	
1.00	0.04	0.144	0.1	0.246	2
1.00	0.04	0.144	0.05	0.062	

Tabelle 3. Ordnung in bezug auf H'.

$(NaNO_3)$	$(KBrO_3)$	(KCl)	(HNO_3)	h	n
1.00	0.04	0.200	0.160	0.696	
1.00	0.04	0.200	0.080	0.174	2
1.00	0.04	0.200	0.040	0.044	
1.00	0.04	0.500	0.040	0.275	2
1.00	0.04	0.500	0.020	0.071	

Tot. Vol. 50 c.c.). Die Klammernausdrücke, ($KBrO_3$) z. B., beziehen sich immer auf analytische Konzentration in Mol pro Liter. Die Anfangsgeschwindigkeit h wird mit der minutlichen Jodausscheidung (d. h. Anzahl c c. der N/50 Thiosulfatlösung) in den KJ-Vorlagen bezeichnet. n bedeutet die berechnete Reaktionsordnung.

Aus den vorliegenden Tabellen ist die Reaktionsordnung in bezug auf BrO_3', Cl' bzw. $H^\cdot$ in ganz exakter Weise als 1,2 bzw. 2 festzustellen. Wir sehen, dass die Brönstedsche Theorie auch hier mit den Tatsachen schön übereinstimmt.

Für den primären, geschwindigkeitsbestimmenden Vorgang können wir daher schreiben:

$$BrO_3' + 2Cl' + 2H^\cdot \rightarrow BrO' + 2HClO\,.$$

Darauf folgen die praktisch momentan verlaufenden Reaktionen nach den Gleichungen:

$$H^\cdot + BrO' + HCl \rightarrow BrCl + H_2O\,, \quad \text{und} \quad 2HClO + 2HCl \rightarrow 2Cl_2 + 2H_2O\,.$$

Die Bruttogleichung lautet also:

$$HBrO_3 + 5HCl \rightarrow BrCl + 2Cl_2 + 3H_2O\,.$$

Die kinetische Gleichung ergibt sich wie folgt:

$$-\frac{d(BrO_3')}{dt} = kF\,(BrO_3')(Cl')^2(H^\cdot)^2\,,$$

wo k die Geschwindigkeitskonstante, F den kinetischen Aktivitätsfaktor bedeutet und kF sich aus den vorigen Tabellen gleich 1.1 bei 30°C. berechnet.

II. Die Reaktion zwischen Chlorsäure und Bromwasserstoffsäure. Aus Tabelle 4 bis 6 ist leicht ersichtlich, dass sich die Reaktionsordnung auch hier ganz einfach und exakt ermitteln lässt.

Die primäre Reaktion verläuft also nach der Gleichung:

$ClO_3' + Br' + 2H^\cdot (= HClO_3 + HBr) \rightarrow HClO_2 + HBrO$ langsam und messbar, worauf die sekundären Reaktionen nach:

$$HClO_2 + HBr \rightarrow HClO + HBrO\,,$$

$$HClO + HBr \rightarrow HCl + HBrO\,,$$

und $3HBrO + 3HBr \rightarrow 3Br_2 + 3H_2O$ praktisch momentan erfolgen.

Die kinetische Gleichung lautet:

$$-\frac{d(ClO_3')}{dt} = kF\ (ClO_3')(Br')(H^{\cdot})^2,$$

wo $kF = 6 \times 10^{-4}$ bei 40°C. ist.

Anhang. Kinetische Untersuchungen über eine eigentümliche, in Gegenwart von Schwefelsäure resp. von Phosphorsäure auftretende Nebenreaktion. Während sich, wie oben gezeigt, in salpetersauren Lösungen die Ordnung der $HClO_3$-HBr-Reaktion in ganz einfacher Weise feststellen liess, wurde dagegen in schwefelsauren und auch in phosphorsauren Medien gefunden, dass neben der Hauptreaktion eine eigentümliche, ebenfalls aber Br_2 liefernde Nebenreaktion simultan fortschreitet. Es wies zunächst nämlich in den beiden letzteren Medien der Einfluss der Bromidkonzentration auf die Br_2-Bildungsgeschwindigkeit, anstatt einer streng linearen Beziehung wie beim Chlorateinfluss, ein einander ganz ähnliches, ausgeprägt anomales Verhalten auf, wie es beispielsweise in Fig. 2 graphisch dargestellt ist. Wie daraus ersichtlich, verlaufen die (KBr)-h- Kurven zwar im Bereich der Bromidkonzentrationen über etwa 0.0125 Mol streng linear, von 0.006 Mol herab müssten sie aber mit starker Krümmung dem Anfangspunkt zulaufen, da bei (KBr) = 0 stets auch h praktisch gleich null erwiesen ist. Ein derartiger Zusammenhang zwischen h und (Br′) konnte auch in andern Fällen mit H_2SO_4- bzw. H_3PO_4-Zusätzen vielfach beobachtet werden, so dass es mir zweckmässig erschien, an jeder (KBr)-h-Kurve den geradlinig auf (Br′) = 0 extrapolierten h-Wert h_0 zu benennen und die quantitativen Eigenschaften des letzteren etwas eingehend zu untersuchen, weil dabei zu vermuten war, dass h_0 die Geschwindigkeit einer noch unbekannten Nebenreaktion darstellte.

Tabelle 4. Temp. 40°C.
Ordnung in bezug auf ClO_3'.

(KBr)	(HNO_3)	($KClO_3$)	h	n
0.800	0.796	0.100	0.498	
0.800	0.796	0.050	0.249	1
0.800	0.796	0.025	0.125	

Tabelle 5. Temp. 50°C.
Ordnung in bezug auf Br′.

($KClO_3$)	(HNO_3)	(KBr)	h	n
0.90	0.20	0.20	0.181	
0.90	0.20	0.10	0.089	1
0.90	0.20	0.05	0.044	

Tabelle 6. Temp. 50°C.
Ordnung in bezug auf H·.

($KClO_3$)	(KBr)	(HNO_3)	h	n
0.30	1.00	0.20	0.310	
0.30	1.00	0.10	0.080	2
0.30	1.00	0.05	0.020	

Nota. (i) Bei derartigen Kombinationen der Konzentrationen der Reaktanten und bei derartiger Trägheit der Reaktion scheint der Zusatz eines indifferenten Neutralsalzes so gut wie überflüssig, da es aus dem Gesichtspunkte der Ionenaktivitäten gleichgültig ist, ob die im konstanten Überschuss, sich befindlichen starken Elektrolyten an den chemischen Umsetzungen beteiligt sind oder nicht. (ii) Die Reversibilität ist hier als ganz unbedeutend erwiesen.

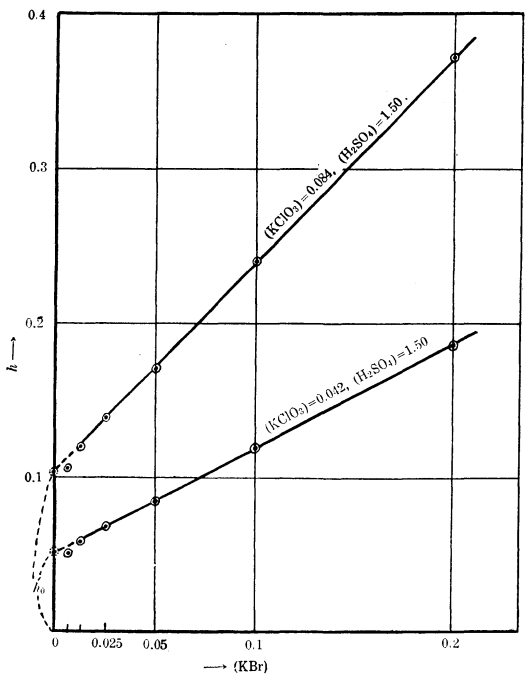


Fig. 2. Temp. 30°.

Um nun wirklich zu zeigen, dass die in schwefelsauren Medien z.B. gemessene Reaktionsgeschwindigkeit wirklich der Geschwindigkeitssumme der vorher untersuchten $HClO_3$-HBr- und unserer fraglichen Nebenreaktion entspricht, wurde zuerst zweckmässigerweise an der schon studierten $HBrO_3$-HCl-Reaktion, welche einen ähnlichen Reaktionstyp besitzt, festgestellt, dass 0.5000 morale Salpetersäure einerseits und 0.4570 molare Schwefelsäure anderseits einander gleiche kinetische Aktivität besitzen, wie in Tabelle 7 angegeben wird.

Es wurde alsdann in dem hier behandelten Fall die Reaktions- bzw. Brombildungsgeschwindigkeit für die beiden Säurearten unter variierten Bromidkonzentrationen gemessen.

Tabelle 7. Temp. 30°C.

Geschwindigkeit der $HBrO_3$-HCl-Reaktion.

$(KBrO_3)$	(KCl)	$(H^{\cdot})$	h
0.012	0.06	$(HNO_3) = 0.5000$	0.199
0.012	0.06	$(H_2SO_4) = 0.4570$	0.199

Tabelle 8. Temp. 40°C.

(Br')	h bei $(KClO_3) = 0.320$, $(HNO_3) = 0.5000$	h bei $(KClO_3) = 0.320$, $(H_2SO_4) = 0.4570$	Differenz
0.2	0.145	0.178	0.033
0.1	0.073	0.103	0.030
0.05	0.0365	0.067	0.030
		$h_0 = 0.030$	

Wie aus Tabelle 8 ersichtlich, erwies sich bei praktisch ungeänderter kinetischer Aktivität der Reaktanten die Geschwindigkeit in schwefelsauren Medien um einen konstanten und zwar derjenigen der vermutlichen Nebenreaktion h_0 exakt gleichen Betrag grösser als die in salpetersauren.

In phosphorsauren Medien machten sich ebenfalls ganz analoge Verhältnisse bemerkbar.

Ferner konnte das Jodid, so gut wie das Bromid, die fragliche Nebenreaktion herbeiführen; und die Tatsache, dass in diesen beiden Fällen unter sonst gleichen Versuchsbedingungen die Werte von h_0 miteinander praktisch übereinstimmten, machte es höchstwahrscheinlich, dass es sich hier um ein und dieselbe Reaktion handelt.

Die Temperaturabhängigkeit von h_0 in schwefelsauren Medien erwies sich übrigens gleich 3.0 für $\Delta t = 10°$.

Es muss auch hinzugefügt werden, dass ähnliche Untersuchungen aufs Auftreten von h_0 weiterhin in wässrigen Lösungen verschiedener ein- bis mehrbasischer organischer Säuren (Essigsäure, Oxalsäure, Malonsäure, Bernsteinsäure, Äpfelsäure, Zitronensäure, Weinsäure) ausgeführt wurden, jedoch stets mit negativem Resultate.

Handelt es sich nunmehr um den Einfluss der Konzentrationen der verschiedenen Reaktionskomponenten auf h_0 und h_0', so konnten in schwefelsauren so gut wie auch in phosphorsauren Medien folgende Tatsachengruppen konstatiert werden.

1. Die Reaktionsfortschreitung hat zwar das Vorhandensein von Br' notwendig, bleibt aber über gewisse kleine Br'-Konzentrationen von denselben unbeeinflusst (s. Fig. 2).

2. Wie auch h, ist h_0 bzw. h_0' an sich ebenfalls der Chloratkonzentration bzw.—aktivität proportional. Dies hat natürlich zur Folge gehabt, dass in solchen Medien die Chloratordnung der Hauptreaktion, wenn auch scheinbar, einfach gleich 1 ermittelt werden konnte (s. Fig. 2).

3. Der Effekt der Schwefelsäure- bzw. Phosphorsäurekonzentration auf h_0 bzw. h_0' erwies sich als stark vorhanden und desto stärker, je höher die Säurekonzentration. Es wurde daher zweckmässig gefunden, auf den Einfluss von $H^\cdot$ einerseits und auf denjenigen von Sulfation bzw. von Phosphorsäuremolekül getrennt zu untersuchen. Die Resultate sind in Tabelle 9 und 10 zusammengestellt. Berechnet man hieraus die Reaktionsordnung in bezug auf $H^\cdot$ und event. auch auf Sulfat bzw. (elektrisch neutrale) Phosphorsäure, indem man in Rechnung trägt, dass die Hauptreaktion ($= h - h_0$ bzw. $h - h_0'$), wie schon bewiesen, in bezug auf ClO_3', Br' bzw. $H^\cdot$ erster, erster bzw. zweiter Ordnung ist, so ergeben sich sowohl die Sulfat- als auch die Phosphorsäureordnung praktisch gleich 1, während die $H^\cdot$-Ordnung in schwefelsauren Medien beinahe gleich 1.8, in phosphorsauren 1.9 gefunden wurde (Tabelle 9 und 10).

Auf Grund der oben erwähnten Resultate können wir für die Geschwindigkeit der Nebenreaktion in schwefelsauren Medien

$$h_0 = k_0 F_0 (ClO_3')(Br')^0(SO_4'')(H^\cdot)^{1.8},$$

und für diejenige in phosphorsauren Medien

$$h_0' = k_0' F_0' \, (C\,O_3')(Br')^{\circ}(H_3PO_4)(H^{\cdot})^{1.9}$$

schreiben, wo k_0, k'_0 die zugehörigen Geschwindigkeitskonstanten und F_0, F_0' die zugehörigen kinetischen Aktivitätsfaktoren bedeuten. Aus Tab. 9 und 10 berechnen sich bei 40° $k_0F_0 = 3.7 \times 10^{-5}$ und $k_0'F_0' = 2.2 \times 10^{-5}$.

Tabelle 9. 40°C. Versuche in schwefelsauren Medien.

Nr.	1	2	3	4	5	6	7	8	9
($KClO_3$)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(HNO_3)	1.01	1.01	1.01	0.711	0.711	0.711	0.356	0.356	0.356
(Na_2SO_4)	0	0.106	0.212	0	0.101	0.202	0	0.101	0.202
h bei (KBr) = 0.2	1.18	1.00	0.820	0.488	0.380	0.294	0.0970	0.0596	0.0349
$h-h_0$,,		0.95	0.740		0.362	0.264		0.0563	0.0307
h bei (KBr) = 0.1	0.610	0.534	0.456	0.248	0.205	0.162	0.0493	0.0317	0.0198
$h-h_0$,,		0.484	0.376		0.187	0.132		0.0284	0.0156
h bei (KBr) = 0.05	0.310	0.292	0.268	0.126	0.1115	0.096	0.0247	0.0175	0.0120
$h-h_0$,,		0.242	0.188		0.0935	0.066		0.0142	0.0078
h_0	(0.010)	0.050	0.080	(0.003)	0.018	0.030	(0.0001)	0.0033	0.0042

Nota. Durch Sulfatzusätze vermindert sich in toto die Reaktionsgeschwindigkeit, da sie durch die Herabsetzung der $H^{\cdot}$-Aktivität stärker beeinflusst wird als durch die simultane Beteiligung der Nebenreaktion im entgegengesetzten Sinne.

Tabelle 10. 40°C. Versuche in phosphorsauren Medien.

Nr.	10	11	12	13	14	15	16	17	18
($KClO_3$)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(HNO_3)	0.721	0.721	0.721	0.505	0.505	0.505	0.253	0.253	0.253
(H_3PO_4)	0	0.45	0.90	0	0.45	0.90	0	0.45	0.90
h bei (KBr) = 0.2	0.505	0.706	1.013	0.214	0.312	0.468	0.0465	0.0808	0.145
$h-h_0'$,,		0.676	0.933		0.298	0.431		0.0763	0.134
h bei (KBr) = 0.1	0.259	0.372	0.550	0.108	0.162	0.253	0.0236	0.0427	0.0784
$h-h_0'$,,		0.342	0.470		0.148	0.216		0.0382	0.0672
h bei (KBr) = 0.05	0.130	0.201	0.315	0.054	0.088	0.145	0.0118	0.0236	0.0448
$h-h_0'$,,		0.171	0.235		0.074	0.108		0.0191	0.0336
h_0'	(0.001)	0.030	0.080	(0.000)	0.014	0.037	(0.0000)	0.0045	0.0112

Nota. Der Effekt der Phosphorsäure auf die Reaktionsfortschreitung besteht hier aus drei gleichsinnig befördernd wirkenden Faktoren, d. h. (i) Mediumwirkung der elektrisch neutralen Phosphorsäure, (ii) Beteiligung der fraglichen Nebenreaktion und (iii) Konzentrationserhöhung der $H^{\cdot}$-Ionen.

Handelt es sich schliesslich um Natur und Wesen solcher Nebenreaktionen, so ist man nach Ausschliessung mancher anderer Möglichkeiten zur folgenden wahrscheinlichsten Annahme geführt worden, welche meines Erachtens die beobachteten Tatsachen besser als irgendeine andere zu erklären vermag, obwohl kein direkter experimenteller Beweis für sie zu erbringen wäre.[3]

Es liegen nämlich in Gegenwart von Schwefelsäure bzw. Phosphorsäure die Oxydations-Reduktionsgleichgewichte nach den Formeln:

$$HClO_3 + H_2SO_4 \rightleftarrows HClO_2 + H_2SO_5$$

bzw. $$HClO_3 + H_3PO_4 \rightleftarrows HClO_2 + H_3PO_5$$

zugrunde, wo H_2SO_5 (Sulfomonopersäure) bzw. H_3PO_5 (Permonophosphorsäure) bekanntlich die höhere Oxydationsstufe der Schwefelsäure bzw. Phosphorsäure darstellt.

Diese reversiblen Gleichgewichte stellen sich, thermodynamisch den relativen Affinitäten der $HClO_3$-$HClO_2$- und der H_2SO_5- H_2SO_4- (bzw. H_3PO_5-H_3PO_4-) Systeme entsprechend, stark zugunsten der Reaktanten, d. h. der linken Seite der Reaktionsformeln ein,[4] auf Zusatz von Bromid (oder Jodid) aber, das mit den ganz spurweise vorhandenen Produktanten nach den Formeln:

$$HClO_2 + 4HBr \rightarrow HCl + 2Br_2 + 2H_2O\,,$$

$$H_2SO_5 + 2HBr \rightarrow H_2SO_4 + Br_2 + H_2O\,,$$

bzw. $$H_3PO_5 + 2HBr \rightarrow H_3PO_4 + Br_2 + H_2O$$

relativ sehr rasch zu Brom (oder Jod) reagieren, würde es gestört und mit einer praktisch konstanten Geschwindigkeit (h_0 bzw. h_0'!) fortwährend zugunsten der Produktanten verschoben. Die Bruttogleichung wäre somit dieselbe:

$$HClO_3 + 6HBr \rightarrow HCl + 3Br_2 + 3H_2O\,,$$

---

(3) So konnte etwa das Vorhandensein irgendeiner Chlorat reduzierender Verunreinigung in den verwendeten Schwefel- bzw. Phosphorsäurepräparaten zunächst sicher ausgeschlossen werden. Auf die Möglichkeit der Anwesenheit des Gleichgewichts etwa nach der Formel:

$$2HClO_3 \rightleftharpoons HClO_2 + HClO_4$$

wurde auch Verzicht geleistet, vor allem im Lichte der schon beobachteten Tatsache, dass in salpetersauren Medien mit genügender H^+-Aktivität solch eine Nebenreaktion in keinem messsbaren Grade fortschreitet.

(4) Bei gleichzeitiger Abwesenheit von Br' (oder J') wird aus solchen Gemischen erst nach langer Zeit spurweise Chlordioxyd entwickelt, was mit meiner Annahme im Einklang steht (sekundäre Bildung von ClO_2 aus $HClO_2$, siehe Abschnitt V.)

Tabelle 11.
Ordnung in bezug auf JO_3'. 30°C.

(KNO_3)	(KBr)	(HCl)	(KJO_3)	h	n
0.5	0.1	0.048	0.02	0.363	0.94
0.5	0.1	0.048	0.01	0.190	0.96
0.5	0.1	0.048	0.005	0.098	

Tabelle 12.
Ordnung in bezug auf Br'. 30°C.

(KNO_3)	(KJO_3)	(HCl)	(KBr)	h	n
0.5	0.01	0.096	0.05	0.325	1.93
0.5	0.01	0.096	0.025	0.085	
0.5	0.01	0.048	0.1	0.190	1.99
0.5	0.01	0.048	0.05	0.048	

Tabelle 13.
Ordnung in bezug auf $H^{\cdot}$. 30°C.

(KNO_3)	(KJO_3)	(KBr)	(HCl)[5]	h	n
0.5	0.01	0.05	0.096	0.325	2.76
0.5	0.01	0.05	0.048	0.048	
(KNO_3)	(KJO_3)	(KBr)	(HNO_3)[5]	h	n
0.5	0.01	0.1	0.048	0.188	2.80
0.5	0.01	0.1	0.024	0.027	

wie bei der schon studierten Hauptreaktion, jedoch mit dem charakteristischen Unterschied, dass hier einerseits die scheinbar indifferente Schwefelsäure bzw. Phosphorsäure in der Tat katalytisch befördernd einwirkt und dass anderseits das an der Reaktion mitbeteiligte Bromid (oder Jodid) die Reaktionsgeschwindigkeit überhaupt nicht beeinflussen kann. Wir sehen, dass diese Annahme mit den oben gewonnenen kinetischen Resultaten im ganzen schön übereinstimmt.

III. Die Reaktion zwischen Jodsäure und Bromwasserstoffsäure. Die kinetischen Messresultate bezüglich der HJO_3-HBr-Reaktion sind in Tabellen 11 bis 13 aufgestellt.

Nach diesen Ergebnissen ist die gefundene Reaktionsordnung in bezug auf JO_3', Br' und $H^{\cdot}$ wegen der sichergestellten, grösseren Reversibilität der primären Reaktion nach oben auf 1, 2 und 3 abzurunden. Wir haben hier also einen sehr merkwürdigen Reaktionsverlauf der sechsten Ordnung.

Der primäre, geschwindigkeitsbestimmende Vorgang lautet nämlich:

$$JO_3' + 2Br' + 3H^{\cdot} \rightarrow HJO + 2HBrO\,.$$

Darauf folgen praktisch momentan:

$$HJO + HBr \rightarrow BrJ + H_2O \text{ und } 2HBrO + 2HBr \rightarrow 2Br_2 + 2H_2O\,.$$

Die Bruttogleichung lautet daher wie folgt:

$$HJO_3 + 5HBr \rightarrow BrJ + 2Br_2 + 3H_2O\,.$$

(5) Da bei gleicher $H^{\cdot}$-Aktivität sowohl Salzsäure wie auch Salpetersäure gleichen h-Wert zeigten, so ist etwa die katalytische Beschleunigung durch Cl' gänzlich auszuschliessen.

Für die kinetische Gleichung ergibt sich :

$$-\frac{d(JO_3')}{dt} = kF(JO_3')(Br')^2(H^\cdot)^3,$$

wo sich $kF = 1 \times 10^3$ bei 30°C. berechnet.

IV. Die Reaktion zwischen Jodsäure und Salzsäure. Unter allen Reaktionen zwischen Halogensauerstoff- und Halogenwasserstoffsäuren findet die Reaktion zwischen Jodsäure und Salzsäure am schwierigsten statt. Damit sie merklich fortschreitet, muss sowohl die Temperatur wie auch die Konzentration der reagierenden Stoffe, insbesondere des Chlorids und der Säure, ziemlich hoch angestellt werden, wie man aus Tabellen 14 bis 18 an kinetischen Resultaten leicht entnehmen kann.

Tabelle 14.
Ordnung in bezug auf JO_3'. 60°C.

(HCl)	(KJO_3)	h	n
1.60	0.04	0.588	0.93
1.60	0.02	0.308	0.96
1.60	0.01	0.158	

Tabelle 15.
Ordnung in bezug auf Cl'. 60°C.

(KJO_3)	(H_2SO_4)	(KCl)	h	n
0.032	3.00	0.40	0.650	3.54
0.032	3.00	0.32	0.295	3.50
0.032	3.00	0.20	0.057	

Tabelle 16.
Ordnung in bezug auf Cl'. 55°C.

(KJO_3)	(H_2SO_4)	(KCl)	h	n
0.02	4.70	0.10	0.744	3.42
0.02	4.70	0.07	0.220	

Tabelle 17. 60°C.

(H_2SO_4)	(KJO_3)	(KCl)	h
2.8	0.16	0.2	0.132
2.8	0.01	0.4	0.150

Tabelle 18.
Ordnung in bezug auf H'. 70°C.

(KCl)	(KJO_3)	(HNO_3)	h	n
3.71	0.093	0.408	2.96	3.80
3.71	0.093	0.204	0.213	
4.20	0.074	0.160	0.176	3.64
4.20	0.074	0.112	0.048	

Nota. Bei solch höheren Temperaturen erwies sich der Einfluss der Kondensation der Wasserdämpfe im Reaktionsgemisch als nicht unbedeutend. Um ihn möglichst auszuschalten, versetzte man zweckmässigerweise das in zwei Waschflaschen enthaltene Wasser mit einer indifferenter Salzlösung geeigneter Konzentration.

Aus Tabelle 14 ist die Jodatordnung wegen der deutlich vorhandenen Reversibilität der Reaktion in üblicher Weise nach oben auf 1 abzurunden.

Wie man weiter an Tabelle 15 bis 18 sieht, erweist sich aber der Einfluss der Chlorid- und der Säurekonzentration als ganz auffallend gross. Die gefundene Ordnung ist nämlich in bezug auf Cl' 3.5, in bezug auf $H^{\cdot}$ 3.7 im Mittel. Unter Berücksichtigung der stärkeren Reversibilität aber können sie beide wohl je auf 4 abgerundet werden. In Ubereinstimmung hiermit belehrt beispielsweise die Tabelle 17, dass die Herabsetzung der Reaktionsgeschwindigkeit infolge der Halbierung der Cl'-Aktivität durch 2^4-fache Steigerung der JO_3'-Aktivität ungefähr auszugleichen ist. Somit scheint es sehr wahrscheinlich, dass die studierte Reaktion in bezug auf JO_3', Cl' und $H^{\cdot}$ respektiv 1ster, 4ter und 4ter Ordnung ist: ein meines Wissens noch nie beobachteter Fall der neunten Reaktionsordnung.

Für den wahrscheinlichen Reaktionsmechanismus können wir daher schreiben:

$$JO_3' + 4Cl' + 4H^{\cdot} \rightarrow JO' + 2Cl_2 + 2H_2O \text{ primär langsam,}$$

und sekundär: $JO' + 2H^{\cdot} + Cl' \rightarrow JCl + H_2O$ praktisch momentan.

Es wäre sehr merkwürdig, dass hier das Chlorion primär nicht wie üblich zu Hypochlorit, sondern zu Chlor oxydiert wird.
Die Geschwindigkeitsgleichung lautet folgendermassen:

$$-\frac{d(JO_3')}{dt} = kF\,(JO_3')(Cl')^4(H^{\cdot})^4,$$

wo $kF = 2.3 \times 10^{-5}$ bei (HCl) = 1.60, 60°C. ist.

V. Die Reaktion zwischen Chlorsäure und Salzsäure. Es ist eine altbekannte Tatsache, dass bei der Wechselwirkung von Chlorsäure und Salzsäure Chlor und Chlordioxyd nebeneinander entstehen. Die kinetischen Untersuchungen dieser Reaktion wurden schon im ersten Jahrzenhte dieses Jahrhunderts an Hand mancher Autoren ausgeführt, deren Ergebnisse jedoch einander ganz widerstreitend waren, etwa wie folgt:

Bray[6] nahm für die primäre Reaktion an:		$HClO_3 + HCl \rightarrow HClO_2 + HClO$.
Sand[7]	,,	$ClO_3' + 2HCl \rightarrow ClO' + 2HClO$.
Luther u. Mac Dougall[2]	,,	$2ClO_3' + 2Cl' + 4H^{\cdot} \rightarrow 2ClO_2 + Cl_2 + 2H_2O$.

(6) Bray, *J. Physic. Chem.*, **7** (1903), 92; *Z. physik. Chem.*, **54** (1906), 569, 731; *Z. anorg. Chem.*, **48** (1906), 217.

(7) Sand, *Z. physik. Chem.*, **50** (1904), 465.

Alle diese Schlussfolgerungen erweisen sich heute nicht nur im Lichte der Salzwirkungslehre nicht mehr als richtig, sondern auch vermögen sie nicht wenige beobachtete Tatsachen nur schwierig zu erklären. Ich habe mich daher mit einer experimentellen Revision derselben Reaktion beschäftigt, um den wahren Reaktionsmechanismus ans Licht bringen zu können, worüber im folgenden kurz besprochen werden soll.

1. *Jodometrische Bestimmung von Chlordioxyd neben Chlor.* Nach eigenen zahlreichen Messungen erwies sich bei reinem Chlordioxyd, das in (ca. 0.1 bis 0.2 normale) KJ-Vorlagen abgefangen und dort jodometrisch titriert wurde, das Titrationsverhältnis (= Titration total : Titration neutral) im Mittel gleich 4.62 ± 0.07 anstatt 4.80 nach Brays Daten.[6] Es erfordere nun ein beliebiges Gemisch von ClO_2 und Cl_2 jodometrisch bei neutraler Titration n, bei nachträglicher Titration N Äquivalenten, so berechnen sich, wie leicht ersichtlich, die ClO_2- und die Cl_2-Menge (in Molen) und das Molenverhältnis r wie in folgenden Formeln:

$$ClO_2 = \frac{N}{3.92}, \qquad Cl_2 = \frac{n - 0.276\,N}{2},$$

$$r = \frac{ClO_2}{Cl_2} = \frac{2}{3.92\,n/N - 1.08}.$$

2. *Kinetische Versuchsresultate.* Ungeachtet der etwaigen Kompliziertheit des Reaktionsmechanismus wurden zunächst nach dem schon wiederholt erwähnten Brönstedschen Prinzip orientierende kinetische Versuche angestellt, um die Reaktionsordnung in grossen Zügen ermitteln zu können. In den Tabellen 19 bis 23 sind die gewonnenen Resultate zusammengestellt.

Aus den Tabellen erhalten wir schon überhaupt den Eindruck, als ob die Reaktionsordnung nicht ohne weiteres festzustellen wäre. Aus Tabelle 19 bis 21 jedoch, wo die Chlorentwicklung das ganze Bild beherrscht, dürfen wir wenn auch vorläufig annehmen, dass die untersuchte Reaktion in bezug auf ClO_3' erster und in bezug auf $H^\cdot$ zweiter Ordnung wäre.

Die Resultate in Tab. 22 und 23 verraten uns dagegen einen weit komplizierteren Sachverhalt. Aus Tab. 22 (23) nämlich ist zu entnehmen, dass die Verdoppelung der Chloridkonzentration bzw. -aktivität (Chloratkonzentration bzw. -aktivität) die minutliche Jodausscheidung h 3—3.4 (2.1—2.2) fach vergrössert, dass aber das Verhältnis r relativ wenig beeinflusst (deutlich erhöht). Berechnet man nun aus Tab. 22 an h rein formal die Chloridordnung, so erweist sich diese im Mittel als 1.7. Wäre es aber berechtigt, sie nach Luther und Mac Dougall wegen der Reversibilität der Reaktion ohne weiteres auf 2 abzurunden? Sei dies einstweilen erlaubt, so würde

Tabelle 19. 40°C.

(HCl)	($KClO_3$)	h[8]	n
1.60	0.04	0.400	0.87
1.60	0.02	0.219	0.92
1.60	0.01	0.116	

Tabelle 20. 40°C.

(KCl)	(HCl)	($KClO_3$)	h[8]	n
2.80	0.40	0.096	0.168	1.0
2.80	0.40	0.048	0.084	

Tabelle 21. 45°C.

($KClO_3$)	(KCl)	(HNO_3)	h[8]	n
0.36	3.60	0.20	0.378	2.0
0.36	3.60	0.10	0.094	2.0
0.36	3.60	0.05	0.023	

Tabelle 22. 40°C.

($KClO_3$)	0.2	0.2	0.2
(H_2SO_4)	2.05	2.05	2.05
(KCl)	0.2	0.1	0.05
h	0.578	0.190	0.056
r	0.55	0.53	0.40
n in bez. auf Cl'	1.61	1.76	

Tabelle 23. 40°C.

(KCl)	0.2	0.2	0.2
(H_2SO_4)	2.05	2.05	2.05
($KClO_3$)	0.2	0.1	0.05
h	0.578	0.259	0.122
r	0.55	0.31	0.18
n in bez. auf ClO_3'	1.16	1.09	

hierfür das Sandsche Reaktionsschema gültig sein, oder d. h. es würde primär:

$$ClO_3' + 2H^{\cdot} + 2Cl' \rightarrow ClO' + 2HClO$$ langsam, messbar und sekundär:

$$ClO' + 2H^{\cdot} + Cl' \rightarrow Cl_2 + H_2O$$ und

$$2HClO + 2H^{\cdot} + 2Cl' \rightarrow 2Cl_2 + 2H_2O$$

praktisch momentan erfolgen. Diese Hypothese kann jedoch vor allem das konstante Auftreten von Chlordioxyd nicht erklären und weiteres Verweilen darüber lohnte nichts. So sind wir nunmehr zur andern Hypothese genötigt, nach der die Chloridordnung eine erste wäre. Für den primären Vorgang könnten wir sodann schreiben:

$$ClO_3' + Cl' + 2H^{\cdot} \rightarrow HClO_2 + HClO\,.$$

(8) In diesen Fällen erwies sich die nachträgliche Jodtitration immer als ziemlich klein gegen die neutrale Titration: d.h. die Jodausscheidung war praktisch lauter dem Chlor zuzuschreiben.

Dieses Reaktionsschema schliesst die Möglichkeit der ClO_2- neben Cl_2-Bildung nicht aus, da es schon von Bray[6] bewiesen steht, dass das Zusammenbringen der beiden hypothetischen primären Reaktionsprodukte momentan Chlordioxyd und Chlor liefert. Gestatten wir uns daher auch vorläufig diese Annahme der ersten Chloridordnung, so sind wir doch gar nicht in der Lage, die oben gewonnenen kinetischen Versuchsergebnisse auf Grund der bisherigen zum Teil nur qualitativen, zum Teil mehr provisorischen Kenntnisse früherer Forscher vollständig zu erklären. Deshalb musste ich unternehmen, über das Wesen der $HClO_2$-Zersetzung und der $HClO_2$-HClO-Reaktion unter verschiedenen Reaktionsbedingungen etwas gründlichere experimentelle Untersuchungen auszuführen. Im folgenden sollen diesbezügliche Resultate insoweit kurz berichtet werden, als sie zur Klarlegung des Mechanismus der in Frage stehenden Reaktion unerlässlich erscheinen.

3. *Experimente über die Zersetzung der chlorigen Säure.* (a) *Zersetzungskinetik der chlorigen Säure.* Die Geschwindigkeitsmessungen der Chlordioxydbildung (h) aus angesäuerter 0.015 molarer Chloritlösung bei 20°C. liessen, wie aus Tab. 24 ersichtlich, u. a. folgende Tatsachen konstatieren. Die Durchlüftungsmethode wurde wie üblich angewandt.

i. Das Titrationsverhältnis in KJ-Vorlagen erwies sich stets gleich 4.6 bis 4.7 und änderte sich selbst bei 2 molarer Chloridkonzentration nicht. Daraus ist zu schliessen, dass unter den angegebenen Bedingungen die Jodausscheidung praktisch lauter dem Chlordioxyd zuzuschreiben ist.

ii. Die Verdoppelung der Chlorigsäurekonzentration verdreifacht die Geschwindigkeit der ClO_2-Bildung (Nr. 1 und 2, Tabelle 24).

Tabelle 24. Temp. 20°C. Tot. Vol. 50 c.c.

Nr.	$(NaNO_3)$	$(HClO_2)$	(ClO_3')	(Cl')	(H^+)	h
1	1.00	0.01512	0.01538	0.000025	0.133	0.812
2	1.00	0.03024	0.03076	0.000050	0.116	2.30
3	1.00	0.01512	0.2154	0.000025	0.133	0.863
4	1.00	0.01512	0.3154	0.000025	0.283	0.897
5	1.00	0.01512	0.01538	0.000025	0.283	0.806
6	1.00	0.01512	0.01538	0.100	0.133	1.65
7	1.00	0.01512	0.01538	0.200	0.133	2.96
8	1.00	0.01512	0.01538	0.100	0.283	8.5

iii. Chloratzusätze bewirken überhaupt nur eine unbedeutende Beschleunigung der ClO_2-Bildung (Nr. 1, 3 und 4). Daraus ist zu schliessen, dass wenigstens der Hauptvorgang der ClO_2-Bildung nicht nach der

Oechslischen provisorischen Formel[9]: $HClO_3+HClO_2 \rightarrow 2ClO_2+H_2O$ auszudrücken wäre, da sonst die Erhöhung der Chloratkonzentration die ClO_2-Bildung in entsprechendem Masse beschleunigen müsste.

iv. Die Erhöhung der Chloridkonzentration verstärkt die Reaktion sehr bedeutend, kann dabei aber das Verhältnis r nicht in messbarem Grade beeinflussen (Nr. 1, 6 und 7).

v. Die Erhöhung der Azidität hat bei verschwindend kleinen Chloridkonzentrationen fast keinen Einfluss auf die Reaktionsgeschwindigkeit (Nr. 1 und 5), während sie über ein gewisses Bereich der Chloridkonzentration hinweg ausgeprägt beschleunigend wirkt (Nr. 6 und 8).

(b) *Analysenresultate an* $HClO_2$*-Zersetzung.* Es wurde der stoffliche Umsatz bei vollständiger Zersetzung von 0.09 molarer chloriger Säure bei 40°C. bei verschiedenen Salzsäurekonzentrationen analytisch bestimmt. Das Reaktionsgemisch wurde nämlich während des ganzen Reaktionsverlaufs durchlüftet und die entweichenden Gase wurden in KJ-Vorlagen abgefangen. Das Reaktionsrestgemisch wurde AgCl-gravimetrisch auf Chlorid- und durch Ferrosulfatreduktion auf Chloratgehalt gemessen. Die Resultate sind in folgender Tabelle zusammengestellt.

Tabelle 25. 40°C. Tot. Vol. 50 c.c. $(HClO_2) = 0.0907$.

Nr.	1	2	3
initial $HClO_2$	0.004536	0.004536	0.004536
,, ClO_3'	0.004614	0.004614	0.004614
,, Cl'	0.000008	0.001349	0.004926
,, (H^+)	0.214	0.214	0.723
Reaktionsdauer	2.5-3 Std.	$<$1.5 Std.	$<$10 Min.
Jodtitration (c.c. N/10 Thio.)	128.2	129.5	141.8
ClO_2 gebildet	0.002564	0.002590	0.002836
final ClO_3'	0.005713	0.005613	0.005266
,, Cl'	0.001176	0.002483	0.005965
ClO_3'-Zunahme (gebild.)	0.001099	0.000999	0.000652
Cl'-Zunahme (gebild.)	0.001168	0.001134	0.001039
$ClO_2 : HClO_2$	0.565	0.571	0.625
ClO_3'-Zun. : $HClO_2$	0.242	0.220	0.144
Cl'-Zun. : $HClO_2$	0.258	0.250	0.229

(Jede Stoffmenge ist in Moleinheiten ausgedrückt.)

Wie daraus ersichtlich, konnte die endgültige Bilanz der Umsätze durch folgende empirische Gleichungen ausgedrückt werden:

(9) Oechsli: *Z. Elektrochem.*, **9** (1903), 807.

Nr. 1: init. $(Cl') \fallingdotseq 0$, $(H^{\cdot}) = 0.2$:

$$HClO_2 = 0.565\ ClO_2 + 0.242\ HClO_3 + 0.258\ HCl \qquad (i),$$

Nr. 2: init. $(Cl') = 0.03$, $(H^{\cdot}) = 0.2$:

$$HClO_2 = 0.571\ ClO_2 + 0.220\ HClO_3 + 0.250\ HCl \qquad (ii),$$

Nr. 3: init. $(Cl') = 0.1$, $(H^{\cdot}) = 0.7$:

$$HClO_2 = 0.625\ ClO_2 + 0.144\ HClO_3 + 0.229\ HCl \qquad (iii).$$

Es entstehen also bei $HClO_2$-Zersetzung neben ClO_2 gleichzeitig stets Chlorsäure und Salzsäure. Während die Erhöhung der Salzsäurekonzentration die ClO_2-Bildung immer etwas verstärkt, vermindert sie dagegen die $HClO_3$- und die HCl-Bildung und zwar jene stärker als diese.

(c) *Erklärung über den Reaktionsmechanismus der* $HClO_2$*-Zersetzung.* Nach den obigen Resultaten muss man das Nebeneinanderlaufen von mindestens zwei bis drei Teilreaktionen annehmen. Aus (i) wäre zunächst zu ersehen, dass die Selbstzersetzung nach der folgenden stöchiometrischen Gleichung verläuft:

$$4HClO_2 \rightarrow 2ClO_2 + HCl + HClO_3 + H_2O \qquad (1).$$

Diese Reaktion wäre in zwei Stufen zu zerlegen, d. h. primär: $2HClO_2 \rightarrow HClO_3 + HClO$ (2) langsam, geschwindigkeitsbestimmend und sekundär: $2HClO_2 + HClO \rightarrow 2ClO_2 + HCl + H_2O$ (3) praktisch momentan. Neben diesem Selbstzersetzungsvorgang würde mit steigender HCl-Konzentration die Reaktion nach der Formel: $HClO_2 + HCl \rightarrow 2HClO$ (4), gefolgt ebenfalls von der ClO_2-Bildung nach (3), immer mehr in den Vordergrund treten (ii u. iii). Die Bruttogleichung dafür würde also lauten:

$5HClO_2 \rightarrow 4ClO_2 + HCl + 2H_2O$ (5). Ein durch HCl autokatalysierter Vorgang.

Es bleibt, wie später gezeigt wird, eine dritte Möglichkeit nach der Formel:

$HClO_2 + HClO \rightarrow HClO_3 + HCl$ (6) oder $3HClO_2 \rightarrow 2HClO_3 + HCl$ (6′)

noch übrig. Bei der beobachteten grossen $HClO_2$-Konzentration aber erwies sich die relative Teilnahme dieser Nebenreaktion als nicht sehr bedeutend. Jedenfalls sehen wir aber, dass die Annahme des Simultanverlaufs von (1), (5) und (6′) die Tatsachen wohl erklären kann.

Es ist weiterhin die schon gefundene Beschleunigung der ClO_2-Bildung durch Chloridzusätze hauptsächlich durch die verstärkte Teilnahme der Reaktion (5) leicht erklärlich.

Ferner wäre bemerkenswert, dass selbst bei höheren Salzsäurekonzentrationen praktisch keine Chlorbildung nach der Formel: $HClO + HCl \rightarrow$

Cl_2+H_2O (7)—eine an sich sehr rasch fortschreitende Reaktion!—beobachtet werden konnte. Es würde also die primär gebildete HClO mit der in noch grösserer Konzentration vorhandenen $HClO_2$ weit zu schnell nach (3) zu ClO_2 reagieren, als dass sie mit HCl nach (7) zu Cl_2 reagieren könnte.

4. *Experimente über die Reaktion zwischen chloriger Säure und unterchloriger Säure.* (a) *Analysenresultate an konzentrierteren Lösungen.* Wie schon von Bray qualitativ gezeigt wurde, werden bei der Wechselwirkung von $HClO_2$ und HClO im allgemeinen sehr rasch ClO_2 und Cl_2 entwickelt. In Tabelle 26 sind die Analysenresultate hierfür zusammengestellt.

Tabelle 26. Temp. 20°C. Tot. Vol. 50 c.c. $(H^{\cdot}) = 0.48$.
Durchlüftungsmethode.

Nr.	1	2
initial $HClO_2$	0.002268	0.001512
,, HClO	0.002066	0.002754
,, Cl'	0.008686	0.011579
ClO_2 gebildet	0.002079	0.001159
Cl_2 ,,	0.000810	0.001814
r	2.57	0.639
final Cl'	0.009153	0.010646
Cl' gebildet = Cl'-Zunahme + Cl_2	0.001277	0.000881
ClO_3' gebildet	0.000155	0.000379
Nach (6) verbrauchte $HClO_2$: $HClO_2-ClO_2$	0.000189	0.000353
,, ,, HClO : $HClO-(Cl_2+ClO_2/2)$	0.000216	0.000360
,, gebildete HCl : Cl' gebild $-ClO_2/2$	0.000237	0.000301

Wie hieraus ersichtlich, bemerkt man auch hier das konstante Auftreten von Chlorat und—die Abnahme durch Cl_2-Bildung nach (7) in Rechnung getragen—auch von Chlorid. Berechnet man nun nach den Formeln: $2HClO_2+HClO \rightarrow 2ClO_2+HCl+H_2O$ (3) und $HClO+HCl \rightarrow Cl_2+H_2O$ (7) den auf anderen Wegen als ClO_2- und Cl_2-Bildung erfolgten Umsatz der chloriger, unterchloriger Säure und Salzsäure, und vergleicht man solche Grössen miteinander und auch mit der beobachteten Chlorsäurebildung, so erweisen sich alle diese vier Zahlen einander beinahe gleich innerhalb der Versuchsfehlergrenzen. Somit ist die simultane Fortschreitung der Nebenreaktion nach dem Schema: $HClO_2+HClO \rightarrow HClO_3+HCl$ (6) neben der ClO_2-Bildung nach (3) bestätigt worden.

(b) *Die Reaktion zwischen* $HClO_2$ *und* HClO *in verdünnteren Lösungen.* Ich wandte mich nunmehr auf die wichtigere Aufgabe, zu studieren, welche

chemischen Veränderungen die einander äquimolekulare $HClO_2$ und HClO in sehr verdünnten Regionen erfahren, weil zu erwarten war, dass man hierdurch den Mechanismus der $HClO_3$-HCl-Reaktion klarlegen könnte. In Tabelle 27 sind Beispiele der diesbezüglichen Versuchsresultate unter denselben Reaktionsbedingungen, wie sie früher bei den kinetischen Untersuchungen angestellt wurden, zusammengestellt.

Tabelle 27. 40°C. Tot. Vol. 50 c.c. Durchlüftungsmethode.

Nr.	1	2	3	4	5	6	7	8	9
(H·)	$(H_2SO_4) = 2.05$							$(HNO_3) = 0.36$	
$HClO_2 \times 10^5$	4.85	4.85	2.42	2.42	2.42	1.21	1.21	2.42	1.21
$HClO \times 10^5$	4.88	4.88	4.88	2.44	2.44	1.22	1.22	2.44	1.22
(KCl)	0.1	0.05	0.1	0.1	0.05	0.1	0.05	2.80	2.80
$ClO_2 \times 10^5$	3.31	2.96	1.38	1.27	1.09	0.43	0.33	1.14	0.44
$Cl_2 \times 10^5$	1.83	1.65	3.23	0.83	0.67	0.50	0.43	3.72	2.33
r	1.81	1.80	0.43	1.53	1.62	0.86	0.78	0.31	0.19
j	0.694	0.622	0.687	0.551	0.466	0.433	0.347	0.901	0.945
u	0.01	0.01	0.01	0.03	0.02	0.08	0.07	0.43	0.58
p	0.53	0.45	0.41	0.37	0.30	0.24	0.17	0.70	0.76
q	0.37	0.33	0.66	0.32	0.27	0.36	0.31	0.82	0.89

Aus der Tabelle 27 sind folgende bedeutungsvolle Punkte zu entnehmen:

i. Das Verhältnis $ClO_2 : Cl_2$ (r) wird bei konstanter Säure- und Chloridkonzentration mit abnehmender $HClO_2$- bzw. HClO-Konzentration—und besonders deutlich bei relativ niederen Konzentrationen derselben—vermindert. Bei höheren Konzentrationen derselben nähert es sich dem Grenzwerte 2 an. Der Einfluss der Chloridkonzentration auf r ist weniger auspeprägt. Bei hoher Chloridkonzentration (Nr. 8 u. 9) aber wird r stark verkleinert, und zwar desto stärker, je kleiner die $HClO_2$- bzw. HClO-Konzentration ist.

ii. Der Mitbeteiligungsgrad u der Reaktion: $HClO_2 + HCl \rightarrow 2HClO$ (4) berechnet sich leicht: $u = \frac{\Delta}{HClO_2}$, wo $\Delta = \frac{1}{6}(2Cl_2 - ClO_2)$ ist und Δ speciell die Menge der nach (4) verbrauchten $HClO_2$ bedeutet. u ist zwar bei höheren $HClO_2$- bzw. HClO-Konzentrationen verschwindend klein (dementsprechend $r \doteqdot 2$), nimmt aber mit abnehmender Konzentration derselben, der Verkleinerung von r parallel, immer etwas zu. Bei hoher

Chloridkonzentration steigt es auch sehr beträchtlich an, und zwar auch hier desto stärker, je kleiner die $HClO_2$- bzw. HClO-Konzentration ist.

iii. Der "Jodausscheidungskoeffizient" j

$$= \frac{\text{Jodausscheidung in KJ-Vorlagen}}{\text{Jodtitration des initialen Reaktionsgemisches}} = \frac{5ClO_2+2Cl_2}{4HClO_2+2HClO}$$

ist für die Auseinandersetzung des Reaktionsmechanismus von grösster Bedeutung. Er geht mit $HClO_2$- bzw. HClO-Konzentration und bemerkenswürdigerweise auch mit der Chloridkonzentration parallel. Bei hoher Chloridkonzentration nähert er sich in bedeutendem Masse der Einheit und desto vollständiger, je kleiner die $HClO_2$- bzw. HClO-Konzentration ist.

iv. Der "ClO_2-Bildungskoeffizient" p, womit die relative Teilnahme der ClO_2 bildenden Reaktion (3) gegen die beiden Vorgänge der ClO_2- und ClO_3'-Bildung ((3)+(6)) bezeichnet werden soll, berechnet sich wie folgt: $p = \frac{1/2ClO_2}{(HClO+2J-Cl_2)}$. Gegen $HClO_2$- bzw. HClO- und auch Chloridkonzentration verhält er sich dem Jodausscheidungskoeffizienten ganz parallel. Der Vergleich von Nr. 3 mit Nr. 1 bzw. 4 belehrt aber, dass p weit stärker von der $HClO_2$-Konzentration abhängt als von der HClO-Konzentration. Dies stimmt molekularkinetisch mit den schon angeführten primären Reaktionsformeln (3) und (6) überein, nach denen die ClO_2-Bildung dem potenzierten Konzentrationsprodukte $(HClO_2)^2(HClO)$, die ClO'_3-Bildung dem $(HClO_2)(HClO)$ proportional schnell fortschreiten müsste.

v. Zuletzt soll mit dem "Cl_2-Bildungskoeffizienten" (q) gezeigt werden, welcher Bruchteil der gesamten (sowohl schon vorhandenen wie auch neugebildeten) HClO zu Cl_2 umgewandelt wird; es ist demnach $q = \frac{Cl_2}{HClO+2J}$. Dieser Koeffizient hängt zwar von der $HClO_2$- bzw. HClO-Konzentration wenig ab, wird aber mit zunehmender Chloridkonzentration immer etwas vergrössert und bei hoher Chloridkonzentration nähert er sich der Einheit ziemlich, und dies desto stärker, je niederer die $HClO_2$- bzw. HClO-Konzentration ist.

Auf Grund der oben gefundenen Tatsachen können wir schliessen, dass in einer sehr verdünnten (äquimolekularen) $HClO_2$-HClO-Lösung hauptsächlich vier Reaktionsarten nach den Formeln:

$$2HClO_2+HClO \rightarrow 2ClO_2+HCl+H_2O \quad (3),$$
$$HClO_2+HClO \rightarrow HClO_3+HCl \quad (6),$$
$$HClO+HCl \rightarrow Cl_2+H_2O \quad (7), \text{ und}$$
$$HClO_2+HCl_2 \rightarrow 2HClO \quad (4)$$

neben- und nacheinander auftreten. Die Intensität der einzelnen Prozesse aber hängt von der Konzentration aller Reaktionskomponenten so verschieden stark ab, dass unter variierten Bedingungen bald jene, bald diese Reaktion in den Vordergrund treten würde, wie man es schon in der vorigen Tabelle an r, j, p, q, u, etc. ersehen konnte.

5. *Erklärung der kinetischen Resultate der Chlorsäure-Salzsäure-Reaktion und Feststellung der fraglichen Reaktionsordnung.* Durch die vorhergehenden Untersuchungen bezüglich der $HClO_2$-HClO-Reaktion scheinen nun die weiteren Schicksale der hypothetischen primären Produkte der $HClO_3$-HCl-Reaktion beinahe klargelegt zu sein. Betrachten wir nämlich die früheren kinetischen Resultate über dieselbe Reaktion wieder. Wir sehen zunächst, dass die schon bewiesene, nicht jodausscheidende Reaktion:

$$HClO_2 + HClO \rightarrow HClO_3 + HCl \qquad (6)$$

keine andere als die Gegenreaktion des fraglichen primären Vorganges darstellt. Im Zusammenhang hiermit liesse sich die Ursache der schon beobachteten kinetischen Anomalien vor allem darin suchen, dass die unter jenen Bedingungen sehr bedeutend hohe Reversibilität der Reaktion durch die Konzentrationsänderungen der primären Reaktanten ganz eigentümlich verschieden stark beeinflusst würde. Da dieser Reversibilitätsgrad aber etwa durch $1-j$ (j: Jodausscheidungskoeffizient) ausdrückbar ist, so scheint j—und somit auch p—für die anomalen kinetischen Resultate das ausschlaggebendste zu sein. Vergleichen wir nun Tabelle 22 und 23 mit Tabelle 27, so erweist sich die sämtliche kinetische Kompliziertheit im Lichte der schon klargelegten Reaktionsmechanismen beinahe als leicht verständlich. So beeinflusst z. B. die Chloratkonzentration nur die Geschwindigkeit der primären Reaktion—und somit auch r, j, p, q, u, etc.—in entsprechendem Masse; alle sekundären Reaktionen aber bleiben dabei von ihrem direkten Einfluss verschont. Bei der Chloridkonzentration wäre es anders. Variiert man dieselbe, so wird dadurch nicht nur wie beim Chlorat die primäre, sondern auch fast alle sekundären Reaktionen beeinflusst, wie man aus dem schon beobachteten Parallelismus zwischen j, p, q, u, etc. einerseits und der Chloridkonzentration anderseits entnehmen kann. Dies hätte aber zur Folge, dass sich die unter solchen Bedingungen einfach berechnete Chloridordnung vom wahren Werte stark nach oben abweichend erwies. Somit findet die früher angenommene erste Chloridordnung hier eine experimentelle Bestätigung. Es scheint merkwürdig, dass hier ein kinetischer Sonderfall vorliegt, in dem grössere Reaktionsgeschwindigkeiten gerade mit kleinerer Reversibilität einhergehen.

Handelt es sich weiterhin um die kinetischen Resultate der Tabelle 19, 20 und 21, so wäre in diesen Fällen die Chloridkonzentration im Verhältnis

zu $HClO_2$- und HClO-Bildungsgeschwindigkeiten so übergross, dass praktisch die Chlorbildung nach: $HClO + HCl \rightarrow Cl_2 + H_2O$ (7) und nach: $HClO_2 + HCl \rightarrow 2HClO$ (4), gefolgt ebenfalls von (7), das ganze Reaktionsbild beherrschen würde, was aber nach den schon gefundenen Tatsachen (Nr. 8, 9 der Tabelle 27) mit Recht zu erwarten ist. Wir können nämlich sagen, dass unter solchen Reaktionsbedingungen die zur Erreichung der kinetisch günstigen Bedingungen notwendige, genügende Annäherung von j zu 1 in weit stärkerem Maszstabe durch die Erhöhung von u und q als durch diejenige von p verwirklicht wurde. Die hier gefundene (in bezug auf ClO_3' bzw. $H^\cdot$ 1ste bzw. 2te) Reaktionsordnung kann daher als richtig anerkannt werden. Es sei aber hinzugefügt, dass die Ermittlung der Chloridordnung unter solchen Bedingungen wegen des Hinzutretens der Neutralsalzwirkung nicht einwandfrei richtig ausgeführt werden konnte.

Tabelle 28. Versuche in Gegenwart von Br'. 40°C.

Nr.	1	2	3	4
($KClO_3$)	0.1	0.1	0.1	0.1
(HNO_3)	1.23	1.23	1.23	1.23
(KCl)	0.30	0	0.15	0
(KNO_3)	0	0.30	0	0.15
(KBr)	0.02	0.02	0.01	0.01
h	0.287	0.049	0.157	0.026

n in bezug auf $Cl' = 0.86$.

Es liessen sich auch die kinetischen Resultate von Luther und Mac Dougall auf Grund der eigenen Betrachtungen wohl erklären.

Zuletzt konnten die in Gegenwart der kleinen Mengen von Br' ausgeführten kinetischen Messungen (s. Tabelle 28) die oben ermittelte erste Chloridordnung—die simultane Fortschreitung der $HClO_3$-HBr-Reaktion in Rücksicht getragen—noch sicherer bestätigen, indem erwiesenermassen das Br' mit den primären Reaktionsprodukten praktisch momentan zu Brom reagiert und somit die kinetischen Anomalien beinahe beseitigen könnte.

Schluss. Der primäre Vorgang der $HClO_3$-HCl-Reaktion lautet wie folgt:

$$ClO_3' + Cl' + 2H^\cdot = HClO_3 + HCl \rightleftarrows HClO_2 + HClO\,.$$

Die sekundären Reaktionen verlaufen nach variierten Reaktionsbedingungen in ganz verschiedenen relativen Intensitäten.

VI. **Die allgemeine Übersicht betreffs der Kinetik der Reaktionen zwischen Halogensauerstoffsäuren und Halogenwasserstoffsäuren.** In den vorhergehenden Abschnitten habe ich mich mit den kinetischen Untersuchungen über die bisher noch nicht studierten oder event. revisionsbedürftigen Reaktionen zwischen HXO_3 und HY beschäftigt; sie sind nämlich:

$HBrO_3$-HCl-, $HClO_3$-HBr-, HJO_3-HBr-, HJO_3-HCl- und $HClO_3$-HCl-Reaktion.

Es bleiben natürlich noch vier Reaktionsarten übrig, bei denen aber, im Lichte der Aktivitätslehre betrachtet, die schon altbekannte Reaktionsordnung sich wohl als richtig anerkennbar erweist: $HBrO_3$-HJ-Reaktion (Noyes, Clark),[10] $HBrO_3$-HBr-Reaktion (Judson u. Walker, Clark),[10][11] $HClO_3$-HJ-Reaktion (Bray),[6] HJO_3-HJ-Reaktion (Dushman, Abel u. Stadler).[12][13] So scheint es hier sehr zweckmässig, die an Hand der oben genannten Autoren gewonnenen kinetischen Resultate zum Zwecke der kinetischen Übersicht zu benutzen, wie im folgenden beschrieben werden soll.

1. *Vergleich der Geschwindigkeitskonstanten.* Die Geschwindigkeitskonstante k der HXO_3-HY-Reaktion wird durch die kinetische Gleichung allgemeiner Form:

$$-\frac{d(XO_3')}{dt} = kF\,(XO_3')^x\,(Y')^y\,(H^\cdot)^z$$

gegeben, wo F den kinetischen Aktivitätsfaktor Brönsteds und x, y, z die zugehörige Reaktionsordnung bedeuten. Auf Grund der bisherigen anderer und eigenen Resultate erweist es sich nun als leicht zugänglich, die event. relativen Grössen von F und somit von k grob annähernd zu errechnen. In Fig. 3 sind die so ermittelten Geschwindigkeitskonstanten der sämtlichen HXO_3-HY-Reaktionen ($\log k$), bezogen auf 30°, in Abhängigkeit von den Ordnungszahlen der im betreffenden Oxydanten oder Reduktanten enthaltenen Halogenatome schematisch dargestellt.

Hieraus konstatiert man sogleich folgende Regularitäten:

i. Die Geschwindigkeitskonstante der Reduktion einer bestimmten Art von HXO_3 durch verschiedene HY nimmt, exakt parallel mit dem Reduktionspotential der letzteren, stets in der Reihenfolge HJ > HBr > HCl ab, oder d. h.

$$k_{HXO_3\cdot HJ} > k_{HXO_3\cdot HBr} > k_{HXO_3\cdot HCl}\,.$$

ii. Die Geschwindigkeitskonstante der Oxydation einer bestimmten Art von HY durch verschiedene HXO_3 nimmt, mit einer einzigen Ausnahme der HJO_3-HCl-Reaktion, in der Reihenfolge $HJO_3 > HBrO_3 > HClO_3$ ab, oder d. h.

$$k_{HJO_3\cdot HY} > k_{HBrO_3\cdot HY} > k_{HClO_3\cdot HY}\,.$$

(10) R. H. Clark, *J. Physic. Chem.*, **10** (1906), 679.
(11) J. Walker, *J. Chem. Soc.*, **73** (1898), 410.
(12) Dushman, *J. Physic. Chem.*, **8** (1904), 453.
(13) Abel u. Stadler, *Z. physik. Chem.*, **122** (1926), 49; Abel u. Hilferding, *Z. physik. Chem.*, **136** (1928), 186.

Kein Parallelismus mit dem Oxydationspotential von HXO_3.

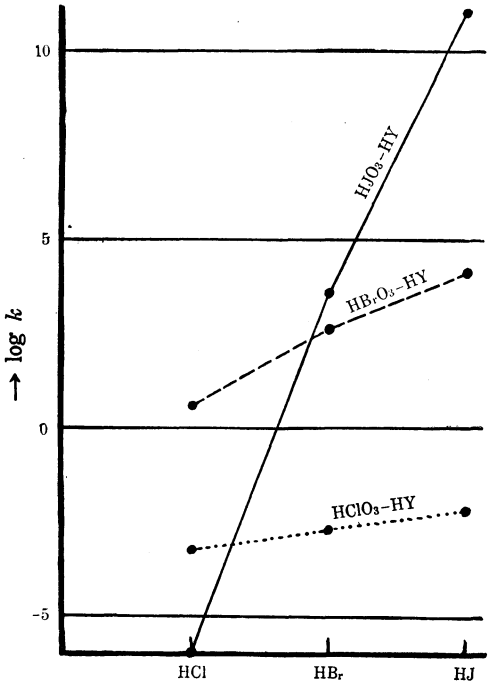


Fig. 3(A). Reduktant variiert.

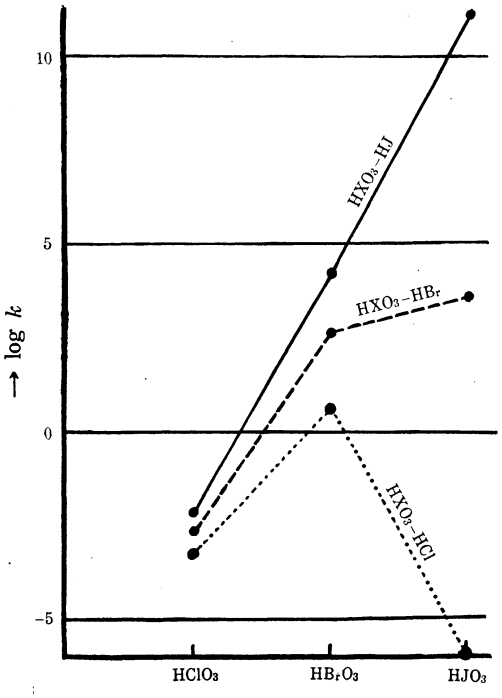


Fig. 3(B). Oxydant variiert.

2. *Übersicht in bezug auf die Reaktionsordnung.* In Tabelle 29 sind die sämtlichen Ordnungswerte (x, y, z) der besprochenen Reaktionen zusammengestellt. Bei jeder Reaktionsart bezieht sich die erste Zahl auf XO_3', die zweite auf Y' und die dritte auf $H^{\cdot}$.

Tabelle 29.

HY \ HXO_3	$HClO_3$	$HBrO_3$	HJO_3
HCl	1, 1, 2	1, 2, 2	1, 4, 4
HBr	1, 1, 2	1, 1, 2	1, 2, 3
HJ	1, 1, 2	1, 1, 2	1, 2, 2[14]

Hieraus können wir einerseits die sämtlichen Reaktionen aus dem Gesichtspunkte des molekularen Mechanismus meiner Ansicht nach in drei folgende Gruppen einteilen:

(14) Nach Abel und Hilferding (1928) tritt bei der HJO_3-HJ-Reaktion bei sehr kleinen J'-Konzentrationen (10^{-7}–10^{-8} Mol) ein lineares Glied in bezug auf dieselben hinzu. Wenn dies auch in molekularkinetischer Hinsicht von hohem Interesse sein müsste, stellen wir hier die allgemein anerkannte Form 1, 2, 2 auf, welche für das gewöhnlich untersuchte J'-Konzentrationsbereich praktisch exakt gültig ist.

Der 1sten Gruppe derselben gehören die Reaktionen des bimolekularen Typus (1, 1, 2), d. h. $HClO_3$-HCl-, $HClO_3$-HBr-, $HClO_3$-HJ-, $HBrO_3$-HBr- und $HBrO_3$-HJ-Reaktion. Molekularkinetisch wäre dafür anzunehmen, dass zwischen den beiden in sehr geringen Konzentrationen vorhandenen undissoziierten Säuremolekülen, welche ihrerseits mit ihren Ionenkomponenten im Gleichgewicht stehen, der geschwindigkeitsbestimmende Vorgang nach der Gleichung: $HXO_3+HY \rightarrow HXO_2+HYO$ stattfindet.

Der 2ten Gruppe gehören die Reaktionen des trimolekularen Typus (1, 2, 2 und 1, 2, 3), d. h. $HBrO_3$-HCl, HJO_3-HJ- und HJO_3-HBr-Reaktion. Molekularkinetisch stiesse entweder ein nacktes Ion oder ein neutrales Säuremolekül des Oxydanten mit zwei Neutralmolekülen des Reduktanten zum kritischen Komplex zusammen, etwa wie folgt:

$$XO_3'+2HY \rightarrow XO'+2HYO \quad (1, 2, 2),$$
$$HXO_3+2HY \rightarrow HXO+2HYO \quad (1, 2, 3).$$

Der letzten Gruppe gehört die Reaktion des pentamolekularen Typus, d. h. HJO_3-HCl-Reaktion: $XO_3'+4HY \rightarrow XO'+2Y_2+2H_2O$. Anderseits können wir noch folgende bedeutungsvolle Schlüsse herausziehen:

i. Die Reaktionsordnung in bezug auf XO_3' ist konstant als 1 erwiesen, gleichgültig ob das Oxydant als neutrales Säuremolekül oder als nacktes Ion reagiert. Es sei hinzugefügt, dass das XO_3' bloss an primärer Reaktion, und nie an sekundären, teilnimmt.

ii. Die Reaktionsordnung in bezug auf Y' ist sehr variabel (1, 2 oder 4). Bemerkenswert scheint es jedoch, dass das Reduktant immer als undissoziiertes Säuremolekül (homöopolare Bindung) in den primären Vorgang tritt.

iii. Die Reaktionsordnung in bezug auf $H^{\cdot}$ ist zumeist 2; aber 3 und 4 in je einem Falle. Sie ist gleich der Y'-Ordnung resp. um 1 grösser als diese, je nachdem das Oxydant als Ion resp. als Neutralmolekül reagiert. Demnach scheint sie von mehr untergeordneter Bedeutung zu sein.

Nach den oben angeführten Betrachtungen scheint für das ganze Ordnungsbild stets die Y'-Ordnung die wichtigste Rolle zu spielen. Betreffend ihre Verschiedenwertigkeit konstatieren wir überhaupt die Regelmässigkeit, dass sie für variierte Oxydanten in der Reihenfolge $HClO_3 < HBrO_3 < HJO_3$ und für variierte Reduktanten in umgekehrter Reihe $HJ < HBr < HCl$ zuwächst.

Zum Schluss möchte ich Herrn Prof. Dr. S. Kakiuchi für die freundlichen Ratschläge meinen herzlichsten Dank aussprechen.

Biochemisches Institut, Medizinische Fakultät,
Kaiserliche Universität zu Tokyo.

ON THE ACTION OF PHOSPHATE UPON HEXOSES. I. THE FORMATION OF ACETOL FROM GLUCOSE IN ACIDIC SOLUTION OF POTASSIUM PHOSPHATE.

By Ryuzaburo NODZU.

Received January 10th, 1935. Published March 28th, 1935.

Since it was made most probable that in yeast fermentation as well as many other biological processes, zymohexose molecule splits primarily into two C_3-fragments, a considerable interest has been centred in the study of the chemical decomposition of this type. The chemical formation of C_3-compounds—lactic acid, methylglyoxal or acetol—from sugars has been demonstrated by several investigators(1). Almost all of these demonstrations have been accomplished by the action of various alkaline reagents upon sugars. These experiments, however, seem to the present writer an inadequate explanation of the chemism of biochemical C_3-compounds formation which may proceed rather in an acidic medium, for example alcoholic fermentation in which optimum *p*H is 6.2–6.6 for the cell-free yeast preparations(2). From such a point of view, it is desirable to realize chemically an analogous decomposition of hexose in an acidic medium. It is well known, however, that hexoses are generally stable in acidic medium(3), and there are so far only two investigators who have demonstrated the formation of C_3-compound (methylglyoxal) from hexoses in acidic media: namely Cameron(4), by the action of aromatic amines in dilute acetic acid; and Bernhauer(5), by the action of hydrogen peroxide in dilute sulphuric acid in the presence of ferrous sulphate.

(1) A. Emmerling and G. Loges, *Ber.*, **6** (1873), 23; **16** (1883), 837; M. Nencki and N. Sieber, *J. prakt. Chem.*, (2) **24** (1881), 298; H. Kiliani, *Ber.*, **15** (1882), 136, 699, 701; G. Pinkus, *ibid.*, **31** (1898), 31; W. Löb, *Biochem. Z.*, **12** (1908) 78; J. U. Nef, *Ann.*, **335** (1904), 326; **357** (1907), 294; **376** (1910), 1; A. Windaus and F. Knoop, *Ber.*, **38** (1910), 1166; H. D. Dakin and H. W. Dudley, *J. Biol. Chem.*, **15** (1913), 127; C. Neuberg, W. Oertel and B. Rewald, *Biochem. Z.*, **55** (1913), 495; **71** (1915), 144; A. Fernbach and M. Schoen, *Compt. rend.*, **158** (1914), 976; J. Meisenheimer, *Ber.*, **41** (1918), 1009; M. Oppenheimer, *Biochem. Z.*, **45** (1912), 134; O. Baudisch, *ibid.*, **84** (1918), 279; F. Fischler, *Z. physiol. Chem.*, **157** (1926), 1; **165** (1927), 53; K. Bernhauer and coworkers, *Biochem. Z.*, **212** (1929), 443; **219** (1930), 232.

(2) K. Myrbäck, "Homogene Katalyse," II. (1931), p. 114.

(3) F. Fischler (*loc. cit.*) and K. Bernhauer (*Biochem. Z.*, **210** (1929), 186) observed that glucose does not undergo any decomposition into C_3-compounds even on boiling with dilute mineral acids.

(4) C. N. Cameron, *J. Am. Chem. Soc.*, **49** (1927), 1789.

(5) K. Bernhauer, *Biochem. Z.*, **230** (1931), 484.

It has been also observed that even in acidic medium, glucose is instable[6] and fructose is autoxydizable[7] if alkali phosphate is coexistent. It is also well known that inorganic phosphates play an important part in the carbohydrate metabolism and are even indispensable in yeast fermentation[8]. It is now generally admitted that a rôle of the phosphate intervenes in the stage of primary fission of hexose molecule into C_3-fragments[9].

Taking these facts into consideration, the present writer has investigated the action of acidic solution of potassium phosphate on glucose and begun with distillation of their mixture, hoping to get some fragments of glucose molecule in the distillate. By such a distillation method, methylglyoxal has been occasionally proved to be formed from hexoses by the action of some alkaline reagents, e.g., sodium carbonate, sodium sulphite[10], and sodium phosphate[11].

Acetol. After adjusting *p*H to 6.6–6.8, a mixture of glucose and about 40% solution of potassium phosphate was subjected to distillation, the volume of the content of the distilling flask being kept constant by addition of water in small portions. The distillate was almost neutral to litmus paper and gave a marked iodoform reaction and reduced Fehling's solution even in the cold. With phenylhydrazine it produced a yellow, and with *p*-nitrophenylhydrazine a scarlet, flocculent precipitate. These precipitates were recrystallized and identified with bisphenyl- and bis-*p*-nitrophenyl-hydrazones of methylglyoxal. In another experiment with a mixture of *p*H 6.2–6.3 the same result was obtained, except that the distillate was faintly acidic.

At first consideration of these results, it was thought that the distillates contained methylglyoxal, and that the glucose underwent by such treatment decomposition analogous to that engendered by alkaline reagents. These hydrazine derivatives, however, can be formed, of course, either from methylglyoxal itself, or from acetol or from lactic aldehyde[12]. For deciding the true origin of the derivatives, a distillate from the mixture of *p*H 6.2–6.3 was treated with semicarbazide hydrochloride and

(6) L. J. Henderson, *J. Biol. Chem.*, **10** (1911), 3.
(7) O. Warburg and M. Yabusoe, *Biochem. Z.*, **146** (1924), 380.
(8) K. Myrbäck, *Z. physiol. Chem.*, **177** (1929), 158.
(9) A. J. Kluyver and A. P. Struyk, *Naturwiss.*, **14** (1926), 883; O. Meyerhof, *ibid.*, **14** (1926), 1175; H. v. Euler, "Biokatalysatoren," (1930), p. 12.
(10) F. Fischler, *loc. cit.*
(11) H. D. Dakin and H. W. Dudley, *loc. cit.*
(12) A. Wohl, *Ber.*, **41** (1908), 3599.

sodium acetate, and acetolsemicarbazone was obtained as the main reaction product instead of bis-semicarbazone of methylglyoxal. In addition to the acetolsemicarbazone, the reaction product, however, contained always a small quantity of some substance difficultly soluble in hot water. By careful fractional crystallization from hot water, it was separated into hydrazodicarbonamide[13], diacetyl-bis-semicarbazone, and methylglyoxal-bis-semicarbazone. Up to this point, the yields of the latter two were far inferior to that of acetolsemicarbazone. The tests for other probable volatile decomposition products in the distillate, such as formaldehyde, acetaldehyde, acetone, levulinic acid, and furfurol derivatives, were all negative, the distillates if existent being very dilute.

In a series of experiments operated at *p*H 7.0–7.1, 6.6–6.7, 5.9–6.0, and 4.9–5.0, similar results were obtained, and at *p*H 6.3–6.5, an appreciable quantity of acetol was isolated from the distillate.

Estimation of Acetol. It is now desirable to know the yield of acetol from glucose under such conditions. The distillation was continued until the distillate gave no more iodoform reaction or only faintly, and the content of acetol was estimated in the total distillate. For the estimation of acetol, Fischler's iodometry[14] for methylglyoxal was applied, assuming

$$CH_3COCH_2OH + 5I_2 + 9KOH = CHI_3 + C_2O_4K_2 + 7KI + 7H_2O$$

instead of

$$CH_3COCHO + 4I_2 + 7KOH = CHI_3 + C_2O_4K_2 + 5KI + 5H_2O\ .$$

The results of experiments at various *p*H are tabulated in Table 1.

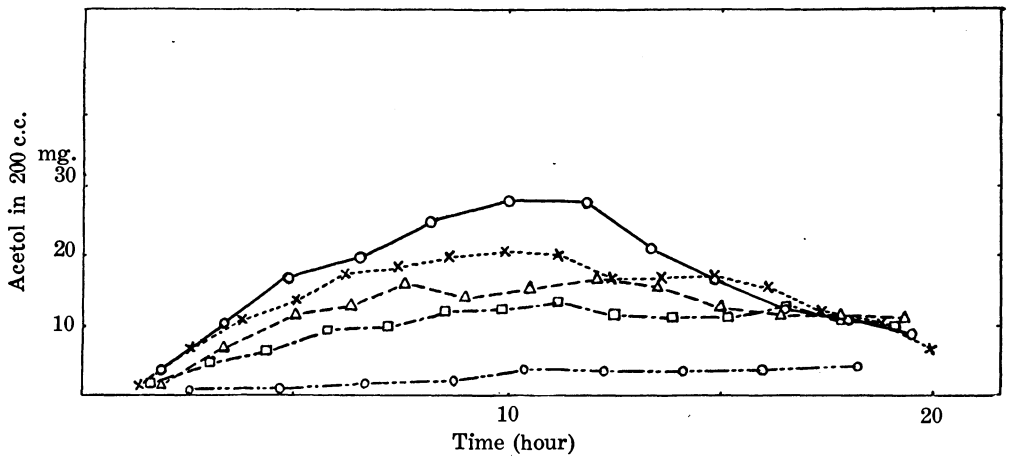
Table 1. Yields of acetol. (5g. glucose+50c.c. 40% phosph. solution.)

*p*H.	Acetol in g.	% on glucose.
7.0–7.1	0.23	4.6
6.5–6.7	0.24	4.8
6.3–6.5	0.20	4.0
5.9–6.0	0.21	4.2

In the region of *p*H studied, the yields were almost alike: 4–5%[15] of glucose used, i.e., 10–12 mol per cent., assuming one molecule glucose gives one molecule acetol. Since, as already mentioned, the distillate is contaminated with some other iodine-consuming substances than acetol, though in a small quantity, the values in the table are naturally approximate.

(13) A condensation product of semicarbazide itself (C. Neuberg, *Biochem. Z.*, **191** (1927), 478.).
(14) F. Fischler and R. Boettner, *Z. analyt. Chem.*, **74** (1928), 28.
(15) In a similar yield, Fischler (*loc. cit.*) got methylglyoxal from glucose by distillation with dilute sodium carbonate solution and neutral sodium sulphite.

Influence of pH. Although the *p*H of the distilling mixture scarcely influenced the yield of acetol, as described above, it had a great effect upon the rate of its formation in the distillate. To compare the rates, the distillations of the mixtures of various *p*H were carried out under similar conditions and at as constant a rate (200 c.c. distillate in 1.5 hrs.) as possible, and the acetol contents were successively estimated in each 200 c.c. of the distillate. The experimental results are summarized in Fig. 1, which is prepared by plotting the acetol content (mg.) against time (hour).



5 g Glucose+50 c.c. of 40% Pot. Phosphate.

—○———○— *p*H 7.0–7.1

---×-----×---- *p*H 6.5–6.7

--△----△-- *p*H 6.3–6.5

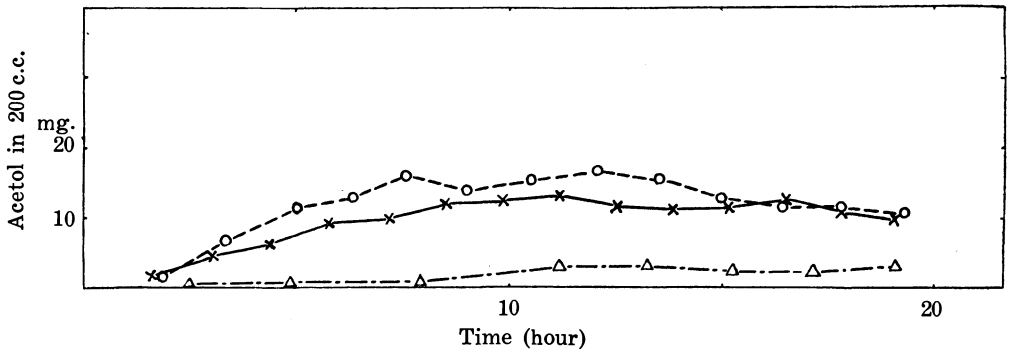
—·□·—·□·— *p*H 5.9–6.0

—··○··—··○··— *p*H 3.0–3.1

Fig. 1.

The maxima of curves in Fig. 1, showing the maximum rates, descend parallel with *p*H values, viz., 28 mg. for *p*H 7.0–7.1; 17 mg. for *p*H 6.3–6.5; 5 mg. for *p*H 3.0–3.1, etc. It is also obvious that the lower in *p*H the distilling mixture, the more the distillation of acetol is prolonged. Hence we may understand the fact that the yield of acetol was almost independent of the *p*H value of the mixture.

Influence of Concentration of the Phosphate. Glucose alone in water or in dilute mineral acids[16] gives no distillate which shows the iodoform reaction. Glucose in 5% phosphate solution (*p*H 5.9–6.3), however, yielded an iodoform-giving distillate. But the iodine-consuming capacity (calc. for acetol) of the distillate was far inferior to that with the corresponding 40% solutions. As shown in Fig. 2, which was plotted



5 g. Glucose+50 c.c. Solution.

---○------○---- 40% Solution, *p*H 6.3–6.5
—×———×—— ,, ,, *p*H 5.9–6.0
- —△- - - —△- — 5% Solution, *p*H 5.9–6.3

Fig. 2.

in the same principle as Fig. 1, the maximum rate of acetol formation is only 3 mg. for 5% solution whereas it is 17 mg. or 13 mg. for 40% solution.

Experimental Part.

Bis-phenylhydrazone and Bis-*p*-nitrophenylhydrazone of Methylglyoxal. Glucose (Merck) (10 g.) was dissolved in 100 c.c. of about 40% potassium phosphate solution which was prepared by mixing[17] 18 g. anhydrous KH_2PO_4, 22 g. anhydrous K_2HPO_4 (Merck), and 60 g. water. After adjusting *p*H of the mixture to 6.6–6.8 with aqueous potassium hydroxide, it was subjected to distillation, keeping the level of the flask-content as constant as possible by adding, drop by drop, distilled water. On continuing the distillation, the flask-content became yellow and then brown in colour, and a dark brown tarry matter appeared after about 10 hours from the beginning. The

(16) F. Fischler, *loc. cit.*; K. Bernhauer, *loc. cit.*

(17) For the further experiments at other *p*H, this ratio of mixing was modified and the minute adjustment of *p*H was made by aqueous phosphoric acid and aqueous potassium hydroxide.

distillate was almost neutral to litmus paper, gave a marked iodoform reaction, and reduced Fehling's solution in the cold. The latter two reactions, however, faded gradually in the course of distillation. On heating about 2 litres of the distillate with phenylhydrazine and acetic acid on a boiling water bath for six hours, a yellow flocculent precipitate was isolated, but the quantity was scant. By repeating the same experiment three times more, about 1 g. of the precipitate was obtained. Recrystallization from aqueous ethyl alcohol gave a light yellow crystalline substance melting at 145–147° in major quantity (0.5 g.), and a less soluble and higher melting substance in minor quantity. The analysis, and the determination of the molecular weight, of the former indicate it is methylglyoxal-phenylosazone. (Found: C, 71.6, 71.1; H, 6.1, 6.3; N, 21.9, 21.8; M, 246.6. Calc. for $C_{15}H_{16}N_4$: C, 71.4; H, 6.3; N, 22.2%; M, 252.2.)

On warming 9 liters of the distillate (about 3 g. as methylglyoxal)[18] from an experiment with 50 g. glucose, on a boiling water bath for four hours with 17 g. *p*-nitrophenylhydrazine (in 30% aqueous acetic acid), a dark red precipitate was obtained. After washed with hot alcohol, it was fractionated by crystallization from nitrobenzene into a substance in deep scarlet needles (m.p. 296–297°, yield 3.5 g.) and a similar appearing but lower melting substance (m.p. 275–278°, yield 1 g.). The former substance (Found: C, 52.8, 52.7; H, 4.4, 4.3; N, 24.4, 24.2. Calc. for methylglyoxal-bis-*p*-nitrophenylhydrazone $C_{15}H_{14}O_4N_4$: C, 52.6; H, 4.1; N, 24.6%) gave the characteristic colour reaction[19] for methylglyoxal-bis-*p*-nitrophenylhydrazone on warming with alcoholic alkali, i.e., a beautiful deep blue colouration which changes slowly to purple then to violet and finally to dull brown. The latter (m.p. 275–278°) gave also similar analytical results and the same colour reaction, and hence was concluded to be the same osazone with a little impurity.

In these experiments the distillation residue became more acidic than the starting mixture, e.g., *p*H shifted from 6.6–6.8 to 6.2–6.3. When a distillation was started with a mixture of *p*H 6.2–6.3, it was observed that almost no change of *p*H took place throughout the distillation, and the distillate gave the same osazones.

Acetolsemicarbazone, Diacetyl- and Methylglyoxal-bis-semicarbazone. The distillate (about 9 litres, 3.1 g. as acetol) prepared from a mixture (*p*H 6.2–6.4) of 200 g. glucose and 2 litres of 40% potassium phosphate solution, was warmed with 23 g. (5 mols) of semicarbazide hydrochloride and 28 g. of sodium acetate on a boiling water bath for half an hour. The reaction product was evaporated[20] to about 200 c.c. under a reduced pressure and in the current of carbon dioxide. The solution was filtered from a little quantity (0.17 g.) of a yellowish white precipitate, which melted over 265°. On further concentration of the filtrate under similar conditions, a faintly brown crystalline deposit amounting to 2.7 g. was obtained, and it melted at about 195°. These two solid substances were fractionated by crystallization from hot water into the following fractions:

---

(18) It was estimated by Fischler's iodometry. *Z. analyt. Chem.*, **74** (1928), 28. See below.

(19) H. D. Dakin and H. W. Dudley, *loc. cit.*

(20) During the course of evaporation, some iodine-consuming substance was distilled and it was estimated 0.5 g. as acetol. It is, however, not sure at present whether it is actually acetol or not.

	m.p.	g.
I.	275—277°	0.04
II.	263—265°	0.01
III.	257—258°	0.01
IV.	236—239°	trace
V.	198—199°	1.75

Fraction (I) melted at 279–280° after a recrystallization from warm acetic acid and this purified sample showed no lowering in melting point when mixed with diacetyl-bis-semicarbazone (Found: C, 35.7; H, 5.6. Calc. for $C_6H_{12}O_2N_6$: C, 36.0; H, 6.0%). Fraction (II) was recrystallized from boiling water in slightly yellow crystalline powder, m.p. 267–268° (Found: N, 45.5. Calc. for $C_5H_{10}O_2N_6$: N, 45.2%)[21], and its melting point was not depressed on admixing with methylglyoxal-bis-semicarbazone[22]. On recrystallization of fraction (III) from hot water, the melting point showed no change. It was identified with hydrazodicarbonamide[23] (a condensation product of semicarbazide itself) by a mixed melting-point determination and an analysis (Found: N, 47.7. Calc. for $C_2H_6O_2N_4$: N, 47.5%.). Fraction (IV) was not further studied. After decolourized with animal charcoal, the hot water solution of fraction (V) was allowed to cool. The substance crystallized out in colourless, glistening, flat needles (about 1.5 g.) which melted at 199–200° alone or with an authentic sample of acetolsemicarbazone[24]. (Found: C, 36.5, 36.4; H, 7.3, 7.2; N, 31.7, 31.8. Calc. for $C_4H_9O_2N_3$: C, 36.6; H, 6.9; N, 32.0%.)

Several other similar experiments were performed with similar results. In the experiments at other *p*H, e.g., 7.0–7.1, 6.6–6.8, 5.9–6.0, 4.8–5.0[25], the same acetolsemicarbazone was actually obtained as the main product. From 4.3 litres of the distillate (0.7 g. acetol) in an experiment at *p*H 6.2–6.3, 0.6 g. of acetolsemicarbazone (in a fairly pure stage, m.p. 196–198°) and 0.05 g. of a difficultly soluble substance was able to be obtained. The yield of acetolsemicarbazone from the distillate was theoretical (61%), if the acetol (0.15 g.)[26] that escaped the reaction with semicarbazide was taken into account.

Acetol. The distillate (8 litres, about 3.2 g. acetol). from an experiment at *p*H 6.2–6.3, was concentrated under a reduced pressure to about 600 c.c. (1.4 g. acetol). About 1 kg. of anhydrous sodium sulphate was added in small portions to the concentrated solution and the resulting solid mass was crushed in a mortar. The powdered mass was extracted three times with two litres of ether each time. The

(21) The pure sample was only few mg. and it was microanalysed with the sample from other similar experiments.

(22) The authentic sample was prepared from aqueous methylglyoxal (C. Neuberg and E. Hoffmann, *Biochem. Z.*, **224** (1930), 491.). When a raw product (m.p. 258–260°) was recrystallized from a large volume of boiling water, it melted at 267–268°.

(23) C. Neuberg, *Biochem. Z.*, **191** (1927), 474.

(24) J. U. Nef, *Ann.*, **335** (1904), 253, 259.

(25) In the course of distillation at *p*H 6.9–7.1 and 6.6–6.8, an adequate quantity of dilute potassium carbonate solution was added from time to time the distilling mixture in order to keep the *p*H as constant as possible. No change in *p*H was observed throughout the distillation at *p*H 5.9–6.0 and 4.8–5.0.

(26) See the foot note (20).

total ethereal extract (about 5 litres) was dried over anhydrous sodium sulphate and then evaporated. The residue was fractionally distilled under a reduced pressure. The main fraction, 0.7 g. of an oil (b.p. 96–98°/159 mm., d_{25}^{25} 1.059, n_D^{25} 1.415) had a characteristic odour, reduced markedly Fehling's solution in the cold, and reacted easily with semicarbazide, giving acetolsemicarbazone.

Estimation of Acetol in the Distillate. In order to get some comparable values of the yields and the rates of formation of acetol in the distillation experiments at various *p*H, all the distillations were carried out in the same apparatus and at as constant a rate as possible. Forty per cent. potassium phosphate solution (50 c.c.) of a certain *p*H was distilled at the rate of 200 c.c. in 90 minutes, adding little by little a solution of 5 g. glucose in 1000 c.c. water and afterward fresh water to make the volume of the distilling flask-content constant. During the distillation, whenever the *p*H of the starting solution was higher than 6.2, it was necessary to add from time to time some aqueous potassium carbonate in order to keep the *p*H constant. The distillation was continued until the iodoform reaction became very faint. It took 25 to 34 hours. In each 200 c.c. of the distillate, the amount of acetol was estimated in the following way. To 10 c.c. of the distillate were added 10 c.c. N/10 iodine solution and 10 c.c. of 10% potassium hydroxide. After the mixture had been left for half an hour at room temperature, it was acidified with 8 c.c. of 15% hydrochloric acid and then titrated back with N/10 sodium thiosulphate solution. One c.c. of N/10 iodine solution is equivalent to 0.73 mg. of acetol, assuming the foregoing equation.

The experiments were made with the solutions of various *p*H, e.g., 7.0–7.1, 6.5–6.7, 6.3–6.5, 5.9–6.0, and 3.0–3.1. Yields of acetol and rates of its distillation in these experiments are summarized in Table 1 and Fig. 1.

As an example, one of experimental records is cited in Table 2.

Table 2. 5 g. glucose, *p*H 6.3–6.5, Distil. temp. 105–107°.

Time (min.) for distilling 200 c.c.	c.c. of 0.0993 N -iodine solution for 10 c.c. distillate.	Acetol (mg.) in 200 c.c. distillate.	Time (min.) for distilling 200 c.c.	c.c. of 0.0993 N -iodine solution for 10 c.c. distillate.	Acetol (mg.) in 200 c.c. distillate.
110	0.10	1.5	85	0.78	11.5
90	0.45	6.6	85	0.52	7.6
100	0.78	11.5	85	0.42	6.2
80	0.88	12.9	90	0.39	5.7
75	1.08	15.9	75	0.34	5.0
85	0.95	13.9	70	0.31	4.6
90	1.03	15.1	75	0.19	2.8
95	1.14	16.8	75	0.18	2.7
85	1.05	15.4			
90	0.87	12.7	Total 1800 min. (30 hrs.)		202.5 mg.
85	0.80	11.7	Distillate . . . . . 4200 c.c.		
85	0.78	11.5	10% K_2CO_3 solution to keep *p*H 6.3-6.5. . . . 7 c.c.		
90	0.74	10.9	Yield . . . . . 4% on glucose		

In order to determine the influence of concentration of potassium phosphate solution, the distillations of 5 g. glucose in 5% and 40% solutions of this salt were investigated under a similar precaution as in the foregoing experiments. The results are plotted in Fig. 2.

Summary.

On steam distillation of a mixture of glucose and about 40% potassium phosphate solution of *p*H from 7.0 to 5.0, an appreciable quantity (4–5% of glucose used) of acetol and a little quantity of diacetyl- and methylglyoxal are found in the distillate. The more concentrated and the nearer to neutrality the phosphate solution is, the more favourable for the formation of acetol.

In conclusion, the writer wishes to thank Prof. S. Komatsu for his valuable advice in this work and the Department of Education for a research grant.

Chemical Institute, Faculty of Science,
Kyoto Imperial University.

ON THE MOLECULAR VOLUME OF UREA IN COMPLEX IONS.

By Haruo NAKAGAWA.

Received January 17th, 1935. Published March 28th, 1935.

Complex salts which contain six molecules of urea co-ordinating with various central metallic atoms in their cations were recently prepared by Okuda and Fujikawa[1], P. Pfeiffer[2], and G. A. Barbieri[3][4]. The present author has studied the molecular volume of urea in complex ions of the complex salts given by the former authors, in order to know

(1) *J. Chem. Soc. Japan*, **40** (1919), 404.

(2) P. Pfeiffer, *Ber.*, **36** (1903), 1926.

(3) Univ. Ferrara, *Atti. accad. Lincei*, **22** (1913), 867; *C. B.*, **1913**, II, 1034; *C.A.*, **7** (1913), 3937.

(4) Univ. Ferrara, *Atti. accad. Lincei*, **24** (1915), 916; *C.B.*, **1916**, I, 924; *C.A.* **9** (1915), 2852.

whether organic molecules contained in a complex ion as "Ligand" generally hold or not the same molecular volume as those in free state.

The following six complex salts were thus used in this study:

$[Ca(ur)_6^*]Br_2$[1], $[Ca(ur)_6]I_2$[1], $[Cr(ur)_6]Cl_3 \cdot 3H_2O$[2], $[Fe(ur)_6]Cl_3 \cdot 3H_2O$[3], $[Al(ur)_6]I_3$[4], $[Al(ur)_6](ClO_4)_3$[4].

Experimentals.

(I) **Specific Gravity Determination.** The determination of the specific gravities of the complex salts mentioned above was performed by the pycnometer method, benzene being used as displacement liquid, for these complex salts are all easily soluble in water. The calculation was made by the following formula:

$$d = \frac{a \cdot s_1}{a+b-c},$$

where a is the weight of the complex salt taken, b the weight of the pycnometer filled with benzene, c the weight of the pycnometer charged with the complex salt and benzene, and s_1 the density of benzene. The results of the observations are given in Table 1.

Table 1.

Molecular formula	Molecular weight	Density D_4^{20}	Molecular volume
C_6H_6	—	0.8778	—
$[Ca(ur)_6]Br_2$	560.20	1.6495	339.62
$[Ca(ur)_6]I_2$	655.20	1.8941	345.91
$[Cr(ur)_6]Cl_3 \cdot 3H_2O$	572.71	1.4774	387.65
$[Fe(ur)_6]Cl_3 \cdot 3H_2O$	576.54	1.5014	384.00
$[Al(ur)_6]I_3$	768.01	1.9973	384.52
$[Al(ur)_6](ClO_4)_3$	685.62	1.7245	397.56
$CO(NH_2)_2$	60.05	1.3289	45.19

(II) **Calculation of Molecular Volume of Urea in Complex Ions.** (1) $[Ca(ur)_6]Br_2$ and $[Ca(ur)_6]I_2$. As shown in Table 2, the molecular volume of urea calculated from the iodide is in good accordance with its value in the free state, but the value obtained from the bromide is somewhat larger than the former.

* The symbol ur represents the molecular formula of urea, $CO(NH_2)_2$.

Table 2.

Salt	$[M(ur)_6]X_2$		MX_2		Molecular volume of urea in complex ion
	D_4^{20}	Molecular volume	D_4^{25}	Molecular volume	
$[Ca(ur)_6]Br_2$	1.6495	339.62	3.352[5]	59.64	46.66
$[Ca(ur)_6]I_2$	1.8941	345.91	3.956[5]	74.29	45.27

(2) $[Cr(ur)_6]Cl_3$ and $[Fe(ur)_6]Cl_3$. These two complex salts contain trivalent metallic central atoms, and the calculated values of molecular volume of urea are practically equal in both cases and do not differ very much from the theoretical within the limit of observation errors, Table 3.

Table 3.

Salt	$[M(ur)_6]X_3 \cdot 3H_2O$		MX_3		Volume of $(ur)_6 \cdot 3H_2O$	Molecular volume of H_2O[7]	Molecular volume of urea[8]
	D_4^{20}	Molecular volume	D_4^{25}	Molecular volume			
$[Cr(ur)_6]Cl_3 \cdot 3H_2O$	1.4774	387.65	2.784[6]	56.89	330.76	19.87	46.10
$[Fe(ur)_6]Cl_3 \cdot 3H_2O$	1.5014	384.00	2.898[6]	55.97	328.03	18.96	45.65

Each of these salts contains three molecules of water of crystallisation, and the author tried also to calculate the molecular volume of water in these complex salts. Formerly W. Biltz obtained 14.4 as the mean molecular volume of water in various complex ions, but the values found by the present author are 19.87 and 18.96[7]. Therefore, it may be said that water molecules existing outside a complex ion show a nearly normal but considerably larger value than that obtained by Biltz for water as "Ligand" in complex ions.

(3) $[Al(ur)_6]I_3$ and $[Al(ur)_6](ClO_4)_3$. From the iodide, a nearly normal value for the molecular volume of urea was again obtained, Table 4.

(5) Baxter and Brink, *J. Am. Chem. Soc.*, **30** (1908), 46; Ruff and Plato, *Ber.*, **32** (1902), 1577.

(6) W. Biltz and Birk, *Z. anorg. Chem.*, **134** (1924), 125.

(7) In this case the calculation was done by taking the normal value, 45.15 for the molecular volume of urea.

(8) In this case the calculation was done by taking the normal value, 18.05 at 20°C. for the molecular volume of water.

Table 4.

Salt	$[Al(ur)_6]I_3$		AlI_3		Molecular volume of urea
	D_4^{20}	Molecular volume	D_4^{20}	Molecular volume	
$[Al(ur)_6]I_3$	1.9973	384.52	3.98	102.5[9]	46.98

In order to calculate this value from the perchlorate, the molecular volume of anhydrous aluminium perchlorate must be found by an indirect way, because its density is yet unknown. For this reason the author chose the two hydrated salts, $[Al(H_2O)_6](ClO_4)_3$ and $[Al(H_2O)_6](ClO_4)_3 \cdot 3H_2O$, for the purpose of calculation of the molecular volume of anhydrous aluminium, Table 5.

Table 5.

Salt	D_4^{20}	Molecular volume	Volume of water (as H_2O, in complex ion = 14.4 and crystalline water = 19.42)			Molecular volume of $Al(ClO_4)_3$
			In complex ion	Water of cryst.	Total	
$[Al(H_2O)_6](ClO_4)_3$	2.1678	199.95	86.4	—	86.4	113.55
$[Al(H_2O)_6](ClO_4)_3 \cdot 3H_2O$	1.9260	253.10	86.4	58.26	144.66	108.44

The mean value 111.00 thus obtained was used for the further calculation of the molecular volume of urea in the aluminium-urea-complex salt.

Table 6.

Salt	D_4^{20}	Molecular volume	Molecular volume of $Al(ClO_4)_3$	Molecular volume of urea
$[Al(ur)_6](ClO_4)_3$	1.7245	397.56	111.00	47.76

The value given in Table 6 is somewhat larger than those obtained from other urea-complex salts. But considering that the last case involves very possibly certain errors in result, because the calculation has been done in a roundabout way, it may perhaps be concluded that the molecular volume of urea does not deviate from its normal value also in the perchlorate.

(9) Biltz and co-worker, *Z. anorg. Chem.*, **121** (1922), 257.

Summary

(1) The molecular volume of urea, which is contained in complex ions of various metallic complex salts, was determined. The average value thus obtained was found nearly equal to the theoretical.

(2) The molecular volume of water which exists as the water of crystallisation in some urea metallic complex salts was also calculated, and found normal, while Biltz gives distinctly smaller values for water contained in complex ions as "Ligand".

In conclusion the author expresses his sincere thanks to Prof. Y. Shibata for his kind guidance during the course of this work.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

SUR LA SOLUBILITÉ MUTUELLE ENTRE LA FLAVONE ET SES DERIVÉS.

Par Tei-ichi ASAHINA et Kôichi YOKOYAMA.

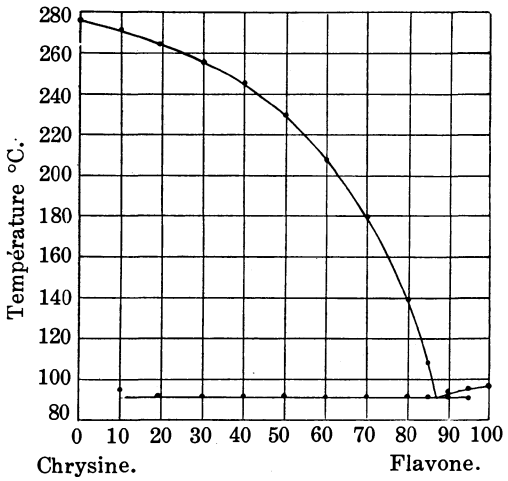
Reçu le 22 janvier 1935. Publié le 28 avril 1935.

Dans un autre mémoire précedent,[1] l'un de nous a constaté de l'existence de solution solide entre la primétine et la flavone. Maintenant on est à examiner s'il y a de telle existence entre la flavone et ses derivés hydroxylés qui sont fréquentés dans la nature comme constituants des plantes. Nous avons fait des études sur les oxyflavones suivantes et, en même temps, sur quelques derivés acétylés et méthylés des oxyflavones. Cependant, nous n'avons pas observé la possibilité d'existence de solution solide jusqu'ici et la solubilité mutuelle des flavones dans l'état solide n'est rien de chose générale. La méthode adoptée est de même que celle précedente.

I. Etude du système: Chrysine (5,6-dioxyflavone) et flavone.

Table 1. (Voyez la Fig. 1.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	de chrysine		
mg.	mg.		
0.0 —	100.0 —	—	275.0
10.0 (1.5)	90.0 (13.5)	95.0	271.0
19.3 (3.1)	80.7 (13.0)	91.5	264.0
30.0 (4.5)	70.0 (10.5)	91.5	255.0
40.0 (6.0)	60.0 (9.0)	91.5	245.0
50.0 (7.0)	50.0 (7.0)	92.0	229.0
60.0 (9.0)	40.0 (6.0)	91.5	208.0
70.0 (10.5)	30.0 (4.5)	91.5	180.0
80.0 (12.0)	20.0 (3.0)	91.5	139.0
85.0 (8.5)	15.0 (1.5)	91.5	108.0
90.0 (13.5)	10.0 (1.5)	92.0	94.5
95.0 (9.5)	5.0 (0.5)	91.3	95.2
100.0 —	0.0 —	—	96.5



Point eutéctique :
91.6°C., 87% de flavone.

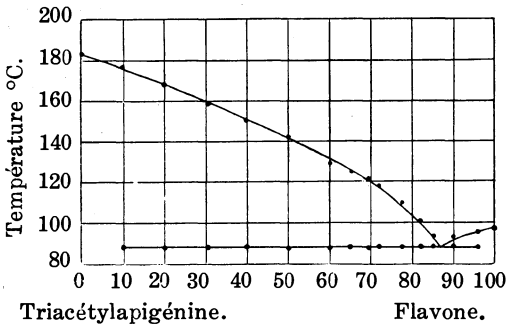
Fig. 1.

(1) T. Asahina, *Acta Phytochimica*, **7** (1933), 187.

II. Etude du système: Triacétylapigénine (5,7,4′-triacétoxyflavone) et flavone.

Table 2. (Voyez la Fig. 2.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	d'acétyl-apigénine		
mg.	mg.		
0.0 —	100.0 —	—	183.3
10.0 (1.2)	90.0 (10.8)	88.5	176.8
20.0 (2.4)	80.0 (9.6)	88.0	168.0
30.0 (3.7)	69.4 (8.4)	88.0	158.5
40.0 (6.0)	60.0 (9.0)	88.0	150.2
50.0 (6.0)	50.0 (6.0)	88.0	142.0
60.0 (7.2)	40.0 (4.8)	88.0	129.0
65.0 (6.5)	35.0 (3.5)	88.0	125.0
69.4 (8.4)	30.6 (3.7)	88.0	122.2
71.7 (7.6)	28.3 (3.0)	88.0	118.0
77.4 (9.6)	22.6 (2.8)	88.0	109.5
82.0 (16.4)	18.0 (3.6)	88.2	101.0
85.0 (8.5)	15.0 (1.5)	88.0	93.0
90.0 (10.8)	10.0 (1.2)	88.0	93.0
96.0 (14.4)	4.0 (0.6)	88.0	95.0
100.0 —	0.0 —	—	96.5



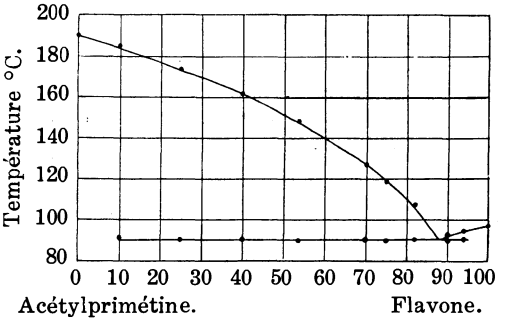
Point eutéctique :
88.0°C., 87% de flavone.

Fig. 2.

III. Etude du système: Diacétylprimétine (5,6-diacétoxyflavone)[2] et flavone.

Table 3. (Voyez la Fig. 3.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	d'acétyl-primétine		
mg.	mg.		
0.0 —	100.0 —	—	190.5
10.0 (1.2)	90.0 (10.8)	91.0	184.8
25.0 (2.5)	75.0 (7.5)	90.0	173.0
40.0 (5.0)	60.0 (7.5)	90.0	161.0
53.6 (7.5)	46.4 (6.5)	89.5	148.0
70.0 (10.5)	30.0 (4.5)	90.0	127.0
75.0 (7.5)	25.0 (2.5)	90.0	118.0
82.0 (12.3)	18.0 (2.7)	90.0	107.0
90.0 (13.5)	10.0 (1.5)	89.7	92.2
94.1 (9.5)	5.9 (0.6)	90.0	94.0
100.0 —	0.0 —	—	96.5



Point eutéctique :
90.0°C., 88% de flavone.

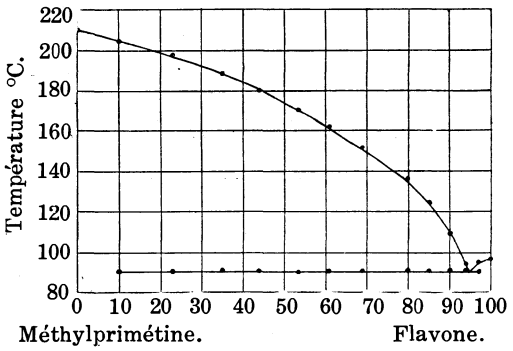
Fig. 3.

(2) W. Nagai et S. Hattori, *Acta Phytochimica*, **5** (1930-1931), 1.

IV. Etude du système: Méthylprimétine (5-oxy-6-méthoxyflavone)[3] et flavone.

Table 4. (Voyez la Fig. 4.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	de méthyl-primétine		
mg.	mg.		
0.0 —	100.0 —	—	210.5
10.0 (1.0)	90.0 (9.0)	90.5	205.0
22.8 (2.3)	77.2 (7.8)	90.0	198.0
35.0 (3.5)	65.0 (6.5)	91.0	188.5
44.0 (4.4)	56.0 (5.6)	90.5	180.0
53.5 (5.4)	46.5 (4.7)	89.5	170.5
60.8 (6.2)	39.2 (4.0)	90.5	161.5
69.0 (7.8)	31.0 (3.5)	90.6	151.2
80.0 (8.0)	20.0 (2.0)	90.5	136.2
85.0 (10.2)	15.0 (1.8)	90.5	122.5
90.0 (9.0)	10.0 (1.0)	90.5	109.5
94.0 (9.4)	6.0 (0.6)	91.0	94.0
97.0 (9.7)	3.0 (0.3)	90.5	95.0
100.0 —	0.0 —	—	96.5



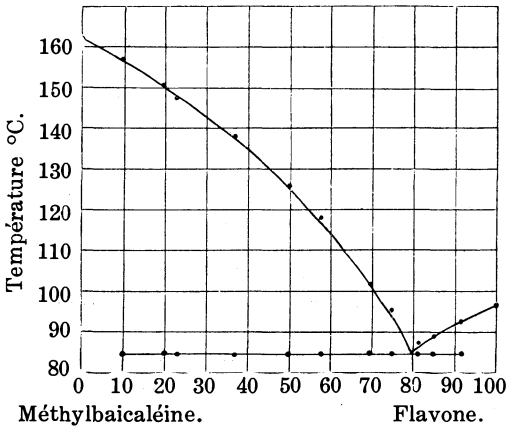
Point eutéctique:
90.5°C., 94.5% de flavone

Fig. 4.

V. Etude du système: Méthylbaicaléine (5,6,7,-triméthoxyflavone)[4] et flavone.

Table 5. (Voyez la Fig. 5.)

Pourcentages		Points de dégel °C.	Points de congel °C.
de flavone	de méthyl-baicaléine		
mg.	mg.		
0.0 —	100.0 —	—	162.0
10.0 (1.1)	90.0 (9.9)	85.0	157.0
19.7 (2.5)	80.3 (10.2)	84.5	150.5
22.9 (2.7)	77.1 (9.1)	84.5	147.5
37.1 (4.3)	62.9 (7.3)	84.5	138.0
50.0 (6.0)	50.0 (6.0)	84.5	125.8
57.7 (6.7)	42.3 (4.9)	84.5	118.0
69.6 (8.0)	30.4 (3.5)	84.5	101.5
75.0 (8.7)	25.0 (2.9)	84.6	95.8
81.3 (10.0)	18.7 (2.3)	84.5	87.5
85.0 (8.5)	15.0 (1.5)	84.5	89.0
91.7 (10.0)	8.3 (0.9)	84.5	92.5
100.0 —	0.0 —	—	96.5



Point eutéctique:
84.6 °C., 79.5% de flavone.

Fig. 5.

En terminant, les auteurs ont l'agréable devoir d'exprimer ses vifs remerciements à MM. W. Nagai et S. Hattori qui les ont aidé par l'envoi

(3) W. Nagai et S. Hattori, *loc. cit.*

(4) S. Hattori, *Acta Phytochimica*, **5** (1930-1931), 108.

de quelques échantillons, et aussi à la Fondation Keimeikai qui leur a donné une part du frais d'expérimentation.

Laboratoire de Chimie, Faculté des Sciences,
Université Impériale de Tokio.

ÜBER DIE KATALYTISCHE HYDRIERUNG VON UNGESÄTTIGTEN ORGANISCHEN VERBINDUNGEN MIT SELEN.

Von Minoru YOKOYAMA und Munio KOTAKE.

Eingegangen am 28. Januar, 1935. Ausgegeben am 28. April, 1935.

Vor kurzer Zeit haben wir die Tatsache[1] gefunden, dass durch Erhitzen mit Selen einige ungesättigte Verbindungen isomerisiert werden können. Ob jedoch ein derartiges Verhalten für organische Verbindungen allgemein ist, schien uns der Nachprüfung wert und so haben wir als erstes Beispiel Oelsäure mit Selen auf 300°C. unter Umrühren 1–1.5 Stunden lang erhitzt. Die experimentellen Resultate waren ganz anders als wir vermutet hatten, indem nämlich Stearinsäure gewonnen wurde. Es ist nicht undenkbar, dass durch Erhitzen mit Selen ungesättigte Verbindungen reduziert werden. Schon Ruzicka[2] hat durch Erhitzen von Oleanolsäure mit Selen unter Abspaltung von CO_2 und H_2O eine gesättigte Substanz Oleanan gewonnen.

Im weitern haben wir die Einwirkung von Selen auf Elaidinsäure, Ricinolsäure, Linolsäure, Erucasäure und Zimtsäure untersucht und von allen diesen Verbindungen hydrierte Substanzen bekommen.

Daraus können wir ableiten, dass man ungesättigte Verbindungen durch Erhitzen mit Selen ziemlich leicht reduzieren kann.

Die Bedingungen der Erhitzung und die Resultate sind in folgender Tabelle zusammengestellt.

Substanzen		Selen	Temp.	Stunden	Resultate	
Oelsäure	50g.	100g.	300°C.	1.5	Stearinsäure	14g.
Elaidinsäure	3	9	300	1.5	Stearinsäure	0.75
Ricinolsäure	35	70	300	1.5	Stearinsäure	6.8
Linolsäure	46	92	300	1.5	Stearinsäure	11
Erucasäure	36	72	300	1	Behensäure	9.4
Zimtsäure	10	20	310	1	Hydrozimtsäure	1.9

(1) Noch nicht veröffentlicht.
(2) *Helvetica Chim. Acta*, **17** (1934), 442.

UNTERSUCHUNGEN ÜBER DIE KATALYTISCHE OXYDATIONS-WIRKUNG KOLLOIDALER SUBSTANZEN. III.

Von Yuji SHIBATA und Kazuo YAMASAKI.

Eingegangen am 31. Januar, 1935. Ausgegeben am 28. April, 1935.

Seit dem Jahre 1918 haben Yuji Shibata, Keita Shibata und ihre Mitarbeiter die Untersuchungen über die oxydasenartige Oxydationswirkung gewisser Metallkomplexsalze fortgeführt,[1] indem u.a. eine interessante Tatsache aufgefunden wurde, dass gewisse Metallkomplexe wie Nickelammine Hydroperoxyd katalytisch zersetzen.[2] Diese Zersetzung erwies sich als eine Reaktion erster Ordnung, genau wie diejenige, die durch Platinsol bewirkt wird.

Angesichts dieses Parallelismus zwischen den Wirkungen der Metallkomplexe und der Metallkolloide bei der Hydroperoxydzersetzung kam man auf den Gedanken, dass die kolloidale Substanzen wie Metallkomplexsalze vielleicht auch die oxydasenartige Oxydation auf Polyphenole leisten vermögen. Zwar wurde diese Tatsache von Y. Shibata und H. Kaneko experimentell bestätigt. In ihren früheren Untersuchungen[3] liessen sie die Hydrosole verschiedener Metalle, Metalloxyde und Silikate auf Pyrogallollösung einwirken, wobei der Reaktionsverlauf mittels eines Spektrophotometers gemessen wurde, da sich Pyrogallol bei der Oxydation bekanntlich rasch braun verfärbt.

Nun haben wir diese Frage wieder aufgenommen, um kennen zu lernen, ob die Oxydation von Phenolsubstanzen durch Metallkolloide auch die Sauerstoffabsorption anzeigen würde. Als kolloidale Metalle wurden hierbei Platin, Gold und Silber verwendet, und wie bei der Oxydationsuntersuchung mit Metallkomplexen wurde der Warburgsche Kapillarmanometer als der Messapparat benutzt.

Diese Experimente ergaben jedoch, dass die Gemische von Pyrogallol und Silber- bzw. Goldsol keine messbare Sauerstoffabsorption zeigten, obzwar dabei die Farbenänderungen der Lösungsgemische deutlich bemerkbar waren. Dagegen absorbierte die Pyrogallollösung, die mit

(1) Die vollständige Literaturangabe findet man in "Untersuchungen über die oxydasenartigen Wirkungen gewisser Metallkomplexsalze. X." von Y. Shibata u. K. Yamasaki, dieses Bulletin, **9** (1934), 2.

(2) Y. Shibata u. H. Kaneko, *J. Chem. Soc. Japan*, **44** (1923), 116.

(3) Y. Shibata u. H. Kaneko, *J. Chem. Soc. Japan*, **45** (1924), 155.

Platinsol versetzt wird, eine bedeutende Menge von Sauerstoff. Es ist sehr interessant zu bemerken, dass die absorbierten Sauerstoffmengen je nach der Bereitungsweise von Platinsol stark verschieden sind.

Beschreibung der Versuche.

Die Oxydationsgeschwindigkeit von Pyrogallol wurde bei 25° mittels eines Warburgschen Manometers gemessen. Das Volum des Reaktionsgefässes beträgt 51.2 c.c. und das Versuchsgemisch bestand aus

Pyrogallol	1/500 Mol	2 c.c.	Hauptraum
30% ige Kalilauge (in Einsatz)		1 c.c.	Hauptraum
Sol		2 c.c.	Ansatzbirne.

Ein gleichartiger Manometer, der im Thermostat neben den Manometer eingestellt wurde, diente zur Bestimmung der Luftdruckschwankung, womit man leicht die beobachtete Druckänderung korrigieren konnte. In jedem Versuch entspricht eine Druckänderung von 1 cm. der Brodie-Lösung einem Sauerstoffverbrauch von 0.04 c.c. Das käufliche Pyrogallol wurde durch wiederholte Sublimation in vacuo gereinigt.

(I) Auto-oxydation von Pyrogallol (Kontrollversuch).

Bekanntlich ist Pyrogallol sehr leicht oxydierbar; daher absorbiert seine wässerige Lösung allmählich den Sauerstoff der Luft. Wir haben also die Sauerstoffmengen, die von Pyrogallollösung ohne oder mit Zusätze von Metallkolloiden absorbiert wurden, in Abb. 1, 2, 3, 4 und 5 dargestellt. Die Ordinaten geben die Druckabnahme in cm. von Brodie-Lösung und auf der Abzisse ist die Zeit in Stunden eingetragen.

(II) Oxydation von Pyrogallol in Gegenwart von Kolloiden.

(1) **Silber.** Die Silbersole wurden nach folgenden Methoden hergestellt: (a) **Reduktion mit Tannin.** Zur Silbernitratlösung wurde Ammoniak zugefügt, bis der einmal gebildete Niederschlag wieder aufgelöst wurde. Zu dieser klaren Lösung wurde eine frisch hergestellte, 1 %ige Tanninlösung zugesetzt. Das so gebildete rotbraune Sol wurde durch Dialyse gegen destilliertes Wasser von Elektrolyten befreit. Der Silbergehalt dieses Sols war 0.040 g. Ag/l. (b) **Die Methode von Kohlschütter.**[4] In eine Flüssigkeit, die das Silberoxyd in Suspension

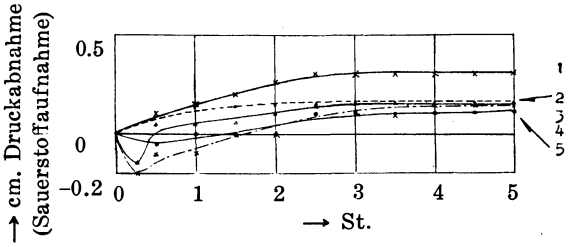
(4) *Z. Elektrochem.*, **14** (1908), 49.

enthält, wurde unter Erwärmung auf 60° ein langsamer Wasserstoffstrom 7 Stunden lang durchgeleitet. Das in Durchsicht gelbbraun und an auffallendem Licht graublau erscheinende Sol, dessen Konzentration 0.071 g. Ag/l. beträgt, wird gegen destilliertes Wasser dialysiert. Die Farbe des Sols veränderte sich dabei zum Rotbraun und der Silbergehalt verminderte sich auf 0.015 g./l. Dieser Verlust an Silbermenge entspricht wahrscheinlich der Menge des Silberoxyds, das durch Dialyse der Lösung entzogen wurde.

Beim Zufügen von nicht dialysiertem Kohlschüttersol zur Pyrogallollösung tritt ein sofortiger Farbenumschlag ins Braun ein und nach einigen Stunden wird eine schwarze Fällung gebildet, dagegen entsteht bei der Verwendung von dialysiertem Sol (sowohl Kohlschüttersol als auch Tanninsol) nur eine schwachgelbe Färbung des Lösungsgemisches, wobei nachher keine Fällung stattfindet. Bei diesen Versuchen erreichte der Sauerstoffverbrauch kaum den Wert des Kontrollversuchs.

Die Niederschläge, die beider Verwendung von nicht dialysiertem Sol gebildet wurden, bestehen aus dem Silbermetall, das wahrscheinlich durch Reduktionswirkung von Pyrogallol auf Silberoxyd gebildet wird. Zum Vergleichszweck wurde die gesättigte Silberoxydlösung zu Pyrogallollösung zugefügt, wobei ein Farbenumschlag ins Dunkelbraun eintrat, ohne dabei keine Vermehrung des Sauerstoffverbrauch aufzuzeigen.

Wie man in Abb. sieht, wurde eine anfängliche Druckzunahme in einigen Fällen beobachtet, was sehr wahrscheinlich durch die lebhafte Entwicklung der Kohlensäure bei der Oxydation von Pyrogallol verursacht wurde.



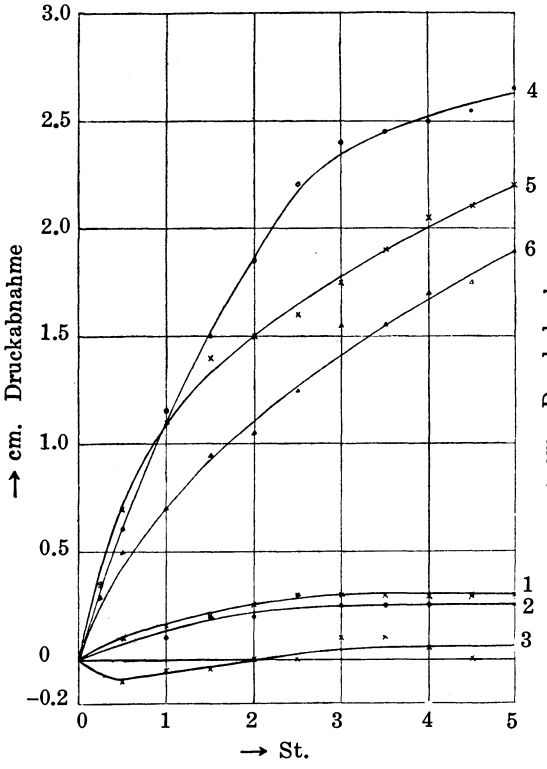
1. Kontrollversuch (Pyrogallol).
2. Nicht dialysiertes Kohlschütter-Sol.
3. Dialysiertes Kohlschütter-Sol.
4. Silberoxydlösung.
5. Silbersol (Reduktion mit Tannin).

Abb. 1. Silber.

(2) **Platin.** Die Platinsole wurden auf folgenden Weisen hergestellt: (a) **Die Bredigsche Methode.** Platin wurde unter reinem Wasser mit Gleichstrom von 100 Volt und 5 Amp. elektrisch zerstäubt. Das so erhaltene schwarzbraune Sol enthielt 0.03 g. Pt/l. (b) **Reduktion mit Formaldehyd.**[5] Eine H_2PtCl_6-Lösung mittels des Gemisches von NaOH

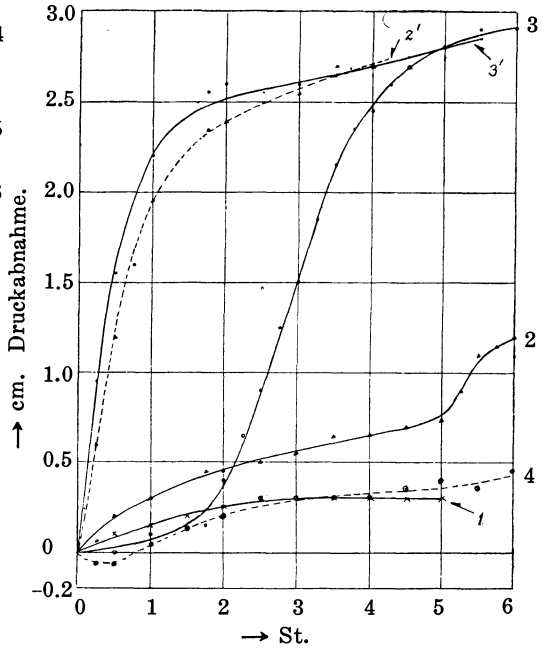
(5) K. Shigena, *Reports Osaka Imp. Ind. Research Lab.*, **8** (1927), 1.

und Formaldehyd in Anwesenheit von Natriumzitrat reduciert und durch Dialyse gereinigt. Die Konzentration war 0.008 g. Pt/l. (c) **Reduktion mit Leuchtgas.**[6] Die Oxydationsflamme des Bunsenbrenners wurde schräg über die Oberfläche der Platinlösung, die sich in einer Porzellanschale befand, gehalten. Nach 10–15 Minuten entstand ein schwarzbraunes Sol, dessen Konzentration 0.037 g. Pt/l. betrug. (d) **Reduktion mit CO.** Ganz neulich haben Sameshima und Sano eine neue Bereitungsmethode von Platinsol veröffentlicht.[7] Leitet man nämlich den Kohlenoxydstrom in eine H_2PtCl_6-Lösung hindurch, so erhält man eine schön



1. Kontrollversuch (Pyrogallol).
2. K_2PtCl_6-Lösung (1.36 g. Pt/l.).
3. H_2PtCl_6-Lösung (0.33 g. Pt/l.).
4. Platinsol (Reduktion mit Formaldehyd).
5. Bredig-Sol.
6. Plationsol (Reduktion mit Verbrennungsgasen)

Abb. 2. Platin.



1. Kontrollversuch.
2, 3, u. 4. Rote Platinsolen (Reduktion mit CO).
2′, 3′. Schwarze gewöhnliche Platinsolen, die beim Stehen von Solen 2 u. 3 im Luft entstanden sind.

Abb. 3. Platin.

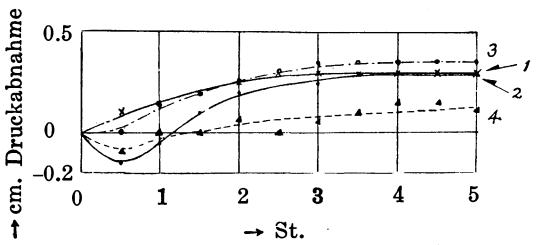
(6) J. Sameshima, *J. Chem. Soc. Japan*, **54** (1933), 695.
(7) Dieses Bulletin, **9** (1934), 320.

tiefrot gefärbte Flüssigkeit. Beim Stehen an der Luft verwandelt sich diese rote Flüssigkeit allmählich ins gewöhnliche schwarze Platinsol (0.03g. Pt/l.). Die zunächst gebildete rote Lösung zeigt manche kolloidale Verhalten, aber ihre Eigenschaften sind noch nicht im näheren bekannt.

Wie man aus der Kurve von Abb. 3 ersieht, gibt die Reaktion dieses roten Sols gegen Pyrogallol sehr unregelmässige und nicht übereinstimmende Resultate, während sich das daraus entstehende schwarze Sol ganz gleich wie andere Pt-Sol verhält. Zum Vergleich wurden H_2PtCl_6– und K_2PtCl_6-Lösung zu Pyrogallollösung zugesetzt, aber man konnte dabei weder Farbenänderung noch Sauerstoffabsorption beobachten.

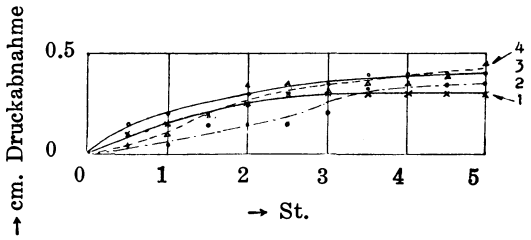
Beim Zusatz von Platinsolen zu Pyrogallol steigt im allgemeinen der Sauerstoffverbrauch und wird gleichzeitig die schwarze Färbung der Lösung hervorgerufen.

(3) **Gold.** Goldsole wurden auch nach verschiedenen Methoden hergestellt: (a) **Reduktion mit Tannin.** Zu 200 c.c. von 0.04%iger Goldchloridlösung wurde 5 c.c. von frisch hergestellter 1%iger Tanninlösung zugefügt. Durch Erwärmung dieses Lösungsgemisches erhielt man ein rot gefärbtes Sol, dessen Konzentration 0.02 g. Au/l. betrug. (b) **Reduktion mit CO.** Das Kohlenoxydgas wurde in Goldchloridlösung eingeleitet. Nach einigen Minuten trat eine Rotfärbung ein. Ihre Konzentration betrug 0.02 g.Au/l. (c) **Reduktion mit Leuchtgas.**[8] Das Goldsol wurde genau in gleicher Weise wie beim Falle von Platinsol hergestellt. Die Konzentration von so erhaltenem Sol war 0.022 g. Au/l. (d) **Die Bredigsche Methode.** Die elektrische Zerstäubung unter reinem Wasser und in KCl-Lösung ($2\cdot10^{-4}$ Mol) mit einer Stromstärke von 4–5 Amp. und einer Spannung von 100 Volt (g. S.) ausgeführt. In reinem



1. Kontrollversuch.
2. $HAuCl_4$-Lösung.
3. Goldsol (Reduktion mit Verbrennungsgasen).
4. Goldsol (Reduktion mit Tannin).

Abb. 4. Gold.



1. Kontrollversuch.
2. Bredig-Sol (KCl-Lösung).
3. Goldsol (Reduktion mit CO).
4. Bredig-Sol (reines Wasser).

Abb. 5. Gold.

(8) J. Sameshima, *loc. cit.*

Wasser erhält man nur eine grobdisperse Suspension, die sich nach etwa 30 Minuten am Boden des Gefässes absetzt. Die schwachviolett gefärbte Mutterlauge, deren Goldgehalt 0.01 g. Au/l. war, wurde zum Versuch verwendet. Das in KCl-Lösung dispergierte, tief rot gefärbte Goldsol ist dagegen sehr beständig und die Konzentration betrug 0.014 g. Au/l.

Die Pyrogallollösung, die mit Goldsole versetzt wurde, zeigte keine messbare Sauerstoffabsorption und auch nach langem Stehen keine auffallende Farbenänderung. Schliesslich wurde die Lösung von $HAuCl_4$ (1 g. Au/l.) zur Pyrogallollösung zugefügt, wobei Aurichlorsäure reduciert wurde und sich das Goldmetall in kolloidaler Form in Flüssigkeit dispergierte. Auch dieses blaue Sol zeigte keine Sauerstoffabsorption in Pyrogallollösung.

Zusammenfassung.

Das Oxydationsvermögen von kolloidalem Platin, Silber und Gold auf Pyrogallollösung wurde manometrisch untersucht. Die Platinsole beschleunigten diese Oxydation immer bedeutend, aber Silber und Gold zeigten keine messbaren katalytischen Oxydationswirkungen.

Anorganisch-Chemisches Laboratorium,
Kaiserliche Universität zu Tokyo.

ON BASKING SHARK LIVER OIL.

By Mitsumaru TSUJIMOTO.

Received February 1st, 1935. Published April 28th, 1935.

Basking shark (Japanese: "Ubazamé" or "Bakazamé"), *Cetorhinus maximus* (Gunner), reaches to a length of 36 feet and is the largest of all the living fish. The chemical examination of basking shark liver oil was first made by the author[1] in 1917; three commercial specimens, which were apparently prepared from adult fish, contained squalene, and in one of them the author discovered a peculiar iso-octadecane (pristane),

(1) *J. Soc. Chem. Ind. Japan*, **20** (1917), 953, 1099; *J. Ind. Eng. Chem.*, **9** (1917), 1098; **12** (1920), 65.

$C_{18}H_{38}$. Then the author[2] and also Y. Toyama[3] examined the liver oils from young basking sharks (length ca. 2.4–2.7 m.); the former found about 8% of cholesterol in the oil. In France, E. André and H. Canal[4] investigated the oils from two adult and a young basking sharks, and observed a reciprocal relation between the contents of cholesterol and squalene.

Basking shark liver oil is sometimes of peculiar properties, for example, a notable amount of pristane being present in it, so it is one of the most interesting liver oils.

For a long time it had been the author's earnest desire to obtain the liver of the adult fish and to prepare the oil in the laboratory. This was recently fulfilled by procuring the following two specimens.

(1) **Basking Shark Liver Oil No. 1.** The fish which gave this oil was a large female basking shark caught in Toyama Bay[5] on December 14, 1933. It was not dissected at the fishing district, but was sent to Kyoto, where it was exhibited as a show under a signboard of a "large monster sea dragon". As it had been known that the fish would be dissected in the city, several negotiations were made with its owner, and a part of the liver was eventually procured to the laboratory on January 12, 1934, after the lapse of nearly one month.

The fish mentioned above had a length of 775 cm.[6] and a weight of about 2000 kg. The liver had a greyish-white colour mingled with blood-red parts, and was of a very oily consistency; in spite of long keeping in the fish body, it showed a comparatively little putrefaction. A batch of 1000 g. of the liver gave, on complete exhaustion, 854 g. i.e., 85.4% of the oil. From 57 kg. of the liver, 45 kg. (ca. 79%) of the oil was obtained by careful heating.

The oil was a pale orange-yellow liquid with a not unpleasant odour; it deposited a little solid substance at room temperature of 6–14° C. With sulphuric acid it gave a brown colour with a slight violet-red tinge; nearly no blue colouration was observed by the $SbCl_3$ test.

---

(2) *Repts. Tokyo Imp. Ind. Research Lab.*, **15** (1920), No. 2, 1, and No. 10, 85.

(3) *J. Soc. Chem. Ind. Japan*, **27** (1924), 601.

(4) *Ann. chim.*, (X), **7** (1927), 69; *Bull. soc. chim.*, (IV), **45** (1929), 598. The lengths of the sharks were 6m., 4.7m., and 3.4m. respectively.

(5) Toyama Bay is an inlet of the Japan Sea and lies to the north of Central Japan, being bounded by Etchu Province (Toyama Prefecture) on the east and south and by Noto Province (Ishikawa Prefecture) on the west.

(6) This figure is due to Mr. Kan-emon Kikuchi of the Toyama High School, who actually measured the fish and to whom the author wishes to express his thanks.

(2) **Basking Shark Liver Oil No. 2.** On January 25, 1934, a telegram from Higashi-Iwase Town Office, Toyama Prefecture, was received by the author, which informed that a large shark was caught again in Toyama Bay. Contrary to the case of the former shark, by easy negotiations and chiefly through the kindness of the above-mentioned office, a part of the liver was procured on January 31. According to a communication of Mr. Awata, a fish-dealer, who treated the shark, it was male in sex, had a length of 24 "shaku" (727 cm.) and a weight of 580 "kwan" (ca. 2170 kg.); the liver weighed 90 "kwan" (337.5 kg.).

The liver was mostly of a dirty, yellowish-grey colour. One kilogram of it contained 838 g., i.e., 83.8% of the oil. From 29 kg. of the liver, about 23 kg. (ca. 79%) of the oil were obtained.

The oil had a pale, orange-yellow colour and did not deposit solids even in winter. Sulphuric acid gave a yellow-brown colour; the $SbCl_3$ test nearly no colouration.

The characteristics, etc., of these oils were found as shown in Table 1.

Table 1.

	d_4^{15}	n_D^{20}	Acid value	Saponif. value	Iodine value (Wijs)	Unsaponif. matter (%)
Oil No. 1 (Female)	0.8973	1.4794	0.16	126.3	185.6	30.35
Oil No. 2 (Male)	0.8808	1.4785	0.21	94.8	191.5	45.13

The oil No. 2 had lower specific gravity and saponification value and higher iodine value. These were chiefly due to the higher proportion of squalene in the oil. The observation that the liver oil of male shark contains more squalene, has already been made in the case of "kuroko-zamé" (*Centroscyllium*).[7]

(3) **Fatty Acids.** After removing the unsaponifiable matter, the soap solution was decomposed with hydrochloric acid. The fatty acids thus liberated had the properties shown in Table 2.

The fatty acids from the oil No. 2, which contained more squalene, showed a far less unsaturation.

(7) Tsujimoto, *Repts. Tokyo Imp. Ind. Research Lab.*, **27** (1932), No. 15, 20.

Table 2.

Fatty acids from	Appearance	Melt. pt.	Neutr. value	Iodine value	n_D^{25}	Ether-insol. bromide (%)	Br content of the bromide (%)
Oil No. 1	Nearly white crystalline mass	Chiefly melted at 24–25°C., became clear at 27°C.	186.4	130.0	—	27.0	70.23
Oil No. 2	Mixture of white solids and a pale yellow liquid	Became clear at 20–21°C.	179.3	88.2	1.4605	9.3	69.63

(4) **Unsaponifiable Matter.** Some of the properties are given in Table 3. (Cholesterol was determined by the digitonine method.)

Table 3.

Unsaponif. matter from	Appearance	n_D^{20}	Iodine value	Cholesterol (%)
Oil No. 1	Pale yellow liquid; deposited a little solid substance in winter	1.4900	338.9	1.83
Oil No. 2	Pale yellow liquid	1.4863	302.4	0.94

The lower refractive index and iodine value of the unsaponifiable matter from the oil No. 2 were due to the notable proportion of pristane.

(5) **Determination of Hydrocarbons.** These were determined by distillation under diminished pressure.[8]

Oil No. 1 (a). The oil (50.3 g.) was distilled under 5 mm. pressure. Above the bath temperature 255°C the distillation began, the thermometer of the flask soon rising to 180°C. At the maximum temperature 247°C. (bath temp. 313°C.) the distillation ended. The distillate was a pale yellow liquid; yield 13.1 g., acid value 2.21. Subtracting the amount of free acids, the yield of hydrocarbons was 25.8%. The refractive index of the distillate, after washing off the acids, was n_D^{20} 1.4897. Its main constituent was squalene. But as an appreciable amount of pristane

(8) Tsujimoto, *J. Ind. Eng. Chem.*, **12** (1920), 71.

appeared also to be present, the lower boiling fraction was determined separately.

Oil No. 1 (b). The oil (50.5 g.) was distilled under the pressure of 5 mm. The distillation began above 250°C. of the bath temperature; the thermometer of the flask soon indicated 144°C. The temperature of the bath was gradually raised to and kept at 270°C., at which nearly no squalene distilled over. The maximum temperature of the distillation was 154°C.; then the temperature sank and the distillation ended. The distillate (colourless liquid) was 1.4 g., and had acid value 1.04. Subtracting free acids, the yield of hydrocarbons (pristane part) was 2.76%. The acid-free substance had n_D^{20} 1.4430 and iodine value 31.8.

Oil No. 2. The oil (50.2 g.) was distilled under 5 mm. pressure. The pristane and squalene parts were determined in one distillation by changing receivers.

Pristane part. Maximum bath temperature 270°C.; maximum distillation temperature 154°C.; distillate (colourless liquid) 3.4 g., acid value 0.202; yield of hydrocarbons 6.76%; the acid-free substance had n_D^{20} 1.4410 and iodine value 18.9.

Squalene part. Maximum bath temperature 320°C.; maximum distillation temperature 246°C.; distillate (nearly colourless liquid) 17.8 g., acid value 0.72; yield of the hydrocarbon 35.34%; the acid-free substance had n_D^{20} 1.4950.

The total yield of the hydrocarbons was 42.1%.

As the above experiments showed, the basking shark liver oils used in the present investigation were notably rich in pristane, especially in the oil No. 2 reaching to about 6%. With such specimens it would not be difficult to prepare pristane in kilogram units, even with ordinary apparatuses of a laboratory. If the total liver of the second shark had been utilized, about 16 kg. (ca. 20 liters) of pristane would have been obtained.

It is also to be noted that the notable occurrence of pristane in basking shark liver oil appears not to be of rare, but of rather frequent instance.

Besides pristane and squalene, there occurred in the oils a new unsaturated hydrocarbon, which is described in the next paper.

Tokyo Imperial Industrial Research Laboratory,
Hatagaya-cho, Shibuya, Tokyo.

ON A NEW HYDROCARBON IN BASKING SHARK LIVER OIL.

By Mitsumaru TSUJIMOTO.

Received February 1st, 1935. Published April 28th, 1935.

In the author's first experiments on the isolation of pristane (at that time described by the name of "iso-octadecane"),[1] the crude hydrocarbon even after alkali-washing and redistillation had iodine value 4.4. In Y. Toyama's elaborate investigation on the occurrence of pristane in various squalene-containing shark liver oils, in which the present name has been proposed for the hydrocarbon,[2] the crude substances corresponding to pristane showed always more or less iodine values (2.3–25.6). It should, however, be mentioned that the specimens of shark liver oil used by him were all meagre in the proportions of pristane, the actual yield being 0.5–0.7%, so that in order to separate the hydrocarbon from the oil a strong heating was necessitated. So Toyama judiciously took the unsaturated compounds more likely to be decomposition products rather than normal constituents of the oils. A few years ago the present author[3] got a similar result with "gonshika" liver oil. Thenceforth the author has been inclined to consider the unsaturation or at least a part of it to be due to some naturally occurring substance or substances in the oils. To decide the question it is necessary to procure a shark liver oil that contains pristane in a fairly large proportion. Advantageously the basking shark liver oils reported in the preceding paper are well suited for the purpose.

(1) **Experiment 1.** The basking shark liver oil No. 1 (1500 g.) was distilled under 4.5–5.5 mm. pressure in batches of 300 g. in a Claisen fiask, the maximum temperatures of the metal bath and the distillation being 270°C. and 146–152°C. respectively. The yield of the distillate was 31.5 g. (2.1%); it had acid value 1.20. On washing off the free acids with alkali, it formed a nearly colourless liquid of n_D^{20} 1.4400 and iodine value 10.1. It (30 g.) was re-distilled under 14 mm. pressure over metallic sodium in

(1) *J. Soc. Chem. Ind. Japan*, **20** (1917), 1099; *J. Ind. Eng. Chem.*, **9** (1917), 1098.

(2) *J. Soc. Chem. Ind. Japan*, **27** (1924), 333; *Chem. Umschau*, **30** (1923), 181.

(3) *Repts. Tokyo Imp. Ind. Research Lab.*, **26** (1931), No. 10, 33. Gonshika is said to be a very large shark, but its scientific name has not yet been ascertained. The properties of its liver oil closely resemble those of basking shark liver oil.

a small flask; the distillation began at the bath temperature 210°C. Up to the distillation temperature 174°C., 28.6 g. distilled; the distillate had n_D^{20} 1.4395 and iodine value 5.2.

As may be seen from the above-mentioned, the pristane part had, even after purification, an appreciable iodine value. For the separation of unsaturated hydrocarbons from the saturated, a method was tried, which consisted in the application of the greater solubility of the former in alcohol or methanol. This method gave, however, unsatisfactory result, at least with a small quantity of the specimen. As there was no simple method applicable, a final resort was found in the so-called "Bromestermethode",(4) which has been proposed for the separation of saturated and unsaturated fatty acids. Of course, the method has a drawback that it requires energetic chemical reactions, viz., bromination and debromination.

The distillate (25.3 g.) was dissolved in 100 c.c. of ether, and with well cooling in ice, about 0.2 c.c. of bromine was added, thereby no precipitate was formed. On removing the excess of bromine with a solution of sodium thiosulphate and bicarbonate, 26 g. of the bromine addition compound was obtained. It was then distilled under 2.5–3 mm. pressure; the maximum temperature of the bath and the distillation were 188°C. and 142°C. respectively. Contrary to expectation the distillation proceeded continuously without a break, so it was stopped appropriately. The distillation residue was a brown-coloured liquid, which on washing with bicarbonate solution, weighed 1.5 g. It was treated with rasped zinc and alcoholic hydrochloric acid. The reaction went on difficulty. The yield of the debrominated product was 1.1 g., which contained still a little bromine as indicated by the CuO flame reaction. It was an orange-yellow liquid of n_D^{20} 1.4533 and iodine value 64.3. No precipitate was formed on saturating its ethereal solution with hydrogen chloride, so squalene was not present in it.

Although no definite compound was isolated by the above experiment, it has been confirmed that there occur in the pristane part of the basking shark liver oil some natural, unsaturated hydrocarbon or hydrocarbons.

(2) **Experiment 2.** The basking shark liver oil No. 2 was distilled in batches of 300 g. under 3–5 mm. pressure, the maximum temperatures of the bath and the distillation being 270°C. and 139–157°C. respectively. On the whole, 3000 g. of the oil gave 196 g. (6.5%) of the distillate. The

(4) A. Grün, "Analyse der Fette und Wachse", Vol. I, p. 223.

latter was a nearly colourless liquid of acid value 0.3; after alkali washing it had n_D^{20} 1.4400 and iodine value 9.5.

The distillate (195 g.) was redistilled under 9–10 mm. pressure in a flask with a Willstätter bulb. Up to the bath temperature 242°C. and the distillation temperature 175°C., 191 g. of the distillate was obtained. In this distillation the distillate was divided into four fractions to see if some separation of the components be effected. But they had nearly equal refractive indices (n_D^{20} 1.4390–1.4394), so they were mixed together. The distillation residue had n_D^{20} 1.4702 and produced a white precipitate with hydrogen chloride in an ethereal solution; this was probably due to the presence of squalene.

Then the distillate (187 g.) was again distilled under 10.5–11 mm. pressure over metallic sodium; the maximum temperature of the bath was 215°C. and that of the distillation 165°C.; the weight of the distillate 183 g., n_D^{20} 1.4389, iodine value 3.4. The residue also contained a small amount of squalene.(5)

Hereupon the "Bromestermethode" was tried on the refined distillate. It (182 g., 235 c.c.) was dissolved in an equal volume of ether and on cooling 1.3 c.c. of bromine was added. The solution showed a little turbidity and on standing a small amount (ca. 0.1 g.) of a white precipitate was formed, probably due to admixed squalene. The solution was filtered from the precipitate, and washed with a solution of sodium thiosulphate and bicarbonate to remove the excess of bromine. On distilling off the ether, 187 g. of the bromine addition product was obtained (a somewhat larger weight was caused by admixed solvent). It was then distilled under 2.5 mm. pressure; the distillation began at the bath temperature 200°C. Up to the bath temperature 210°C. and the distillation temperature 156°C., 227 c.c. of the distillate was obtained. At this point the distillation was interrupted.(6) The distillation residue formed a dark, brownish-yellow liquid and weighed 7.6 g., which in winter deposited a little solid substance. Debromination was effected with rasped zinc, alcoholic hydrochloric acid and petroleum ether. Difficulty was experienced as in the case of the previous experiment. The debrominated product was a dark, brownish-yellow liquid and amounted to 5.7 g.; by the flame reaction, it was found to contain a little bromine. Finally it was refined

(5) The cause why in these distillations squalene was accompanied in the low boiling fractions was not exactly known.

(6) If we assume the unsaturated hydrocarbon to be $C_{18}H_{36}$, by calculating from the iodine value (3.4), its amount is ca. 6 g. or ca. 8 c.c.; hence the amount of the saturated hydrocarbon corresponds to 235−8=227 c.c.

by distilling under 12 mm. pressure. At 175–185°C., 3.9 g. of a pale yellow liquid distilled over; it had d_4^{20} 0.7948, n_D^{20} 1.4470 and iodine value 66.2. It was free from the halogen, and squalene was not present in it.

(Found: C, 85.46; H, 14.66; Mol. wt. (in benzene), 240. Calc. for $C_{18}H_{36}$: C, 85.62; H, 14.33; Mol. wt., 252.3. Calc. for $C_{18}H_{38}$ (pristane): C, 84.94; H, 15.06; Mol. wt., 254.3.)

The substance was, therefore, recognized to be a mixture of an octadecylene, $C_{18}H_{36}$ (calculated iodine value, 100.6) and pristane, the former predominating.

On the assumption that the substance is a simple mixture of the two hydrocarbons, we get by calculation d_4^{20} 0.8006 and n_D^{20} 1.4510 for the values of the octadecylene (according to Toyama, pristane d_4^{20} 0.7835, n_D^{20} 1.4390). Adopting these values, the molecular refraction of the octadecylene is 84.82, which agrees closely with the calculated value $C_{18}H_{36}$|= 84.86.

The experiment to concentrate the unsaturated hydrocarbon by means of methanol was performed as follows: the mixture (2.105 g.) was treated with 100 c.c. of methanol. The soluble part amounted to 1.331 g. (63.2%) and had n_D^{20} 1.4480 and iodine value 70.3. It (1.209 g.) was again treated with 50 c.c. of methanol. The soluble part was 0.653 g. (54.0%) and had n_D^{20} 1.4500 and iodine value 78.4. The operation was interrupted from the want of the material, but it seemed to be possible to concentrate further the unsaturated hydrocarbon. Of course, the insoluble parts had also fairly high iodine values (1st 43.5, 2nd 51.1).

The concentrated substance (iodine value 78.4) was hydrogenated with platinum black as catalyser. The product was a liquid of n_D^{20} 1.4405 and iodine value 1.9. If hydrogenation be carried out completely, the final product appears to be pristane or a very similar compound.

By the above experiments, the occurrence of an octadecylene in the basking shark liver oil has been confirmed. Its amount was, however, far smaller than anticipated.

The objection that unsaturated hydrocarbons might be formed by the decomposition of the oil by over-heating, may be negated from the following grounds, viz., (1) the temperature of the bath was comparatively low (up to 270°C.), so that no appreciable decomposition would be expected to occur, and (2) decomposition products of the dry distillation of squalene are a mixture of hydrocarbons and not a single compound such as octadecylene. Also according to Toyama's experiments, such products, which correspond to pristane, are highly unsaturated hydrocarbons of very high iodine values.

The octadecylene appears to occur not only in basking shark liver oil, but also in other squalene-containing shark liver oils, probably in far smaller proportions.

Although the author has not yet succeeded in isolating this hydrocarbon in pure state, nevertheless as there is little doubt as to its natural occurrence, he has given the name "Zamene" to it (Japanese: "Samé" or "Zamé" = shark).

Summary.

Although small in proportion, a new octadecylene, $C_{18}H_{36}$, has been found to occur, together with pristane, in basking shark liver oil. In far smaller proportions, it probably occurs in many other, squalene-containing shark liver oils in association with pristane. The author has proposed the name "Zamene" for this new hydrocarbon.

Tokyo Imperial Industrial Research Laboratory,
Hatagaya-cho, Shibuya, Tokyo.

A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. X. THE VISCOSITY OF AQUEOUS SOLUTIONS OF ELECTROLYTES.

By Tetsuya ISHIKAWA and Toshitomo BABA.

Received February 2nd, 1935. Published April 28th, 1935.

Much attention has been paid to the study of the viscosity of strong electrolyte solutions since Jones and Dole[1] proposed in 1929 an empirical equation:

$$\eta^* = 1 + A\sqrt{c} + Bc\,,$$

where η^* is the specific viscosity of a salt solution, c the concentration in mols per litre, and A and B constants. Falkenhagen, Dole, and Vernon[2]

(1) Jones and Dole, *J. Am. Chem. Soc.*, **51** (1929), 2950.
(2) Papers summarized in *Phil. Mag.*, **14** (1932), 537.

made a brilliant success in evaluating the coefficient A from the ion-atmosphere theory in terms of the well-known physical constants, i.e.

$$A = \frac{12.78\times10^{-10}\sqrt{\frac{N}{1000}}\sqrt{\frac{P_1z_1}{z_1+z_2}}}{\sqrt{4\pi DkT}}\cdot \frac{\varepsilon}{\eta_0}\left\{\frac{z_1^3}{L_1}+\frac{z_2^3}{L_2}-\frac{\frac{4z_1^3z_2^3}{L_1L_2}\left(\frac{L_1}{z_1^2}-\frac{L_2}{z_2^2}\right)^2}{\left[\sqrt{\frac{L_1}{z_1}+\frac{L_2}{z_2}}+\sqrt{(z_1+z_2)\left(\frac{L_1}{z_1^2}+\frac{L_2}{z_2^2}\right)}\right]^2}\right\}$$

where ε is the unit charge of electricity in e.s.u. ($\varepsilon=4.77\times10^{-10}$), N Avogadro's number ($N=6.06\times10^{23}$), P_1 the number of, say, positive ions formed in dissociation, L_1, L_2, and z_1, z_2, the ionic molar conductance and numerical values of the valencies of positive and negative ions respectively, D and η_0 the dielectric constant and the viscosity of the solvent, k Boltzmann's constant ($k=1.37\times10^{-16}$ ergs/degree), and T the absolute temperature.

Wolfenden and his coworkers[3] pointed out that the approximate additivity for individual ions might exist in the coefficient B.

The Falkenhagen-Dole-Vernon theory tells us that the interionic forces acting on the viscosity of electrolyte solutions may become negligibly small as compared with the rapid increase of the viscosity in suitably high concentration, and the Jones-Dole equation which serves at present only for the estimation of the coefficient A in accord with the former theory has no great rôle in an unknown field of more concentrated solutions.

Experimental works on the viscosity of concentrated solutions of various electrolytes have been done in earlier times and have thrown more interesting problems than that of dilute solutions. Hübner[4], Sprung[5], Wagner[6] and others observed the curious phenomenon showing the viscosities less than that of water which they termed "negative viscosity". In fact, some salts of Cs, Rb, K and NH_4 produce negative viscosities. All electrolytes except these show viscosities greater than that of water. The name of "positive viscosity" is often used as an antonym to negative viscosity.

---

(3) Cox and Wolfenden, *Proc. Roy. Soc. London*, **145** A (1934), 475; Laurence and Wolfenden, *J. Chem. Soc.*, **1934**, 1144.
(4) Hübner, *Pogg. Ann.*, **157** (1873), 130.
(5) Sprung, *ibid.*, **159** (1876), 1.
(6) Wagner, *Z. physik. Chem.*, **5** (1891), 31.

It is generally observed, however, in the case of the negative viscosity that the viscosity lowers with the increase of concentration more and more in a certain range of concentration, but this tendency suddenly ceases at a suitable concentration, thus showing a minimum value, and at still higher concentration the viscosity increases acceleratedly with the increasing concentration even showing the positive viscosity. The temperature also influences the negative viscosity remarkably in such a manner that it gradually turns out to the positive viscosity as the temperature rises.

In certain cases the inter-ionic forces veil the negative viscosity at extremely low concentration as readily understood from the sign of the sum of the second and third terms in the Jones-Dole equation.

Among many proposed explanations for this anormalous phenomenon of negative viscosity the suggestions made by Jones and Veazay[7] and by Getman[8] are worth mentioning first. These authorities stated that it was due to the cations to lower the viscosity of the solvent while the anions and the undissociated molecules always increased it, and moreover Jones and Veazay pointed out that the salts of K, Rb, and Cs having the highest atomic volumes known showed the marked negative viscosity. Tammann and Rabe[9] who discovered the parallelism between the curve viscosity versus concentration and the curve viscosity versus pressure for aqueous solutions of salts emphasized that the negative viscosity was due to this effect of salts to increase the internal pressure of the solvent. Rabinovich[10] made an extensive study on the cause of the negative viscosity in consideration of many factors acting upon the viscosity of solutions, especially those lowering the internal friction of the solvent, and came to the conclusion that the depolymerization of solvent molecules alone was adequate to explain the negative viscosity and that what was stated by the above-mentioned investigators was self-explaining from this consideration.

Judging from Rabinovich's idea which seems to represent all the explanations hitherto made on this subject, it may be acknowledged that the negative viscosity depends solely on the action of ions—especially of cations, but not on the action of undissociated molecules.

Recently one of the present writers[11] has put forward the assumption that an associated molecule of a liquid is a grouping of single mole-

(7) Jones and Veazay, *Am. Chem. J.*, **37** (1907), 405.
(8) Getman, *J. Am. Chem. Soc.*, **30** (1908), 721.
(9) Tammann and Rabe, *Z. anorg. allgem. Chem.*, **168** (1927), 73.
(10) Rabinovich, *J. Am. Chem. Soc.*, **44** (1922), 954.
(11) Ishikawa, this Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155.

cules 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, and has deduced the following viscosity formula for a binary mixture which is fairly calculable from the constants of the constituents provided that no chemical reactions take place on mixing them:

$$\eta = \frac{\eta_1 k_1 a_1 (1-z_m) + \eta_2 k_2 a_2 z_m}{k_1 a_1 (1-z_m) + k_2 a_2 z_m} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where η, a, k, with suffixes 1 and 2 signify the viscosities, the association degrees and his so called "field constants" of component 1 and 2 respectively; z_m a formal molar fraction of component 2. The above formula indicates that the share of each component viscosity consists of two factors of equal importance, the molecular attraction force presumably proportionate to the association degree and the number of molecules, i.e. it is expressed, in fraction, by $\frac{k_1 a_1 (1-z_m)}{k_1 a_1 (1-z_m) + k_2 a_2 z_m}$ for component 1 or $\frac{k_2 a_2 z_m}{k_1 a_1 (1-z_m) + k_2 a_2 z_m}$ for component 2. The validity of this equation has been already justified with numerous examples of organic non-electrolytes, and has proved to be valid and always superior to other noted empirical equations containing several arbitrary constants. It has also been shown that his equation is fairly applicable to the special case where one of the component is a solid substance such as naphthalene or diphenyl. Ishikawa has made a further success in expressing the viscosity of a binary mixture which forms a molecular compound in solution, i.e.

$$\eta = \frac{\eta_1 k_1 a_1 (1-z_m) + \eta_2 k_2 a_2 z_m}{k_1 a_1 (1-z_m) + k_2 a_2 z_m} + C(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \cdots\cdots\cdots \quad (2)$$

where ν_1 and ν_2 are respectively the molecular numbers of component 1 and 2 in the molecular compound, and C is a constant which varies with the temperature or more closely

$$C = C_0 (\eta_1^{\nu_1} \eta_2^{\nu_2})^{\frac{m}{\nu_1 + \nu_2}}$$

in which C_0 and m are constants independent of the temperature and concentration.

He has also found that m in the above relation takes the value 2 if the molecular compound firmly exists without dissociation, but takes a lower value if the molecular compound suffers ionic or molecular dis-

sociation. Equation (2) has merits that it furnishes us with a reliable means for determining the composition of the molecular compound formed as well as it expresses quantitatively the viscosity of a binary mixture of any kind.

For one more example, the mixture of pyridine (1) and acetic acid (2) will be here adopted from the recent measurements done by Swearingen and Heck[12] over a wide range of temperature. The fusion curve of this mixture studied quite recently by Swearingen and Ross[13] indicated two maxima: one corresponded to a compound $C_5H_5N{\cdot}CH_3COOH$ and the other, a hidden maximum, corresponded probably to $C_5H_5N{\cdot}4CH_3COOH$ or $C_5H_5N{\cdot}5CH_3COOH$ according to their opinion. The curve viscosity versus concentration, however, showed no peculiarity at the former composition, but a marked maximum at the latter.

Now for the estimation of the products ka of the respective liquids we have fortunately the viscosity data at 30°C. of a physical mixture of pyridine and ethyl acetate observed by Puschin and Pinter[14], from which we have evaluated that of pyridine to be 0.76 as referred to that of benzene. Take this value and 0.82 for acetic acid as previously obtained, or put $\frac{k_2a_2}{k_1a_1} = \frac{0.82}{0.76} = 1.08$, which is presumably invariant for the temperature studied, in equation (2). Then the difference between the observed viscosity values (η) and thus calculated (η_0) (η_0^* as appears in other tables means its specific value) can be obtained. Fig. 1 illustrates the values $\eta - \eta_0$ divided by $(1-z_m)z_m$ as ordinate and z_m as abscissa. The horizontal line up to z_m=0.45 indicates the existence of $C_5H_5N{\cdot}CH_3COOH$ which can not be found directly from the curve viscosity versus concentration, and a curve which begins at z_m=0.5 and increases rapidly upwards at higher concentration is the strong indication of $C_5H_5N{\cdot}5CH_3COOH$ as clearly seen from Fig. 2 in which the values $\eta - \eta_0$ divided by $(1-z_m)z_m^5$ is taken as ordinate. The temperature variation of C of these compounds are completely expressed by the following equations respectively:

$$\log C_{1:1} = 1.145 + \frac{1.44}{1+1} \log (\eta_1 \eta_2)$$

and

$$\log C_{1:5} = 3.537 + \frac{2.00}{1+5} \log (\eta_1 \eta_2^5) .$$

(12) Swearingen and Heck, *J. Phys. Chem.*, **38** (1934), 395.
(13) Swearingen and Ross, *J. Phys. Chem.*, **38** (1934), 1085.
(14) Puschin and Pinter, *Z. physik. Chem.*, **151** (1930), 135.

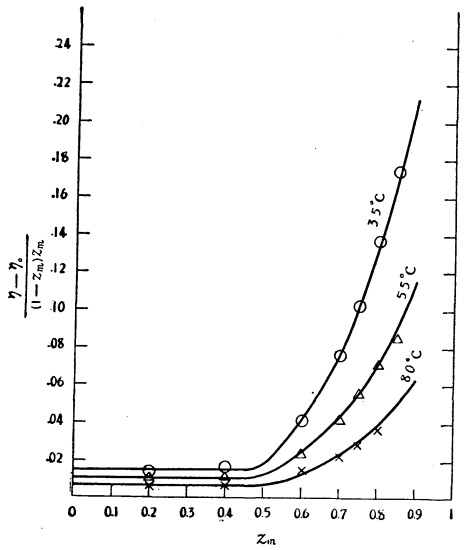


Fig. 1.

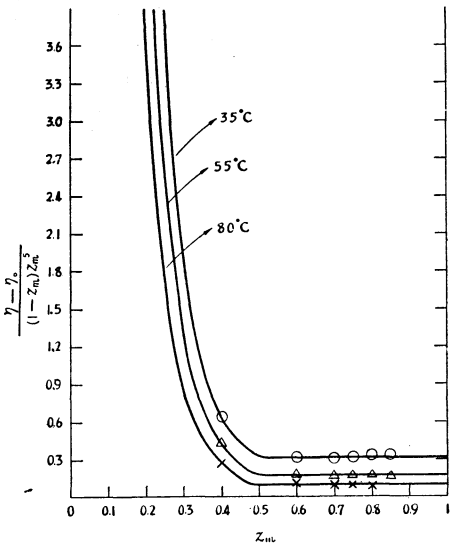


Fig. 2.

The extreme coincidence between the observed and calculated values is shown in Table 1.

Table 1.

t°C.	Molecular compound $C_5H_5N \cdot CH_3COOH$		Molecular compound $C_5H_5N \cdot 5CH_3COOH$	
	$C_{obs.}$ (mean)	$C_{calc.}$	$C_{obs.}$ (mean)	$C_{calc.}$
35	0.0156	0.0155	0.327	0.324
45	0.0129	0.0122	0.235	0.230
55	0.0107	0.0102	0.175	0.177
65	0.0077	0.0087	0.138	0.140
75	0.0074	0.0074	0.108	0.110
80	0.0068	0.0068	0.097	0.096

The present paper is contributed to the study of the viscosity of electrolyte solutions from the same standpoint of view, the Falkenhagen effect being taken into account.

Before entering into further study, the writers have, in this place, to introduce their conception upon the negative viscosity : The chief factor of the negative viscosity depends on no other than the viscosity of the solute or, more correctly to say, the solutional viscosity of the salt, though other investigators considered it to be the depolymerizing action of cations against solvent molecules. As regards the solutional viscosity there have been few descriptions in the literature. Rabinovich supposed it to be of high value enough to compare with the viscosity of

a solid, but Kendall[15] estimated it to be of the same order as that of ordinary organic solvents by using his cube-root formula. Ishikawa also calculated the solutional viscosities of naphthalene and diphenyl to be nearly equivalent as estimated by Kendall, i.e. 0.0265 and 0.0541 at 25°C. respectively. Quite recently Castiglioni[16] observed that camphor and menthol in oleic acid had the solutional viscosities less than the solvent, giving the additional proof for the validity of the Ishikawa formula, although unfortunately we find his mistake in recalculating molar fractions of the solute from its weight percentages: i.e. the solutional viscosity of menthol at 20°C. has the value 0.02596 against the value of the solvent 0.03235 at the same temperature.

It may be probable to consider such a case that the solutional viscosity of a salt differs not so much from the viscosity of water, and if the former is less than the latter, the negative viscosity results according to our theory. The question why the negative viscosity disappears when the concentration sufficiently increases may be easily answered by postulating the solvation or hydration effect as in the pyridine-acetic acid mixture above cited.

In general, the following three cases for the solutional viscosity less than the viscosity of water may be assumed: Firstly, no hydration takes place and negative viscosity is observed throughout the concentration; secondly, a slight hydration takes place so that negative viscosity appears distinctly at low concentration but becomes less distinct or disappears in high concentration; and thirdly, a marked hydration takes place in such a degree that no negative viscosity is perceptible even in low concentration. That when solutional viscosity is greater than the viscosity of water the positive viscosity results is self-evident from the above consideration.

In the following treatment, aqueous solutions of alkali chlorides and nitrates will be taken as adequate examples of the different cases mentioned above.

For simplicity, we rewrite equation (2) in the following form:

$$\eta^{**} = 1 + \frac{(H-1)Kz_m}{1-z_m+Kz_m} + C^*(1-z_m)^{\nu_1}z_m^{\nu_2} \quad \cdots\cdots\cdots\cdots \quad (3)$$

where H is the specific solutional viscosity of the solute, the viscosity of water being taken as unity, K a positive characteristic constant of the solute relative to that of water, and C^* a constant independent of the

(15) See Hatschek's "The Viscosity of Liquids", London (1928).

(16) Castiglioni, *Gazz. chim. ital.*, **63** (1933), 395; **64** (1934), 465.

concentration but dependent on the temperature. η^{**} denotes the difference between the observed specific viscosity and the viscosity caused by the inter-ionic forces according to the Falkenhagen-Dole-Vernon theory, though this correction may not be strictly rigorous in high concentration, yet the error thereby may be inappreciable.

Differenciate equation (3) and take the limit when z_m tends to 0, we have

$$\lim_{z_m \to 0}\left(\frac{d\eta^{**}}{dz_m}\right) = (H-1)K + C^{*}\nu_2 \lim_{z_m \to 0} z_m^{\nu_2-1} \quad \cdots\cdots\cdots\cdots \quad (4)$$

As readily seen from equations (3) and (4), since $\lim_{z_m \to 0}\left(\frac{d\eta^{**}}{dz_m}\right)$ is not always negative even when H is smaller than unity unless $C^{*}=0$ or $\nu_2 > 1$, the positive viscosity is not always an indication of H greater than unity, when hydration takes place.

As it has been proved in the previous studies that the value of K is invariant in the small range of temperature, the following two equations at 18° and 25°C. are obtained:

$$\eta_{18}^{**} = 1+\frac{(H_{18}-1)Kz_m}{1-z_m+Kz_m} + C_{18}^{*}(1-z_m)^{\nu_1}z_m^{\nu_2} \quad \cdots\cdots\cdots\cdots \quad (5)_1$$

$$\eta_{25}^{**} = 1+\frac{(H_{25}-1)Kz_m}{1-z_m+Kz_m} + C_{25}^{*}(1-z_m)^{\nu_1}z_m^{\nu_2} \quad \cdots\cdots\cdots\cdots \quad (5)_2$$

where suffixes 18 and 25 denote the respective values at 18° and 25°C.

Putting $\frac{H_{25}-1}{H_{18}-1} = q$ and $\frac{\eta_{25}^{**}-1}{\eta_{18}^{**}-1} = r$, we have

$$(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1) = (C_{25}^{*}-qC_{18}^{*})(1-z_m)^{\nu_1}z_m^{\nu_2}$$

or

$$r = q+(C_{25}^{*}-qC_{18}^{*})\frac{(1-z_m)^{\nu_1}z_m^{\nu_2}}{\eta_{18}^{**}-1} \quad \cdots\cdots\cdots\cdots\cdots \quad (6)$$

In the simplest case where no hydration takes place, equation (6) reduces to

$$r = q = \text{a constant}, \quad \cdots\cdots\cdots\cdots\cdots \quad (7)$$

since C_{18}^{*} and C_{25}^{*} vanish.

Also from equations $(5)_1$ and $(5)_2$ the following equations readily come, if no hydration occurs,

$$\eta_{18}^{**} = 1 + \frac{(H_{18}-1)Kz_m}{1-z_m+Kz_m} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (8)_1$$

$$\eta_{25}^{**} = 1 + \frac{(H_{25}-1)Kz_m}{1-z_m+Kz_m} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (8)_2$$

For these special cases, a method of determining the values of H and K has been given in Part V, yet again another will be shown below. Transform, say, equation $(8)_1$, then we obtain

$$\frac{z_m}{\eta_{18}^{**}-1} = \frac{1}{(H_{18}-1)K} + \frac{(K-1)}{(H_{18}-1)K} z_m \quad \cdots\cdots\cdots\cdots\cdots \quad (9)$$

A linear relation exists between $\frac{z_m}{\eta_{18}^{**}-1}$ and z_m, which enables us to find H and K by the use of ordinary graphical method.

Among the salts studied, the three salts CsCl, RbCl, and $CsNO_3$ are found to be good examples of this simple case. They have no hydrates in the studied concentration range and all show the solutional viscosities less than the viscosity of water. The coincidence between the observed and calculated viscosity values are satisfactory as seen from Tables 2, 3, and 4.

Table 2. CsCl.[17]

z_m	18°C.		25°C.		r	
	$\eta_{obs.}^{*}$	η_0^{*}	$\eta_{obs.}^{*}$	η_0^{*}		
0.00448	0.986	0.986	0.992	0.9925	0.64	mean 0.60
0.00893	0.973	0.973	0.985	0.985	0.61	
0.01771	0.952	0.953	0·975	0.974	0.57	
0.03478	0.927	0.927	—	—	—	

$A_{18} = 0.00472$ $H_{18} = 0.8296$ } $K = 24.28$
$A_{25} = 0.00489$ $H_{25} = 0.8997$ }

Table 3. RbCl.[17]

z_m	18°C.		25°C.		r	
	$\eta_{obs.}^{*}$	η_0^{*}	$\eta_{obs.}^{*}$	η_0^{*}		
0.00448	0.990	0.990	0.995	0.995	0.58	mean 0.56
0.00893	0.980	0.980	0.990	0.990	0.56	
0.01771	0.965	0.965	0.983	0.982	0.55	
0.03478	0.943	0.941	—	—	—	

$A_{18} = 0.00472$ $H_{18} = 0.8577$ } $K = 21.37$
$A_{25} = 0.00488$ $H_{25} = 0.9194$ }

Table 4. $CsNO_3$, (Merton).[18]

z_m	18°C.		25°C.		r	
	$\eta_{obs.}^{*}$	η_0^{*}	$\eta_{obs.}^{*}$	η_0^{*}		
0.000419	0.9986	0.9979	0.9988	0.9986	(0.92)	
0.000929	0.9960	0.9949	0.9970	0.9964	(0.81)	
0.001976	0.9899	0.9889	0.9926	0.9918	0.77	mean 0.77
0.002885	0.9844	0.9838	0.9882	0.9881	0,79	
0.004665	0.9752	0.9746	0.9811	0.9811	0.79	
0.006059	0.9681	0.9680	0.9761	0.9761	0.77	
0.008853	0.9561	0.9561	0.9671	0.9671	0.77	
0.01132	0.9470	0.9469	0.9604	0.9601	0.77	
0.01516	0.9347	0.9345	0.9518	0.9508	0.76	

$A_{18} = 0.00486$ $H_{18} = 0.7939$ } $K = 33.37$
$A_{25} = 0.00504$ $H_{25} = 0.8415$ }

(17) Quoted from Internat. Crit. Tab. V.
(18) Merton, *J. Chem. Soc.*, **97** (1910), 2454.

In the cases of $RbNO_3$, KCl, and KI, it is observed generally that r takes a constant value at low concentration, but that it soon rapidly increases or decreases when the concentration reaches a point at which the amount of hydrating molecules begins discontinuously to be appreciable.

Provided that equation (9) is fortunately applicable to these solutions at the concentration range containing no hydrates, it is not difficult to require the composition of hydrates as well as H and K, because the viscosity increase owing to the hydrates can be easily calculated by the use of equation (5), though some ambiguity may exist in the determination of ν_1 unless accurate measurements of viscosities of the wide range of concentration can be had. The calculation thus made are tabulated in Tables from 5 to 7.

Table 5. $RbNO_3$, (Smith, Wolfenden and Hartley).[19]

zm	18°C.					25°C.					r	
	$\eta_{obs.}{}^*$	$\eta_0{}^*$	$\eta^*-\eta_0{}^*$	$\frac{\eta^*-\eta_0{}^*}{(1-zm)zm^3}$	$\eta_{calc.}{}^*$	$\eta_{obs.}{}^*$	$\eta_0{}^*$	$\eta^*-\eta_0{}^*$	$\frac{\eta^*-\eta_0{}^*}{(1-zm)zm^3}$	$\eta_{calc.}{}^*$		
0.00169	0.9925	0.9920	0.0005	—	—	0.9942	0.9945	-0.0003	—	—	(0.81)	
0.00265	0.9877	0.9873	0.0004	—	—	0.9910	0.9912	-0.0002	—	—	0.75	
0.00342	0.9839	0.9838	0.0001	—	—	0.9885	0.9887	-0.0002	—	—	0.75	
0.00468	0.9785	0.9785	0.0000	—	—	0.9849	0.9849	0.0000	—	—	0.73	mean 0.74
0.00911	0.9628	0.9623	0.0005	—	—	0.9738	0.9733	0.0005	—	—	0.73	
0.00914	0.9623	0.9623	0.0000	—	—	0.9733	0.9733	0.0000	—	—	0.74	
0.01416	0.9483	0.9482	0.0001	—	—	0.9631	0.9631	0.0000	—	—	0.74	
0.01817	0.9410	0.9390	0.0020	(3.4×10^2)	0.9413	0.9588	0.9566	0.0022	(3.7×10^2)	0.9591	0.72	
0.02039	0.9374	0.9347	0.0027	(3.3×10^2)	0.9379	0.9563	0.9534	0.0029	(3.4×10^2)	0.9570	0.72	
0.02737	0.9313	0.9234	0.0079	4.0×10^2	0.9312	0.9542	0.9454	0.0088	4.4×10^2	0.9539	0.69	
0.03495	0.9306	0.9141	0.0165	4.0×10^2	0.9301	0.9572	0.9387	0.0185	4.5×10^2	0.9564	0.65	
0.04187	0.9339	0.9073	0.0266	3.8×10^2	0.9348	0.9639	0.9339	0.0300	4.2×10^2	0.9642	0.59	
				mean 3.9×10^2					mean 4.3×10^2			

$A_{18} = 0.00485$ $H_{18} = 0.8387$
$A_{25} = 0.00498$ $H_{25} = 0.8814$ $K = 37.19$

(19) Smith, Wolfenden and Hartley, *J. Chem. Soc.*, **1931**, 403.

Table 6. KCl.[17]

z_m	18°C.					25°C.					r	
	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^3}$	$\eta_{calc.}^*$	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^3}$	$\eta_{calc.}^*$		
0.00180	0.998	0.998	0.000	—	—	0.999	1.000	-0.001	—	—	(0.79)	
0.00448	0.995	0.994	0.001	—	—	0.998	0.999	-0.001	—	—	(0.76)	
0.00893	0.990	0.989	0.001	—	—	0.997	0.997	0.000	—	—	0.48	mean 0.44
0.01335	0.985	0.986	-0.001	—	—	0.996	0.996	0.000	—	—	0.43	
0.01771	0.982	0.983	-0.001	—	—	0.995	0.995	0.000	—	—	0.43	
0.02632	0.980	0.978	0.002	(1.0×10^2)	0.981	0.997	0.994	0.003	(1.7×10^2)	0.998	0.35	
0.03478	0.982	0.975	0.007	(2.1×10^2)	0.982	1.002	0.993	0.009	2.2×10^2	1.002	0.20	
0.04315	0.987	0.973	0.014	1.8×10^2	0.986	1.010	0.992	0.018	2.3×10^2	1.009	-0.12	
0.05130	0.994	0.972	0.022	1.7×10^2	0.993	1.021	0.992	0.029	2.3×10^2	1.020	-0.91	
0.06725	1.017	0.970	0.047	1.7×10^2	1.018	1.050	0.992	0.058	2.0×10^2	1.054	5.13	
				mean 1.7×10^2					mean 2.2×10^2			

$A_{18} = 0.00484 \quad H_{18} = 0.9471$
$A_{25} = 0.00500 \quad H_{25} = 0.9765$
$K = 40.39$

Table 7. KI.[17]

z_m	18°C.					25°C.					r	
	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^2}$	$\eta_{calc.}^*$	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^2}$	$\eta_{calc.}^*$		
0.00180	0.9908	0.9907	0.0001	—	—	0.993	0.992	0.001	—	—	(0.79)	
0.00448	0.9768	0.9768	0.0000	—	—	0.981	0.981	0.000	—	—	0.84	mean 0.84
0.00893	0.9561	0.9561	0.0000	—	—	0.964	0.964	0.000	—	—	0.84	
0.01771	0.9228	0.9227	0.0001	—	—	0.936	0.936	0.000	—	—	0.84	
0.03478	0.898	0.877	0.021	17.8	0.898	0.915	0.898	0.017	(14.5)	0.919	0.85	
0.05130	0.892	0.848	0.044	17.8	0.892	0.916	0.873	0.043	17.1	0.917	0.79	
0.08266	0.916	0.802	0.114	18.2	0.912	0.951	0.844	0.107	17.0	0.953	0.63	
0.1120	0.978	0.790	0.188	16.8	0.987	1.030	0.826	0.204	18.3	1.021	-0.51	
0.1191	1.003	0.787	0.216	17.3	1.007	—	—	—	—	—	—	
				mean 17.6					mean 17.5			

$A_{18} = 0.00481 \quad H_{18} = 0.6929$
$A_{25} = 0.00497 \quad H_{25} = 0.7420$
$K = 20.20$

It is worth mentioning that there appears to exist in solution as yet unknown hydrates such as $3RbNO_3 \cdot H_2O$, $3KCl \cdot H_2O$, and $2KI \cdot H_2O$, these salts, however, having long been considered to form no hydrates. The reason of the missing of these hydrates depends probably on the neglect because of their small water contents when expressed in weight percentage.

It happens, of course, that in the cases where hydration takes place at zero concentration as are the cases NaCl, LiCl, and $LiNO_3$, no methods of calculating H and K are employable and consequently ν_1 and ν_2 are not determined directly. The determination of ν_1 and ν_2 in such cases, however, may be done by the help of equation (6) as follows.

At first, calculate the values of r i.e. $\frac{\eta_{25}^{**}-1}{\eta_{18}^{**}-1}$. Remembering that q and $(C_{25}^{*}-qC_{18}^{*})$ are constants, r is linear against the values $\frac{(1-z_m)^{\nu_1} z_m^{\nu_2}}{\eta_{18}^{**}-1}$ provided that the suitable values of ν_1 and ν_2 are taken, and therefore the graphical method is applicable in the determination of the values of ν_1 and ν_2 as well as of q, these values having, of course, to be checked by the relation:

$$\frac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^{\nu_1} z_m^{\nu_2}} = \text{a constant.}$$

Table 8. NaCl.[17]

z_m	η_{18}^{*}(obs.)	η_{25}^{*}(obs.)	r	$\frac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^2 z_m}$	η_{25}^{*}(calc.) fr. η_{18}^{*}(obs.)
0.00180	1.0085	1.009	1.059	(0.50)	1.009
0.00448	1.0205	1.022	1.080	(0.58)	1.023
0.00893	1.0405	1.046	1.148	(0.90)	1.045
0.01771	1.0840	1.094	1.127	(0.89)	1.091
0.03478	1.192	1.205	1.071	(0.80)	1.203
0.05130	1.329	1.341	1.038	0.74	1.341
0.06725	1.498	1.509	1.021	0.73	1.509
0.08266	1.700	1.706	1.007	0.75	1.706
				mean **0.74**	
				q = **0.932**	

$A_{18} = 0.00585$ $A_{25} = 0.00601$

Table 9. $LiNO_3$.[17]

z_m	η_{18}^{*}(obs.)	η_{25}^{*}(obs.)	r	$\frac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^3 z_m}$	η_{25}^{*}(calc.) fr. η_{18}^{*}(obs.)
0.00090	1.0060	1.0060	1.000	—	(1.0064)
0.00180	1.0109	1.0116	1.080	0.44	1.0116
0.00448	1.0259	1.0277	1.075	0.43	1.0277
0.00893	1.0503	1.0534	1.068	0.40	1.0535
0.01771	1.0996	1.1063	1.070	0.42	1.1060
0.03478	1·2110	1.2230	1.058	0.39	1.2226
0.05130	1.341	1.358	1.048	0.41	1.358
0.06725	1.492	1.514	1.046	0.45	1.511
0.08266	1.670	1,694	1.035	0.43	1.692
0.09761	1.874	1.898	1.027	0.41	1.897
				mean **0.42**	
				q = **0.991**	

$A_{18} = 0.00685$ $A_{25} = 0.00696$

The results thus calculated from the viscosity values of the solution of NaCl, and $LiNO_3$ are shown in Tables 8 and 9 with the reference of Fig. 3 for $LiNO_3$. These salts appear to have a hydrate throughout the concentration studied, although the accurate composition of their hydrate may not be hoped for on account of the difficulty of deciding ν_1, yet it may be sure that one and only one molecule of these salts combines with water molecules more than one i.e. hydrates $NaCl \cdot mH_2O$ and $LiNO_3 \cdot nH_2O$, the plausible values of m and n being 2 and 3 respectively. Lowitz[20] obtained $NaCl \cdot 2H_2O$ as a monoclinic crystal, and Mellor[20] mentioned two hydrates $LiNO_3 \cdot 3H_2O$ and $2LiNO_3 \cdot H_2O$, the transition point lying at 29.6°C.

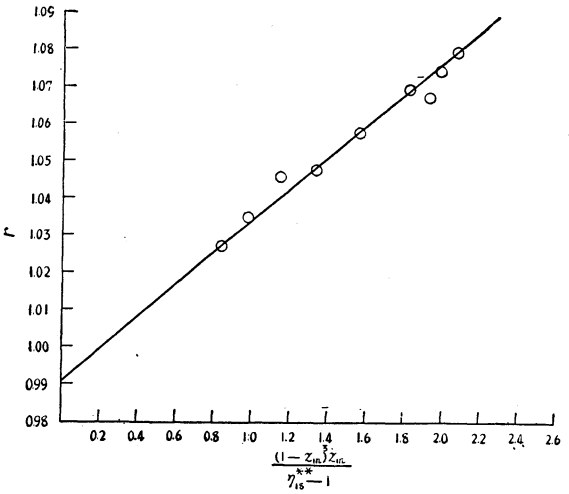


Fig. 3.

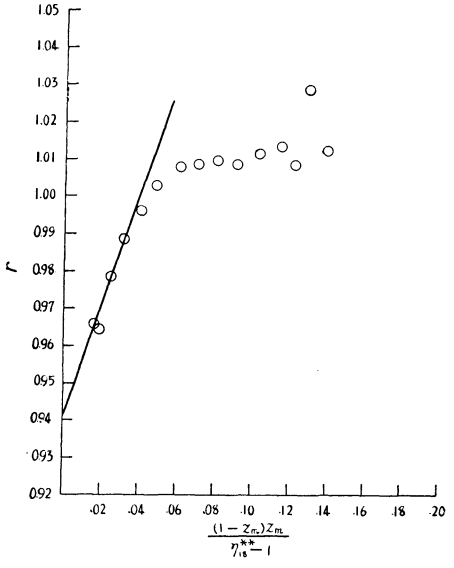


Fig. 4.

With regard to LiCl somewhat different manner is observed as compared with NaCl and $LiNO_3$. The curve r versus $\frac{(1-z_m)z_m}{\eta_{18}^{**}-1}$ in Fig. 4 apparently shows two or more sets of lines, one being distinctly an inclined straight line and others being curved, points, however, lying somewhat complicatedly. The former indicates the existence of a hydrate $LiCl \cdot H_2O$, and the value of q (0.941) obtained from the intersection of this line and the vertical axis may be considered as more reliable than the values obtained from other lines, in which H and K take negative values. Taking this

(20) See Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", II, London (1922), 554, 815, 542.

q, we proceed to the further calculation as shown in Table 10. In this case two hydrates more are postulated: $LiCl \cdot 2H_2O$ and $2LiCl \cdot 4H_2O$ besides $LiCl \cdot H_2O$. Bogorodsky[20] obtained three hydrates $LiCl \cdot 3H_2O$, $LiCl \cdot 2H_2O$, and $LiCl \cdot H_2O$, the transition temperature of $LiCl \cdot 3H_2O$ to $LiCl \cdot 2H_2O$ being $-15°C.$, while that of $LiCl \cdot 2H_2O$ to $LiCl \cdot H_2O$ being $12.5°C$. From this reference it may be concluded that in the aqueous solution of LiCl exist two hydrates $LiCl \cdot H_2O$ and $LiCl \cdot 2H_2O$ with this double molecules, but not $LiCl \cdot 3H_2O$ at the temperature range between 18° and 25°C.

Table 10. LiCl, (Green).[21]

z_m	η_{18}^*(obs.)	η_{25}^*(obs.)	γ	$\frac{(\eta_5^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^{\nu_1} z_m^{\nu_2}}$		η_{25}^*(calc.) fr. η_{18}^*(obs.)
0.0018	1.0136	1.0137	1.009	(0.44)		1.0140
0.0036	1.0271	1.0273	1.008	(0.45)	mean	1.0280
0.0090	1.0692	1.0700	1.013	0.51	**0.63**	1.0711
0.0180	1.144	1.148	1.029	0.69	($\nu_1 = 2$,	1.147
0.0271	1.225	1.227	1.009	0.60	$\nu_2 = 1$)	1.228
0.0362	1.312	1.316	1.014	0.65		1.315
0.0543	1.511	1.517	1.012	0.72		1.513
0.0727	1.747	1.754	1.009	12.8		1.754
0.0912	2.035	2.046	1.010	12.3	mean	2.048
0.1098	2.401	2.413	1.009	12.2	**12.7**	2.417
0.1284	2.878	2.893	1.008	12.9	($\nu_1 = 4$,	2.891
0.1473	3.530	3.539	1.011	13.4	$\nu_2 = 2$)	3.531
0.1663	4.430	4.417	0.9961	13.8		4.403
				(1.33)		(4.431)
0.1854	5.707	5.653	0.9886	1.44	mean	5.652
0.2046	7.550	7.409	0.9786	1.46	**1.43**	7.404
0.2240	10.102	9.777	0.9642	(1.16)	($\nu_1 = 1$,	9.824
0.2289	11.523	11.159	0.9656	1.38	$\nu_2 = 1$)	11.168
				$q = 0.941$		

$A_{18} = 0.00662$ $A_{25} = 0.00665$

As already stated, no method of finding the values of H and K are available in case a solution shows positive viscosity, but even in such a case it is possible only to know whether H is greater than unity or not. Since H is known to become greater as the temperature rises, we may have the following simple relation:

$$\left.\begin{array}{lll} & \text{If } q > 1, & H_{18},\ H_{25} > 1, \\ \text{and} & \text{If } 1 > q > 0, & H_{18},\ H_{25} < 1. \end{array}\right\} \quad \cdots\cdots\cdots \quad (10)$$

(21) Green, *J. Chem. Soc.*, **93** (1908), 2023.

By the use of the criterion it may be obvious that the solutional viscosities of NaCl and LiCl also must be smaller than the viscosity of water. As for $LiNO_3$, q being nearly unity, such decision may not be hoped for, yet H is undoubtedly nearly unity.

From the several examples given above the following conclusion may be reached: The negative viscosity is entirely due to the smaller solutional viscosity of the solute than the viscosity of water, but not to the ionic behaviours suggested by other investigators. The viscosity formula formerly proposed and developed by Ishikawa for a binary mixture of liquids proves to have a general applicability in a new field of aqueous solutions of electrolytes, and at the same time, to play an important rôle in finding their hydrates in solution.

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

DIPOLMOMENT DES CHLORWASSERSTOFFES UND LÖSUNGSMITTEL.

Von San-ichiro MIZUSHIMA, Katsuji SUENAGA und Kunio KOZIMA.

Eingegangen am 25. März, 1935. Ausgegeben am 28. April, 1935.

Von zahlreichen Messungen[1] an Dielektrizitätskonstante und Dichte verdünnter Lösungen von HCl, wurde die extrapolierte Molekularpolarisation P bestimmt und daraus das Dipolmoment μ berechnet, wobei die Summe der Elektronen- und Atompolarisation gleich 7.1 angesetzt wurde.

Der Wert des Momentes in Hexanlösung ist, innerhalb des Messfehlers, gleich dem in Gaszustand (1.03×10^{-18}) [2], was wir von der nichtpolaren Natur des Hexanmoleküles von vornherein vermuten können. In Übereinstimmung mit der Beobachtung Fairbrothers[3] haben wir in Benzollösung ein grosses Moment gefunden; Benzol ist makroskopisch sicher nichtpolar, doch mikroskopisch hat es ein starkes Feld, welches ihrgendeine Änderung im HCl-Molekül verursachen kann.[4] In Toluol-

(1) Betr. Messmethode vgl.: Mizushima, Morino und Higasi, *Sci. Pap. Inst. Phys. Chem. Research, Tokyo*, **25** (1934), 159.
(2) Zahn, *Phys. Rev.*, **24** (1924), 400.
(3) Fairbrother, *J. Chem. Soc.*, **1932**, 43; *ibid.*, **1933**, 1541; *Trans. Faraday Soc.*, **30** (1934), 862.
(4) Vgl. auch: Mizushima, Morino u. Higasi, *Physik. Z.*, **35** (1934), 905.

lösung ist das Moment ebenso gross wie das in Benzollösung und der Zunahme des Momentes im Vergleich mit dem in Gaszustand ist in diesem Falle auch dem Benzolkern zuzuschreiben.[4] Obwohl Äthyläther und Chloroform wegen ihrer ähnlichen Werte in Dielektrizitätskostante und in Moment eine analoge Beeinflussung auf den gelösten Stoff erwarten lassen, haben wir dagegen in der Tat einen auffälligen Unterschied zwischen HCl-Momenten in beiden Lösungen gefunden. Während der Wert in Chloroformlösung gleich dem in Gaszustand ist, findet man in Ätherlösung einen beträchtlich grossen Wert, welcher fast gleich der Summe der Momente von Äther und HCl ist. Für das Solvat in der Ätherlösung, wenn es überhaupt ein solches gibt, kann man also ein Gebilde gleichgerichteter Momente vorstellen.

Lösungsmittel	Temp.	P	$\mu\times10^{18}$
Hexan	20	30.0	1.04
Benzol	10	38.7	1.20
,,	20	38.5	1.22
,,	25	37.8	1.21
Toluol	20	39.5	1.24
Chloroform	30	28.9	1.03
Äthyläther	20	111.3	2.22
Cyclohexan (Fairbrother)[3]			1.32
Benzol (″)			1.26
Tetrachlorkohlenstoff (″)			1.32

Handelt es sich hier um die Änderung der Bindungsart von HCl? Dafür bewährt sich besonders die Berücksichtigung der Placzekschen Auswahlregel[5] in Ramaneffekt. West und Arthur[6] konnten in verdünnter Chloroformlösung die Ramanlinie von HCl beobachten, was mit der bei Dipolmessung beobachteten Tatsache gut übereinstimmt; d.h. die Bindungsart von HCl in der Chloroformlösung ist nichtpolar. Unsere Beobachtung an Ramanspektrum konzentrierter Ätherlösung (Molenbruch von HCl über 40%), die zwar nur vorläufig ausgeführt wurde, zeigt dagegen, dass keine starke Linie von HCl weder einzeln noch mit Ätherlinie überdeckt vorhanden ist. Es ist sehr wahrscheinlich, dass die Bindungsart von HCl in Ätherlösung von derjenigen in Gaszustand verschieden ist. Die Untersuchung an Ramaneffekt wird fortgesetzt und vervollständigt.

Herrn Prof. M. Katayama sowie Herrn Dr. M. Morino danken wir bestens für ihre Ratschläge an dieser Arbeit. Ferner danken wir dem Nippon-Gakujutsushinkôkai, das die zur Durchführung notwendigen Mittel zur Verfügung gestellt hat.

Chemisches Institut der Kaiserlichen Universität zu Tokio.

(5) Placzek, *Z. Physik*, **70** (1931), 84.
(6) West und Arthur, *J. Chem. Physics*, **2** (1934), 215.

LES SPECTRES D'ABSORPTION DES COMPOSÉS AZOÏQUES MIXTES ET CEUX DE LEURS ISOMÈRES.[1]

Par **Taku UÉMURA** et **Yasuo INAMURA.**

Reçu le 9 février 1935. Publié le 28 mai 1935.

Un des auteurs du présent travail a déjà étudié[2] une quarantaine de composés oxyazoïques au moyen de leurs spectres d'absorption et a discuté leurs constitution chimiques en leur appliquant les courbes Hartley et Baly. Il y a encore ajouté des recherches plus détaillées[3] sur leur absorption ultra-violette en vue de déterminer leur structure moléculaire en solution aqueuse, en faisant varier leur concentration des ions d'hydrogène d'un certain nombre de ces composés.

Le mémoire actuel a une certaine relation avec nos recherches antérieures. On a pris la photographie des spectres d'absorption en se servant du spectrographe en quartz de l'Anglais Adam Hilger et étudié les bandes d'absorption dans les photographies prises. Nous avons, cependant, préparé des échantillons des substances azoïques mixtes (gemischte Azokörper[4]) et leurs isomères, afin d'observer les relations qui peuvent exister entre les chromophores contenus dans ces matières colorantes azoïques et leurs spectres d'absorption.

Procédé expérimental et préparation des corps étudiés. Le spectre d'absorption présenté dans le mémoire actuel a été pris par la méthode appliquée pour la première fois par Hartley et Baly (courbes Hartley-Baly), c'est-à-dire les logarithmes des épaisseurs des solutions liquides correspandant à la concentration de 1/10000 mol en axe des ordonnées dans les courbes, et la réciproque d'une longueur d'onde (la fréquence) en abcisse. Les photographies ont été prises sur une plaque orthochromique "Tôyô" (marque japonaise) par le spectrographe anglais ci-dessus décrit. La source lumineuse a été fournie par le courant continu (4 à 5 ampères à 100 volts) d'un arc métallique en fer. On a compté 15 secondes en moyenne comme temps de pose photographique et pris

(1) Traduit de la publication originale publiée dans le Bulletin de Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku Gakuhô), **3** (1934), 467. Exposé fait lors de la Séance de la Société chimique du Japon, le 14 juillet 1934.

(2) Ce bulletin, **1** (1926), 290; **2** (1927), 10, 48, 229, 249; **3** (1928), 105.

(3) *Arch. phys. biol.*, **9** (1931), 29; *J. Chem. Soc. Japan*, **54** (1933), 265.

(4) Radical azoïque lié d'une part par un aryle, et de l'autre par un alcoyle.

l'alcool absolu comme dissolvant des corps étudiés. Les solutions alcooliques ont été obtenues en dissolvant l'échantillon purifié en fiole graduée. On en a préparé plusieurs espèces de concentrations des solutions: 1/10, 1/100 ou 1/10000 mol pour les utiliser convenablement.

On a préparé les 21 corps suivants par synthèse chimique, excepté l'azobenzène et la diphénylamine qui ont été obtenus l'un et l'autre dans le commerce.

(1) *Azobenzène,* $C_6H_5 \cdot N:N \cdot C_6H_5$. L'échantillon d'azobenzène utilisé par nous est produit par la compagnie Kahlbaum (marque allemande). C'est un cristal jaune-orange qui fond à 68°C.

(2) *Phénylazométhane,* $C_6H_5 \cdot N:N \cdot CH_3$. Le phénylazométhane qui a été préparé par Baly et Tuck[5] en faisant réagir la phénylhydrazine sur le formaldéhyde qui a été déjà examiné par Stobbe et Nowak[6], et ils le signalaient comme un produit impur. Nous avons donc adopté la méthode proposée par Tafel[7], c'est-à-dire méthyliser, saponifier la dibenzoylphénylhydrazine et l'oxyder par l'action de l'oxyde de mercure. Le composé ainsi obtenu est un corps jaune et huileux qui a une odeur spéciale et bout entre 52 et 54°C. sous 11 mm. de basse pression.

(3) *Phénylazoéthane,* $C_6H_5 \cdot N:N \cdot C_2H_5$. Ce corps synthétiquement formé d'après la méthode proposée par Fischer[8] est jaune et huileux avec une odeur caractéristique. Nous l'avons purifié par la distillation à vide deux fois répétée. Le composé ainsi obtenu bout entre 62 et 65°C. sous une pression de 10 à 12 mm.

(4) *Phénylazopropane,* $C_6H_5 \cdot N:N \cdot C_3H_7$. Suivant le procédé employé par Fischer[9] pour opérer la synthèse du phénylazoéthane et du phénylazopropène, on a fait réagir la phénylhydrazine en présence de l'éther sur le bromure de propyle pendant 30 heures, à la température ordinaire, et le résultat n'a pas été défavorable. On a dosé 15 g. de phénylhydrazine pour y ajouter 30 c.c. d'éther, et on a laissé reposer le mélange pendant 30 heures après l'avoir fait réagir sur 7 g. de bromure de propyle à la température ordinaire. Nous filtrons la phénylhydrazine ainsi précipitée et obtenons un sel incolore, puis nous faisons évaporer l'éther qui se trouve dans le filter, et nous éliminons la phénylhydrazine non réagie comme le hydrochlorate par le moyen de l'acide hydrochlorique concentré, puis nous neutralisons l'eau mère par la soude caustique pour

(5) E. C. C. Baly et W. B. Tuck, *J. Chem. Soc.*, **89** (1906), 986.
(6) H. Stobbe et R. Nowak, *Ber.*, **47** (1914), 578.
(7) J. Tafel, *Ber.*, **18** (1885), 1742.
(8) E. Fischer, *Ber.*, **29** (1896), 793.
(9) E. Fischer et O. Knoevenagel, *Ann.*, **239** (1887), 203.

obtenir le produit huileux jaune-brun dans l'éther. Cette solution éthérique est oxydée par l'action de l'oxyde de mercure et séchée par le carbonate de potasse. Nous procédons alors à une distillation à vide et nous obtenons une substance huileuse jaune qui bout à 85°C. sous une pression de 20 mm. Son rendement est de 0.5 g., et l'analyse chimique montre 0.513 c.c. (23°C., 760 mm.) d'azote de 3.074 mg. de l'échantillon; cela correspond à 19.03%, tandis que la valeur calculée est de 18.92%.

(5) *Phénylazobutane,* $C_6H_5{\cdot}N{:}N{\cdot}C_4H_9$. Nous avons synthétisé ce corps par une méthode semblable à celle qui a été appliquée au composé précédent.

Ayant pris 50 g. de phénylhydrazine, nous y ajoutons 100 c.c. d'éther et 25 g. de bromure de butyle. Nous laissons reposer le mélange pendant 30 heures à la température ordinaire, puis nous filtrons le sel incolore de phénylhydrazine ainsi cristallisé et après, nous éliminons la phénylhydrazine non attaquée par l'action de l'acide chlorhydrique concentré; nous neutralisons la solution éthérique au moyen de l'oxyde de mercure, nous séchons le tout avec le carbonate de potasse et distillons à vide pour obtenir un produit huileux, d'un jaune citron. Son rendement est de 1.1 g. et son point d'ébullition indique 90°C. sous pression réduite (19 mm.). L'analyse chimique révèle la présence de 0.677 c.c. (24°C., 757 mm.) d'azote sur 4.402 mg. de substance; cela correspond à 17.42%, tandis que la valeur calculée est de 17.28%.

(6) *Phénylazophénylméthane,* $C_6H_5{\cdot}N{:}N{\cdot}CH_2{\cdot}C_6H_5$. Nous avons préparé ce corps suivant les indications fournies par Thiele[10] et le produit jaune et huileux a une odeur caractéristique.

(7) *ω-Azotoluène,* $C_6H_5{\cdot}CH_2{\cdot}N{:}N{\cdot}CH_2{\cdot}C_6H_5$. La benzalazine est réduite par l'amalgame de sodium en solution alcoolique,[11] et, d'après la méthode de Thiele,[12] en l'oxydant avec l'eau oxygénée, on peut obtenir l'ω-azotoluène, cristal incolore, ayant son point de fusion à 31.5°C.

(8) *Formaldéhydephénylhydrazone,* $C_6H_5{\cdot}NH{\cdot}N{:}CH_2$. Ce composé a été synthétiquement obtenu, d'après les indications de Walker,[13] en présence de l'acide acétique. Lorsque deux mols de phénylhydrazine réagissent sur la solution aqueuse d'une mol d'aldéhyde formique, on obtient, mais non sans peine, un corps ayant son point de fusion à 155°C. Nous avons cependant réussi à stabiliser le corps au point de fusion ci-dessus nommé après les trois essais d'expériences, et le produit a été

(10) J. Thiele, *Ann.*, **376** (1910), 267.
(11) Th. Curtius, *J. prakt. Chem.*, **62** (1900), 90.
(12) J. Thiele, *Ann.*, **376** (1910), 265.
(13) J. W. Walker, *J. Chem. Soc.*, **69** (1896), 1282.

recristallisé dans le benzène. Comme ce composé est peu soluble dans l'alcool, sa photographie d'absorption n'a été prise qu'en utilisant sa solution à 1/10000 mol. Nous avons mis le reste du corps étudié dans le dessicateur pendant deux ou trois jours et avons observé qu'une transformation s'opérait dans cette substance et que son point de fusion s'élevait à 183°C. Nous avons encore des doutes sur l'existence de ce corps à l'état pur, non polymérisé, même du point de vue du spectre d'absorption.

(9) *Acétaldéhydephénylhydrazone,* $C_6H_5 \cdot NH \cdot N : CH \cdot CH_3$. La substance obtenue d'après le procédé de Lockemann et de Liesche[14] se liquéfie entre 98 et 101°C. C'est un cristal incolore qui correspond au type *α* nommé par Fischer[15].

(10) *Propylaldéhydephénylhydrazone,* $C_6H_5 \cdot NH \cdot N : CH \cdot C_2H_5$. D' après la méthode de préparation employée par Fischer,[16] on a fait réagir dans l'éther la phénylhydrazine sur l'aldéhyde propylique en quantités égales, on a éliminé l'eau qui s'est produite, on a desséché le corps par le carbonate de potasse et on l'a distillé sous pression réduite. Le produit ainsi obtenu qui bout à 135°C. sous la pression 18 mm. a une apparence huileuse.

(11) *Butylaldéhydephénylhydrazone,* $C_6H_5 \cdot NH \cdot N : CH \cdot C_3H_7$. Ce corps a été préparé d'après la même méthode que les composés précédents, et suivant les indications données par Brunner;[17] c'est-à-dire qu'on fait réagir, en présence de l'éther, la phénylhydrazine sur l'aldéhyde normal-butylique prises l'une et l'autre en quantités égales, puis on en élimine l'eau et on dessèche au moyen du carbonate de potasse, puis on distille sous pression réduite. Le produit huileux ainsi obtenu a son point d'ébullition entre 141 et 143°C. sous 15 mm. de pression réduite, exposé à la lumière solaire, il devient jaunâtre.

(12) *Propanonephénylhydrazone,* $C_6H_5 \cdot NH \cdot N : C(CH_3)_2$. Appliquant la méthode indiquée par Fischer,[18] nous ajoutons de la phénylhydrazone à l'excès d'acétone, nous éliminons l'eau qui s'est produite, puis nous desséchons au moyen du carbonate de potasse. Le corps obtenu par distillation sous pression réduite est une substance incolore et huileuse qui a son point d'ébullition à 135°C., sous 27 mm. de pression et qui devient jaune sous l'action de la lumière solaire.

(13) *Butanonephénylhydrazone,* $C_6H_5 \cdot NH \cdot N : C(CH_3) \cdot C_2H_5$. Ce corps s'obtient par la méthode de préparation proposée par Arbusow et

(14) G. Lockemann et O. Liesche, *Ann.*, **342** (1905), 14.
(15) E. Fischer, *Ber.*, **29** (1896), 795.
(16) E. Fischer, *Ann.*, **236** (1886), 137.
(17) K. Brunner, *Monatsh.*, **16** (1895), 184.
(18) E. Fischer, *Ann.*, **236** (1886), 126.

Tichwinsky,[19] mais il peut se former également en partant de la phénylhydrazine et de la méthyléthylcétone, qui entrent en quantités égales, et sont traités dans l'éther. On élimine l'eau qui s'est produite, on dessèche avec le carbonate de potasse et on fait la distillation sous pression réduite. Le composé ainsi obtenu est huileux et incolore, il bout à 140°C., sous 15 mm. de pression et devient jaunâtre sous l'action de lumière.

(14) *Benzaldéhydephénylhydrazone,* $C_6H_5{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_5$. La préparation de ce corps a été faite d'après les indications de Biltz,[20] et le produit ainsi obtenu, le soi-disant type α de Biltz, se présente sous l'aspect d'un cristal incolore ayant son point de fusion à 155°C. Il devient jaune sous l'action de la lumière.

(15) *Benzalbenzylhydrazone,* $C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_5$. Ce corps fut confondu d'abord par Curtius et Quedenfeldt[21] avec la benzylhydrazine symétrique. Nous l'avons cependant préparé suivant les procédés indiqués par Curtius[22], en employant la benzalazine réduite par l'amalgame de sodium. Le produit obtenu est un cristal incolore, qui a son point de fusion à 65°C.

(16) *Diazoaminobenzène,* $C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5$. Ce composé se forme d'après la méthode indiquée par Griess.[23] Le corps ainsi obtenu est un cristal jaune qui a son point de fusion à 96°C.

(17) *Diméthyldiphényltétrazone,* $C_6H_5{\cdot}N(CH_3){\cdot}N{:}N{\cdot}N(CH_3){\cdot}C_6H_5$. Suivant la méthode de synthèse de la diéthyldiphényltétrazone indiquée par Fischer,[24] une légère quantité de phénylhydrazone réagissant sur l'iodure de méthyle donne un cristal incolore qui a son point de fusion à 137°C.

(18) *Hydrazobenzène,* $C_6H_5{\cdot}NH{\cdot}NH{\cdot}C_6H_5$. Ce corps s'obtient, d'après les indications de l'ouvrage écrit par Vanino,[25] par la réduction basique de l'azobenzène en solution alcoolique sous l'action du zinc.

(19) *Diphénylamine,* $C_6H_5{\cdot}NH{\cdot}C_6H_5$. Le produit chimique fabriqué par Kahlbaum (marque allemande) est un cristal incolore qui a son point de fusion à 54°C.

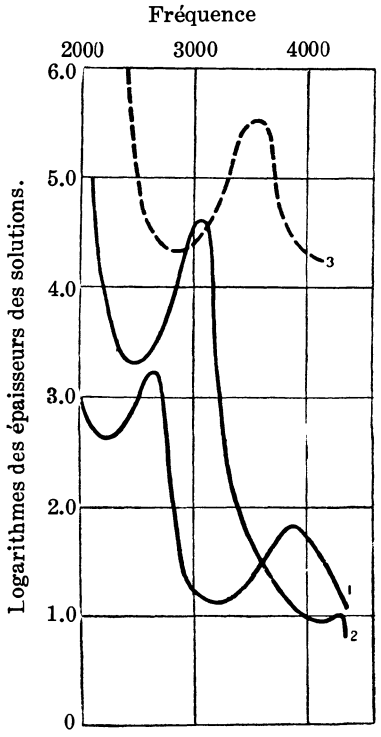
(20) *Benzalazine,* $C_6H_5{\cdot}CH{:}N{\cdot}N{:}CH{\cdot}C_6H_5$. D'après la méthode indiquée par Curtius et Jay,[26] par l'action d'aldéhyde benzoïque sur la

(19) A. E. Arbusow et W. M. Tichwinsky, *Ber.*, **43** (1910), 2301.
(20) H. Biltz, *Ann.*, **305** (1899), 170.
(21) Th. Curtius et E. Quedenfeldt, *J. prakt. Chem.*, **58** (1898), 374.
(22) Th. Curtius, *J. prakt. Chem.*, **62** (1900), 90.
(23) P. Griess, *Ann.*, **121** (1862), 257.
(24) E. Fischer, *Ann.*, **190** (1877), 169; *Ber.*, **29** (1896), 793.
(25) L. Vanino, "Präparative Chemie", II (1923), 505.
(26) Th. Curtius et R. Jay, *J. prakt. Chem.*, **39** (1889), 27.

solution de hydrazine, on a un produit insoluble dans l'eau. Ce qu'on obtient par recristallisation dans l'alcool est un cristal jaune présentant la forme d'aiguilles et qui fond à 93°C.

(21) *Benzalaniline,* $C_6H_5 \cdot CH:N \cdot C_6H_5$. Suivant les indications fournies par l'ouvrage écrit par Vanino,[27] ce corps se recristallise dans l'alcool et donne un cristal jaunâtre qui a son point de fusion entre 53 et 54°C.

Spectres d'absorption. (1) *Azobenzène,* (2) *Phénylazométhane,* et *Azométhane.* Il semblerait que, dans les spectres d'absorption de ces trois composés (fig. 1) l'absorption des rayons lumineux par le radical azoïque –N=N– dépende grandement de la double liaison conjuguée qu'il a avec le noyau benzénique. C'est pourquoi, en substituant le radical alcoylé à un radical d'aryle, soit R–N=N–R, Ar–N=N–R et Ar–N=N–Ar (Ar: un aryle, R: un alcoyle) les bandes d'absorption varient régulièrement trahissant des influences bathochromiques et hyperchromiques. La fréquence indiquée par la centre de la bande d'absorption se porte vers une longueur d'onde plus élevée, en substituant un méthyle à un phényle (à peu près une différence de 300 dans la fréquence par chaque substitution).



1. C_6H_5-N=N-C_6H_5 (1)
2. C_6H_5-N=N-CH_3 (2)
3. CH_3-N=N-CH_3

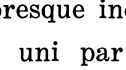
Fig. 1.

Quant au spectre d'absorption donné par l'azométhane, nous avons pris la courbe (ligne pointillée dans la figure 1) indiquée par Hantzsch et Lifschitz,[28] pour faire une comparaison avec deux autres corps: azobenzène et phénylazométhane.

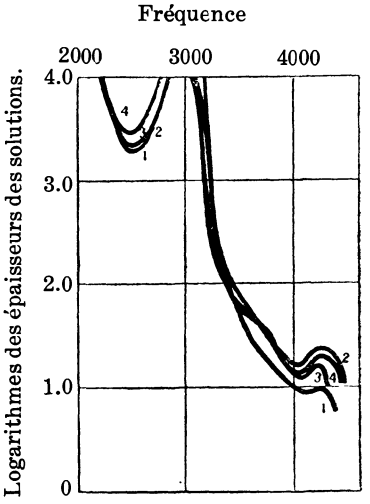
(2) *Phénylazométhane,* (3) *Phénylazoéthane,* (4) *Phénylazopropane,* et (5) *Phénylazobutane.* La figure 2 rend compte de la comparaison entre les spectres d'absorption obtenus par les quatre composés azoïques mixtes en prolongeant l'union chaînée contenue

(27) L. Vanino, "Präparative Chemie", II (1923), 468.
(28) A. Hantzsch et J. Lifschitz, *Ber.*, **45** (1912), 3011.

dans les corps étudiés. Nous avons ajouté deux nouveaux corps, le phénylazopropane et le phénylazobutane, qu'on n'a pas trouvés dans les comptes rendus de chimie.

La position du centre des spectres d'absorption est presque la même dans les quatre composés indiqués, et cela nous montre que la longueur du radical alcoylé est presque indépendante de l'absorption lumineuse et que le radical azoïque uni par le noyau benzénique () représente la cause principale de l'absorption lumineuse.

Baly et Tuck[29] ont les premiers exposé le résultat des spectres d'absorption du phénylazométhane, mais leurs résultats ne sont pas d'accord avec les nôtres. Puis, Hantzsch et Lifchitz,[30] Stobbe et Nowak[31] ont observé l'absorption du phénylazométhane, et ils ont admis que le phénylazométhane est obtenu d'après la méthode indiquée par Baly et Tuck, et que leur phénylazoéthane a les mêmes spectres d'absorption. Le phénylazométhane préparé par le moyen indiqué par Tafel[7] présente aussi les mêmes courbes d'absorption que le phénylazoéthane. D'après ces résultats, nous constatons que l'échantillon préparé par Baly et Tuck n'était pas pur. Quant à la bande d'absorption, nos résultats présentent un caractère plus hyperchromique que ceux obtenus par Stobbe et Nowak. Le corps utilisé par nous est, semble-t-il, plus pur et son point d'ébullition plus stabilisé.



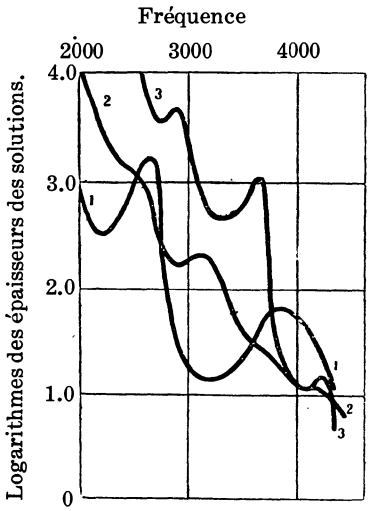
1. C_6H_5-N=N-CH_3 (2)
2. C_6H_5-N=N-CH_2-CH_3 (3)
3. C_6H_5-N=N-CH_2-CH_2-CH_3 (4)
4. C_6H_5-N=N-CH_2-CH_2-CH_2-CH_3 (5)

Fig. 2.

(1) *Azobenzène,* (6) *Phénylazophénylméthane,* et (7) *ω-Azotoluène.* Les deux composés dans lesquels l'hydrogène contenu dans le méthyle des deux corps déjà montrés dans la figure 1 est remplacé par les radicaux du phényle, ont été préparés pour être comparés avec l'azobenzène. La figure 3 représente donc la comparaison de l'azobenzène avec ces deux corps qui n'ont pas de liaison conjuguée entre le noyau benzénique et le radical azoïque. En comparant la figure 3 avec la figure 1, on note que les

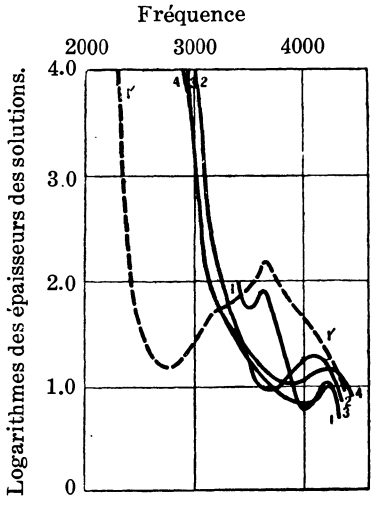
(29) E. C. C. Baly et W. B. Tuck, *J. Chem. Soc.*, **89** (1906), 982.
(30) A. Hantzsch et J. Lifschitz, *Ber.*, **45** (1912), 3011.
(31) H. Stobbe et R. Nowak, *Ber.*, **46** (1913), 2887; **47** (1914), 578.

deux corps de la figure 3 contiennent le radical azoïque qui est plutôt facile à transformer en type "*hydrazone*" plus stable qu'en type azoïque; ils ne montrent pas nettement l'absorption du radical azoïque, mais ils sont plus hypsochromiques et hypochromiques que l'azobenzène. Ceci nous explique l'influence plus ou moins grande que produit la rupture des liaisons conjuguées entre le radical azoïque et le noyau benzénique. La différence qui existe entre les colorations présentées par ces trois corps, cristal jaune-orange dans l'azobenzène, jaune et huileux dans le phénylazophénylméthane, cristal incolore dans l'ω-azotoluène, est d'accord avec la



1. C_6H_5-N=N-C_6H_5 (1)
2. C_6H_5-N=N-CH_2-C_6H_5 (6)
3. C_6H_5-CH_2-N=N-CH_2-C_6H_5 (7)

Fig. 3.



1. C_6H_5-NH-N=CH_2 (8)
1′. ,, (Baly et Tuck)
2. C_6H_5-NH-N=CH-CH_3 (9)
3. C_6H_5-NH-N=CH-CH_2-CH_3 (10)
4. C_6H_5-NH-N=CH-CH_2-CH_2-CH_3 (11)

Fig. 4.

variation de la courbe d'absorption comme le montre la figure 3. La série de trois composés déjà indiqués dans la figure 1 n'est pas suffisante pour expliquer la liaison conjuguée. Les variations de la courbe d'absorption présentées par la figure 1 risqueraient d'être attribuées aux différences qui existent entre le méthyle et le phényle. L'aparition d'une influence hypsochromique que l'on remarque dans la figure 3 pourra, cependant, en définitive provenir des relations conjuguées de liaison double, union directe du phényle avec le radical azoïque.

(8) *Formaldéhydephénylhydrazone,* (9) *Acétaldéhydephénylhydrazone,* (10) *Propylaldéhydephénylhydrazone,* et (11) *Butylaldéhydephénylhydrazone.* La figure 4 présente des courbes d'absorption du type

"hydrazone" des corps montrés dans la figure 2. Il existe déjà un certain nombre de publications concernant le spectre d'absorption observé dans l'isomérie, *"azo"* et *"hydrazone"*, mais le présent mémoire représente un spectre mesuré dans des conditions identiques, et il nous amène à admettre la différence nette qui existe entre le type *"azo"* et le type *"hydrazone"* contenus dans les composés azoïques mixtes.

Les trois courbes 2,3 et 4 données dans la figure 4 approximativement d'accord entre elles. La position du centre de leur bande d'absorption se trouve entre 3700 et 4000 de la fréquence. Tous ces corps qui contiennent le radical –N=CH– ne présentent pas d'absorption sélective dans une région visible comme l'on peut l'observer dans la figure 6. La cause en est probablement dans ce fait que le chromophore faible –N=CH– n'est pas directement joint au noyau benzénique.

Comme nous l'avons déjà dit, notre formaldéhydephénylhydrazone préparée d'après la méthode donnée par Walker a son point de fusion à 155°C., ce que Richter et Anschütz n'ont pas admis dans leur ouvrage[32] où ils ont indiqué un polymère $(C_6H_5N_2)_2(CH_2)_3$ (triméthylènephénylhydrazine) dont le point de fusion est à 183°C. Nous avons pu, par cette mesure, contrôler les dires de Richter et Anschütz qui soutenaient la non-existence de la formaldéhydephénylhydrazone et nous avons pu comprendre la différence remarquable qui existe la courbe 1 et les autres, dans la figure 4. La courbe d'absorption 1 donnée par Baly et Tuck[29] a été étudiée par ceux-ci comme la résultante d'un mélange d'un polymère ci-dessus indiqué avec un autre corps. Nous concevons des doutes sur la différence qui existe entre les courbes 1 et 1′ et l'accord global, entre la courbe 1′ et celle que présente la benzaldéhydephénylhydrazone dans la figure 6.

Notre courbe d'acétaldéhydephénylhydrazone est à peu près d'accord avec celles qu'ont données par Baly et Tuck,[29] Stobbe et Nowak[31] et Stevens et Ward;[33] d'autre part notre courbe d'absorption observée par la propylaldéhydephénylhydrazone n'est pas très différente de celle qui est représentée dans le mémoire de Baly et Tuck.[29]

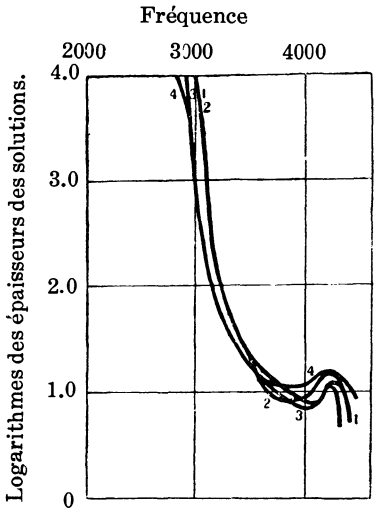
On peut, dans les figures 2 et 4, admettre semble-t-il la différence observée dans les spectres d'absorption des deux types *"azo"* et *"hydrazone"*. Nous l'étudierons plus minutieusement et nous la discuterons dans d'autres circonstances.

---

(32) Richter-Anschütz, "Chemie d. Kohlenstoffverbindungen", I (12e édit., 1928), 276.

(33) H. R. Stevens et F. W. Ward, *J. Chem. Soc.*, **125** (1924), 1328.

(10) *Propylaldéhydephénylhydrazone,* (11) *Butylaldéhydephénylhydrazone,* (12) *Propanonephénylhydrazone,* et (13) *Butanonephénylhydrazone.* La figure 5 nous montre la comparaison entre la phénylhydrazone jointe au radical alcoylé sans chaîne normale et celle qui est unie par l'alcoyle contenu une chaîne normale et qui a le même nombre d'atomes de carbone. Tous les quatre corps représentés dans la figure 5 sont du type "*hydrazone*" et se ressemblent à peu près d'après les formes de leurs courbes d'absorption. La petite différence observée dans la fréquence du centre de la bande d'absorption décèle des radicaux isopropyle et isobutyle, c'est-à-dire cétonehydrazones. Ceux-ci, à la fin de l'absorption, ont des longueurs d'onde plus courtes que celles présentées par les aldéhydephénylhydrazones.



1. C_6H_5-NH-N=C$<^{CH_3}_{CH_3}$ (12)
2. C_6H_5-NH-N=C$<^{CH_3}_{CH_2\text{-}CH_3}$ (13)
3. C_6H_5-NH-N=CH-CH_2-CH_3 (10)
4. C_6H_5-NH-N=CH-CH_2-CH_2-CH_3 (11)

Fig. 5.

Baly et Tuck[29] ont déjà déterminé la courbe de la propanonephénylhydrazone laquelle est presque semblable à la nôtre.

(6) *Phénylazophénylméthane,* (7) *ω-Azotoluène,* (14) *Benzaldéhydephénylhydrazone,* et (15) *Benzalbenzylhydrazone.* Nous avons pris la benzaldéhydephénylhydrazone et la benzalbenzylhydrazone qui correspondent respectivement aux isomères déjà étudiés, phénylazophénylméthane et ω-azotoluène, pour comparer les courbes de deux types "*azo*" et "*hydrazone*".

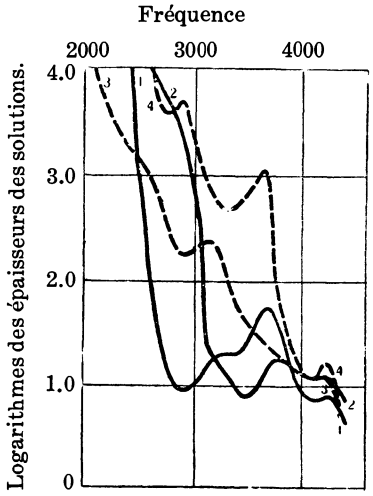
En comparant deux par deux les courbes 1 et 3, 2 et 4 de la figure 6, nous voyons que, dans les courbes 3 et 4, la bande d'absorption caractéristique donnée par "*azo*" se rapproche du type "*hydrazone*" auquel on a ajouté du phényle, en tenant compte de la courbe présentée par le phénylazométhane et l'azométhane, dans la figure 1. Ces deux courbes 3 et 4 peuvent être considérées comme celles qui sont données par le mélange des deux type "*azo*" et "*hydrazone*".

La courbe donnée par la benzaldéhydephénylhydrazone peut se retrouver dans les mémoires déjà publiés par Baly et Tuck,[29] ou par Stobbe et Nowak[34] où elle n'est guère différente de la nôtre. Stevens et Ward[33] l'ont quantitativement étudiée.

(34) H. Stobbe et R. Nowak, *Ber.*, **46** (1913), 2888.

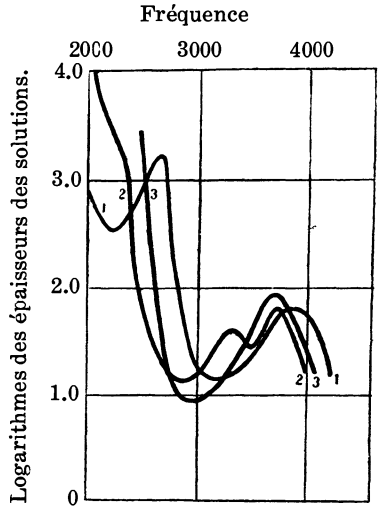
(1) *Azobenzène,* (16) *Diazoaminobenzène,* et (17) *Diméthyldiphényltétrazone.* Ley a fait remarquer les variations de couleur; orange, jaune et incolore, présentée par les trois composés, azobenzène, diaminobenzène et diphényltétrazone. A propos de cette série de corps, il a écrit, dans le "Handbuch d. Physik",[35] sur la diminution graduelle du pouvoir absorbant que présente le chromophore azoïque, quand il combine avec un radical azoté comme NH.

Puisque la diphényltétrazone, troisième composé, prise par Ley n'est pas encore connue, nous avons préparé la diméthyldiphényltétrazone,



1. C_6H_5-NH-N·CH-C_6H_5 (14)
2. C_6H_5-CH_2-NH-N·CH-C_6H_5 (15)
3. C_6H_5-N·N-CH_2-C_6H_5 (6)
4. C_6H_5-CH_2-N·N-CH_2-C_6H_5 (7)

Fig. 6.



1. C_6H_5-N·N-C_6H_5 (1)
2. C_6H_5-N·N-NH-C_6H_5 (16)
3. C_6H_5-N(CH_3)-N·N-N(CH_3)-C_6H_5 (17)

Fig. 7.

cristal incolore, d'après les indications données par Fischer,[23] pour comparer son spectre d'absorption avec celui de l'azobenzène et du diazoaminobenzène.

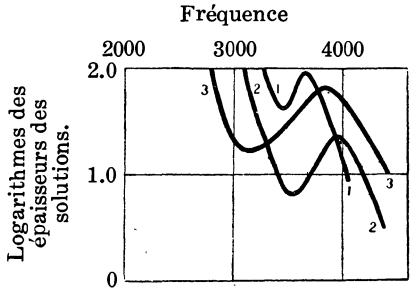
Comme nous pouvons l'observer dans la figure 7, à la fin de l'absorption, la région visible se transforme graduellement en une longueur d'onde plus petite en s'éloignant de la liaison conjuguée du radical azoïque avec le noyau benzénique. Cette variation des courbes, dans la figure 7, est en accord avec les changements que subissent les couleurs des corps ci-dessus nommés. Le centre d'absorption sélective ultra-violette donnée par le diazoaminobenzène et la diméthyldiphényltétrazone présente un carac-

(35) "Handbuch der Physik", XXI, "Licht u. Materie", (1929), 128.

tère plus bathochromique que l'azobenzène et cela nous semble se baser sur l'absorption du radical NH lui-même.

Nous notons, dans la figure 7, le pouvoir absorbant remarquable montré par la liaison conjuguée du radical azoïque avec le noyau benzénique, mais nous le voyons plus facilement, dans la figure 3, sans l'insertion du radical NH qui a une absorption ultra-violette. Notre étude actuelle a plutôt donné une explication spectrochimique de l'opinion émise par Ley et a rendu plus évidente la conclusion concernant la comparaison des courbes d'absorption que représente la figure 3.

(1) *Azobenzène,* (18) *Hydrazobenzène,* et (19) *Diphénylamine.* Pour préciser l'absorption de la phénylhydrazone en considérant l'influence exercée par le radical NH, nous avons ajouté le hydrazobenzène et la diphénylamine à l'azobenzène pour les comparer dans la figure 8.



1. C_6H_5-NH-NH-C_6H_5 (18)
2. C_6H_5-NH-C_6H_5 (19)
3. C_6H_5-N=N-C_6H_5 (1)

Fig. 8.

Le centre de bande d'absorption, dans une fréquence de 3500, est clairement observé par la diphénylamine et le hydrazobenzène, qui ne diffère par sa position avec le centre de la bande, est sensiblement hypochromique. Purvis et McCleland[36] ont déjà étudié le spectre d'absorption du hydrazobenzène, et ils n'y ont pas cependant trouvé de différence nette et rationelle concernant l'absorption que présente l'azobenzène. C'est à ce même résultat que nous sommes nous-mêmes arrivés. Ils ont probablement observé le spectre d'absorption du hydrazobenzène qui s'est déjà, en grande partie, transformé en azobenzène. Quant aux spectres d'absorption de la diphénylamine, nous en avons déjà plusieurs, et les observations de Baker[37] ne diffèrent guère des nôtres, mais elles sont un peu différentes de celles qui ont été faites par Purvis et McCleland[36] ou Lifschitz.[38]

(20) *Benzalazine,* et (21) *Benzalaniline.* Nous avons pris les deux corps préparés ci-dessus nommés pour étudier l'influence exercée par le radical –CH=N– sur l'absorption de la phénylhydrazone.

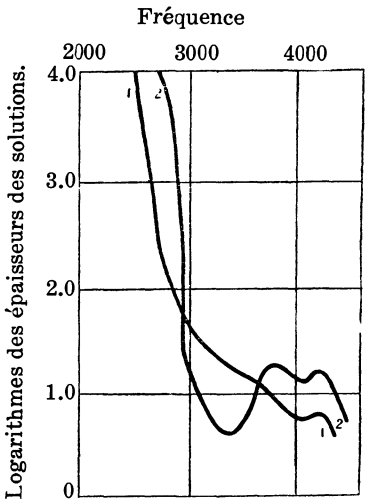
La benzalaniline jaunâtre et la benzalazine jaune ne donnent pas d'absorption sélective dans une région visible comme nous l'observons dans

(36) J. E. Purvis et N. P. McCleland, *J. Chem. Soc.*, **101** (1912), 1514.
(37) F. Baker, *J. Chem. Soc.*, **91** (1907), 1490.
(38) J. Lifschitz, *Rec. trav. chim.*, **43** (1924), 403.

la figure 9. Dans la benzalazine, le centre de bande d'absorption apparaît vers 3400 de fréquence, ce qui vient de ce que sa bande est basée sur -CH=N-. Le chromophore -CH=N- ne présente qu'un pouvoir absorbant fort hypsochromique quand il se trouve tout seul, et c'est la liaison conjuguée par rapport au noyau benzénique qui doit être considérée comme le cas du radical azoïque.

Dans le cas de la phénylhydrazone (fig. 6), puisque le noyau benzénique s'unit indirectement, en laissant un intervalle entre le radical -NH-, et le radical -CH=N-, son pouvoir absorbant est supposé plus petit que les deux composés indiqués dans la figure 9.

Baly, Tuck et Marsden[39] ont déjà publié le spectre d'absorption de la benzalaniline qui est un peu différent du résultat que nous avons obtenu.



1. C_6H_5-CH=N-C_6H_5 (21)
2. C_6H_5-CH=N-N=CH-C_6H_5 (20)

Fig. 9.

Résumé.

(1) Lorsque le radical azoïque se présente comme un chromophore bien fort, il se forme une double liaison conjuguée avec le noyau benzénique, et cette relation présente, dans ce cas, deux bandes d'absorption remarquables qui sont surtout nettement observées par la solution d'azobenzène (voir fig. 1, 2, 3 et 7).

(2) La position du centre de deux bandes d'absorption produites par les composés azoïques mixtes est indépendante de la longueur de l'alcoyle. Il nous semble que cette conclusion peut aussi confirmer le paragraphe (1) de ce résumé (voir fig. 2).

(3) Nous observons que le type *"azo"* donne naissance à deux bandes d'absorption tandis que le type *"hydrazone"* n'en montre qu'une seule (comparer fig. 2 et 4).

(4) Le spectre d'absorption observé dans le type *"hydrazone"* des corps azoïques mixtes est presque indépendant de la forme de l'alcoyle (chaîne normale ou chaîne latérale) (voir fig. 5).

(39) E. C. C. Baly, W. B. Tuck et E. G. Marsden, *J. Chem. Soc.*, **97** (1910), 590.

(5) Le pouvoir absorbant du radical azoïques dans les composés azoïques mixtes s'affaiblit par l'introduction du phényle à l'alcoyle contenu. Ce radical azoïque se change partiellement en type "*hydrazone*" plus stable (voir fig. 6).

(6) Nous avons étudié l'influence spectrochimique du radical –NH– (voir fig. 7 et 8).

(7) Nous avons examiné le pouvoir absorbant montré par le chromophore –CH=N– (voir fig. 9).

En terminant cette publication, nous avons à exprimer nos sincères remerciements à la Société "Hattori Hôkôkaï" qui a bien voulu se charger d'une partie des frais de nos expériences.

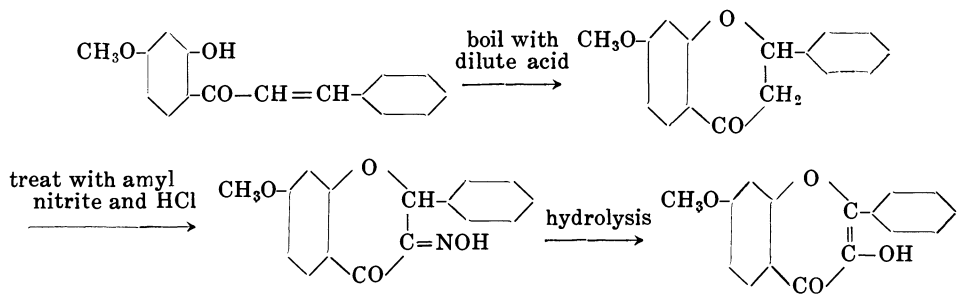
Laboratoire de Chimie minérale, Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku).

A NEW GENERAL METHOD FOR THE SYNTHESIS OF THE DERIVATIVES OF FLAVONOL.*

By Taichiro OYAMADA.

Received February 13th, 1935. Published May 28th, 1935.

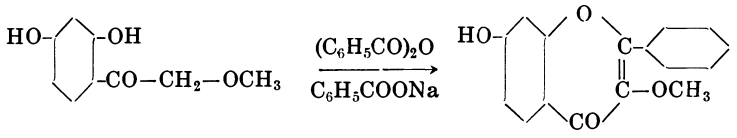
The derivatives of flavonol were first synthesised by Kostanecki and Lampe[1] from the derivatives of *o*-hydroxychalkone through isonitroso-flavanones, as shown in the following scheme:



* Translation from the original, *J. Chem. Soc. Japan*, **55** (1934), 1256.

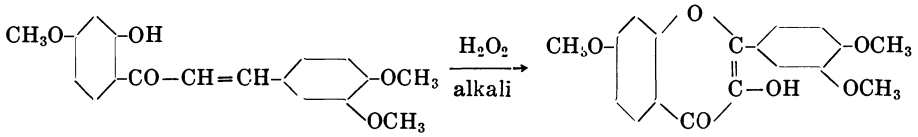
(1) *Ber.*, **37** (1904), 773.

About ten years ago, Robinson and Allan[2] suggested a new general method for their preparation:



By means of these methods a large number of the derivatives of flavonol have hitherto been synthesised.

The present author has observed that the derivatives of *o*-hydroxychalkone show an extreme facility in forming derivatives of flavonol by the action of hydrogen peroxide in the presence of alkali. A methyl alcoholic solution of 4,3′,4′-trimethoxy-2-hydroxychalkone containing hydrogen peroxide and alkali was kept at 0–5° for 12 hours, and, on acidifying, a pale yellow substance separated out. This substance, melting at 185°, was proved to be identical with 7,3′,4′-trimethoxy-3-hydroxyflavone by the mixed melting point. The yield amounted to about 80%.

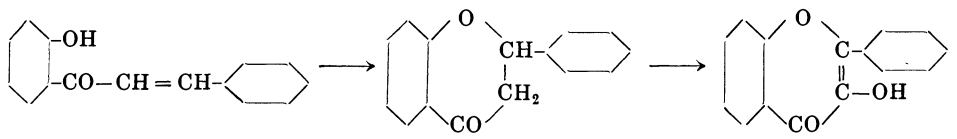


The similar reactions were carried out with 2-hydroxychalkone, 2-hydroxy-4′-methoxychalkone, and 2-hydroxy-3′,4′-dimethoxychalkone, and the corresponding derivatives of flavonol were obtained in good yields. It can naturally be considered that this method is generally applicable for synthesis of the derivatives of flavonol. Owing to the simplicity of the procedure and to the excellent yield, it may be said to be a new convenient method for preparation.

Weitz and Scheffer[3] first studied the action of hydrogen peroxide on chalkone in the aqueous-alcoholic solution and obtained benzalacetophenone-oxide from benzalacetophenone. Recently, Baker and Robinson[4] applied this reaction to 2-acetoxy-4-methoxychalkone, but without success, and reported that the reaction resulted merely in the hydrolysis of the acetoxy-group. But the present author has observed that the above-mentioned derivatives of *o*-hydroxychalkone easily give the correspond-

(2) *J. Chem. Soc.*, **125** (1924), 2192.
(3) *Ber.*, **54** (1921), 2344.
(4) *J. Chem. Soc.*, **1932**, 1798.

ing flavonols under the conditions described above. Now it is interesting to consider the mechanism of the formation of flavonol from *o*-hydroxychalkone. We first suppose that the formation of the oxide as an intermediate product may take place, but it is difficult to explain how the oxide is converted into flavonol. On the other hand, we can also consider that *o*-hydroxychalkone isomerises to flavanone which may be oxidised to flavonol under these conditions. The latter view was supported by the experimental fact that *o*-hydroxychalkone easily gives flavanone with alkali alone and the resulting flavanone is subsequently converted into flavonol in an excellent yield by the action of hydrogen peroxide in the presence of alkali. Hence, the mechanism of the formation of flavonol is accounted for by the following scheme:



That of the formation of the other three derivatives of flavonol will also be explained as in the above case.

By the action of hydrogen peroxide in the presence of alkali, 4′-methoxyflavanone and 7,3′,4′-trimethoxyflavanone were oxidised to 4′-methoxyflavonol and 7,3′,4′-trimethoxyflavonol respectively in good yields. It is of interest to note that a derivative of flavanone is directly converted into a derivative of flavonol by such a simple oxidation. In the early stage of the investigation of the derivatives of flavonol, attempts to obtain flavonol from flavone by oxidation were made by Kostanecki and his collaborators,[5] but without success. The present author has succeeded in preparing it from flavanone by oxidation.

Experimental.

Preparation of 7, 3′, 4′-Trimethoxy-3-hydroxyflavone from 4, 3′, 4′-Trimethoxy-2-hydroxychalkone. To a solution of 4,3′,4′-trimethoxy-2-hydroxychalkone (1.5 g.) in methyl alcohol (30 c.c.), 15% aqueous hydrogen peroxide (4 c.c.) and 16% aqueous sodium hydroxide (10 c.c.) were added under cooling. After being allowed to stand at 0–5° for 12 hours, the solution was acidified with dilute sulphuric acid and diluted with water. The precipitate was recrystallised from alcohol, pale yellow needles melting at 185°, and showing no depression of melting point by admixture with 7,3′,4′-trimethoxy-3-hydroxyflavone synthesized by the Kostanecki method. The yield was 1.2 g. (Found: C, 65.62; H, 5.05. Calc. for $C_{18}H_{16}O_6$: C, 65.85; H, 4.87%.)

(5) *Ber.*, **35** (1902), 1679.

Preparation of 3-Hydroxyflavone (Flavonol) from *o*-Hydroxychalkone. *o*-Hydroxychalkone (1 g.) was dissolved in methyl alcohol (20 c.c.), and 15% aqueous hydrogen peroxide (3 c.c.) and 16% aqueous sodium hydroxide (5 c.c.) were added. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water, when a colourless substance separated out. It was recrystallised from alcohol, needles melting at 169–170°. This melting point coincides with that of flavonol.[6] The yield was 0.8 g. (Found: C, 75.35; H, 4.58. Calc. for $C_{15}H_{10}O_3$: C, 75.63; H, 4.20%.)

3-Methoxyflavone (Methylflavonol). 3-Hydroxyflavone (0.5 g.) was methylated with diazomethane in ethereal solution. On recrystallising from alcohol, colourless needles, m.p. 114°, were obtained. The yield was 0.5 g. 3-Methoxyflavone which prepared by Hattori[7] melts at 107°. (Found: C, 75.97; H, 4.98. Calc. for $C_{16}H_{12}O_3$: C, 76.19; H, 4.76%.)

3-Acetoxyflavone. 3-Hydroxyflavone (0.5 g.) was acetylated with acetic anhydride and fused sodium acetate. The product forms colourless crystals melting at 110–111°. Kostanecki and Szabranski[8] gave 110-111° as its melting point. Yield, 0.2 g. (Found: C, 73.00; H, 4.56. Calc. for $C_{17}H_{12}O_4$: C, 73.21; H, 4.29%.)

Preparation of 4′-Methoxy-3-hydroxyflavone from 4′-Methoxy-2-hydroxychalkone. To a solution of 4′-methoxy-2-hydroxychalkone (1 g.) in methyl alcohol (35 c.c.), 15% aqueous hydrogen peroxide (2 c.c.) and 16% aqueous sodium hydroxide (2 c.c.) were added under cooling. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water. The pale yellow crystals which separated were collected and recrystallised from alcohol, pale yellow needles, m.p. 230–232°. Edelstein and Kostanecki[9] gave 231–232° as the melting point. Yield, 0.7 g. (Found: C, 71.57; H, 4.70. Calc. for $C_{16}H_{11}O_4$: C, 71.64; H, 4.48%.)

3,4-Dimethoxyflavone. 4′-Methoxy-3-hydroxyflavone (0.5 g.) was methylated with diazomethane in ethereal solution. The raw product was recrystallised from alcohol, when it melted at 90–92°. The yield was 0.3 g. (Found: C, 72.15; H, 5.21. Calc. for $C_{17}H_{14}O_4$: C, 72.34; H, 4.96%.)

Preparation of 3′,4-Dimethoxy-3-hydroxyflavone from 3′,4′-Dimethoxy-2-hydroxychalkone. 3′,4′-Dimethoxy-2-hydroxychalkone (1.3 g.) was dissolved in methyl alcohol (15 c.c.), and 15% aqueous hydrogen peroxide (2 c.c.) and 16% aqueous sodium hydroxide (3 c.c.) were added under cooling. After standing overnight in the ice-chest, the alkaline solution was acidified with dilute sulphuric acid and diluted with water, when a yellow substance separated out. On recrystallising from alcohol, pale yellow crystals m.p. 200–202° were obtained. Hattori[10] gave 202° as its melting point. Yield, 1 g. (Found: C, 68.66; H, 4.84. Calc. for $C_{17}H_{14}O_5$: C, 68.79; H, 4.69%.)

3,3′,4′-Trimethoxyflavone. 3′,4′-Dimethoxy-3-hydroxyflavone (0.5 g.) was methylated with diazomethane in ethereal solution and the product was then purified, when

(6) *Ber.*, **37** (1904), 2820.
(7) *Acta Phytochimica*, **4** (1928), 44.
(8) *Ber.*, **37** (1904), 2820.
(9) *Ber.*, **38** (1905), 1507.
(10) This Bulletin, **2** (1927), 175.

almost colourless crystals, m.p. 168–169°, were obtained. Hattori[10] gave 168–169° as its melting point. The yield was 0.2 g. (Found: C, 69.04; H, 5.36. Calc. for $C_{18}H_{16}O_5$: C, 69.23; H, 5.12%.)

Preparation of Flavanone from *o*-Hydroxychalkone. To a solution of *o*-hydroxychalkone (1 g.) in methyl alcohol (15 c.c.), 16% aqueous sodium hydroxide (4 c.c.) was added. After standing overnight in the ice-chest, the solution was diluted with water, when a colourless substance separated out. On recrystallising from dilute alcohol, colourless prisms, m.p. 75–76°, were obtained. No alternation of melting point was observed on mixing it with flavanone obtained by the usual method. Yield, 0.8 g.

Preparation of 3-Hydroxyflavone (Flavonol) from Flavanone. Flavanone (0.3 g.) in methyl alcohol (15 c.c.) was mixed with 15% aqueous hydrogen peroxide (2 c.c.) and 16% sodium hydroxide (3 c.c.) under cooling. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water. The colourless crystals which separated were recrystallised from alcohol, colourless needles, m.p. 169–170°. No alternation of melting point was observed on mixing it with flavonol obtained by the method described on page 185. Yield, 0.25 g.

Preparation of 4′-Methoxy-3-hydroxyflavone from 4′-Methoxyflavanone. 4′-Methoxyflavanone (0.5 g.) was dissolved in methyl alcohol (10 c.c.), and 15% aqueous hydrogen peroxide (2 c.c.) and 16% aqueous sodium hydroxide (2 c.c.) were added under cooling. After standing overnight in the ice-chest, the solution was acidified with dilute sulphuric acid and diluted with water, when a pale yellow substance separated out. It was recrystallised from alcohol, pale yellow needles, m.p. 232°. It proved to be identical with 4′-methoxy-3-hydroxyflavone by the mixed melting point. Yield, 0.4 g.

Preparation of 7, 3′, 4′-Trimethoxy-3-hydroxyflavone from 7, 3′, 4′-Trimethoxyflavanone. 7,3′,4′-Trimethoxy-3-hydroxyflavone was directly prepared from 7,3′,4′-trimethoxyflavanone similarly as described above.

In conclusion, the author wishes to express his sincere thanks to Professor Kinzo Kafuku for his kind guidance and encouragement.

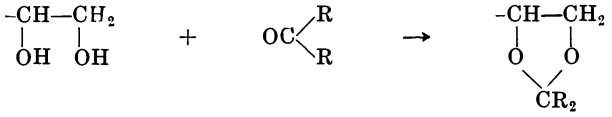
Laboratory of Organic Chemistry,
Faculty of Science and Agriculture,
Taihoku Imperial University.

ACETONE-COMPOUNDS OF SOME α-HYDROXY-ACIDS AND THEIR RAMAN SPECTRA.*

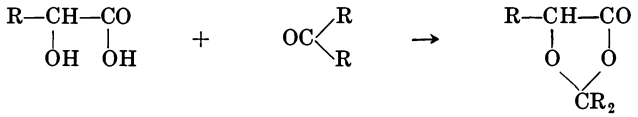
By Haruomi ÔEDA.

Received February 22nd, 1935. Published May 28th, 1935.

Polyhydric compounds, which contain two hydroxyls in α-positions, condense with a carbonyl compound producing cyclic acetals in the presence of dehydrating agents.



It is known that some α-hydroxy-acids behave similarly towards carbonyl and form compounds having a heterocyclic ring of the same type.



The preparation of such derivatives of α-hydroxy-acids was reported by Wallach,[1] Leipen,[2] van Ekenstein,[3] and several other investigators. Formaldehyde, benzaldehyde, and acetone can be mentioned as the reactants on α-hydroxy-acids. Restricting to the acetone compounds, following works are cited from the literature.

In 1923 Willstätter[4] prepared acetone compounds of glycollic acid (b.p. 41° under 11 mm.), mandelic acid (m.p. 47.5–48°), and benzilic acid (m.p. 48°). In 1927 those of tartaric acids (*l* and *d*, m.p. 102°; *r*, 88.5°; *i*, 96–97°) and of quinic acid (m.p. 141°) were synthesized by H. O. L. Fischer.[5] As the dehydrating agent, Willstätter used concentrated sulphuric acid or anhydrous copper sulphate, while zinc chloride and

---

* Studies on Hydroxy-acids and their Derivatives. II.

(1) O. Wallach, Th. Heymer, *Ber.*, **9** (1876), 545.

(2) R. Leipen, *Monatsh.*, **9** (1888), 45.

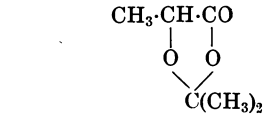
(3) W. A. Ekenstein, C. A. Lobry de Bruyn, *Rec. trav. chim.*, **18** (1899), 305; **20** (1901), 331; **21** (1902), 310.

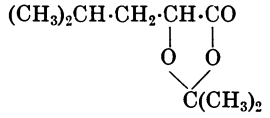
(4) R. Willstätter, Fr. Königsberger, *Ber.*, **56** (1923), 2107.

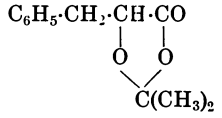
(5) H. O. L. Fischer, C. Taube, *Ber.*, **60** (1927), 485.

phosphorus pentoxide were recommended by H. O. L. Fischer and Smith[6] respectively.

The present author tried the preparation of acetone compounds of other α-hydroxy-acids and isolated the following:

Acetone-lactic acid  b.p. 49–49.5° under 11 mm.

Acetone-leucic acid  b.p. 84.5-85.5° under 13 mm.

Acetone-phenyl-lactic acid  m.p. 63-64°.

The latter two are formed by dehydration either with sulphuric acid or zinc chloride (better yield is obtained with the former), but the acetone compound of lactic acid is very sensitive to hydrolysis and can be prepared only with sulphuric acid under the special precautions that it never come in contact with water during its isolation.

Little was studied on the properties of acetone-hydroxy-acids and the only fact hitherto described is their instability towards warm dilute alkali. The author intends to carry out some investigations on the compounds of this class and the Raman spectra were first studied.

Raman Spectra. The acetone compounds of lactic acid and leucic acid were selected as materials. At room temperature, they are liquid, which provides every facility for the study of Raman spectra.

On the Raman spectra of compounds having five-membered saturated ring, informations are few except cyclopentane and its derivatives[7] and some of the anhydrides of dibasic acids.[8] From the Raman spectra of two above-mentioned compounds photographed by the author, the following conclusion can be derived.

(a) C·H-Frequencies. In both of the spectra, the frequencies close up and over 2900 cm.$^{-1}$ (2869, 2940, 2993 in acetone-lactic acid (I) and

(6) L. Smith, J. Lindberg, *Ber.*, **64** (1931), 505.

(7) Weiler, *Z. Physik*, **69** (1931), 586; Canal, *Compt. rend.*, **194** (1932), 1574. L. Piaux, *Compt. rend.*, **197** (1933), 1647; **198** (1934), 1496.

2868, 2902, 2939, 2994 in acetone-leucic acid (II)) are lines usually assigned as "C·H-valency-frequencies". No C·H-frequency which exceeds 3000 cm.$^{-1}$ is found in the spectra. The frequencies 1448 cm.$^{-1}$ in I and 1446 cm.$^{-1}$ in II are assigned as "C·H-deformation-frequencies".

(b) C:O-Frequency. The present compounds contain a carbonyl group in the molecules. The frequencies 1790 cm.$^{-1}$ in I and 1787 cm.$^{-1}$ in II can be attributed to this group, although the values observed here seem rather high for such frequencies.

According to the detailed study of Kohlrausch,[8] the C:O-frequency is said to be sensible to the constitutive effect of adjacent groups. It shows minimum value in free acids (mean 1660 cm.$^{-1}$) and it increases in ketones, aldehydes, and esters (mean of esters 1732 cm.$^{-1}$) in the order mentioned. In acid anhydrides, which show some similarity in structure with the present compounds, the value increases furthermore; 1740–1754 cm.$^{-1}$ are observed in six kinds of anhydrides of monobasic acids and 1774–1782 cm.$^{-1}$ in four kinds of anhydrides of dibasic acids (inner anhydrides). In addition to these, it was pointed out also by Kohlrausch that the more sensitive the compound to hydrolysis, the higher is the value of C:O-frequency, Table 1.

Table 1.

Phthalide	$C_7H_4<\begin{matrix}CO\\CH_2\end{matrix}>O$	1753
Phthalic anhydride	$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>O$	1775
Benzoic anhydride	$C_6H_5\cdot CO\cdot O\cdot OC\cdot C_6H_5$	1776
Benzoyl peroxide	$C_6H_5\cdot CO\cdot O\cdot O\cdot OC\cdot C_6H_5$	1781
Acetone-lactic acid	$CH_3\cdot CH(O{-}C(CH_3)_2{-}O)CO$	1790
Acetone-leucic acid	$(CH_3)_2CH\cdot CH_2\cdot CH(O{-}C(CH_3)_2{-}O)CO$	1787

The present compounds have the similar cyclic structure as anhydrides of dibasic acids and show marked sensitivity to hydrolysis and it is easily understood from the study of Kohlrausch that the C:O-frequencies in these compounds show the values as high as 1787–1790 cm.$^{-1}$.

(c) Other frequencies. Among other frequencies, the two adjacent ones, 623, 706 cm.$^{-1}$ in I and 623, 700 cm.$^{-1}$ in II are sharp and strong and are very conspicuous in each of two spectra.

(8) K. Kohlrausch, A. Pongratz, R. Seka, *Ber.*, **66** (1933), 1.

Experimental Part.

Preparation of acetone-compounds of α-hydroxy-acids.

Acetone-lactic acid. Lactic acid (Takeda; 100 g.) was dissolved in dry acetone (400 c.c.). The solution was kept at -5--10° and concentrated sulphuric acid (300 g.) was added with mechanical stirring in the course of two hours. Benzene was poured repeatedly (total volume, 1000 c.c.) to the above solution and the product was thoroughly extracted.

To the combined benzene solution freshly ignited sodium sulphate was added and dry ammonia was passed to neutralize the remaining acid. After standing overnight, the benzene was removed under reduced pressure and the residual oil was subjected to vacuum distillation, when the main part distilled at 57–58° under 18 mm. and it amounted to 43.2 g., corresponding to 30 mol% assuming that the lactic acid was pure. After refractionation, the part distilling at 49–49.5° under 11 mm. was taken for analysis. The acetone-compound is readily hydrolyzed with warm dilute alkali and the components can be determined as follows: The weighed sample was completely hydrolyzed with an excess of N/10-alkali by warming on water bath. After cooling, the remaining alkali was titrated with N/10-acid. (Found: Saponification equivalent, 130.6. Calc. for $C_6H_{10}O_3$: 130.1). The weighed sample was hydrolyzed with an excess of N-alkali in a tightly stoppered bottle. After cooling, acetone was determined by Messinger's method as usual. (Found: acetone, 44.07. Calc. for $C_6H_{10}O_3$: 44.65%.)

Acetone-leucic acid. (a) *By sulphuric acid method.* Leucic acid (40 g., 0.30 mol) (m.p. 73°, prepared from natural leucine) was dissolved in acetone (110 c.c.) and the solution was cooled at -10--20°. Concentrated sulphuric acid (25 g.) was gradually added with constant stirring. After 30 minutes, the reaction product was poured into an excess of ice-cooled 10% sodium carbonate solution to remove acid, whereupon an oil gradually accumulated on the surface of the solution. The oily layer was separated and the carbonate solution was thoroughly extracted with ether, to which the above oil was put together. After removing ether, the residual oil was distilled in vacuum; the part distilling at 90–92.5° under 18 mm. amounted to 33.7 g., corresponding to 64 mol%. (Found: Saponification equivalent, 173.6; acetone, 33.32. Calc. for $C_9H_{16}O_3$: sap. equ., 172.1; acetone, 33.72%.)

(b) *By zinc chloride method.* Leucic acid (20 g., 0.15 mol.) was dissolved in dry acetone (50 c.c.), to which a suspension of zinc chloride (40 g.) in acetone (100 g.) was gradually added. After standing overnight, acetone was distilled off in vacuum and ether (500 c.c.) was added and the mixture was extracted with water to remove zinc chloride. After drying, ether was expelled and the residual oil was subjected to distillation. The part distilling at 91–95° under 21 mm. (3.9 g., corresponding to 15 mol%) was collected, but it was contaminated with mesityl oxide. It required repeated fractionation to remove the impurity completely.

Acetone-phenyl-lactic acid. (a) *By sulphuric acid method.* Phenyl-lactic acid (40 g., 0.24 mol) (m.p. 124°; prepared from natural phenylalanine) was put into acetone (110 c.c.) and was treated with concentrated sulphuric acid (24 g.) just in the same manner as in the case of leucic acid. The solution was poured into an excess of ice-cooled 10% sodium carbonate solution and the acetone compound separated as crystals. It amounted to 43 g. after drying overnight. Yield, 88 mol%. It melted

at 63–64° after recrystallisation from alcohol. (Found: saponification equivalent, 206.4; acetone, 27.82. Calc. for $C_{12}H_{14}O_3$: sap. eq., 206.1; acetone, 28.17%.)

(b) *By zinc chloride method.* From 15 g. of the hydroxy-acid, 50 c.c. of dry acetone, and 23 g. of zinc chloride; 5.2 g. of the acetone-compound was obtained, yield 28 mol%.

Raman Spectra.

The Raman spectra were taken in the laboratory of Prof. Mizushima by his and his collaborators' courtesy. Every appliance for Raman spectrum here used is of

Table 2. Acetone-lactic acid.

No.	Intensity	$\Delta\nu$ in cm.$^{-1}$	No. in which $\Delta\nu$ is equal
1	m.	k- 114	1–15
2	w.	k- 258(q-2941)	2–26–31
3	w.	k- 310(q-2993)	3–27–32
4	w.	k- 348(p-2996)	4–27–32
		(o-2936)	4–26–31
5	w.	k- 412(o-3000)	5–27–32
6	w.	k- 526	6–18
7	v.s.	k- 623	7–19
8	s.	k- 705	8–20
9	s.	k- 786	9–21
10	w.	k- 813(i- 624)	10- 7–19
11	w.	k- 883	11–22
12	w.	k- 934	12–23
13	w.	k- 984	13–24
14	m. b.	k-1449	14–28
15	s.	e- 115	15- 1
16	w.	e- 250	—
17	m.	e- 329	—
18	w.	e- 529	18- 6
19	v.s.	e- 622	19- 7
20	s.	e- 707	20- 8
21	s.	e- 784	21- 9
22	w.	e- 884	22–11
23	w.	e- 933	23–12
24	w.	e- 987	24–13
25	m.	e-1099(k-2868)	25–30
26	v.s.	e-1176(k-2943)	26–31
27	v.s.	e-1227(k-2994)	27–32
28	s. b.	e-1447	28–14
29	m.	e-1790	—
30	m.	e-2870	30–25
31	v.s.	e-2937	31–26
32	v.s.	e-2992	32–27

$\Delta\nu$: 115(s.), 250(w.), 329(m.), 528(w.), 623(v.s.), 706(s.), 785(s.), 884(w.), 934(w.), 986(w.), 1448(s. b.), 1790(m.), 2869(s.), 2940(v.s.), 2993(v.s.).

Table 3. Acetone-leucic acid.

No.	Intensity	$\Delta\nu$ in cm.$^{-1}$	No. in which $\Delta\nu$ is equal
1	w.	k- 223(p-2871)	1–26–32
2	m.	k- 258(q-2941)	2–28–34
3	w.	k- 278(o-2866)	3–26–32
4	m.	k- 317(q-3000)	4–29–35
5	w.	k- 352(o-2940)	5–28–34
		(p-3000)	5–29–35
6	w.	k- 415(o-3003)	6–29–35
7	w.	k- 518	7–19
8	v.s.	k- 623	8–20
9	s.	k- 699	9–21
10	w.	k- 808(i- 619)	10- 8–20
11	s.	k- 828	11–22
12	w.	k- 925	12–23
13	w.	k- 958	13–24
14	w.	k-1009	14–25
15	w.	k-1141(e+ 626)	15- 8–20
16	s. b.	k-1447	16–30
17	w.	e- 359	—
18	w.	e- 429	—
19	w.	e- 524	19- 7
20	v.s.	e- 622	20- 8
21	s.	e- 700	21- 9
22	s.	e- 829	22–11
23	w.	e- 928	23–12
24	m.	e- 957	24–13
25	w.	e-1001	25–14
26	s.	e-1103(k-2870)	26–32
27	s.	e-1136(k-2903)	27–33
28	v.s.	e-1172(k-2939)	28–34
29	v.s.	e-1229(k-2996)	29–35
30	s. b.	e-1444	30–16
31	m.	e-1787	—
32	s.	e-2865	32–26
33	s.	e-2901	33–27
34	v.s.	e-2939	34–28
35	v.s.	e-2992	35–29

$\Delta\nu$: 359(w.), 429(w.), 521(w.), 623(v.s.), 700(s.), 829(s.), 927(w.), 958(m.), 1005(w.), 1446(s. b.), 1787(m.), 2868(s.) 2902(s.), 2939(v.s.), 2994(v.s.).

their own construction.[9] 1. Light source: two mercury lamps, 30 cm. long (100 v.–10 amp.). 2. Spectrograph: an apparatus with large aperture (1:5) having a dispersion of 12 Å per mm. at 4000 Å. 3. The breadth of the slit: 0.1 mm. 4. Photographic plates: "Agfa Isochromplatten." 5. Time of exposure: 2.5 hours (3.5 hrs. in the case when quinine sulphate filter was used). 6. The relative intensity of Raman spectra was classified into four grades (by visual estimation), namely, very strong (v.s.), strong (s.), medium (m.) and weak (w.). 7. The Raman apectra were taken twice for each sample, once with the filter, and the mean value of the frequencies in both plates are shown in Tables 2 and 3. 8. Materials: purified by repeated fractionation in vacuum through a 6 cm. Widmer column, in each experiment, 25 c.c. of the pure sample was put into the scattering tube.

Acetone-lactic acid,	b.p. 58.0–58.5°C. under 18 mm.
Acetone-leucic acid,	b.p. 84.5–85.5°C. under 13 mm.

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author wishes to express his sincere thanks to Prof. K. Matsubara for the kind inspection of this paper. His best thanks are also due to Prof. S. Mizushima and Mr. Y. Morino for their valuable instructions in the study of Raman spectrum and to Dr. Y. Takayama for his constant encouragements during this work.

(9) The detailed description of the apparatus is given by Mizushima, Morino, and Higasi, *Scientific Papers of the Institute of Physical and Chemical Research, Japan*, **25** (1934), 159–221; *Physik. Z.*, **35** (1934), 905–911.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL.
II. THE CONSTITUTION OF HIRAGONIC ACID $C_{16}H_{26}O_2$.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received February 25th, 1935. Published May 28th, 1935.

In the previous paper,(1) the authors described the isolation of hiragonic acid $C_{16}H_{26}O_2$ from Japanese sardine oil. The present paper records the results of the experiments concerning the constitution of this acid.

---

* Translated from the paper published in Japanese in the Report of Tokyo Imperial Industrial Research Laboratory, **27** (1932), No. 2.

(1) Toyama and Tsuchiya, this Bulletin, **4** (1929), 83.

For the determination of the positions of three ethylenic linkings in hiragonic acid, its methyl ester was oxidised by the permanganate method and also by the ozonide method, and the products were examined. Among the oxidation products of methyl hiragonate by the permanganate method, acetic acid $CH_3 \cdot COOH$, succinic acid $HOOC \cdot (CH_2)_2 \cdot COOH$, and methyl hydrogen adipate $HOOC \cdot (CH_2)_4 \cdot COOCH_3$ were identified. The products obtained by the ozonide method contained, besides the above-mentioned three compounds, acetaldehyde $CH_3 \cdot COH$ and semi-aldehyde of methyl hydrogen adipate $HOC \cdot (CH_2)_4 \cdot COOCH_3$, and also the presence of semi-aldehyde of succinic acid $HOC \cdot (CH_2)_2 \cdot COOH$ and succinic aldehyde $HOC \cdot (CH_2)_2 \cdot COH$ (or its polymerised products) was indicated. It is seen from these results that the free hiragonic acid has the groups: $CH_3 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_4 \cdot COOH$, of which hiragonic acid should contain two of the $=CH \cdot (CH_2)_2 \cdot CH=$ group, since it has three ethylenic linkings. This is also verified by the fact that the actual yield of the oxidation products having four carbon atoms was considerably higher than the value obtainable by assuming only one $=CH \cdot (CH_2)_2 \cdot CH=$ group. The constitution of hiragonic acid was thus established as $\Delta^{6:7,\ 10:11,\ 14:15}$-hexadecatrienoic acid which is expressed by the following formula:

$$CH_3 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_4 \cdot COOH$$

Besides hiragonic acid, two other unsaturated C_{16}-acids have hitherto been found with certainty in natural fatty oils. These are zoomaric acid, which occurs widely in marine animal oils, and lycopodium-oleic acid in lycopodium oil. In comparison of these two acids, it should be mentioned here that the positions of three ethylenic linkings in hiragonic acid differ entirely from those in zoomaric and lycopodium-oleic acids. Whilst the ethylenic linking of zoomaric acid[2] lies in 9:10-position and that of lycopodium-oleic acid[3] in 12:13-position, hiragonic acid has three ethylenic linkings in 6:7-, 10:11- and 14:15-positions, but no ethylenic linking in 9:10- or in 12:13-position.

Experimental.

1. Preparation of Methyl Hiragonate. For the preparation of methyl hiragonate used in these experiments, a methyl ester fraction containing a large amount of highly unsaturated C_{16}- and C_{18}-acids as their methyl esters was prepared first from the sardine oil, and it was then converted into bromides, from which the ether insoluble,

(2) Toyama, *J. Soc. Chem. Ind. Japan*, **30** (1927), 603.
(3) K. H. Bauer and W. Piners, *Pharm. Zentralhalle*, **71** (1930), 33.

but benzene soluble portion was separated. Debromination of this portion followed by a repeated fractionation gave a fraction corresponding to methyl hiragonate.

(i) *Preparation of methyl ester fraction in which highly unsaturated* C_{16}- *and* C_{18}-*acid are concentrated.* The Japanese sardine oil used in these experiments had d_4^{20} 0.9265, n_D^{20} 1.4795, saponification value 190.0, iodine value by the Rosenmund-Kuhnhenn method 164.0, and the mixed fatty acids yielded 54.14% of ether insoluble bromides. It was converted into ethyl esters[4] by ethanolysis, and the latter were subjected to the distillation, by which the fraction boiling below 215°/10 mm. and the fraction boiling over 215°/10 mm. were collected separately. Whilst the fraction boiling below 215°/10 mm. was used in these experiments, the higher fraction was used for the examination of highly unsaturated C_{20} and C_{22}-acids which will be reported later. Sixty kg. of the ethyl esters gave 28.5 kg. of the fraction boiling below 215°/10 mm. This was converted into free fatty acids by saponification followed by acidification in the usual way, the latter were dissolved in 5 times of their weight of 85% methanol, allowed to cool down to about 10°, and the separated crystals consisting largely of saturated fatty acids were filtered. The filtrate was neutralised with aqueous lithium hydroxide solution (2.5%), the insoluble lithium soaps formed were removed by filtration, and on acidification of the filtrate there were obtained 7.5 kg. of 85% methanol, allowed to cool down to about 10°, and the separated crystals consistjected to fractional distillation, which yielded 5.9 kg. of a fraction boiling below 215°/15 mm. It had saponif. value 199.6 and iodine value by the Rosenmund-Kuhnhenn method 182.8, and was considered to contain a large proportion of highly unsaturated C_{16}- and C_{18}- acids as their methyl esters.

(ii) *Preparation of ether insoluble bromides and separation of the bromides by means of benzene.* From the methyl ester fraction boiling below 215°/15 mm., the ether insoluble bromides were prepared in the following manner: 100 g. of the methyl ester fraction was dissolved in 1 l. of ether and cooled to −10°. Bromine, dissolved in an equal part of glacial acetic acid, was added with constant stirring until the brown colouration remained permanent. After standing for 15 hours at 2–3°, the supernatant ethereal solution was removed by decantation, the residual precipitate of insoluble bromides was washed 2 to 3 times with cold ether by decantation as before, and then transferred on the filter where it was washed thoroughly until the washings became colourless. In total, about 2 l. of ether was used for washings. The precipitate appeared to be soluble in ether to a certain extent. For the recovery of the solid bromides dissolved in the washings, the united washings were treated with sodium thiosulphate to remove the excess of bromine, concentrated by distilling off a portion of ether, and on cooling the solid bromides separated from the solution. In our previous experiment,[5] the precipitate of solid bromides to be recovered was filtered and washed with ether, but a large amount of ether was required in order to remove oily bromides which adhere tenaciously to the precipitate, and the washing of precipitate was not successful as the precipitate itself dissolved in ether before it was completely washed. In this experiment, the precipitate was filtered and it was boiled with five volumes of alcohol, then cooled down to room temperature and filtered with suction. By repeating the washing in this way with the use of alcohol four times, the filtrate became

(4) Excepting this case, the methyl esters were used instead of the ethyl esters.
(5) This Bulletin, **4** (1929), 83.

colourless and a white powder of bromide was obtained. The latter was added to the main portion of ether insoluble bromides obtained before. The ether insoluble bromides thus obtained were then treated with benzene in the following manner: 20 g. of ether insoluble bromides were refluxed with 1.5 l. of benzene for about 40 minutes, and filtered while hot. From the filtrate, the dissolved bromides were recovered by distilling off benzene. By these treatments, 5.9 kg. of the methyl ester fraction yielded 1.5 kg. of benzene soluble, but ether insoluble bromides and 900 g. of benzene insoluble bromides.

(iii) *Debromination of benzene soluble, but ether insoluble bromides and fractionation of debrominated products.* For the debromination of benzene soluble bromides, 100 g. of the bromides was mixed with 50 g. of zinc powder, and the mixture was dropped gradually into a flask containing 150 c.c. of alcohol. The flask was immersed in cold water to avoid a violent heat evolution. When no further evolution of heat occurred, the flask was placed on the water-bath, and 150 c.c. of 5N alcoholic solution of hydrogen chloride was added in the course of 1.5 hours; during the reaction further 50 g. of zinc powder was added in several portions. After all the alcoholic solution of hydrogen chloride has been added, the solution was refluxed for another 1 hour, and the filtered. The residue, which seemed to contain some unchanged bromides, was heated with 100 c.c. of alcohol and 25 g. of zinc powder on the water-bath with an addition of 50 c.c. of alcoholic solution of hydrogen chloride during 30 minutes. After heating for one hour more, the alcoholic solution was filtered. The alcoholic solutions and the washings obtained by these treatments were combined and the debrominated product which was separated by an addition of a large quantity of water was taken up with ether. Since it was suspected that the debrominated product might contain a small portion of unsaponifiable substance, it was saponified, the unsaponifiable substance was removed by extraction with ether, and the fatty acids liberated from the soap solution on acidification were reconverted into methyl esters. These were subjected to a repeated fractionation, by which a fraction boiling at 186–188°/15 mm. was finally obtained as methyl hiragonate; yield 58 g. It had the following constants: d_4^{15} 0.9155, d_4^{20} 0.9122, n_D^{15} 1.4783, n_D^{20} 1.4764, molecular refraction 81.74 (calc. for $C_{17}H_{28}O_2$⊨$_3$: 80.96), saponif. value 212.8 (calc. 212.4), iodine value by the Rosenmund-Kuhnhenn method 288.7 (calc. 288.2). On brominating in ethereal solution, it gave an ether-insoluble bromide (yield 57%) which melted at about 180° to a light yellow liquid (Found: Br, 64.61. Calc. for $C_{17}H_{28}O_2Br_6$: Br, 64.47%).

Hiragonic acid was obtained on saponification of its methyl ester followed by acidification (Found: C, 76.69; H, 10.32. Calc. for $C_{16}H_{26}O_2$: C, 76.74; H, 10.47%). It had the following constants: d_4^{15} 0.9330, d_4^{20} 0.9296, n_D^{15} 1.4870, n_D^{20} 1.4850, molecular refraction 77.13 (calc. for $C_{16}H_{26}O_2$⊨$_3$: 76.22), neutralisation value 223.1 (calc. 224.2), iodine value by the Rosenmund-Kuhnhenn method 303.1 (calc. 304.4). Bromination of hiragonic acid in ethereal solution gave an ether insoluble bromide (yield 57%) which melted at about 190° (Found: Br, 65.84. Calc. for $C_{16}H_{26}O_2Br_6$: Br, 65.71%). Hydrogenation of hiragonic acid yielded palmitic acid which after recrystallisation from 90% alcohol showed neutralisation value 218.5 (calc. 219.0), m.p. and mixed m.p. 62.5°. It should be noted here that hiragonic acid and its methyl ester showed a slight exaltation of molecular refraction; the cause of this exaltation is unknown to us.

2. Oxidation of Methyl Hiragonate by the Permanganate Method. Methyl hiragonate (20 g.) was dissolved in 200 g. of acetone, the solution was gently boiled.

and 200 g. of powdered potassium permanganate was added in the course of 5 hours. When all the permanganate has been added, the solution was continued to reflux for 5 hours more, and then the acetone was removed by distillation. The residue was mixed with 400 c.c. of water, and a current of sulphur dioxide was passed through the mixture until the excess of permanganate and the insoluble oxides of manganese have disappeared completely. An oily portion (**A**), which separated from the aqueous solution, was collected on a filter, and the filtered solution was shaken with 2 l. of ether and allowed to separate into two layers. For a further recovery of the oxidation products dissolved in the aqueous layer, alcohol was added until the greater portion of inorganic salts separated out from the solution, and the filtered solution was then neutralised with alkali, evaporated to dryness, acidified with hydrochloric acid, and extracted with 300 c.c. of ether. The ethereal solutions were united and the ether distilled off. The residue was extracted three times with petroleum ether, using 150 c.c. for each extraction, and separated into petroleum ether soluble portion (**B**) and petroleum ether insoluble portion (**C**). The three portions thus obtained were examined separately.

(i) *Oily portion* (**A**). Yield 10.5 g. This portion contained neutral substance which escaped oxidation, besides acidic substance. Sodium carbonate solution was added to this portion, and the resulting soap solution was treated with ether, by which 2.5 g. of neutral substance was obtained from the ethereal extract. The soap solution yielded on acidification an oily liquid having neutr. value 338.5 and saponif. value 691.6 (calc. for methyl hydrogen adipate $C_7H_{12}O_4$: neutr. value 350.5 and saponif. value 700.9). The free acid obtained on saponification followed by acidification consisted of a crystalline solid which crystallised from ethyl acetate in needles; neutr. value 767.1 (calc. for adipic acid $C_6H_{10}O_4$: 768.2), m.p. 152.5–153°, which was unaltered when admixed with an authentic specimen of adipic acid (Found: C, 49.09; H, 6.95. Calc. for $C_6H_{10}O_4$: C, 49.29; H, 6.90%).

(ii) *Petroleum ether soluble portion* (**B**). The petroleum ether solution was heated on the water-bath until the petroleum ether was driven off, and then the residue (2.8 g.) heated in an oil-bath. About 1 g. of a colourless liquid distilled before the temperature of the bath reached 150°, beyond which nearly nothing distilled out; and when the temperature of the bath reached about 210°, the residue showed an indication of decomposition. The petroleum ether which distilled first showed acid reaction. On neutralising it with barium hydroxide solution, it precipitated barium acetate (Found: Ba, 53.66. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The distillate boiling below 150° (temperature of bath) was found to consist of acetic acid, since silver acetate was obtained by neutralising with sodium hydroxide and then adding silver nitrate (Found: Ag, 64.59. Calc. for $C_2H_3O_2Ag$: Ag, 64.64%).

(iii) *Petroleum ether insoluble portion* (**C**). Yield 12.8 g. This portion consisted of a crystalline solid, and on recrystallisation from ethyl acetate it gave succinic acid; neutr. value 948.6 (calc. 950.6), m.p. and mixed m.p. 182.5–183° (Found: C, 40.60; H, 5.22. Calc. for $C_4H_6O_4$: C, 40.66; H, 5.12%). It is considered that this portion consists almost exclusively of succinic acid, and its yield is about 64% of the methyl hiragonate used for the oxidation. This is considerably higher than the theoretical yield of succinic acid, 44.68%, with the assumption that methyl hiragonate has only one $=CH\cdot(CH_2)_2\cdot CH=$ group.

3. Ozonolysis of Methyl Hiragonate. Methyl hiragonate (5 g.) was dissolved in chloroform (50 c.c.), and on cooling with ice-salt, a current of ozonised oxygen was passed through the solution until it became saturated. On distilling off the solvent under reduced pressure, the ozonide remained as a light yellow sirup. Twenty g. of methyl hiragonate yielded 32.2 g. of ozonide (161.0%). The yield calculated for normal ozonide $C_{17}H_{28}O_{11}$ and ozonide peroxide $C_{17}H_{28}O_{12}$ are 154.5 and 160.6%, respectively. The ozonide obtained here is probably ozonide peroxide. Water (200 c.c.) was added to the ozonide, and the liquid was heated in a flask on the water-bath for 30 minutes, a gentle current of hydrogen being passed into the flask. In order to recover the volatile decomposition products (**A**) which were carried over with hydrogen, the flask was attached by a delivery tube to other three flasks which were connected in succession, the first (**a**) being filled with 200 c.c. of water and cooled with ice, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The liquid remained in the initial flask consisted of aqueous solution and reddish orange oil ($\mathbf{B_1}$) which separated on the bottom of the flask. These were separated, and the clear aqueous solution was extracted with 2 l. of ether. After distilling off ether from the ethereal solution, 50 c.c. of water was added to the residue, of which a portion remained undissolved as an orange yellow oil ($\mathbf{B_2}$), and was separated from the aqueous solution (**C**). By these treatments, the decomposition products of ozonide were separated into (i) volatile substance (**A**), (ii) oily substance ($\mathbf{B_1}$ and $\mathbf{B_2}$) and (iii) the portion dissolved in water (**C**).

(i) *Volatile substance* (**A**). The aqueous solution of volatile substance collected in the flask (**a**) produced a pink colouration with Schiff's reagent, and a deep blue colouration with diethylamine and sodium nitroprusside, indicating that acetaldehyde is present in the aqueous solution. On adding *p*-nitrophenylhydrazine in hydrochloric acid, *p*-nitrophenylhydrazone of acetaldehyde separated, which crystallised from 50% alcohol in yellow needles; m.p. 126.5–127°, which was not lowered when admixed with a pure specimen, m.p. 127.5–128° (Found: N, 23.23. Calc. for $C_8H_9O_2N_3$: N, 23.46%). The aqueous solution showed also acid reaction, and gave a deep red colouration on adding ferric chloride after neutralisation. The barium salt, obtained from the solution by neutralisation with barium hydroxide, was found to be barium acetate (Found: Ba, 53.50. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%).

The barium hydroxide solution in the flask (**b**) was found to contain a small quantity of precipitate of barium carbonate (0.1528 g.), which indicated the formation of carbon dioxide by the decomposition of ozonide. But the yield of carbon dioxide calculated from the quantity of precipitated barium carbonate is only 0.17% of the methyl hiragonate used for ozonolysis. If a highly unsaturated acid having the $=CH\cdot CH_2\cdot CH=$ group is subjected to ozonolysis, carbon dioxide is formed by secondary decomposition of the oxidation products derived from that group thus: $HOOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COOH + CO_2$ and $HOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COH + CO_2$. It is, however, found from the results of our experiments which will be reported later that the secondary decomposition takes place to a considerable extent, though not to a quantitative extent, and it never gives such a small yield of carbon dioxide. Consequently, the formation of carbon dioxide in such a minute amount as in the case of above experiment gives an indication of the absence of the $=CH\cdot CH_2\cdot CH=$ group in methyl hiragonate; it is probably due either to the contamination of highly unsaturated acids having the $=CH\cdot CH_2\cdot CH=$ group or to an abnormal decomposition of a small portion of the ozonide of methyl hiragonate.

(ii) *Oily substance* (B_1 and B_2). Yield 10.9 g. It was separated into neutral and acidic portions by adding sodium hydroxide solution and extracting the resulting soap solution with ether. The neutral portion (2.4 g.) obtained from the ethereal solution had saponif. value 379.0 (calc. for semi-aldehyde of methyl hydrogen adipate $C_7H_{12}O_3$: 389.4). This was saponified and then oxidised with potassium permanganate in alkaline solution. The crystalline products obtained on acidification yielded pure adipic acid after recrystallising from ethyl acetate; neutr. value 766.8 (calc. for $C_6H_{10}O_4$: 768.2), m.p. and mixed m.p. 152–153°.

The acidic portion (8.5 g.) which was obtained from the soap solution on acidification and was collected by using ether, had neutr. value 340.0 and saponif. value 690.2 which are close to the corresponding values for methyl hydrogen adipate (neutr. value 350.5 and saponif. value 700.9). Adipic acid liberated from the ester in the usual way showed neutr. value 767.0 and m.p. 152–153° after recrystallising from ethyl acetate (Found: C, 49.16; H, 6.91. Calc. for $C_6H_{10}O_4$: C, 49.29; H, 6.90%).

(iii) *The portion dissolved in water* (C). Sodium carbonate solution was added to the aqueous solution of this portion, and the resulting soap solution was shaken with 2 l. of ether and allowed to separate into two layers. After removal of the ether from the ethereal solution, there remained 1.2 g. of neutral substance (C_1). The soap solution was decomposed with hydrochloric acid, extracted with 2 l. of ether, and on distilling off the ether from ethereal extract, 17 g. of acidic substance (C_2) was obtained.

The neutral substance (C_1) showed aldehyde reaction. It was subjected to a further oxidation with alkaline permanganate solution, and the product, which after acidification was collected by using ether, was treated with a little water in which a portion remained undissolved. The insoluble portion had neutr. value 342.6 and saponif. value 691.2 (calc. for methyl hydrogen adipate: neutr. value 350.5 and saponif. value 700.9), and the free acid obtained on acidification of the saponified product melted at 149–150° and was considered to be an impure adipic acid. The aqueous extract on evaporation left behind a crystalline solid which melted at 175°, and it was likely to be an impure succinic acid. From these experiments, it is seen that the neutral substance (C_1) contains semi-aldehyde of methyl hydrogen adipate and succinic aldehyde (or its polymerised products).

The acidic substance (C_2) was extracted three times with petroleum ether, using 150 c.c. for each extraction. The united petroleum ether solution was heated on the water-bath to remove petroleum ether. The distilled petroleum ether showed an acid reaction and had an odour of acetic acid. The barium salt, obtained on neutralising the petroleum ether with barium hydroxide, was found to consist of barium acetate (Found: Ba, 53.60. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). After distilling off petroleum ether, the residue (2 g.) was heated in an oil-bath, and a small quantity of distillate was obtained before the temperature of oil-bath reached 150°. Beyond 150°, practically nothing distilled over, and when the temperature of bath reached about 200°, the distillation was stopped since there were the indications of decomposition. The silver salt, prepared from the distillate by neutralising with sodium hydroxide and adding silver nitrate, was found to consist of silver acetate (Found: Ag, 64.50. Calc. for $C_2H_3O_2Ag$: Ag, 64.64%). The final residue from distillation was oxidised with alkaline permanganate solution, and the product obtained after acidification was found to be an impure succinic acid, m.p. 177–177.5°.

The petroleum ether insoluble portion (14.5 g.) consisted of a mixture of crystalline solid and liquid. It was oxidised with alkaline permanganate solution, and the product obtained after acidification was recrystallised from ethyl acetate to yield succinic acid; neutr. value 948·7, m.p. 182.5–183° (Found: C, 40·61; H, 5·10. Calc. for $C_4H_6O_4$: C, 40.66; H, 5.12%). Twenty g. of methyl hiragonate gave 14.5 g. or 72.5% yield of petroleum ether insoluble portion. Since it is considered that the petroleum ether insoluble portion consists almost entirely of succinic acid and its semi-aldehyde, methyl hiragonate should have two $=CH\cdot(CH_2)_2\cdot CH=$ group. (The maximum yield of succinic acid will be 44.68% if it has only one of such group.)

Summary.

Methyl hiragonate has been prepared from Japanese sardine oil, and it was subjected to the oxidation by the permanganate method and by the ozonide method. Among the oxidation products obtained by the permanganate method, succinic acid, acetic acid and methyl hydrogen adipate were identified. The products obtained by the ozonide method contained, besides the above-mentioned three acidic compounds, acetaldehyde and semi-aldehyde of methyl hydrogen adipate, and also the presence of semi-aldehyde of succinic acid and succinic aldehyde (or its polymerised products) was indicated. Accordingly, the constitution of hiragonic acid is $\Delta^{6:7,\ 10:11,\ 14:15}$-hexadecatrienoic acid as expressed by the following formula:

$$CH_3\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_4\cdot COOH$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

HETEROGENEOUS CHEMICAL REACTIONS IN THE SILENT ELECTRIC DISCHARGE. XIII.* REACTIONS BETWEEN HYDROGEN AND SOLID INORGANIC COMPOUNDS.

By Susumu MIYAMOTO.

Received February 27th, 1935. Published May 28th, 1935.

Investigations on the reduction of a number of solid inorganic substances by hydrogen under the silent electric discharge were carried out;

* Heterogeneous chemical reactions in the silent electric discharge. XII; *Kolloid-Z.*, **69** (1934), 179.

there follows an account of the results obtained since the publication of the previous papers.[1] The apparatus and the method of investigation are essentially the same as those mentioned in the previous papers.[1]

(1) **Selenious acid.** The quantity of selenious acid, H_2SeO_3, employed = 2 g. Time of silent electric discharge = 2 hours. The white powder became yellowish red soon after the electric current was passed, and the wall of the discharge tube was gradually covered with a thin yellow film of metallic selenium.

The reaction product was dissolved in water; red metallic selenium remained. The formation of a thin metallic film on the wall of the discharge tube suggests that hydrogen selenide is produced first, and the reactions in the discharge tube seem to be expressed by the following equations:

$$H_2SeO_3 + 3H_2 = SeH_2 + 3H_2O,$$
$$SeH_2 = Se + H_2.$$

(2) **Selenic acid.** Selenic acid, H_2SeO_4, employed = 2 g. Time of silent electric discharge = 2 hours. As selenic acid is an extremely hygroscopic compound, it had absorbed a small quantity of water, which was not determined. The white powder became red, showing the liberation of metallic selenium. The reduction products were shaken with water, and filtered. Red powder of metallic selenium remained. The presence of selenious acid in the filtrate was proved in the normal manner.[2]

The reaction products are selenious acid and metallic selenium, and the reactions in the discharge tube are expressed by the following equations:

$$H_2SeO_4(\text{solid}) + H_2 = H_2SeO_3 + H_2O,$$
$$H_2SeO_3 + 2H_2 = Se + 3H_2O.$$

(3) **Sodium selenate.** Sodium selenate, $Na_2SeO_4 \cdot 10H_2O$, employed = 3 g. Time of silent electric discharge = 3 hours. The powder became red, showing the liberation of metallic selenium. Water was added to the discharge tube, well shaken and filtered. Red metallic selenium remained. The presence of selenite in the filtrate was proved quite the same way as in the case of selenic acid.

---

(1) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 724, 788, 914, 933; **54** (1933), 85, 202, 705, 1223; **55** (1934), 320.

(2) Treadwell-Hall, "Analytical Chemistry", 8th Edition, Vol. I, p. 541.

The principal reaction products are selenite and metallic selenium, and the reactions in the discharge tube are expressed by the following equations:

$$Na_2SeO_4(solid) + H_2 = Na_2SeO_3 + H_2O,$$
$$Na_2SeO_3 + 2H_2 = Se + 2NaOH + H_2O.$$

(4) **Tellurous acid.** Tellurous acid, H_2TeO_3, employed = 2 g. Time of silent electric discharge = 2 hours. Not only the white powder became black, but the wall of the discharge tube was also covered with a thin film of metallic tellurium, forming a beautiful mirror.

The formation of tellurium mirror suggests that hydrogen telluride is first produced, and the reactions in the discharge tube are expressed by

$$H_2TeO_3(solid) + 3H_2 = TeH_2 + 3H_2O,$$
$$TeH_2 = Te + H_2.$$

It is an interesting fact that when selenious or tellurous acid is reduced under the silent electric discharge, metallic hydride is first produced, quite in the same way as in the case of the reduction of arsenic[3] or antimony compounds.[4]

(5) **Sodium tellurite.** Sodium tellurite, Na_2TeO_3, employed = 2 g. Time of silent electric discharge = 4 hours. White powder became black soon after the electric current was passed, showing the liberation of metallic tellurium. In this case no appreciable amount of metallic tellurium was deposited on the wall of the discharge tube. The reaction in the discharge tube is expressed by

$$Na_2TeO_3(solid) + 2H_2 = Te + 2NaOH + H_2O.$$

(6) **Telluric acid.** Telluric acid, $H_2TeO_42H_2O$, employed = 3 g. Time of silent electric discharge = 4 hours. White powder became black soon after the electric current was passed, and the wall of the discharge tube was gradually covered with a thin film of metallic tellurium.

Alkaline solution was added to the discharge tube, well shaken, and filtered. Metallic tellurium remained. The filtrate contained tellurite.[5] The principal reaction products are tellurous acid and metallic tellurium, and the reactions in the discharge tube seem to be expressed by

---

(3) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 734, 735.
(4) *Ibid.*, **53** (1932), 789, 790, 791.
(5) Treadwell-Hall, "Analytical Chemistry", 8th Edition, Vol. I., p. 545.

$$H_2TeO_4(\text{solid}) + H_2 = H_2TeO_3 + H_2O,$$
$$H_2TeO_3 + 3H_2 = TeH_2 + 3H_2O,$$
$$TeH_2 = Te + H_2.$$

(7) **Potassium thiosulphate.** Exp. 1. The production of potassium sulphate, hydrogen sulphide, and sulphur was proved quite in the same way as in the case of sodium thiosulphate.[6]

Exp. 2. The quantity of hydrogen sulphide produced was determined. The quantity of potassium thiosulphate employed = 7.0 g. Time of silent electric discharge = 7 hours. Volume of sodium thiosulphate solution of 0.01000 normal, equivalent to the quantity of hydrogen sulphide produced = 3.82 c.c.

It seems that the principal reactions in the discharge tube are expressed by the following equations:

$$K_2S_2O_3 + H_2 = K_2SO_3 + H_2S,$$
$$4K_2S_2O_3 = 3K_2SO_4 + K_2S_5,$$
$$K_2S_5 = K_2S + 4S,$$
$$K_2S + 2H_2O = 2KOH + H_2S,$$
$$S + H_2 = H_2S.$$[7]

(8) **Silver carbonate.** Silver carbonate, Ag_2CO_3, employed = 2 g. Time of silent electric discharge=4 hours. On leaving the discharge tube the gas was passed through an absorption bottle, containing barium hydroxide solution.

Soon after the electric current was passed, the powder in the discharge tube became black, and in the absorption bottle white precipitate was produced, showing the production of metallic silver and carbon dioxide. The reaction products in the discharge tube were shaken with hot dilute sulphuric acid to dissolve silver carbonate remained and silver oxide produced. A small quantity of white powder remained. On rubbing the powder with a glass rod, it manifested metallic lustre, showing that it is metallic silver.

The principal reactions in the discharge tube are expressed by

$$Ag_2CO_3(\text{solid}) = Ag_2O + CO_2,$$
$$Ag_2O + H_2 = 2Ag + H_2O.$$[8]

---

(6) S. Miyamoto, *J. Chem. Soc. Japan*, **55** (1934), 1145.
(7) *Ibid.*, **53**
(8) *Ibid.*, **53** (1932), 796.

According to Losanitsch,[9] the following reaction is also possible in the present case.

$$CO_2 + H_2 = HCOOH.$$

(9) **Lithium chlorate.** Exp. 1. The formation of lithium chloride was proved quite in the same way as in the case of potassium chlorate.[10]

Exp. 2. The quantity of lithium chloride produced was determined by Volhard's method.[11] Lithium chlorate, $LiClO_3 \cdot \frac{1}{2} H_2O$, employed = 7.0 g. Time of silent electric discharge = 6 hours. Volume of silver nitrate solution of 0.01000 normal, equivalent to the quantity of lithium chloride produced = 26.10 c.c.

The reaction in the discharge tube is expressed by

$$LiClO_3(solid) + 3H_2 = LiCl + 3H_2O.$$

(10) **Sodium bromate.** Exp. 1. Sodium bromate, $NaBrO_3$, employed =4 g. Time of silent electric discharge = 6 hours. No appreciable change was observed in the appearance of the powder.

The reaction product was dissolved in water and the solution was acidified with dilute sulphuric acid. The solution became yellow and it decolourizes methylorange, showing the liberation of free bromine:

$$HBrO_3 + 5HBr = 3Br_2 + 3H_2O.$$

It proves the formation of potassium bromide in the the discharge tube.

Exp. 2. The quantity of sodium bromide produced was calculated by the determination of the quantity of sodium bromate remained. Sodium bromate employed = 6.1851 g. Time of silent electric discharge = 5 hours. Volume of arsenious acid solution of 0.1000 normal, equivalent to the quantity of sodium bromide produced = 58.5 c.c.

The reaction in the discharge tube is expressed by

$$NaBrO_3(solid) + 3H_2 = NaBr + 3H_2O.$$

Summary.

The chemical reactions under the silent electric discharge were studied when hydrogen reacts with the following inorganic solid substances.

(9) *Ber.*, **30** (1897), 135.
(10) S. Miyamoto, *J. Chem. Soc. Japan*, **53** (1932), 731.
(11) Treadwell-Hall, "Analytical Chemistry", 7th Edition, Vol. II, p. 603.

	Reacting substance	Reaction products
(1)	Selenious acid	Selenium
(2)	Selenic acid	Selenium and selenious acid
(3)	Sodium selenate	Selenium and sodium selenite
(4)	Tellurous acid	Tellurium
(5)	Sodium tellurite	Tellurium and sodium hydroxide
(6)	Telluric acid	Tellurium and tellurous acid
(7)	Potassium thiosulphate	Potassium sulphite, hydrogen sulphide, and sulphur
(8)	Silver carbonate	Silver and carbon dioxide
(9)	Lithium chlorate	Lithium chloride
(10)	Sodium bromate	Sodium bromide

The author acknowledges with thanks the receipt of a grant from the Japanese Imperial Academy.

Laboratory of Physical Chemistry,
Hiroshima University.

DIE KONZENTRATION DER SCHWEREN ISOTOPE IN KOHLENHYDRATEN.

(Vorläufige Mitteilung.)

Von **Toshizo TITANI** und **Masao HARADA.**

Eingegangen am 15. April, 1935. Ausgegeben am 28. Mai, 1935.

Früher[1] haben wir gefunden, dass das Wasser aus der Rohrzuckermelasse um 2.8 γ schwerer als gewöhnliches Wasser ist. Dies hat uns veranlasst das aus dem Zucker selbst durch Verbrennung erhaltene Wasser zu untersuchen. Es wurde dabei gefunden, dass das Wasser aus dem gereinigten Rohrzucker um 7.4 γ und das aus dem Rübenzucker um 6.5 γ schwerer als das Osaka-Leitungswasser waren. Weil dies nun die Vermutung nahe legte, dass eine Anreicherung von schweren Isotopen in allen Kohlenhydraten allgemein vorhanden ist, untersuchten wir möglichst viele Sorten von Substanzen, die Kohlenhydrate als Hauptbestandteil enthalten, nach ihren Gehalt an schweren Isotopen. Die Substanzen wurden direkt im Luftstrom verbrannt, das dabei erhaltene Wasser wurde sorgfältig gereinigt und sein spezifisches Gewicht bei 8°C. mit dem ebenso gereinigten Osaka-Leitungswasser verglichen. Wir fanden dabei, wie erwartet, dass das Probewasser aus den Substanzen, die Glukose, Laktose, Stärke, Dextrin, Galaktan, Mannan und Zellulose als Hauptbestandteil enthalten, durchschnittlich um 6 γ schwerer als das Normalwasser waren. Die Einzelheiten sollen später in diesem Bulletin berichtet werden.

Kaiserliche Universität zu Osaka
und
Schiomi-Institut für Physikalische
und Chemische Forschungen.

---

(1) Vgl. T. Titani und M. Harada, dies Bulletin, **10** (1935), 31.

ISOTOPENZUSAMMENSETZUNG DES REGEN- UND SCHNEEWASSERS.

(Vorläufige Mitteilung.)

Von Masao HARADA und Toshizo TITANI.

Eingegangen am 15. April, 1935. Ausgegeben am 28. Mai, 1935.

Während des Versuchs über den Deuterium-Gehalt von Wasserproben in verschiedenen natürlichen Vorkommen, fanden wir kleine, aber untrügliche Schwankungen in der Dichte des Regenwassers. Nach einigen Versuchen überzeugten wir uns, dass das Regenwasser, am Anfang eines Regenfalls immer schwerer als gewöhnliches Bodenwasser ist und gegen Ende allmählich leichter wird. Wir sammelten z.B. bei einem Regenfall das Wasser separat in drei Mengen. Die Anfangsmenge, deren Volumen 340 c.c. betrug, erwies sich um 1.6 γ schwerer als das Normalwasser. Dagegen fanden wir, dass die mittlere Menge, deren Volumen 1180 c.c. betrug, um 1.3 γ leichter und die letzte Menge von 30 c.c. um 1.9 γ leichter als das Normalwasser waren. Diese Ergebnisse kann man vielleicht entweder durch die fraktionierte Kondensation oder durch Verdampfung erklären.

Das Schneewasser, das wir dann untersuchten, erwies sich ausnahmslos leichter als das Normalwasser. Der grösste Unterschied, den wir bisher gefunden haben, betrug sogar 3.3 γ und der kleinste 0.5 γ, durchschnittlich etwa 2 γ. Die Erklärung für diese Ergebnisse kann man vielleicht darin finden, dass die Feuchtigkeit in der Atmosphäre sich unter den Wirkung der Gravitationskraft befindet. Die Einzelheiten sollen später in diesem Bulletin berichtet werden.

Kaiserliche Universität zu Osaka
und
Schiomi-Institut für Physikalische
und Chemische Forschungen.

ON THE ABSORPTION OF HYDROGEN CHLORIDE INTO VARIOUS ORGANIC LIQUIDS AND CALCULATION OF THE HEAT OF ABSORPTION. II.

By Senzo HAMAI.

Received March 4th, 1935. Published June 28th, 1935.

In a previous paper,[1] we published the results of the absorption of hydrogen chloride into various organic liquids such as 1,1,2,2-tetrachlorethane, ethylene chloride, carbon tetrachloride, and ethylene bromide, and also presented the purpose of this investigation along with necessary discussions in connection with it in detail. The present paper is a further report of similar measurements of the absorption of hydrogen chloride into several other organic liquids of the same series as the previous ones.

Experimental Procedure. The method of measuring the absorption of hydrogen chloride into these liquids is exactly the same as before and the apparatus remains essentially the same as that described previously except that the water-jacketed gas burette has been used with constant temperature water flowing in the jacket, and the measurements of the absorption have been carried out at 20°, 15°, and 12°C. and at various pressures.

Materials. Hydrogen chloride was prepared similarly as described in the previous report by dropping concentrated hydrochloric acid into pure concentrated sulphuric acid, passing the generated gas through two sulphuric acid bubblers, and condensing it twice by liquid nitrogen. Only the middle portion of it was used, after passed finally through a calcium chloride tube before it was allowed to fill the burette and reservoir.

1,1,2-Trichlorethane, b. p. 112.5°–113°C.[2] Eastman's product was distilled twice and once under reduced pressure.

Pentachlorethane, b.p. 158.5°–159.5°C.[2] Eastman's product was distilled twice and the constant boiling part was again distilled under reduced pressure.

---

(1) S. Hamai, this Bulletin, **10** (1935). 5.

(2) The boiling points of both liquids are somewhat lower than those given in the literature but they are distilled at essentially constant temperature.

Results. The results of the absorption measurements with these organic liquids—the volume of hydrogen chloride absorbed per 20 c.c. of each liquid is reduced to the corresponding volume at 25°C.—are tabulated in Tables 1 and 2 with their corresponding molal fractions and mole percent.

The treatment of these results is exactly similar to that already published, namely the volume of hydrogen chloride absorbed is plotted against respective pressure at which the system finally reached an equilibrium, as shown, for an example, in Fig. 1 for 1,1,2-trichlorethane. The volume of hydrogen chloride to be absorbed at one atmosphere is obtained by extrapolation and this is converted into mole fraction and then the solubility of hydrogen chloride in respective liquids, i.e. N_{HCl} when P_{HCl} equals 760 mm., is obtained by assuming Henry's law is obeyed. In calculating the mole fractions for both liquids, the densities of the liquids at 20°, 15°, and 12°C. are obtained by interpolating those data given in Beilstein's Handbook. Table 3 shows N (20°, 15°, and 12°C.), $\log N$, and $(1/T) \times 10^{-3}$ and these are plotted in Fig. 2 and 3. ΔH for the heat of absorption can be calculated from

$$d \log N/d(1/T) = -\Delta H/(2.303 \times R).$$

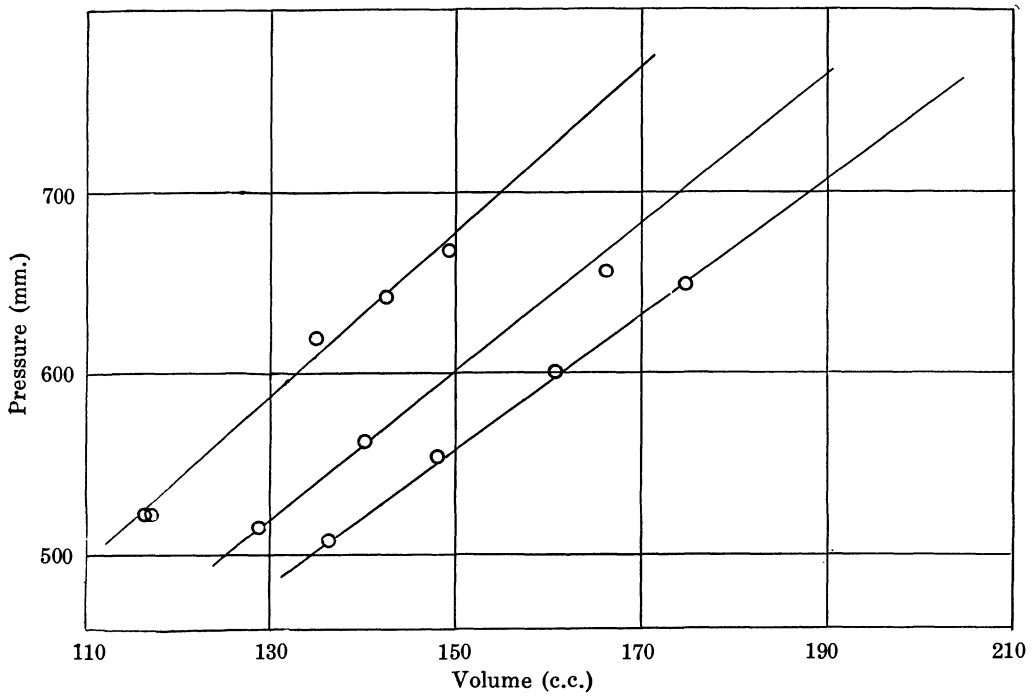
The values of ΔH thus found are also listed in Table 3.

Table 1. Absorption of Hydrogen chloride per 20 c.c. of 1,1,2,-Trichlorethane at 20°, 15°, and 12°C.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mole fraction N	Mole per cent.
		20°C.		
1	620.0	134.33	0.02489	2.49
2	523.5	116.81	0.02171	2.17
3	667.0	149.57	0.02781	2.78
4	640.5	142.33	0.02633	2.63
5	620.0	134.24	0.02488	2.49
6	523.5	116.48	0.02166	2.17
		15°C.		
7	562.0	140.33	0.02588	2.59
8	516.0	128.70	0.02378	2.38
9	655.0	166.50	0.03056	3.06
		12°C.		
10	556.5	147.23	0.02705	2.71
11	649.0	174.77	0.03195	3.195
12	508.5	136.59	0.02514	2.51
13	601.5	160.11	0.02935	2.94

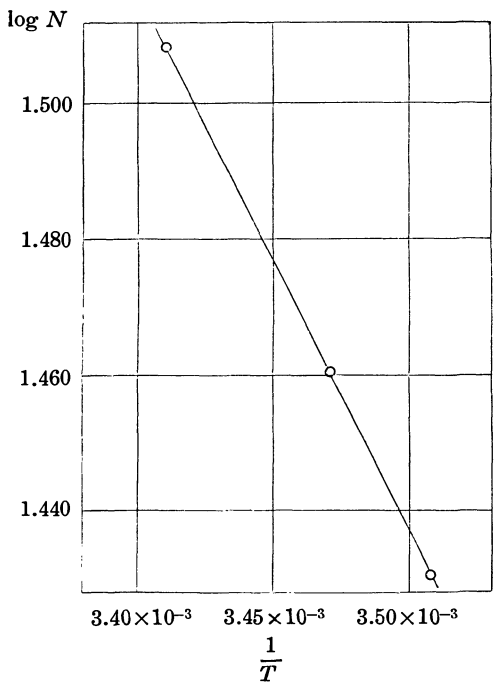
Table 2. Absorption of Hydrogen Chloride per 20 c.c. of Pentachlorethane at 20°, 15°, and 12°C.

Exp. No.	Pressure P mm.	Vol. of absorbed HCl reduced to $V_{25°}$ c.c.	Mole fraction N	Mole per cent.
		20°C.		
1	718.0	87.44	0.02125	2.13
2	565.5	68.25	0.01666	1.67
3	614.0	75.43	0.01838	1.84
4	666.0	79.58	0.01937	1.94
5	339.5	40.33	0.009946	0.995
		15°C.		
6	661.5	86.60	0.02096	2.10
7	611.5	79.76	0.01934	1.93
8	562.0	73.74	0.01790	1.79
9	661.5	86.60	0.02096	2.10
		12°C.		
10	712.5	98.90	0.02381	2.38
11	611.5	83.50	0.02018	2.02
12	560.5	76.86	0.01865	1.87
13	657.5	91.20	0.02199	2.20



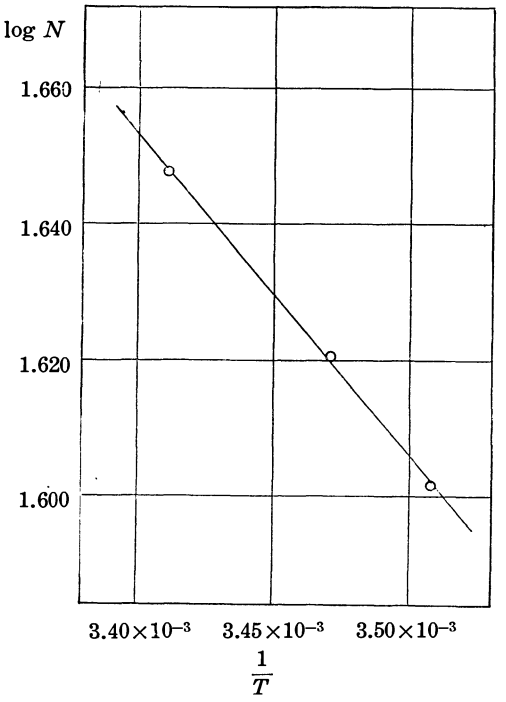
Volume of Hydrogen Chloride Absorbed per 20 c.c. of 1,1,2,-Trichlorethane at 20°, 15°, and 12°C, and at Various Pressures.

Fig. 1.



Variation of the Absorption of Hydrogen Chloride into 1,1,2-Trichlorethane with Respect to Temperature.

Fig. 2.



Variation of the Absorption of Hydrogen Chloride into Pentachlorethane with Respect to Temperature.

Fig. 3.

Table 3.

Substance	N(HCl)	log N	$(1/T)\times10^{-3}$
20°C.			
1,1,2-Trichlorethane	0.03101	1.5085	3.411×10^{-3}
Pentachlorethane	0.02250	1.6478	,,
15°C.			
1,1,2-Trichlorethane	0.03463	1.46055	3.471×10^{-3}
Pentachlorethane	0.02396	1.6205	,,
12°C.			
1,1,2-Trichlorethane	0.03715	1.43004	3.508×10^{-3}
Pentachlorethane	0.02502	1.6017	,,

The Heat of Absorption ΔH/mole in cal.

	ΔH
1,1,2-Trichlorethane	3600 cal./mole
Pentachlorethane	2200 ,,

Table 5.

Bond	Bond energy	Substance	Total bond energy
C-Cl	3.22*v.e.	$C_2H_4Cl_2$	27.40 v.e.
C-Br	2.89*	$C_2H_4Br_2$	26.74 ,,
C-H	4.34	$C_2H_3Cl_3$	26.28 ,,
C-C	3.60	$C_2H_2Cl_4$	25.16 ,,
		C_2HCl_5	24.04 ,,
		CCl_4	12.88 ,,

Total Bond Energy

$C_2H_4Cl_2>C_2H_4Br_2>C_2H_3Cl_3>C_2H_2Cl_4>C_2HCl_5>CCl_4$

Solubility (N 20°C.)

$C_2H_4Cl_2>C_2H_4Br_2>C_2H_3Cl_3>C_2H_2Cl_4>C_2HCl_5>CCl_4$

* Average values of the various authors are used (A. Sherman and C. E. Sun, *J. Am. Chem. Soc.*, **56** (1934), 1096).

Table 4.

Substance	N(20°C.)	D.C.(20°)	$\mu\times10^{18}$	Mol. volume	Eötvös K	$T\frac{\alpha}{\beta}$	$E/V^{\frac{1}{3}}$
$ClCH_2\cdot CH_2Cl$	0.03993	10.8	1.8	78.90	2.15	4158	17.0
$BrCH_2\cdot CH_2Br$	0.03441	6.3	1.4	86.20	2.19	4455 4760	17.2
$Cl_2CH\cdot CH_2Cl$	0.03101	—	1.15*	92.31	2.21	—	—
$Cl_2CH\cdot CHCl_2$	0.02744	8.2	1.6	105.30	2.26	3362 3690	15.58
C_2HCl_5	0.02250	—	1.0*	120.59	2.32	—	—
CCl_4	0.01550	2.24	0.0	97.10	2.20	—	14.3

	Total bond energy	$(n-1)L/V$	$\frac{5200+30t_b}{V}$	Van Laar's a	$\gamma/V^{\frac{1}{3}}$	Sutherland	Mathews
$ClCH_2\cdot CH_2Cl$	27.40 v.e.	406	97.45	475	7.5	—	—
$BrCH_2\cdot CH_2Br$	26.74 ,,	422	105.23	549	8.7	710	3900
$Cl_2CH\cdot CH_2Cl$	26.28 ,,	—	93.05	335	—	—	—
$Cl_2CH\cdot CHCl_2$	25.16 ,,	368	90.72	555	7.71	—	—
C_2HCl_5	24.04 ,,	—	82.8	503	—	—	—
CCl_4	12.88 ,,	308	77.06	496	5.78	490	2660

* Van Arkel and Snock (unpublished) (C. P. Smyth, " Dielectric Constant and Molecular Structure ").

Discussion of Results. As we expected, the absorption of hydrogen chloride into 1,1,2-trichlorethane is much greater than into pentachlorethane as obvious from the tables; furthermore, by comparison with the data already published,[1] we find that the order of the solubilities in these various substances are not quite concordant with the order expected either from internal pressures as measured by various different methods or from polarities as indicated by several different ways, e.g. dielectric constant, electric moment, etc., as shown in Table 4, where the various quantities listed have significances as explained in our previous report. Also as already pointed out, we can hardly find any regularity with respect to molal volumes as well as Eötvös's K but they are well in the order of the total bond energies, as illustrated in Table 5.

Thus the solubilities of hydrogen chloride in these various halogen derivatives of the aliphatic hydrocarbon are not well accounted for either in the light of various criteria which are already considered elsewhere but they are well taken into account in the term of bond energies which have been more fully discussed in our previous paper.[1]

Summary.

(1) The absorption of hydrogen chloride into 1,1,2-trichlorethane and pentachlorethane at 20°, 15° and 12°C. has been measured.

(2) The heat of absorption of hydrogen chloride into these organic substances has been calculated.

(3) The order of the solubilities of hydrogen chloride into these liquids including those mentioned in our previous paper, is found to be well fitted in a scheme already described, namely they are in the order of the total bond energies of these substances.

In conclusion, the author wishes to express the best thanks to Prof. S. Mitsukuri for his kind advices and criticisms in the course of this investigation also hearty appreciation to generosity that a part of the expenses of this research has been covered by the grant given to Prof. S. Mitsukuri by the Saito Gratitude Foundation.

Laboratory of Theoretical Chemistry, Faculty of Science.
Tohoku Imperial University, Sendai, Japan.

Correction to the previous paper (this volume, p. 5):

Read Ethyl bromide *for* Ethylene bromide *in Table 7 on page 13 and in line 2 on page 14.*

ON THE FATTY ACIDS OF JAPAN WAX.

By Mitsumaru TSUJIMOTO.

Received March 13th, 1935. Published June 28th, 1935.

The chemical composition of Japan wax (fruit-coat fat from the berries of "Hazé", *Rhus succedanea* L.) was chiefly investigated by foreign chemists and the specimens used by them were the bleached white wax. As the results of these researches Japan wax has been ascertained to consist mainly of tripalmitin and free palmitic acid. Besides them, of saturated acids small amounts of dibasic acids and of soluble acids (isobutyric?) were found. In some old books on fats and oils, stearic and arachidic acids were mentioned to occur in Japan wax. However, they could not be detected by A. C. Geitel and G. van der Want.(1) In the modern books, these acids, especially the latter, are usually omitted. Of unsaturated acids a small amount of oleic acid was stated to occur. Later Tassily(2) isolated pelargonic acid and an acid of the suggested formula $C_{15}H_{30}O_2$. Traces of stearic and oleic acids were also detected.

It is no wonder that oleic acid in Japan wax was rather neglected by foreign investigators, inasmuch as it is markedly changed or oxidised by the severe treatment of insolation on bleaching the wax. Also the presence of volatile or soluble acids is due to sun-bleaching process.

More than twenty years ago, the author(3) suggested the following composition of Japan wax fatty acids: palmitic acid 84%, oleic acid 14%, japanic acid(?) 2%. Nowadays the above amount of the dibasic acids has been found to be too small.(4)

The present experiments were made to reconfirm the components of the fatty acids (the dibasic acids being excepted) of genuine Japan wax. As the results the occurrence of stearic and arachidic acids has been ascertained, thus confirming the correctness of the description of the old books.

Experimental Part.

(1) **General Properties of the Specimen of Japan Wax.** The specimen used in this investigation was a raw or fresh wax, especially prepared from the berries

(1) *J. prakt. Chem.*, **61** (1900), 151.
(2) J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," Vol. II (5th Edition), 654.
(3) *J. Soc. Chem. Ind. Japan*, **14** (1911), 321.
(4) Concerning the dibasic acids see M. Tsujimoto, this Bulletin, **6** (1931), 325.

("Komi"[5] or old berries) of *Rhus succedaneae* L. from the Prefecture of Kumamoto by the Higo Seirô Kaisha (Higo Wax Manufacturing Company), which contained no kernel oil.[6]

It was a brownish-yellow solid, which, though coherent and tenacious, was rather brittle. The characteristics, etc., were as follows:[7] Melt. pt. 53–53.5°C., d_4^{99} 0.8608, acid value 15.9, saponification value 208.1, iodine value 13.4, Reichert-Meissl value 0.38, unsaponifiable matter 0.77%.

As the specimen was free from the kernel oil, its iodine value was lower than those of commercial samples (iodine value, sometimes up to 20). The Reichert-Meissl value was very small indicating a negligible amount of volatile water-soluble acids.

The unsaponifiable matter was a brownish-yellow fine crystalline mass and produced a large amount of precipitate with digitonin in alcoholic solution.

The fatty acids formed a brownish-yellow crystalline mass of the following properties: Melt. pt. 63°C. (mainly liquefied at 61–62°C.), neutralisation value 215.3, iodine value 12.7, dibasic acids 6.3%.

The fatty acids were dissolved in acetone and on cooling the deposited solid acids were separated. By concentrating the filtrate, the crystallisation was repeated several times. The liquid acids were separated from the acids of the final filtrate by means of the lead-salt-ether method. They were of a brownish-yellow colour and had neutralisation value 193.1, iodine value 87.1, and n_D^{20} 1.4620. These figures nearly corresponded to those of oleic acid. On bromination in petroleum ether solution, they gave a small amount (ca. 1.7%) of a white precipitate; in ether solution, a little turbidity was observed, but nearly no precipitate. It appeared, therefore, that there occurred in the liquid acids a small proportion of linolic acid, but linolenic acid was almost absent in them.

(2) **Identification of the Component Fatty Acids.** The mixed fatty acids (unsaponifiable matter not removed) from the specimen of Japan wax were changed into methyl esters by boiling with half the weight of methanol containing 3% of H_2SO_4 upon a water bath for three hours. The ester mixture thus obtained was a brownish-yellow liquid in summer; it had still acid value 2.34, but was used without further treatment.

The methyl esters (1000 g.) were distilled (in batches of 250 g.) under 15 mm. pressure into the following fractions:

Fract.	Dist. temp.	Yield		Saponif. value	Iodine value	n_D^{20}
		(g.)	(%)			
I	Up to 200°	555.3	55.5	2.5.9	7.4	1.4389
II	200–205°	221.1	22.1	202.8	13.0	1.4395
III	205–210°	77.6	7.8	201.6	20.5	1.4410
IV	210–219°	60.2	6.0	198.7	32.1	1.4430

Distillates (total) 914.3 g. (91.4%). Residue 85.2 g. (8.5%)

(5) This Bulletin, **6** (1931), 326, foot-note.

(6) According to the author's experiments, the kernels of the berries of *Rhus succedanea* contained 4–9% of the oil. The oil had the following properties: d_4^{15} 0.9254–0.9289, acid value 2.16–4.32, saponification value 189.6–193.6, iodine value 125.2–133.2.

(7) All the iodine values were determined by Wijs method.

The residue consisted mainly of the methyl esters of the dibasic acids and the unsaponifiable matter.

The fractions were re-distilled under 15 mm. pressure. The results corresponding to 950 g. of the original esters were as follows:[8]

Fract.	Dist. temp.	Yield		Appearance (at 20°C.)	Saponif. value	Iodine value	n_D^{20}
		(g.)	(%)				
1	Up to 190°	0.7	0.07	White crystals	204.3	—	1.4375
2	190–200°	632.7	66.6	,,	205.0	6.2	1.4380
3	200–205°	120.6	12.7	White crystals and a little liquid	200.6	19.0	1.4400
4	205–210°	56.0	5.9	Nearly colourless liquid	198.6	26.7	1.4415
5	210–215°	23.8	2.5	,,	195.7	36.9	1.4431
6	215–222°	22.4	2.4	Pale yellow liquid	193.6	42.9	1.4450

Distillates (total) 856.2 g. (90.1%). Residue (brownish-yellow, crystalline mass) 11.0 g. (1.2%).

The distillation temperature soon rose above 180°C. The residue of the first fractionation was not re-distilled.

The fractions, especially the higher-boiling ones, showed notable unsaturation; this was apparently due to the methyl ester of oleic acid.

Each fraction was then examined for its component fatty acids.

Fraction 1 (up to 190°C./15 mm.). The yield was very small. Judged from its boiling point and saponification value, myristic acid and the lower homologues appeared not to be present. The free acid obtained from it, when crystallised from 90% alcohol, melted at 63°C., and by mixed test, was identified to be palmitic acid.

Fraction 2 (190–200°C./15 mm.). This was the principal constituent of the esters. To separate the solid part, 600 g. of the fraction was dissolved in about twice of its volume of acetone and well cooled with ice; the deposited solid was separated by a suction funnel. From the filtrate the acetone was distilled, and the remaining substance was again treated similarly. By these treatments 388 g. of a solid substance was obtained. It formed a beautiful, white crystals of m.p. 29°C., saponification value 206.7 and iodine value 0.64. Although it contained a very small amount of unsaturated substance, its properties nearly coincided with those of methyl palmitate (m.p. 30°C., saponif. value 207.6). The free acid obtained from it by saponification, on crystallising from alcohol, melted at 62°C. and had neutralisation value 218.7. So it consisted of palmitic acid (m.p. 62.6°C., neutr. value 218.9).

From the acetone-filtrate the solvent was distilled off, and on saponifying the remaining esters, 196. g. of fatty acids comparatively rich in liquid components were obtained. These were dissolved in four times of their volume of acetone, and kept at 18–20°C. overnight; the deposited solid was separated and the filtrate was again treated similarly.

(8) Though not strictly accurate, the following procedure was adopted. A fraction was distilled to a prescribed temperature and the residue was mixed to the next fraction and distilled; the distillate coming over to the temperature was mixed to the former fraction.

Such treatment was repeated several times, finally by cooling with ice. As the result, 170 g. of solid acids and 25 g. of crude liquid acids were obtained.

The solid acids melted at 60–60.5°C. and had neutralisation value 212.3 and iodine value 7.8. By crystallising the acids from alcohol, palmitic acid was isolated.

The crude liquid acids had iodine value 73.7 and were still admixed with solids. They were dissolved in 250 c.c. of 95% alcohol, and while hot, 5 g. of lead acetate was added to complete solution. On keeping at room temperature (18°C.) for five hours, the precipitate was filtered off, and on decomposing the insoluble and soluble lead salts, 5.8 g. of solid acids and 18.5 g. of liquid acids were obtained.

The solid acids had neutralisation value 203.4 and iodine value 53.9; so they contained more than half of the weight of unsaturated acids. On crystallisation from alcohol, the crystals melted at 52–52.5°C. By mixed test the chief component appeared to be palmitic acid.

The liquid acids were of an orange-yellow colour and had neutralisation value 194.7, iodine value 86.5, and n_D^{20} 1.4590. They were changed into methyl esters, and 18 g. of the esters were fractionally distilled under ca. 15 mm. pressure. The results were as follows:

Fract.	Dist. temp.	Yield (g.)	Appearance	Saponif. value	Iodine value	n_D^{20}
a	Up to 200°	0.5	Pale yellow liquid	179.9	70.5	1.4500
b	200–210°	10.8	,, ,, ,,	189.5	79.6	1.4520
c	210–216°	5.5	Light yellow liquid	187.8	83.9	1.4520

Residue (brownish-yellow liquid) 0.5 g.

The amount of fraction a was very small; its low saponification value was caused by the admixture of the remaining solvent. The fatty acids from this fraction had neutralisation value 193.5.

The saponification and iodine values of fractions b and c nearly corresponded to those of methyl oleate (saponif. value 189.3, iodine value 85.7). By the elaidin test (Hg and HNO_3), the free acids from these fractions solidified easily and gave elaidic acid of m.p. 44–44.5°C. The acids consisted, therefore, mainly of oleic acid. Hexadecenoic acid, $C_{16}H_{30}O_2$, did not appeared to occur in the present specimen of Japan wax. The presence of the oleic ester in the comparatively low-boiling fraction was due to the fact that a small amount of it was carried over with a large amount of methyl palmitate in the distillation.

Fraction 3 (200–205°C./15 mm.). On saponification, 111.7 g. of the fatty acids were obtained from 117 g. of this fraction. They were treated with acetone and then separated into solid and liquid acids by the lead-salt-alcohol method in the similar manner as described in the case of the previous fraction. Thus the acids were separated as follows:

	Yield (g.)	Neutralisation value	Iodine value
Solid acids (A) deposited from acetone	97	209.3	12.0
,, ,, (B) obtained by lead-salt-alcohol method	4.6	206.5	32.3
Liquid acids ,, ,, ,,	10	197.7	84.8

On crystallising solid acids A from 90% alcohol, crystals of m.p. 60–60.5°C. were obtained; by mixed test they were identified to be palmitic acid. Solid acids B melted, after second recrystallisation, at 53–53.5°C.; the main component of their saturated acids consisted also of palmitic acid. By the elaidin test, the liquid acids were confirmed to consist mainly of oleic acid.

Fraction 4 (205–210°C./15 mm.). The fraction (54 g.) gave 51.4 g. of the fatty acids, which were treated similarly as previously described.

	Yield (g.)	Neutralisation value	Iodine value
Solid acids (C) deposited from acetone	38	207.1	14.6
,, ,, (D) obtained by lead-salt-alcohol method	4.7	208.3	37.1
Liquid acids ,, ,, ,,	8.1	196.6	87.6

Solid acids C, when recrystallised from 90% alcohol, melted at 55°C.; the high boiling point of the fraction indicated the presence of some saturated acids (possibly stearic acid) higher than palmitic acid. Solid acids D melted, after recrystallisation, at 53°C.; they appeared still to contain palmitic acid. The liquid acids consisted mostly of oleic acid.

Fraction 5 (210–215°C./15 mm.). This fraction was mostly liquid at 15°C., though a notable amount of crystals was deposited. On saponification 20.9 g. of the fatty acids were obtained from 22 g. of the fraction. They were dissolved in 70% acetone and cooled with ice; the deposited solid acids were separated from the solution. The fatty acids remaining on evaporating off the acetone were then dissolved in 100 c.c. of 95% alcohol, and the still admixed solid acids were precipitated by adding 1 g. of lead acetate. By these procedures the following results were obtained:

	Yield (g.)	Melt. pt.	Neutralisation value	Iodine value	n_D^{20}
Solid acids (E) deposited from acetone	12.6	51–52°	206.0	12.0	—
Solid acids (F) obtained by lead-salt-alcohol method	1.2	61°	213.1	23.5	—
Liquid acids ,, ,, ,, ,,	7.1	—	198.7	85.6	1.4600

Solid acids E (10 g.) were dissolved in 300 c.c. of 95% alcohol and fractionally precipitated with magnesium acetate as follows:

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st precipitate	1.9	57 – 57.5°C.	201.2
,, ,, ,, 2nd ,,	1.9	54.5–55°C.	205.2
,, ,, ,, 3rd ,,	1.8	54 – 54.5°C.	208.4
,, ,, ,, 4th ,,	1.9	54 – 54.5°C.	212.7
,, ,, ,, 5th ,,	1.5	57 – 57.5°C.	212.8

As the above results show, besides palmitic acid, the presence of stearic acid in the acids would be expected. By fractionally precipitating the fatty acids from the 1st precipitate, 0.3 g. of a solid of m.p. 61.5–62°C. and neutralisation value 189.9 was obtained. Judged from the neutralisation value, this substance appeared to be a mixture of stearic and the higher saturated acids.

Solid acids F contained a fairly large amount of unsaturated acids; as the neutralisation value was high, their main component was probably palmitic acid.

The liquid acids readily formed elaidic acid (m.p. 43.5–44°C.), so the main component was oleic acid.

Fraction 6 (215–222°C./15 mm.). This fraction formed a soft crystalline mass at 15°C. It (20 g.) gave 19.3 g. of the fatty acids, which were treated in the same way as those of preceding fraction.

	Yield (g.)	Melt. pt.	Neutralisation value	Iodine value	n_D^{20}
Solid acids (G) deposited from acetone	8.1	64°C. (mainly liquid at 60°C.)	202.5	0.8	—
Solid acids (H) obtained by lead-salt-alcohol method	2.6	52°C.	213.2	37.4	—
Liquid acids ,, ,, ,, ,,	8.3	—	195.2	86.2	1.4600

The solid acids G consisted mostly of saturated acids. As they were found to contain a small amount of the dibasic acids, 7.8 g. of them were dissolved in about 50 times of their volume of petroleum ether in the hot and kept at room temperature of 22–25°C; the deposited dibasic acids (0.4 g.) were then filtered off.

The acids (6.5 g.) thus freed from the dibasic acids were dissolved in 200 c.c. of 95% alcohol and fractionally precipitated with magnesium acetate.

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st precipitate	1.5	61 - 61.5°C.	192.3
,, ,, ,, 2nd ,,	1.5	60 - 60.5°C.	195.8
,, ,, ,, 3rd ,,	1.8	60.5–61°C.	202.1
,, ,, ,, 4th ,,	1.3	55 - 55.5°C.	208.8

The last mother liquor gave, on evaporation, a soft crystalline mass.

The fatty acids from the 1st and 2nd precipitates were mixed and repeatedly recrystallised from alcohol with the following results:

	Yield (g.)	Melt. pt.	Neutralisation value
Fatty acids from 1st recrystallisation	1.4	63°C.	—
,, ,, ,, 2nd ,,	0.8	64.5–65°C.	—
,, ,, ,, 3rd ,,	0.4	70 - 70.5°C.	183.5

The last acids, when mixed with an equal part of arachidic acid (m.p. of the specimen 75°C.), melted at 72–72.5°C. On analysis the substance gave the following results: Found: C, 76.80; H, 13.06. Calc. for $C_{20}H_{40}O_2$: C, 76.84; H, 12.91%. The substance was, therefore, confirmed to be somewhat impure arachidic acid (m.p. 77°C., neutr. value 179.6).

The mother liquor of the arachidic acid was twice concentrated, the deposited solid (yield ca. 1 g.) separated, and on further concentration 0.45 g. of crystals was obtained.

This substance melted at 63–64°C. and had neutralisation value 194.0; mixed with stearic acid (equal part) it melted at 66–66.5°C. Found: C, 75.44; H, 12.93. Calc. for $C_{18}H_{36}O_2$: C, 75.98; H, 12.76%. Thus the substance consisted of stearic acid.

The acids intermediately deposited (neutr. value 188.3 and 193.5) were mixtures of arachidic and stearic acids.

The fatty acids from the 4th precipitate appeared to be a mixture of stearic and palmitic acids.

The solid acids H contained a notable amount of unsaturated acids; on crystallising them from 90% alcohol, crystals having m.p. 57–58°C. and neutralisation value 212.2 were obtained, so they consisted mainly of palmitic acid. It was rather unexpected to find the presence of palmitic acid in such a high-boiling fraction, though the amount was very small; this indicated the difficulty of thoroughly separating fatty acids from one another by simple fractional distillation of their methyl esters.

The liquid acids formed elaidic acid of m.p. 43.5°C., so they were identified to be oleic acid.

The distillation residue of the second fractionation of the original esters consisted mainly of the esters of the dibasic acids. It should be noted that notwithstanding their high boiling points these esters distilled over together with those of the fatty acids, but their amount was comparatively small.

(3) **On the Free Fatty Acids in Japan Wax** The amounts of free acids in commercial samples of Japan wax vary somewhat markedly and are usually rather high, but the unbleached wax contains a far smaller amount than the sun-bleached one. The following brief experiment was performed to ascertain the components of the free acids.

The specimen of Japan wax (50 g.) was heated with 200 c.c. of 90% alcohol to dissolve out the free acids; on cooling the wax sank and solidified, hereupon the upper solution was decanted. The wax was again treated with 100 c.c. of alcohol. The alcoholic solutions, which deposited notable amounts of solids, were united, neutralised with alcoholic NaOH solution, and evaporated to dryness. The solid residue was mixed with sand and extracted with petroleum ether in a Soxhlet apparatus to remove neutral wax. The soap was then decomposed with diluted hydrochloric acid.

The free acids thus separated amounted to 2.7 g. They formed a pale brownish-yellow solid, and had neutralisation value 195.4, saponification value 212.9, and iodine value 26.7; the content of the dibasic acids was 5.1%. A further treatment of the extraction of neutral wax was made to ensure the complete removal of it. Then the acids had neutralisation value 206.2 and iodine value 27.1.

From the above results, it has been concluded that the components of the free acids were nearly the same as the mixed acids of the wax, but oleic acid was present in a far larger proportion.

Summary.

The component fatty acids of a specimen of unbleached Japan wax, which contains no kernel oil, have been examined.

In agreement with the description in fat literature, palmitic acid is, of course, the main component. Myristic acid and the lower homologues appear not to be present; volatile lower acids stated to occur in Japan wax by old investigators are undoubtedly decomposition products formed by bleaching process. On the other hand, stearic and arachidic acids occur in appreciable proportions. The unsaturated acids consist mostly of oleic acid. A small proportion of linolic acid is present. Hexadecenoic and linolenic acids are probably not present.

It is difficult to mention the quantitative proportion of the individual acids, but rough approximation would be as follows: Palmitic acid 77%, stearic and arachidic acids 5%, oleic acid 12%, linolic acid small amount (less than 1%), dibasic acids 6%.

The above proportion of stearic and arachidic acids would be rather high; in their relative amounts the former seems to predominate.

It is interesting to observe that whereas myristic acid can not be detected in Japan wax obtained from *Rhus succedanea,* it occurs abundantly in the wax of "Tsutaurushi", *Rhus toxicodendron, var. vulgaris,* a viny shrub belonging to the same genus *Rhus.*(9)

The free acids in Japan wax have nearly the same composition as the mixed acids of the wax, but oleic acid is present in a far larger proportion.

Tokyo Imperial Industrial Research Laboratory,
Hatagayacho, Shibuya, Tokyo.

(9) This Bulletin, **6** (1931), 340, foot-note.

STUDIES OF THE RAMAN EFFECT OF ORGANIC SUBSTANCES. PART IV. RAMAN EFFECT OF CEDRENE.

By Kichimatsu MATSUNO and Kwan HAN.

Received March 22nd, 1935. Published June 28th, 1935.

Introduction.

In the present paper, the Raman effect of cedrene is reported, the constitution of which has been studied by Prof. K. Kafuku[1] and others[2] on the standpoint of the organic chemistry. The result of the Raman effect in the present investigation seems to provide an evidence for the organic chemists' idea regarding the constitution. The further discussion will be reported after studying the Raman spectra of the derivatives of cedrene and other terpenes, which are in the course of experiments.

Experimental.

The so-called "artificial cedrene" (b.p. 116–118°/10 mm., n_D^{30} 1.494) obtained by the dehydration of cedrol, was kindly supplied by Ass. Prof. T. Nozoe and Mr. K. Kuraoka. The Raman spectrum of this sample was taken by means of a spectrograph with two prisms. Six hours' exposure was enough for obtaining an intense Raman spectrum (Plate 1) in the total region of the visible part. The experiments were repeated by using a new sample obtained by dehydrating cedrol (m.p. 86°) supplied by Dr. Ichikawa of the Central Research Institute of Formosa. Using this new sample of cedrene, the Raman spectrum was obtained with a spectrograph of three prisms[3] by using a saturated solution of sodium nitrite as a filter (Plate 2). A longer exposure of 12–14 hours was required in this case. No difference was found in the above-mentioned two results. The data of the Raman spectrum are shown in Table I.

For the purification, the substances were dehydrated over calcium chloride, and then redistilled over metallic sodium in vacuum (b.p. 116–117°/10 mm., n_D^{30} 1.4943).

(1) K. Kafuku, *J. Chem. Soc. Japan*, **55** (1934), 1235.
(2) Simonsen, "The Terpenes", Vol. II (1932), p. 530.
(3) This Bulletin, **9** (1934), 327.

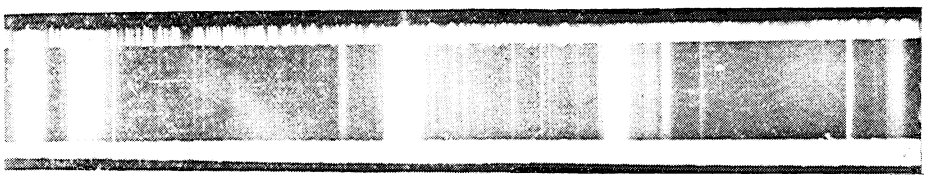


Plate 1. Raman Spectrum of Cedrene (I)

Plate 2. Raman Spectrum of Cedrene (II)

Table I. Raman Spectrum of Cedrene.

No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)	No.	ν(cm.$^{-1}$)	I	$\nu_0-\Delta\nu$(cm.$^{-1}$)
1	24560	4	q-2828(k-145)	25	23885	3	k- 820(i-631)
2	24525	½(d)	p-2828(k-180)	26	23855	2(d)	k- 850(i-661)
3	24474	4(d)	q-2914(k-231)	27	23787	2(b, d)	k- 918
4	24443	5(d)	k- 262(p-2910)	28	23763	3(d)	k- 942
5	24418	5(d)	q-2970	29	23737	2	k- 968
6	24391	5(b)	k- 314	30	23704	3(d)	k-1001
7	24381	½	p-2972	31	23680	½	k-1025
8	24362	½	k- 343(q-3026)	32	23666	3(b, d)	k-1039(i-850)
9	24314	2(b)	k- 391	33	23637	3(d)	k-1068
10	24293	1(b)	k- 412	34	23601	2	k-1104
11	24269	2(b, d)	k- 436	35	23579	4(b)	k-1126(i-937)
12	24250	2(b)	k- 455	36	23563	4(b)	k-1142
13	24211	2	k- 494	37	23537	3(b, d)	k-1168
14	24171	3	k- 534	38	23503	2	k-1202
15	24131	5	k- 574	39	23485	3(d)	k-1220
16	24116	2	k- 589	40	23465	3(d)	k-1240
17	24092	2	k- 613	41	23432	4	k-1273(i-1084)
18	24073	½	k- 632	42	23404	2	k-1301
19	24048	2	k- 657	43	23385 ?	0	k-1320
20	24006	2	k- 699	44	23354	4	k-1351
21	23973	5(d)	k- 732	45	23330	4	k-1375
22	23942	½	i- 574	46	23295	½(d)	i-1221
23	23925	5	k- 780(i-591)	47	23271	6	k-1434
24	23905	½	k- 800(i-611)	48	23257	6(b, d)	k-1448

Table I. (*Concluded*)

No.	ν(cm.$^{-1}$)	*I*	$\nu_0-\Delta\nu$(cm.$^{-1}$)	No.	ν(cm.$^{-1}$)	*I*	$\nu_0-\Delta\nu$(cm.$^{-1}$)
49	23251	6(b, d)	k-1454	85	22088	4(b, d)	e- 850(f-907)
50	23228	3(d)	k-1477	86	22065	½(d)	f- 930(e-873)
51	23195	2(d)	e+257	87	22026	5(b, d)	e- 912
52	23124	2(d)	e+186	88	22001	6 b, d)	e- 937
53	23080	3(b)	i-1436(e+142)	89	21973	5(b, d)	e- 965
54	23039	?	k-1666(hg)	90	21952	3(d)	e- 986?(f-1043)
55	22851	2(b, d)	e- 87	91	21937	5(d)	e-1001
56	22814 ?	0(d)	e- 124	92	21914	2	e-1024
57	22794	4(bb, d)	e- 144	93	21901	3	e-1037
58	22749	3(b, d)	e- 189	94	21874	6	e-1064(f-1121)
59	22701	½(d)	e- 237	95	21851	2	e-1087?(f-1144)
60	22680	4(b, d)	e- 258(f-315)	96	21831	6(d)	e-1107(k-2874)
61	22650	0	e- 288	97	21811	5(b)	e-1127
62	22630	4	e- 308	98	21795	6(b)	e-1143
63	22621	3	e- 317				(k-2914, f-1200)
64	22598	1	e- 340	99	21771	6(b)	e-1167(k-2934)
65	22574	2	e- 364	100	21737	6(b)	e-1201(k-2968)
66	22549	3(b, d)	e- 389	101	21719	2	e-1219
67	22528	3	e- 410	102	21704	3(b, d)	e-1234
68	22501	2(d)	e- 437	103	21669	2(d)	k-3036
69	22485	2(d)	e- 453	104	21660	5	e-1278
70	22469	0(d)	f- 526	105	21641	5	e-1297(f-1354)
71	22447	3	e- 491	106	21608	2 dd)	e-1330
72	22406	5	e- 532	107	21588	5	e-1350
73	22388	½	e- 550(f-607)	108	21563	5	e-1375(f-1432)
74	22367	8	e- 571(f-628)	109	21504	8	e-1434
75	22351	4	e- 587	110	21486	8	e-1452
76	22327	4	e- 611	111	21465	6(bb)	e-1473
77	22308	2	e- 630	112	21292	½	e-1646
78	22282	3	e- 656	113	21272	10	e-1666
79	22240	3	e- 698	114	21106	2(b)	e-2832
80	22205	8(b, d)	e- 733	115	20063	2	e-2875(f-2932)
81	22158	8	e- 780	116	20020	6(b, d)	e-2918
82	22136	2	e- 802	117	19999	6(b)	e-2939
83	22119	6	e- 819	118	19971	6(d)	e-2967(f-3024)
84	22105	½	e- 833	119	19914	2(d)	e-3024

$\Delta\nu$: (87) (2b, d); (124) (0d) ?; 144 (4bb, d); 189 (3b, d); 237 (½d); 260 (4b, d); (288) (0); 308 (4); 317 (3); 340 (1); (364) (2); 389 (3b, d); 410 (3); 437 (2d); 454 (2d); 491 (3); 532 (5); (550) (½) ?; 571 (8); 587 (4); 611 (4); 630 (2); 656 (3); 698 (3); 733 (8b, d); 780 (8); 802 (2); 819 (6); (833) (½); 850 (4b, d); (873) (½d) ?; 915 (5b, d); 938 (6b, d); 965 (5b, d); (986) (3d) ?; 1001 (5d); 1024 (2); 1038 (3); 1066 (6); (1087) (2) ?; 1105 (2d); 1127 (5b); 1143 (6b); 1167 (6b); 1201 (6b); 1219 (2); 1237 (3b, d); 1275 (5); 1297 (5); 1325 (2dd); 1350 (5); 1375 (5); 1434 (8); 1452 (8); 1475 (6b, d); (1646) (½) ?; 1666 (10); 2830 (2b); 2875 (2); 2916 (6b, d); 2937 (6b); 2967 (6b); 3030 (2d)

Discussion.

The Raman spectrum of cedrene is the most complicated one. It contains one-hundred-nineteen lines. And some of the Raman lines are

observed at the equal intervals. The mean interval between them is 25 cm.$^{-1}$, as shown below:

317		1101		1325	
	23		26		25
340		1127		1350	
	24				25
364		1143		1375	
	25		24		
389		1167			
	21				
410		1271			
	27		26		
437		1297			

According to the usual estimation, the lower frequencies may be ascribed to the deformation of the carbon linkages. And when we put

$$\omega_1 = 144,\quad \omega_2 = 308,\quad \omega_3 = 317,\quad \omega_4 = 364,\quad \omega_5 = 389,\quad \omega_6 = 410,\quad \omega_7 = 437,$$
$$\omega_8 = 454,\quad \omega_9 = 491,\quad \omega_{10} = 532,\quad \omega_{11} = (550),\quad \omega_{12} = 571,\quad \omega_{13} = 587,\quad \omega_{14} = 611,$$

we find that a number of the Raman lines higher than $\Delta\nu$ 630 cm.$^{-1}$ are two times as great as the above-mentioned frequencies as shown in Table II. These lines may be taken as the overtone of the corresponding lower ones.

Table II. The Frequencies Associated with the Overtone.

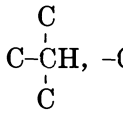
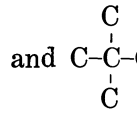
$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}-\omega_{obs.}$	$\omega_{cal.}$	$\omega_{obs.}$	$\omega_{cal.}-\omega_{obs.}$
$2\omega_1 = 288$	(288)(0)	0	$2\omega_8 = 908$	915 (5b, d)	-7
$2\omega_2 = 616$	611 (4)	5	$2\omega_9 = 982$	(986)(3d)?	-4
$2\omega_3 = 634$	630 (2)	4	$2\omega_{10} = 1064$	1066 (6)	-2
$2\omega_4 = 728$	733 (8)	-5	$2\omega_{11} = 1100$	1105 (2d)	-1
$2\omega_5 = 778$	780 (8)	-2	$2\omega_{12} = 1142$	1143 (6b)	-1
$2\omega_6 = 820$	819 (6)	1	$2\omega_{13} = 1174$	1167 (6b)	7
$2\omega_7 = 874$	(873)($\frac{1}{2}$)	1	$2\omega_{14} = 1222$	1219 (2)	3

From the result compared in Table II, it seems to be impossible to assign the intense lines of $\Delta\nu$ 733(8), 780(8), 915(5b, d), 1066(6), 1143(6b), and 1167(6b), simply as the overtone of the above-mentioned frequencies. Another origin must be taken into consideration.

As the usual assignment, the frequencies in the region of $\Delta\nu$ 733–1066 cm.$^{-1}$ may be attributable to the valency frequencies of the C–C bond. It will be noted that the organic chemists' picture[4] of the molecule indicates that:

(4) Cf. (2).

(1) Cedrene is a tricyclic compound.

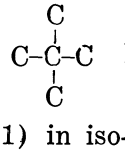
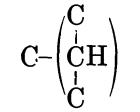
(2) There are carbon atoms holding one, two, three, and none hydrogen atoms, that is,  , $-CH_2-$, $-CH_3$ and  .

(3) The molecule includes more possibly a 1-methyl-cyclopentene-(1) than a 1-methyl-cyclohexene-(1) ring.

From these points of view, let us compare, in the first place, the Raman spectrum of cedrene with those of the other simple paraffine molecules which have been observed by Kohlrausch and Köppl[5]. As shown in Table III, in the paraffine series, the frequencies of ca. $\Delta\nu$ 840 and 890 cm.$^{-1}$ are found in the normal compounds, while the corresponding shifts in their isomerides are ca. $\Delta\nu$ 780 and 950 cm.$^{-1}$. It is also found that $\Delta\nu$ 1335 cm.$^{-1}$ disappears in the normal compounds, and $\Delta\nu$ 1066 cm.$^{-1}$ does in the iso-compounds.

Table III. Raman Frequencies of the Normal- and Iso-Praffines.

C_nH_{2n+2}	a	b	c	d	e	f	g	h	i	j	k	l
C_4H_{10} (*n*)	298	—	825	(873)	895	—	1058	1006	—	1299	—	1447
C_5H_{12} (*n*)	—	—	841		895	1027	1066	1110	—	1301	—	1446
C_6H_{14} (*n*)	269	—	822	863	889	1026	1069	1112	—	1302	—	1446
C_7H_{16} (*n*)	256	—	845		886	1021	1069	1113	1169	1300	—	1445
C_4H_{10} (*i*)	335	427	(789)	832	954	(1029)	—	1120	1168	1298	1334	1454
C_5H_{12} (*i*)	(366)	424	773	826	953	(1030)	—	1123	1167	(1295)	1337	1453

In the second place, let us consider the Raman spectrum of tetramethyl-methane which was studied by the above authors[7] and Rank.[6] Kohlrausch and Köppl[7] have ascribed ω_1 732(10), ω_2 332(4b), ω_3 921 (7b), and ω_4 416(1) in tetramethyl-methane to the vibration frequencies of the  linkage, while ω_1 795(9), ω_2 371(4b), ω_3 965(4b) and ω_4 437(1) in iso-butane to the  linkage. From the fact that

(5) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, (B) **24** (1934), 377.

(6) D. H. Rank, *J. Chem. Phys.*, **1**, (1933), 572.

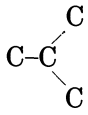
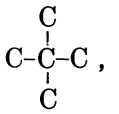
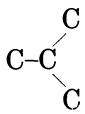
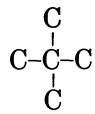
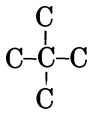
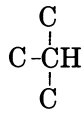
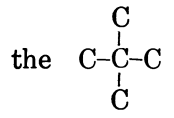
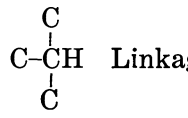
the above-mentioned Raman lines are also observed in the other isomerides of paraffines and their derivatives having the valency bond of  or  , as shown in Table IV, and the fact of the disappearance and the displacement of the frequencies in the normal compounds of the paraffine series as shown in Table III, we may ascribe the frequencies in the regions of 732–795 and 915–965 cm.$^{-1}$ to the valency frequencies of the  or  linkage.

Table IV. Raman Frequencies Possibly Associated with the  or  Linkage.

Molecule	ω_1	ω_2	ω_3	ω_4
Tetramethyl-methane[7]	732 (10)	333 (4b)	921 (7b)	416 (1)
Tertiary butylcarbinol[8]	744 (9)	333 (2b) 350 (2b)	933 (4)	407 ($\frac{1}{2}$)
Tertiary amylcarbinol[8]	714 (4) 726 (3)	350 (2)	903 (2) 931 (2)	405 (0) 441 ($\frac{1}{2}$)
Isobutane[7]	795 (9)	371 (4b)	965 (4b)	437 (1)
Isopentane[9]	762 (5) 796 (4)	366 (1)	906 (2) 948 (2)	469 (4)
Isobutyl alcohol[9]	782 (2)	361 ($\frac{1}{2}$)	953 (3b)	494 (4)
Isobutyl amine[9]	792 (5b)	363 (2b)	952 (3)	480 (4b)
Methyl-isopropylcarbinol[8]	757 (2b) 786 (3)	358 (1)	930 (3) 954 (2)	462 ($\frac{1}{2}$) 496 ($\frac{1}{2}$)
2,5-Dimethyl-hexane[10]	778 (2)	313 (2)	962 (3br)	444 (4b)

(7) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, (B) **26** (1934), 219.
(8) K. W. F. Kohlrausch and F. Köppl, *Monatsh.*, **63** (1933), 269.
(9) H. Kopper, R. Seka and K. W. F. Kohlrausch, *Monatsh.*, **61** (1932), 403.
(10) John W. Murry, *J. Chem. Phys.*, **2** (1934), 618.

Table V. The Vibration Frequencies Associated with the  or  Linkage.

Molecule	ω_1	ω_2	ω_3	ω_4
Isobutane	785 (9)	371 (4b)	965 (4b)	437 (1)
Cedrene	780 (8) 733 (8)	389 (3b, d) 317 (3)	965 (5b) 915 (5b, d)	427 (2d) 410 (3)
Tetramethyl-methane	732 (10)	332 (4b)	921 (7b)	416 (1)

Table VI. The Valency Frequencies of the Carbon Bonds.

Cedrene	α-Pinene		β-Pinene[12]	Sabinene[13]
	V.B.[11]	M.H.[13]		
733 (8)	—	—	—	729 (1d)
780 (8)	774 (2)	774 (6)	786 (5)	786 (5)
802 (2)	—	—	—	—
819 (5)	816 (0)	818 (2)	—	808 (4d)
850 (4b, d)	844 (2)	844 (7)	850 (5)	—
(873)(½)	878 (0)	885 (2)	879 (5)	882 (2d)
915 (5b, d)	904 (1)	908 (4)	—	916 (6d)
938 (6b, d)	931 (0)	933 (2)	—	930 (1)
965 (5b)	949 (3)	954 (5d)	942 (4)	953 (6b)
986 (3)	—	—	—	989 (3)

It may, therefore, be possible to assign the frequensies of $\Delta\nu$ 733, 780, 915, and 965 cm.$^{-1}$ in cedrene as due to these linkages in the cedrene molecule. The vibration frequencies associated with the linkage in question in cedrene are compared also with those in iso-butane and tetramethyl-methane as shown in Table V. It is interesting that the relation of the intensities of these lines in the latter are similar to that in the former. As to the other Raman lines in the region of 802–850 cm.$^{-1}$, they may be attributable to the $-CH_2-CH_2-$ linkage of the ring.

Further, let us compare the Raman lines which are possibly associated with the valency frequencies of the carbon linkages in cedrene with those

(11) S. Venkateswaran and S. Bhagavantam, *Ind. J. Phys.*, **7** (1933), 585.
(12) G. Dupont, P. Daure and J. Allard, *Bull. soc. chim.*, **49** (1932), 1401.
(13) The details will be published shortly in this Bulletin.

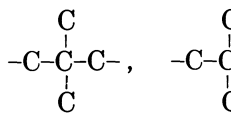
in the other terpenes, such as α-pinene, β-pinene, and sabinene, which have been known to have the carbon linkages of  , , $-CH_2-$ and $-CH_3$ (Table VI). The frequencies of $\Delta\nu$ 780, 873, and 965 cm.$^{-1}$ in cedrene are also found in α-pinene, β-pinene, and sabinene. The frequencies of $\Delta\nu$ 819, 915 and 938 cm.$^{-1}$ appear in cedrene, α-pinene, and sabinene, but not in β-pinene. The frequency of $\Delta\nu$ 850 cm.$^{-1}$ appears in cedrene, α-pinene, and β-pinene, but not in sabinene. The fact that all the shifts between $\Delta\nu$ 733 and 986 cm.$^{-1}$ in cedrene are found also in α-pinene, β-pinene, or sabinene seems to give a verification of the organic chemists' idea regarding the constitution of cedrene.

Table VII. Comparison of the Raman Frequencies in Cedrene, 1-Methyl-cyclopentene-(1) and 1-Methyl-cyclohexene-(1).

Methyl-cyclopentene		Cedrene	Methyl-cyclohexene (Godchot, etc.)[15]	Methyl-cyclopentene		Cedrene	Methyl-cyclohexene (Godchot, etc.)[15]
(Godchot, etc.)[15]	(Piaux)[16]			(Godchot, etc.)[15]	(Piaux)[16]		
—	—	308	—	—	928	938	—
333	325	317	—	—	—	965	—
		340		—	—	(986)?	990
—	—	364	—	—	1008	1001	—
—	—	389	—	1017	1026	1024	—
—	—	410	—	—	—	1038	—
437	432	437	437	—	—	1066	1069
—	—	454	—	1083	—	(1087)?	1087
—	—	491	495	—	—	1105	—
—	—	532	—	—	1133	1127	—
578	578	571	—	—	1148	1143	1152
—	—	587	588	—	—	1167	—
—	—	611	618	—	1207	1201	—
—	—	630		—	—	1219	—
—	648	656	—	1278	1259	1275	1266
—	—	698	695	—	1295	1297	1309
—	—	733		1336	1333	1325	1367
—	790	780	758	—	—	1350	—
—	—	802	—	1385	1383	1375	—
—	821	819	821	1445	1439	1434	1445
—	851	850	859		1465	1452	
879	881	(873)?	—			1475	
—	903	915	—	1660	1658	1666	1675

(14) The details will be published shortly in this Bulletin.

(15) Marcet Godchot, Etienne Canales, and Germaine Cauquil, *Compt. rend.*, **197** (1933), 1408.

(16) Leon Piaux, *Compt. rend.*, **199** (1934), 67.

The facts that almost all the Raman lines observed in cyclohexane occur also in decahydro-naphthalene and decahydro-acenaphthene[14] and that many of the Raman lines of cedrene coinside with those of 1-methyl-cyclopentene-(1) and 1-methyl-cyclohexene-(1) (Table VII) give an another evidence of the organic chemists' constitution of cedrene.

The most intense line at $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is attributable to the inner vibration of the C=C bond. This frequency is generally influenced rather remarkably by the adjacent atoms or atom groups of the bond in the molecule. The frequency of $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is compared with that in the other molecules which have the C=C linkage, as shown in Table VIII.

From the results we may summarize that the Raman frequency due to the C=C linkage indicates a constant value for each type of the molecules. And by the substitution of a methyl or methylene group for a hydrogen atom attached to the double bond of the carbon atoms the frequency is increased about 20 cm.$^{-1}$, with an exception of cyclopentene in which it is increased about 40 cm.$^{-1}$, as shown below:

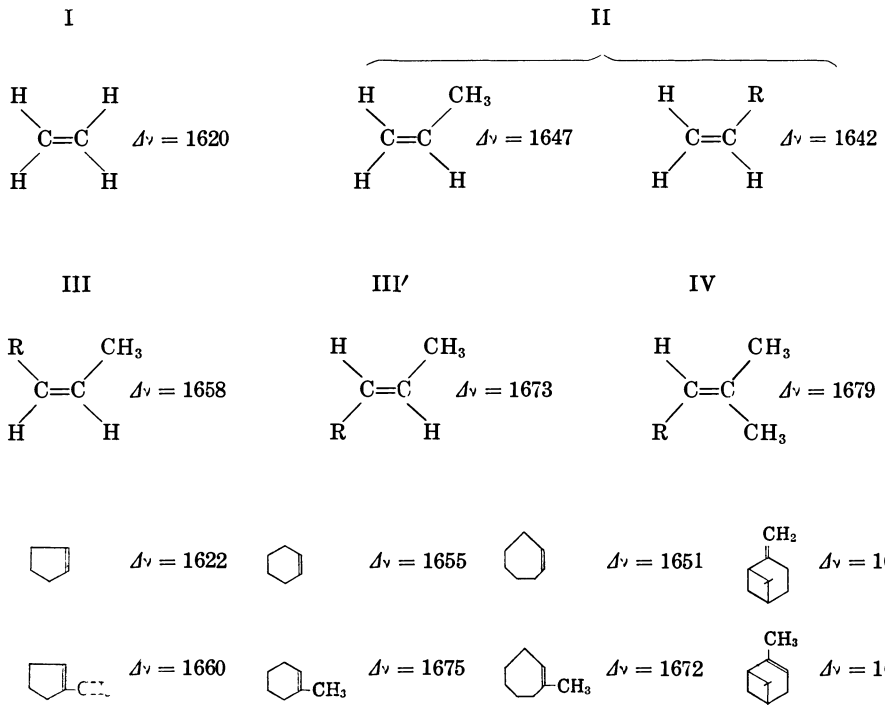
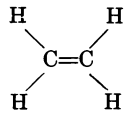
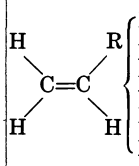
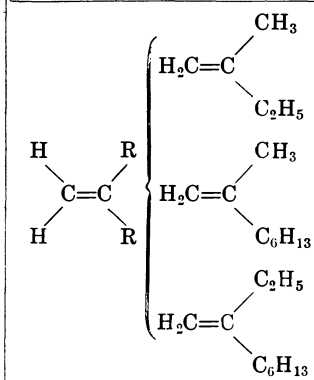
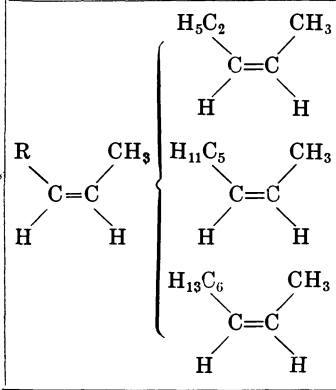
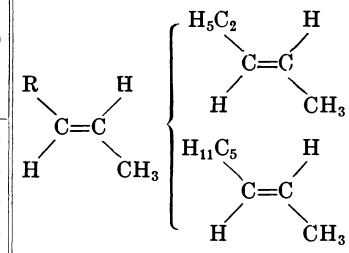
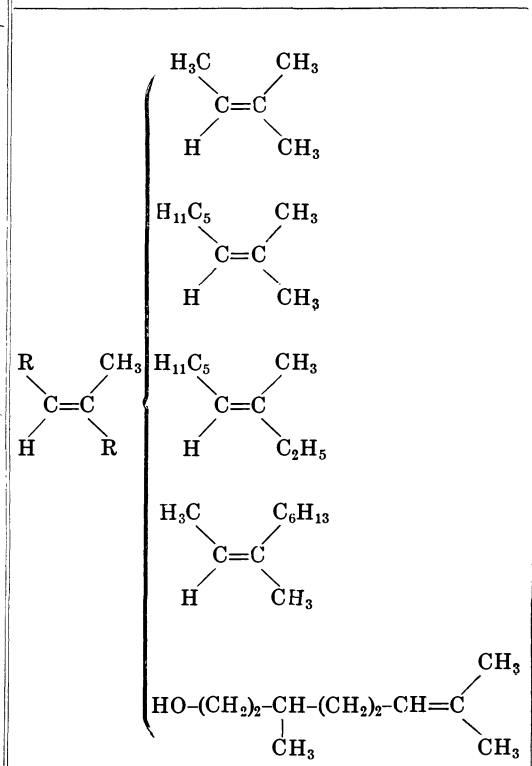


Table VIII. Raman Frequencies Associated with the C=C Bond.

 $H_2C=CH_2$	1620[17]
 $H_2C\text{-}CH\text{-}CH_3$	1647[17]
$H_2C\text{-}CH\text{-}CH_2OH$	1646[17]
$H_2C\text{-}CH\text{-}CH_2Cl$	1640[17]
$H_2C\text{-}CH\text{-}CH_2\text{-}C_6H_5$	1642[17]
$H_2C\text{-}CH\text{-}C_nH_{2n+1}$ (n=2–8)	1642[17]
	1652[19]
	1647[18]
	1646[18]
	1658[20]
	1658[20]
	1658[20]
	1674[20]
	1673[20]
	1679[21]
	1677[18]
	1670[18]
	1672[18]
	1675[27]

(17) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 495.
(18) B. Gredy, *Compt. rend.*, **195** (1932), 313.
(19) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 480.
(20) M. Bourguel, B. Gredy, and L. Piaux, *Compt. rend.*, **195** (1932), 129.
(21) M. Bourguel, *Bull. soc. chim.*, **53** (1933), 474.

Table VIII. (*Concluded*)

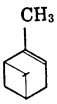
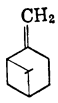
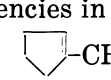
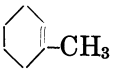
	1622[22]		1655[22]		1651[22]		
	1660[23]		1650[23]		1672[23]		1660[25]
	1660[23]		1675[23]				
	1656[24]		1675[23]				1641[26]
			1680[23]				
			1677[23]				

Table IX. The Raman Frequencies Associated with the $-C=\underset{\displaystyle CH_3}{\overset{|}{C}}-$ Linkage.

Butadiene[28]	—	Geraniol[29]	1388
1-Methyl-butadiene[23]	1370	Linalool[30]	1383
Isoprene[28]	1380	Carvone[31]	1378
2,3-Dimethyl-butadiene[28]	1377	Pulegone[32]	1379
Phenyl-ethylene[28]	—	Cyclopentene[22]	—
Phenyl-methyl-ethylene[28]	1376	1-Methyl-cyclopentene-(1)[23]	1385
Chloroprophylene[28]	1375	Cyclohexene[22]	—
Methyl crotonate[28]	1375	1-Methyl-cyclohexene-(1)[22]	1367
Methyl iso-crotonate[29]	1367	Cycloheptene[22]	—
Crotonic acid[28]	1381	1-Methyl-heptene-(1)[23]	1379
α-Pinene[25]	1383	Octene[22]	—
β-Pinene[26]	—		

From these results, we may conclude that the most intense line corresponding to the frequency of $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is attributable to the C=C bond in the type of $H_{20}C_{12}\overset{CH}{\underset{C-CH_3}{\diagup\!\!\diagdown}}$, as described by the organic chemists. By comparing with the corresponding Raman

(22) M. Godchot, etc., *Compt. rend.*, **196** (1933), 780.
(23) M. Godchot, etc., *ibid.*, **197** (1933), 1407.
(24) L. Piaux, *ibid.*, **199** (1934), 67.
(25) Cf. (13).
(26) Cf. (12).
(27) G. B. Bonino, and P. Cella, *Mem. Accad. Italia*, **3** (1932), No. 4, 20.
(28) Kohlrausch, "Smekal-Raman-Effekt", (1931), p. 322–327.
(29) G. B. Bonino and P. Cella, *Mem. Accad. Italia*, **3** (1932), No. 4, 22.
(30) *Ibid.*, p. 21. (31) *Ibid.*, p. 8. (32) *Ibid.*, p. 6.

shift in 1-methyl-cyclopentene-(1) ($\Delta\nu$ 1660 cm.$^{-1}$) and 1-methyl-cyclohexene-(1) ($\Delta\nu$ 1675 cm.$^{-1}$), it seems that the frequency in question appears more likely in the case of 1-methyl-cyclopentene-(1) than in the case of 1-methyl-cyclohexene-(1). The difference is, however, too small to distinguish the latter from the former, as the frequency $\Delta\nu$ 1666 cm.$^{-1}$ in cedrene is situated between the frequencies in 1-methyl-cyclopentene-(1) and 1-methyl-cyclohexene-(1). That is:  $\Delta\nu$ 1660 cm.$^{-1}$; cedrene $\Delta\nu$ 1666 cm.$^{-1}$;  $\Delta\nu$ 1675 cm.$^{-1}$. This fact gives an evidence of the presence of a methyl group attached to the carbon atom of the double bond. The question whether the molecule of cedrene contains 1-methyl-cyclopentene-(1) ring or 1-methyl-cyclohexene-(1) ring is still unanswered from the study of the Raman effect.

Another possible evidence of the existence of the $-C=\underset{\displaystyle CH_3}{\overset{|}{C}}-$ linkage in cedrene may be given by the occurrence of the Raman frequency of $\Delta\nu$ 1375 cm.$^{-1}$. This frequency has been observed in the Raman spectra of such molecules as methyl-butadiene, isoprene, chloropropylene, geraniol, linalool, pulegone, 1-methyl-cyclopentene-(1), 1-methyl-cyclohexene-(1), 1,2-dimethyl-cyclohexene, and 1-methyl-cycloheptene-(1), etc., but not in butadiene, cyclopentene, cyclohexene, and cycloheptene, etc., as shown in Table IX.

Summary.

The Raman spectrum of cedrene has been studied. The frequencies of $\Delta\nu$ 733, 780, 915 and 965 cm.$^{-1}$ are established to be attributable to the valency frequencies of the linkage, $-C-HC\overset{C}{\diagdown}$ or $-C-\overset{|}{\underset{|}{C}}-C-$ in the molecule of cedrene. The most intense line at $\Delta\nu$ 1666 cm.$^{-1}$ is assigned to characterize the C=C bond. The occurrence of the Raman line at $\Delta\nu$ 1375 cm.$^{-1}$ seems to give an evidence of the $-C=\underset{\displaystyle CH_3}{\overset{|}{C}}-$ linkage in the cedrene molecule, $H_{20}C_{12}\overset{CH}{\underset{C-CH_3}{\diagup\!\!\diagdown}}$.

In conclusion, the authors wish to express their thanks to Ass. Prof. T. Nozoe for his kind advices and supply of the sample. The authors express their indebtedness also to Dr. Ichikawa for his supply of cedrol.

Laboratory of Physical and Inorganic Chemistry,
Taihoku Imperial University, Taihoku, Japan.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. III. THE ISOLATION AND CONSTITUTION OF MOROCTIC ACID $C_{18}H_{28}O_2$.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received March 25th, 1935. Published June 28th, 1935.

In the first paper(1) of this series it was shown concerning the highly unsaturated C_{18}-acids of sardine oil that the sardine oil contained an octadecatetraenoic acid $C_{18}H_{28}O_2$, and also the occurrence of an octadecatrienoic acid $C_{18}H_{30}O_2$ was indicated. In this paper the results of our further experiments concerning the octadecatetraenoic acid are described. Whilst this acid could not be isolated in the previous experiments, we have this time achieved its isolation by using a large quantity of sardine oil. Although the occurrence of octadecatetraenoic acid in sardine oil and in other marine animal oils has hitherto been stated by various authors, the acids described as an octadecatetraenoic acid by earlier authors represented, in some cases, a mixture of several highly unsaturated acids, and no octadecatetraenoic acid appears to have been isolated with certainty before our experiments. We designate the octadecatetraenoic acid isolated from sardine oil as moroctic acid.(2)

In order to determine the constitution of moroctic acid, methyl moroctate was oxidised by the ozonide method in the first place. Among the decomposition products of the ozonide, propionic acid, propyl aldehyde, succinic acid, succinic semi-aldehyde, acetic acid, acetaldehyde, carbon dioxide, methyl hydrogen succinate and the corresponding semi-aldehyde were recognised; the presence of malonic acid was also indicated. Of these decomposition products, propionic acid and propyl aldehyde are derived from the $CH_3{\cdot}CH_2{\cdot}CH=$ group, while succinic acid and its semi-aldehyde from the $=CH{\cdot}(CH_2)_2{\cdot}CH=$ group, and it was found from the yield of succinic acid and its semi-aldehyde that methyl moroctate contained two of the $=CH{\cdot}(CH_2)_2{\cdot}CH=$ group. The presence of acetic acid, acetaldehyde, carbon dioxide together with malonic acid is explainable

* Translated from the paper published in Japanese in the Report of Tokyo Imperial Industrial Research Laboratory, **27** (1932), No. 2.

(1) Toyama and Tsuchiya, this Bulletin, **4** (1929), 83.

(2) The name is derived from "Morokuti" (Japanese) which is one of a few other names given to Japanese sardine.

on condition that methyl moroctate has the $=CH\cdot CH_2\cdot CH=$ group which on oxidation yields primarily malonic acid and the corresponding aldehyde, from which acetic acid, acetaldehyde and carbon dioxide are formed by the secondary decompositions thus: $HOOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COOH + CO_2$ or $HOC\cdot CH_2\cdot COOH \rightarrow CH_3\cdot COH + CO_2$. Finally the methyl hydrogen succinate and the corresponding semi-aldehyde are derived from the $=CH\cdot(CH_2)_2\cdot COOCH_3$ group, showing that free moroctic acid has the $=CH\cdot(CH_2)_2\cdot COOH$ group. From these results, moroctic acid is found to contain the following groups: $CH_3\cdot CH_2\cdot CH=$, $=CH\cdot CH_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot CH=$ (two), and $=CH\cdot(CH_2)_2\cdot COOH$. Accordingly its constitution is expressed by one of the following formulae:

$$CH_3\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (I)$$

$$CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (II)$$

$$CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (III)$$

In order to determine which of these formulae is correct, we have successfully applied the principle of selective addition of thiocyanogen to the poly-ethylenic acids.[3] After having found by determining the thiocyanogen value of methyl moroctate that thiocyanogen adds selectively to two of the four ethylenic linkings in methyl moroctate, yielding a tetrathiocyanate, we have prepared tetrathiocyanate of methyl moroctate and subjected the latter to ozonolysis. Among the decomposition products, propionic acid, propyl aldehyde, acetic acid, acetaldehyde, carbon dioxide and an oily substance containing thiocyano-groups were recognised; also malonic acid seemed to be present. Of these products, propionic acid and propyl aldehyde are derived from the $CH_3\cdot CH_2\cdot CH=$ group, and acetic acid, acetaldehyde and carbon dioxide together with malonic acid are considered to come from the $=CH\cdot CH_2\cdot CH=$ group. It is seen from these results that the two groups, $CH_3\cdot CH_2\cdot CH=$ and $=CH\cdot CH_2\cdot CH=$, in methyl moroctate remained unsaturated when thiocyanogen was allowed to act upon methyl moroctate. Of the three formulae given above, only the formula (I) is consistent with these facts, and it should be concluded that tetrathiocyanate of methyl moroctate is formed by the selective addition of thiocyanogen to the two ethylenic linkings (4:5 and 8:9) lying near the carboxyl group in the formula (I), leaving the other two ethylenic linkings (12:13 and 15:16) unsaturated. The oily substance formed on ozonolysis of tetrathiocyanate had still thiocyano-groups. It must, therefore, contain monomethyl ester of 3,4,7,8-tetrathiocyano-

(3) P. H. Kaufmann, *Arch. Pharm.*, **263** (1925), 675.

decane- 1,10-dicarboxylic acid. This was verified by the fact that on elimination of thiocyanogen from the oily substance followed by hydrolysis, there was obtained a decadiene-dicarboxylic acid ($\Delta^{8:9,\ 7:8}$-decadiene-1,10-dicarboxylic acid) which yielded on hydrogenation decane-dicarboxylic acid. From these results, the constitution of moroctic acid is established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid expressed by the formula (I).

Of the unsaturated C_{18}-acids found in the natural fats and oils, the most widely distributed acids are oleic ($\Delta^{9:10}$), linolic ($\Delta^{9:10,\ 12:13}$), and linolenic ($\Delta^{9:10,\ 12:13,\ 15:16}$) acids. Comparing these acids with moroctic acid, there exist the following relations between the positions of respective ethylenic linkings. Thus the 9:10 ethylenic linking is common to oleic, linolic and linolenic acids, but it does not occur in moroctic acid; the 12:13 ethylenic linking is common to linolic, linolenic and moroctic acids, while the 15:16 ethylenic linking is common to linolenic and moroctic acids. Although there are found, besides the above-mentioned acids, petroselinic ($\Delta^{6:7}$), vaccenic ($\Delta^{11:12}$), γ-linolenic ($\Delta^{6:7,\ 9:10,\ 12:13}$),[4] and elaeostearic ($\Delta^{9:10,\ 11:12,\ 13:14}$) acids as naturally occurring unsaturated C_{18}-acids, neither 4:5 nor 8:9 ethylenic linking occurs in these acids except moroctic acid.

Experimental.

1. **The Isolation and Properties of Moroctic Acid and its Methyl Ester.** The ethyl esters (60 kg.) obtained by ethanolysis of sardine oil were subjected to distillation, and the distillate (28.5 kg.) boiling below 215°/10 mm. was collected separately. This was converted into free fatty acids, and the latter were dissolved in 85% methanol and cooled to separate crystalline solids which were filtered off. An aqueous solution of lithium hydroxide was added to the filtrate, and the insoluble lithium soaps were filtered. From the filtrate, the remaining fatty acids (7.5 kg.) were recovered and converted into methyl esters, from which a fraction (5.9 kg.) boiling below 215°/15 mm. was obtained on distillation. This was brominated in ethereal solution, and the ether insoluble bromides obtained were separated by means of benzene. The details of the above experiments were already described in the previous report[5] in which the benzene soluble bromides (1.5 kg.) were worked up for the isolation of hiragonic acid. In this paper the benzene insoluble bromides (900 g.) were debrominated and the product was fractionated to yield methyl moroctate. The debromination of the benzene insoluble bromides was carried out as follows: to the mixture of 100 g. of the bromides and 50 g. of zinc powder, 150 c.c. of alcohol was added. Unlike the case with the benzene soluble bromides described in the previous report, no appreciable heat evolution occurred. The mixture was gently refluxed by heating on the

(4) A. Eibner, L. Widenmayer and E. Schild, *Chemische Umschau Fette, Oele, Wachse und Harze*, **34** (1927), 312.

(5) This Bulletin, **10** (1935), 192.

water-bath, and 150 c.c. of 5 N alcoholic solution of hydrogen chloride was added in the course of 2.5 hours, another 50 g. of zinc powder being added in several portions. When all the alcoholic solution of hydrogen chloride has been added, heating was continued for one hour more, after which the alcoholic solution was removed by decantation. The residual insoluble substance was again refluxed with alcohol and zinc powder, and alcoholic solution of hydrogen chloride was added as before. The alcoholic solution was filtered, and the final residue was washed with alcohol. From the united alcoholic solution, the debrominated products were separated on addition of a large quantity of water, and extracted with ether. Since the products obtained from the ethereal solution were suspected to contain unsaponifiable substance, though it might have been a minute amount, they were saponified and the resulting soap solution was extracted with ether to remove unsaponifiable substance, after which the soap solution was decomposed with hydrochloric acid to yield the free fatty acids, and then the latter were reconverted into methyl esters. From 900 g. of the bromides there were obtained 220 g. of debrominated methyl esters. These were repeatedly fractionated, and a fraction (48 g.) boiling at 208–213°/15 mm. was finally obtained as methyl moroctate; d_4^{15} 0.9174, d_4^{20} 0.9140, n_D^{15} 1.4849, n_D^{20} 1.4829, mol. refr. 90.66 (calc. for $C_{19}H_{30}O_2$: 89.73), saponification value 193.3 (calc. 193.3), iodine value by the Rosenmund-Kuhnhenn method 344.6 (calc. 349.8), thiocyanogen value 173.1 (calc. for the formation of tetrathiocyanate $C_{19}H_{30}O_2(SCN)_4$: 174.9). On brominating methyl moroctate in ethereal solution, it yielded 57% of ether insoluble bromide which melted at about 215° to a tar-like substance (Found: Br, 68.65. Calc. for $C_{19}H_{30}O_2Br_8$: Br, 68.78%).

Moroctic acid liberated from its methyl ester in the usual way had the following constants (Found: C, 78.12; H, 10.25. Calc. for $C_{18}H_{28}O_2$: C, 78.20; H, 10.22%): d_4^{15} 0.9334, d_4^{20} 0.9297, n_D^{15} 1.4930, n_D^{20} 1.4911, mol. refr. 86.00 (calc. for $C_{18}H_{28}O_2$: 84.99),[6] neutralisation value 201.7 (calc. 203.1), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 372.6 and 361.9 respectively (calc. 367.6). On brominating moroctic acid in ethereal solution, it yielded 58% of ether insoluble bromide which melted at about 220° to a tar-like substance (Found: Br, 69.72. Calc. for $C_{18}H_{28}O_2Br_8$: Br, 69.83%). The hydrogenation product of moroctic acid yielded, after recrystallisation from 95% alcohol, a pure stearic acid; neutr. value 196.7 (calc. 197.4), m.p. and mixed m.p. 69.5–70°.

2. **Ozonolysis of Methyl Moroctate.** Methyl moroctate (5 g.) was dissolved in chloroform (50 c.c.), cooled with ice-salt, and a current of ozonised oxygen was passed through the solution until it became saturated, after which the chloroform was distilled by heating on the water-bath under diminished pressure. As it was found by a preliminary experiment that the ozonide was exceedingly unstable and decomposed explosively on undue heating, the temperature of water-bath was kept at about 40°C. When most of the chloroform was driven off, the distillation was stopped since there was a danger of frothing of the residue. The ozonide remained as a light yellow viscous liquid which is probably not a normal ozonide but an ozonide peroxide. From

(6) It should be noted here that moroctic acid and its methyl ester, like hiragonic acid, showed a slight exaltation of mol. refr. This was also observed with decadiene-dicarboxylic acid which was obtained in the experiments of the ozonolysis of tetrathiocyanate described below. The cause of this exaltation of mol. refr. is unknown to us.

20 g. of methyl moroctate, there was obtained 35 g. of ozonide (175%) which was not thoroughly freed from chloroform. The calculated yields for normal ozonide $C_{19}H_{30}O_{41}$ and ozonide peroxide $C_{19}H_{30}O_{15}$ are 165.9 and 171.4%, respectively. Water (200 c.c.) was then added to the ozonide in a flask, and the liquid was heated for about 30 minutes on the water-bath in a current of hydrogen. In order to recover the volatile decomposition products carried over with hydrogen, the flask was attached by a delivery tube to another three flasks which were connected in succession, the first (**a**) being filled with 200 c.c. of water and cooled with ice, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The products of ozonolysis were thus separated into two parts: (i) volatile decomposition products and (ii) decomposition products which were not carried over with hydrogen.

(i) *Volatile decomposition products.* These were collected in three flasks (**a**, **b** and **c**) as stated above. The aqueous solution in the flask (**a**) gave a pink colouration with Schiff's reagent and indicated the presence of acetaldehyde by a deep blue colouration produced on adding diethylamine and sodium nitroprusside. On adding phenylhydrazine, it yielded an oily phenylhydrazone which, after being washed with acetic acid, was heated with zinc chloride to 180°, when a smell of scatol was recognised, and consequently the presence of propyl aldehyde in the aqueous solution in the flask (**a**) was indicated. In order to effect a partial separation of acetaldehyde and propyl aldehyde, 50 c.c. of the aqueous solution was heated in a flask ($\mathbf{a}_1$) to 45°, and a current of carbon dioxide was passed through the solution to drive off the volatile portion at 45°; it was then caught by means of passing through an ice-cold water in another flask ($\mathbf{a}_2$) which was connected to the flask ($\mathbf{a}_1$) by a delivery tube. The solution remained in the flask ($\mathbf{a}_1$) precipitated, on adding *p*-nitrophenylhydrazine and hydrochloric acid, 0.7 g. of *p*-nitrophenylhydrazone which on recrystallisation from 50% alcohol yielded an impure *p*-nitrophenylhydrazone of propyl aldehyde in orange yellow needles; m.p. 121.5–122° (Found: N, 21.82. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The solution in the flask ($\mathbf{a}_2$) yielded 0.5 g. of *p*-nitrophenylhydrazone which, on fractional crystallisation from 50% alcohol, gave 1st crop with m.p. 116.5–117°, 2nd crop with m.p. 115.5–116° and 3rd crop with m.p. 113–113.5°. The 1st crop was found to consist of a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde by analysis (Found: N, 22.83. Calc. for $C_9H_{11}O_2N_3$: N, 21.76. Calc. for $C_8H_9O_2N_3$: N, 23.46%).

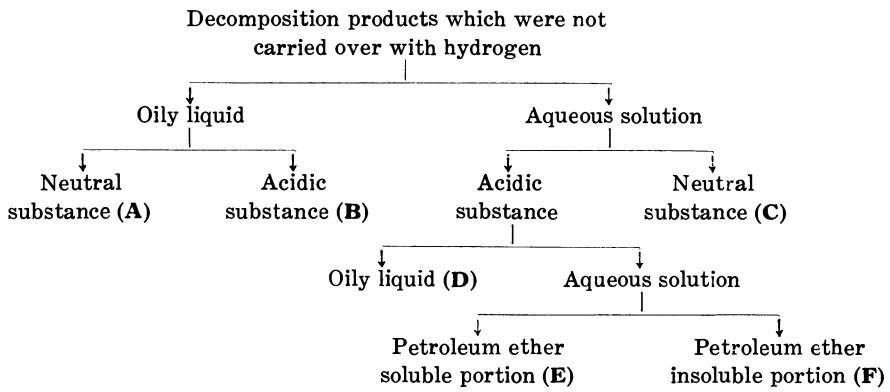
The solution in the flask (**a**) showed also acid reaction. On neutralising this solution (100 c.c.) with barium hydroxide and evaporating to dryness, there remained 0.25 g. of barium salt which was found to be barium acetate by analysis (Found: Ba, 53.30. Calc. for $C_4H_6O_4Ba$: Ba, 53.73%).

The barium hydroxide solution in the flask (**b**) was found to contain precipitate of barium carbonate, which was also formed in a smaller amount in the solution of the flask (**c**). The quantity of carbon dioxide formed by the ozonolysis is calculated from the quantity of the barium carbonate as 2.58 g. or 12.9% of the methyl moroctate used for ozonolysis. The formation of carbon dioxide in such a large amount is explainable on condition that methyl moroctate has the $=CH\cdot CH_2\cdot CH=$ group. The latter on ozonolysis yields malonic acid and its semi-aldehyde which, however, undergo secondary decompositions with the formation of carbon dioxide together with acetaldehyde and acetic acid, and the yield of carbon dioxide is 15.2% of methyl moroctate when the secondary decompositions take place to a quantitative extent. The reason

why the yield of carbon dioxide was not quantitative in this experiment may be attributed to the fact that a part of the primary decomposition products escaped the secondary decomposition and remained unchanged.

(ii) *Decomposition products which were not carried over with hydrogen.* A portion of these products separated under aqueous solution as an oily liquid. This was neutralised with sodium carbonate solution, the resulting solution was extracted with ether, and after distilling off the ether from ethereal solution, there remained a neutral substance (**A**). The neutralised solution, separated from ethereal extracts, was acidified with hydrochloric acid and an acidic substance (**B**) liberated was taken up with ether. The aqueous solution, separated from the oily liquid, was shaken with 2 l. of ether in order to extract the decomposition products thoroughly from the aqueous solution. The ethereal solution was concentrated to about 200 c.c., and then shaken with sodium carbonate solution to remove the acidic substance as sodium salts. The ethereal solution left behind a neutral substance (**C**) on distilling off ether. The carbonate solution containing the sodium salts of acidic substance was acidified, and the acidic substance liberated was taken up with ether. After distilling off the ether, 60 c.c. of water was added to the residue; a portion remained undissolved as an oily liquid (**D**) which was separated by filtration. The aqueous solution which contained dissolved substances was extracted with ether, and the product obtained on distilling off the ether was then treated with petroleum ether in order to effect a separation into petroleum ether soluble portion (**E**) and petroleum ether insoluble portion (**F**). The portions obtained by these separative operations are shown in Table 1.

Table 1.



Neutral substance (**A**). Yield 0.7 g. It had saponif. value 477.4 which is close to the saponif. value 483.4 for methyl ester of succinic semi-aldehyde $C_5H_8O_3$. After saponification it was subjected to oxidation with potassium permanganate in alkaline solution, and the crystalline product obtained on acidification showed, after being washed with a little ether, neutr. value 948.1 (calc. for succinic acid $C_4H_6O_4$: 950.6) and m.p. 180–180.5° which was not lowered when the substance was admixed with a pure specimen of succinic acid, m.p. 182.5–183°.

Acidic substance (**B** and **D** united). Yield 6.3 g., neutr. value 422.9, saponif. value 830.5 Although the neutr. value agrees with the calculated value for methyl hydrogen succinate $C_5H_8O_4$ (neutr. value 424.9; saponif. value 849.7), and the saponif. value is also close to the calculated value for methyl hydrogen succinate, the acidic substance obtained is an oily liquid at the ordinary temperature and it is considered to contain some other compounds besides methyl hydrogen succinate, since the melting point of the latter is recorded as 58° by Bone, Sudborough, and Sprankling.[7] The free acid obtained on saponification followed by acidification yielded, however, a pure succinic acid with neutr. value 948.5 and m.p. 182–183° after being recrystallised from ethyl acetate.

Neutral substance obtained from aqueous solution (**C**). Yield 1.2 g. It consisted of an orange yellow liquid and had saponif. value 380.4. After saponification, it was subjected to the permanganate oxidation in alkaline solution, and the crystalline product obtained on acidification showed neutr. value 940.9 and m.p. 178.5–179° after being washed with a little ether, and it was considered to be an impure succinic acid. Accordingly, this portion seems to contain methyl ester of succinic semi-aldehyde and in addition succinic aldehyde (or its polymerised products).

Petroleum ether soluble portion (**E**). On distilling off the petroleum ether from the solution, the distillate showed acid reaction. The barium salt prepared from the distillate was found to consist mainly of barium acetate by analysis (Found: Ba, 53.01. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The residue (2.7 g.) obtained on distilling off petroleum ether was a reddish orange liquid. On heating in an oil bath, about 1 g. of colourless distillate was obtained between 120–180° (temperature of bath). The distillate was neutralised with sodium hydroxide solution, and silver nitrate solution was added to precipitate silver salts fractionally; those were found to be a mixture of silver acetate and silver propionate by analyses (Found for 1st precipitate: Ag, 60.61. Found for 2nd precipitate: Ag, 62.45. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

Petroleum ether insoluble portion (**F**). Yield 15.4 g. This portion consisted of a reddish orange liquid and a crystalline solid. On oxidation with alkaline permanganate, there was obtained, after acidification, a white crystalline product which yielded succinic acid on recrystallisation from ethyl acetate; neutr. value 948.1, m.p. 182.5–183°. On concentrating the mother liquor, a further quantity of succinic acid separated, and after all the ethyl acetate being driven off, there remained a soft solid. A little water was added to the residue, a small portion of insoluble substance was removed, and the aqueous solution was shaken with ether in order to extract the substance dissolved in aqueous solution. After distilling off the ether from ethereal solution, there remained a crystalline solid (0.8 g., neutr. value 1010, m.p. 124.5–125°), which decomposed on heating at 140–150° with the formation of carbon dioxide, and it was considered to contain malonic acid (neutr. value 1079, m.p. 133°). From these results, the petroleum ether insoluble portion is found to consist principally of succinic acid and its semi-aldehyde though a little malonic acid was contained in addition to these compounds. Whilst the maximum yield of succinic acid is 40.67% if methyl moroctate has only one $=CH\cdot(CH_2)_2\cdot CH=$ group, the yield of petroleum ether insoluble portion obtained in these experiments is 77% of the methyl moroctate

(7) *J. Chem. Soc.*, **85** (1904), 539.

used for ozonolysis. Accordingly, methyl moroctate must have two of the $=CH\cdot(CH_2)_2\cdot CH=$ group.

3. **Ozonolysis of Methyl Tetrathiocyano-moroctate.** Methyl moroctate (5 g.) was dissolved in 50 c.c. of glacial acetic acid, and 350 c.c. of 1/2 N thiocyanogen solution in glacial acetic acid was added. After being allowed to stand for 24 hours, the excess of thiocyanogen was removed by sodium thiosulphate solution. Methyl tetrathiocyano-moroctate was extracted with chloroform, and the chloroform solution was washed with water, dehydrated, and then concentrated to about 50 c.c. A current of ozonised oxygen was passed through the solution cooled with ice-salt until it became saturated. After distilling off chloroform from the solution, the ozonide remained as a reddish orange syrup. The last traces of chloroform could not be driven off owing to the frothing of the residual ozonide. Fifteen g. of methyl moroctate yielded 35 g. of ozonide (probably ozonide peroxide), from which the chloroform was not thoroughly removed. The calculated yield for ozonide peroxide $C_{10}H_{20}O_9(SCN)_4$ is 32.8 g. Water (150 c.c.) was added to the ozonide thus obtained, and the liquid was heated on the water-bath for 30 minutes. During heating, a current of hydrogen was passed through the flask containing the ozonide, and the volatile substance was carried over with hydrogen into another three flasks which were connected in succession, the first (**a**) being filled with 150 c.c. of water, the second (**b**) and the third (**c**) being filled with 400 c.c. of approximately 1/3 N barium hydroxide solution. The decomposition products remained in the initial flask consisted of aqueous solution and insoluble oil which separated under aqueous layer. By these treatments, the decomposition products of ozonide were separated into three portions: (i) volatile substance, (ii) aqueous solution and (iii) oily substance.

(i) *Volatile substance.* The volatile substance collected in three flasks (**a**, **b** and **c**) was examined. In the aqueous solution of the flask (**a**), the presence of acetaldehyde was indicated by a deep blue colouration exhibited on adding diethylamine and sodium nitroprusside. Also the presence of propyl aldehyde was indicated by preparing phenylhydrazone and heating the latter with zinc chloride to 180°, when a smell of scatol was recognised. A partial separation of two aldehydes was attempted by passing carbon dioxide through the solution (50 c.c.) in a flask ($\mathbf{a}_1$) which was kept at 45°, and by collecting the volatilised portion, carried over with carbon dioxide, in another flask ($\mathbf{a}_2$) containing ice-cold water. The solution remained in the initial flask ($\mathbf{a}_1$) yielded 0.6 g. of crystalline *p*-nitrophenylhydrazone which melted at 121–121.5° after recrystallising from 50% alcohol and was considered to be an impure *p*-nitrophenylhydrazone of propyl aldehyde (Found: N, 21.94. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The aqueous solution in the flask ($\mathbf{a}_2$) yielded 0.5 g. of *p*-nitrophenylhydrazone which melted at 115.5–116° after recrystallising from 50% alcohol and was considered to be a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde (Found: N, 22.73. Calc. for $C_8H_9O_2N_3$: N, 23.46. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The aqueous solution in the flask (**a**) contained also acetic acid which was identified by preparing the barium salt (Found: Ba, 53.51. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%).

The barium hydroxide solution in the flask (**b**) was found to contain a precipitate of barium carbonate which was also precipitated in the solution of the flask (**c**) in a smaller amount. The quantity of carbon dioxide formed by the ozonolysis is

calculated from the quantity of the precipitate of barium carbonate as 12.1% of the methyl moroctate used in these experiments.

(ii) *Aqueous solution.* The decomposition products dissolved in water were extracted with 2 l. of ether. On removal of ether from the ethereal solution, the residue was treated with petroleum ether in order to separate it into petroleum ether soluble portion and petroleum ether insoluble portion. The petroleum ether which was driven off from the solution had the odour of acetic acid. The barium salt prepared from the petroleum ether distillate was found to consist mainly of barium acetate by analysis (Found: Ba, 53.42. Calc. for $C_4H_6O_4Ba$: Ba, 53.79%). The residue (1.8 g.) obtained after distilling off petroleum ether was heated in an oil bath, and there was obtained about 0.5 g. of a colourless liquid distilling below 136°. The silver salts fractionally precipitated from the distillate were found to be a mixture of the silver salts of acetic and propionic acids (Found for 1st precipitate: Ag, 60.48. Found for 2nd precipitate: Ag, 62.58. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

The petroleum ether insoluble portion consisted of a soft solid (0.8 g.). On adding a little water, a portion remained insoluble and was removed, and the aqueous solution was extracted with ether. After distilling off the ether from ethereal solution, there remained a crystalline solid (0.3 g., neutr. value 1020, m.p. 125–126°), which decomposed at about 140° forming carbon dioxide and was considered to consist mainly of malonic acid.

(iii) *Oily substance.* Yield 21 g. For the elimination of thiocyano-groups, 30 c.c. of alcohol and 20 g. of zinc powder were added to the oily substance, the mixture gently refluxed, and 30 c.c. of 5 N alcoholic solution of hydrogen chloride gradually added. The product was extracted with ether, and after distilling off ether from ethereal solution, the residue was saponified and the resulting soap solution was shaken with ether in order to remove the unsaponifiable portion. On acidification of soap solution, a reddish orange oil was obtained. This was converted into methyl ester and the latter was fractionated, yielding a fraction boiling at 170–180°/10 mm., from which a free acid consisting of decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid) was liberated in the usual way (Found: C, 63.57; H, 8.13. Calc. for $C_{12}H_{18}O_4$: C, 63.68; H, 8.02%). It had d_4^{20} 0.9989, n_D^{20} 1.4535, mol. refr. 61.25 (calc. for $C_{12}H_{18}O_4$[=]: 59.76), neutr. value 495.0 (calc. 496.2), iodine value by the Rosenmund-Kuhnhenn method 220.1 (calc. 224.5). On hydrogenation it yielded decane-1,10-dicarboxylic acid after recrystallising from 50% alcohol; neutr. value 484.8 (calc. for $C_{12}H_{22}O_4$: 487.5), m.p. 124.5–125°. Nördlinger[8] gives m.p. 124.5–125.5°; Chuit[9] gives m.p. 127.5–128°.

Summary.

Moroctic acid $C_{18}H_{28}O_2$ has been isolated from a large quantity of Japanese sardine oil. For the determination of its constitution, methyl moroctate was subjected to ozonolysis. Among the products of ozonolysis, propionic acid, propyl aldehyde, succinic acid, succinic semi-aldehyde,

(8) *Ber.*, **23** (1890), 2356.

(9) *Helvetica Chim. Acta*, **9** (1926), 264.

methyl hydrogen succinate, methyl ester of succinic semi-aldehyde, carbon dioxide, acetic acid and acetaldehyde were found. Three last named compounds are considered to be formed by the secondary decomposition of malonic acid and the corresponding aldehyde which are derived from the $=CH\cdot CH_2\cdot CH=$ group. The presence of malonic acid, though in a small quantity, in the products of ozonolysis was also indicated. In the next place, tetrathiocyano-derivative was prepared from methyl moroctate, and it was subjected to ozonolysis. Among the products of ozonolysis, propionic acid, propyl aldehyde, carbon dioxide, acetic acid, acetaldehyde and an oily thiocyano-compound were recognised. The oily thiocyano-compound yielded, on elimination of thiocyanogen followed by hydrolysis, a decadiene-dicarboxylic acid ($\Delta^{3:4,\ 7:8}$-decadiene-1,10-dicarboxylic acid). Hence, the constitution of moroctic acid is established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid which is expressed by the following formula.

$$CH_3\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot (CH_2)_2\cdot CH=CH\cdot (CH_2)_2\cdot CH=CH\cdot (CH_2)_2\cdot COOH$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. IV. THE SEPARATION OF HIGHLY UNSATURATED C_{20}-ACIDS.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received March 25th, 1935. Published June 28th, 1935.

In previous reports[1] of this series, the highly unsaturated C_{16}- and C_{18}-acids of sardine oil were studied with the results that two individual components, hiragonic acid $C_{16}H_{26}O_2$ and moroctic acid $C_{18}H_{28}O_2$, were isolated and their constitutions were established as follows:

(1) This Bulletin, **4** (1929), 83; *ibid.*, **10** (1935), 192, 232.

Hiragonic acid: $CH_3{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_4{\cdot}COOH$

Moroctic acid: $CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}CH{=}CH{\cdot}(CH_2)_2{\cdot}COOH$

The present paper deals with the highly unsaturated C_{20}-acids in sardine oil. The occurrence of highly unsaturated C_{20}-acids, such as $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$, in sardine oil has already been reported by several authors, among whom Majima and Okada,[2] Tsujimoto,[3] and Brown and Beal[4] may be mentioned. Furthermore, such highly unsaturated C_{20}-acids have been found to occur also in various kinds of marine animal oils besides the sardine oil. Thus, we[5] found the acids $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$ in several kinds of whale oils (oils obtained from the whales belonging to *Mysticete*), in cod liver oil, in sperm body oil, in several kinds of liver oils from *Elasmobranch* fish, and also in pilot-whale head and body oils. Tsujimoto and his coworkers[6] reported the presence of highly unsaturated C_{20}-acids in giebel oil, herring roe oil, eel oil, the liver oil from *Chionecetes phalangium*, cod liver oil, the oil from *Atheresthes evermanni*, halibut liver oil, and in the liver oil from *Paralithodes camtschatica*. According to Ueno and Iwai,[7] menuke oil and the liver oil from *Scoliodon laticaudes* contain a highly unsaturated acid $C_{20}H_{32}O_2$. Suzuki and his coworkers,[8] examining the glycerides of marine animal oils, stated the occurrence of an acid $C_{20}H_{32}O_2$ as glycerides in whale oil, cod liver oil, herring oil, sardine oil, sand eel oil, cuttle-fish oil, red salmon oil, shark oil and in the liver oil from *Theragra chalcogramma*. A glyceride containing an acid component $C_{20}H_{30}O_2$ was stated by I. Okada[9] to occur in tunny oil, whereas an acid $C_{20}H_{32}O_2$ was considered by Tomiyama[10] to occur in tunny liver oil. Bull[11] stated the occurrence of the acids $C_{20}H_{30}O_2$ and $C_{20}H_{28}O_2$ in cod

(2) *J. Tokyo Chem. Soc.*, **35** (1914), 13.

(3) *J. Soc. Chem. Ind. Japan*, **26** (1923), 1013.

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

(5) Toyama, *J. Soc. Chem. Ind. Japan*, **28** (1925), 95, 104; *ibid.*, **29** (1926), 531, 538, 624; *ibid.*, **30** (1927), 519; Toyama and Tsuchiya, *ibid.*, **30** (1927), 63, 116, 207; Toyama, *Report of the Tokyo Imperial Industrial Research Laboratory*, **27** (1932), No. 2.

(6) Tsujimoto, *Report of the Tokyo Imperial Industrial Research Laboratory*, **18** (1923), No. 2; Tsujimoto and Koyanagi, *ibid.*, **25** (1930), No. 4; Tsujimoto, *ibid.*, **26** (1931), No. 10; *ibid.*, **27** (1932), No. 15; Tsujimoto and Kimura, *J. Soc. Chem. Ind. Japan*, **26** (1923), 1162; Tsujimoto, *ibid.*, **30** (1927), 402; *ibid.*, **31** (1928), 136, 1191.

(7) *J. Soc. Chem. Ind. Japan*, **37** (1934), 121, 562.

(8) *Proc. Imp. Acad. Japan*, **5** (1929), 265, 269.

(9) *Journal of the Imperial Fisheries Institute*, **28** (1932), 105.

(10) *Bulletin of the Japanese Society of Scientific Fisheries*, **2** (1933), No. 1.

(11) *Tidskrift Kemi Farm. Terapi*, **14** (1917), 11.

liver oil. Brown and Beal[12] indicated the presence of two highly unsaturated C_{20}-acids, $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$, in menhaden, cod liver, herring and salmon oils besides sardine oil. It is seen from the foregoing notes that the highly unsaturated C_{20}-acids, such as $C_{20}H_{32}O_2$ and $C_{20}H_{30}O_2$, occur widely in various kinds of marine animal oils, including sardine oil, but no individual acid has hitherto been isolated with certainty, and little has been known regarding the properties of these acids.

The above is a review of the most important works in literature on highly unsaturated C_{20}-acids in sardine and other marine animal oils. A survey of the literature shows that the highly unsaturated C_{20}-acids have also been found to occur in terrestrial animal oils. Thus Hartley[13] found an acid $C_{20}H_{32}O_2$ in the liver fats of pig and ox, which was termed afterward arachidonic acid by Lewkowitsch.[14] The presence of arachidonic acid in the fats from the organs of domestic animals has frequently been reported since then, but it appears not to have been isolated in a state of purity.

In the experiments described below, the highly unsaturated C_{20}-acids have been separated from sardine oil, and on a further separation into individual components, an eicosatetraenoic acid $C_{20}H_{32}O_2$ has been isolated in fairly pure state, and also a concentrated fraction of eicosapentenoic acid $C_{20}H_{30}O_2$ has been separated. Although the eicosatetraenoic acid in marine animal oils is described as arachidonic acid by some authors, it should not be assumed without experimental evidence that both acids are identical. In order to decide whether the eicosatetraenoic acid isolated from sardine oil, the constitution of which will be reported in a succeeding paper, is identical with arachidonic acid or not, it is necessary to gain a fuller information concerning arachidonic acid.

Experimental.

1. **Separation of Highly Unsaturated C_{20}-Acids.** As described in the second report,[15] 60 kg. of the ethyl esters, prepared by the ethanolysis of sardine oil, were subjected to distillation, and there was obtained 27 kg. of a fraction boiling over 215°/10 mm. Fifteen kg. of this fraction was used for this experiment. It was first

(12) *Loc. cit.*, (4).

(13) *J. Physiol.*, **38** (1909), 353.

(14) "Chemical Technology and Analysis of Oils, Fats and Waxes", 6th Edition, Vol. I, p. 215.

(15) This Bulletin, **10** (1935), 192.

treated by sodium-soap-acetone method,[16] and crude highly unsaturated acids having neutralisation value 179.3 and iodine value[17] 327.6 were obtained from the acetone-soluble sodium soaps. These were converted into methyl esters, and 8 kg. of the latter were subjected to fractional distillation with the results shown in Table 1.

During the distillation of the fraction (7), the temperature of bath was raised to about 260°, the pressure was reduced to 5 mm., and the distillation was continued till the rate of distillation became very slow. The large yield of the residue is probably caused by a partial polymerisation of methyl esters having high boiling point.

Table 1.

Fraction	B.p./10 mm.	Yield (g.)	n_D^{20}	Saponif. value	Iodine value
(1)	Below 210°	750	1.4700	189.0	245.7
(2)	210–215°	650	1.4766	181.4	275.8
(3)	215–220°	1020	1.4800	177.8	300.4
(4)	220–222°	900	1.4852	175.3	315.2
(5)	222–225°	850	1.4872	173.0	328.7
(6)	225–230°	600	1.4891	170.9	334.3
(7)	Over 230°	2050	1.4930	163.0	353.2
Residue and loss	—	1180	—	—	—

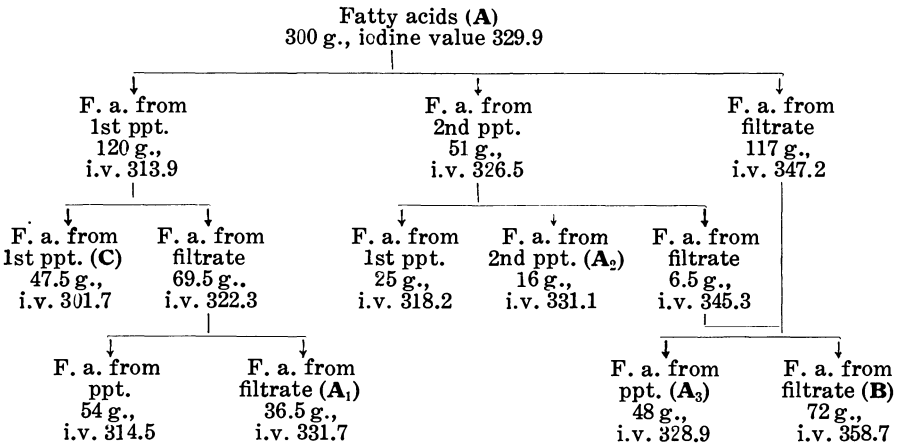
The fractions (3) and (4) were subjected to a further fractionation, and there was obtained a fraction boiling at 217–221°/10 mm.; saponif. value 177.0 and iodine value 303.0. Since this fraction was considered to contain a little of less unsaturated methyl esters, it was again treated by sodium-soap-acetone method, by which a small amount of acetone-insoluble sodium soaps was formed. The fatty acids liberated from acetone-soluble sodium soaps were then reconverted into methyl esters, and the latter were repeatedly fractionated to give 580 g. of a fraction boiling at 217–221°/10 mm.; saponif. value 177.0 and iodine value 316.0. The free fatty acids (**A**) obtained from this methyl ester fraction showed neutralisation value 185.0 and iodine value 329.9, and yielded 101% of ether insoluble bromides which had Br-content 69.41%. Hydrogenation yielded arachidic acid which had neutr. value 178.9 (calc. for $C_{20}H_{40}O_2$: 179.6) and m.p. 74–74.5° after recrystallisation from 95% alcohol. The melting point was not lowered when the substance was admixed with an authentic specimen of arachidic acid which was prepared from erucic acid by fusion with caustic potash and had m.p. 74.5–75°. Accordingly, the fatty acids (**A**) are proved to consist essentially of highly unsaturated C_{20}-acids. It is true that their iodine value is close to the calculated value (337.7) for the acid $C_{20}H_{32}O_2$, but they are found by the separative methods described below to contain other acids of different degrees of unsaturation in addition to the acid $C_{20}H_{32}O_2$.

(16) Toyama and Tsuchiya, *Chemische Umschau Fette, Oele, Wachse und Harze*, **32** (1925), 204; *ibid.*, **34** (1927), 51; also *J. Soc. Chem. Ind. Japan*, **28** (1925), 653, 962.

(17) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

2. **Fractional Precipitation of Sodium Soaps in Acetone.** The fatty acids (**A**) obtained above were fractionally precipitated from an acetone solution as their sodium soaps, and were separated into the portions of different degrees of unsaturation. The separative operation was carried out in the following manner: 50 g. of the fatty acids (A) were dissolved in 1 l. of acetone, and a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 50 c.c. of water and 100 c.c. of 95% alcohol was added to effect a partial neutralisation of the fatty acids, by which there was formed a precipitate of sodium soaps. After the precipitated sodium soaps were once brought into solution by a gentle boiling of the solution under a reflux condenser, the solution was allowed to cool to reprecipitate the sodium soaps which were then filtered. The filtrate was again neutralised partially by adding a portion of the sodium hydroxide solution, and after being treated as before, the precipitate of sodium soaps was filtered. Each precipitate of sodium soaps (1st and 2nd precipitates) was decomposed with hydrochloric acid to liberate the fatty acids. The remaining fatty acids in the filtrate were recovered by removing the solvent followed by acidification. The fatty acids (**A**) were thus separated into three portions, and each portion was subjected to a further separation by a similar operation as before. In these experiments, 300 g. of the fatty acids (**A**) were used instead of all the quantity of the fatty acids (**A**) obtained by the foregoing procedure. The results are given in Table 2.

Table 2.

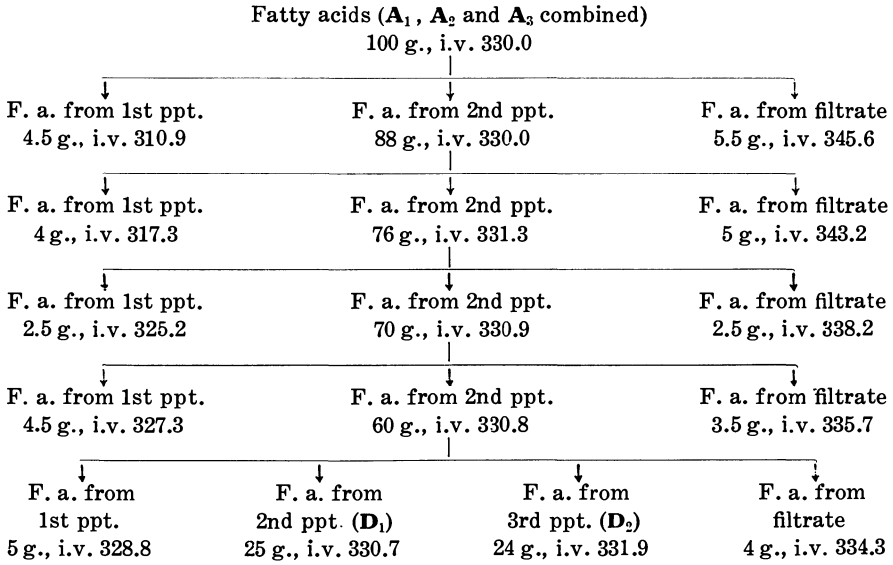


From their iodine values, the fatty acids fractions (A_1), (A_2) and (A_3) are considered to consist essentially of an acid $C_{20}H_{32}O_2$; the fraction (**B**) contains a more highly unsaturated acid $C_{20}H_{30}O_2$ in addition to the acid $C_{20}H_{32}O_2$, while the fraction (**C**) contains less unsaturated acids besides the acid $C_{20}H_{32}O_2$.

3. **Isolation of Eicosatetraenoic Acid $C_{20}H_{32}O_2$.** In order to isolate the eicosatetraenoic acid $C_{20}H_{32}O_2$ from the fatty acids fractions (A_1), (A_2) and (A_3), 100 g. of the combined fractions (iodine value 330.0) were dissolved in 2.5 l. of acetone, and a small portion of the sodium hydroxide solution prepared by dissolving 50 g.

of sodium hydroxide in 50 c.c. of water and 100 c.c. of 95% alcohol was added, by which a small amount of the precipitate (1st precipitate) of sodium soaps was formed. This was filtered, and the filtrate was then neutralised completely with the same solution of sodium hydroxide. The precipitated sodium soaps (2nd precipitate) were filtered, and the fatty acids liberated on acidification were again subjected to fractional precipitation of sodium soaps in acetone as before. These separative operations were repeated till the results shown in Table 3 were obtained. In the final fractionation, the fatty acids were separated into four portions.

Table 3.



The fatty acids fractions obtained by the final fractionation in Table 3 showed the iodine values which were close to each other. The fractions (D_1) and (D_2) were converted into methyl esters, and the latter were subjected to a repeated fractional distillation which yielded a fraction boiling at 217–220°/10 mm. as methyl eicosatetraenoate. It had the following constants: d_4^{15} 0.9140, d_4^{20} 0.9106, n_D^{15} 1.4854, n_D^{20} 1.4834, mol. refr. 99.87 (calc. for $C_{21}H_{34}O_2$: 98.96), saponif. value 176.0 (calc. 176.3), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 321.2 and 309.5 respectively (calc. 319.0), thiocyanogen value 160.5 (calc. for the formation of tetrathiocyanate: 159.5). Bromination in ethereal solution yielded 103% of ether insoluble bromide (Found: Br, 67.02. Calc. for $C_{21}H_{34}O_2Br_8$: Br, 66.76%).

The eicosatetraenoic acid liberated from the methyl ester in the usual way showed the following constants: d_4^{15} 0.9300, d_4^{20} 0.9263, n_D^{15} 1.4935, n_D^{20} 1.4915, mol. refr. 95.16 (calc. for $C_{20}H_{32}O_2$: 94.23), neutralisation value 184.3 (calc. 184.4), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 334.0 and 323.1 respectively (calc. 333.7), thiocyanogen value 167.1 (calc. for the formation of tetrathiocyanate: 166.9). Bromination in ethereal solution yielded 103% of ether insoluble

bromide which turned black at about 240° without melting (Found: Br, 68.06. Calc. for $C_{20}H_{32}O_2$: Br, 67.76%).

4. **Separation of a Concentrated Fraction of Eicosapentenoic Acid $C_{20}H_{30}O_2$.** Seventy g. of the fatty acid fraction (**B**) recorded in Table 2 was dissolved in 1.8 l. of acetone, and a small quantity of the same solution of sodium hydroxide as used in the preceding separative operation was added in order to precipitate the less unsaturated fatty acids as their sodium soaps, which were filtered. The more highly unsaturated fatty acids recovered from the filtrate were again treated with the sodium hydroxide solution as before, the less unsaturated portion was removed as insoluble sodium soaps, and after several repetitions of these separative operations, there was obtained 8 g. of a fatty acid fraction from the final filtrate which had the following constants: d_4^{15} 0.9399, n_D^{15} 1.5019, neutr. value 185.1, iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 392.7 and 378.4 respectively, thiocyanogen value 167.9 (calc. for $C_{20}H_{30}O_2$: neutr. value 185.6, iodine value 419.9, thiocyanogen value calc. for the formation of tetrathiocyanate 168.0). Bromination in ethereal solution yielded 104% of ether insoluble bromide which turned black at about 240° without melting (Found: Br, 71.28. Calc. for $C_{20}H_{30}O_2Br_{10}$: Br, 72.56%). As the iodine value of this fraction is still considerably lower than the value calculated for $C_{20}H_{30}O_2$, it must contain an appreciable amount of $C_{20}H_{32}O_2$ in addition to $C_{20}H_{30}O_2$. Although the acid $C_{20}H_{30}O_2$ could not be isolated in pure state, its existence in sardine oil is thus proved by the present experiments.

5. **Examination of the Less Unsaturated Portion.** Forty-seven g. of the fatty acid fraction (**C**) recorded in Table 2 was dissolved in 1 l. of acetone and was partially neutralised by adding a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 100 c.c. of water and 200 c.c. of 95% alcohol. The solution was refluxed until all the insoluble sodium soaps formed once disappeared, and then it was allowed to cool to reprecipitate the insoluble sodium soaps. By these treatments, the following two portions were separated.

	Yield (g.)	Neutr. value	Iodine value
(i) Fatty acids from insoluble sodium soaps	17	186.0	276.6
(ii) Fatty acids from the filtrate	29	185.0	315.9

The iodine value of the fatty acids (i) was more close to the calculated value for $C_{20}H_{34}O_2$ (248.6) than that for $C_{20}H_{32}O_2$ (333.7), but they yielded 71% of an ether insoluble bromide having Br-content 67.06% which was considerably higher than the Br-content of $C_{20}H_{34}O_2Br_6$ (61.02%) and was close to the Br-content of $C_{20}H_{32}O_2Br_8$ (67.76%). On the other hand, when the lithium soaps prepared from the fatty acids (i) were treated with 50% alcohol, there was obtained a small amount of the lithium soaps insoluble in 50% alcohol, and the latter yielded on acidification fatty acids with an iodine value 91.3 which indicated that the fatty acids (i) contained also a small amount of less unsaturated fatty acids such as $C_{20}H_{38}O_2$ (iodine value 81.8). Accordingly, the fatty acids (i) were found to be a mixture of the fatty acids of different degrees of unsaturation, and though the presence of $C_{20}H_{34}O_2$ was not proved with certainty, it was most probable.

Summary.

Highly unsaturated C_{20}-acids have been separated from sardine oil and they were further separated into the portions of different degrees of unsaturation with the results that an eicosatetraenoic acid $C_{20}H_{32}O_2$ was isolated and also the presence of an eicosapentenoic acid $C_{20}H_{30}O_2$ was proved by separating a fraction, in which this acid is concentrated.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

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

By Tetsuya ISHIKAWA.

Received March 25th, 1935. Published June 28th, 1935.

The nature of the solutional viscosity of solids in liquids. In the latest publication,[1] we have laid stress on the solutional viscosity in accordance with the Ishikawa's theory for elucidating the viscosity of aqueous solutions of electrolytes, and evaluated those values of a few strong electrolytes.

Table 1.

Substance	Solutional viscosity at t°C.	t°C.
Naphthalene	0.02653	25
Diphenyl	0.05413	25
KCl	0.01003	18
	0.00874	25
KI	0.00735	18
	0.00664	25
$RbNO_3$	0.00889	18
	0.00789	25
$CsNO_3$	0.00842	18
	0.00753	25

Since his formula for binary mixtures, the component viscosities of which being alike treated, has the validity for the solution of solids in liquids, one may arrive at the supposition that the solutional viscosity of a solid calculated by it touches a fundamental nature of the molecular constitution, and must have, in con-

(1) T. Ishikawa and T. Baba, this Bulletin, **10** (1935), 153.

sequence, an intimate relationship with the viscosity of its molten state.

The equations expressing the viscosity variation of liquids with temperature have been proposed numerously. Among them the one proposed by Raman[2] and developed by Andrade[3] and his follower[4] is simple but sufficient within the limit of experimental error:

$$\log \eta = \alpha + \frac{\beta}{T} \quad \cdots\cdots\cdots\cdots\cdots \quad (1)$$

in which η denotes the viscosity, T the absolute temperature, α and β constants. The equation also proved to be valid for molten salts such as $NaNO_3$, KNO_3, and $PbBr_2$, but failed for some salts such as $PbCl_2$, for which, however, a slightly modified formula which was also proposed by Andrade was shown to be applicable:

$$\log \eta = \alpha + \frac{\beta}{T-\theta} \quad \cdots\cdots\cdots\cdots\cdots \quad (2)$$

where θ is a constant.

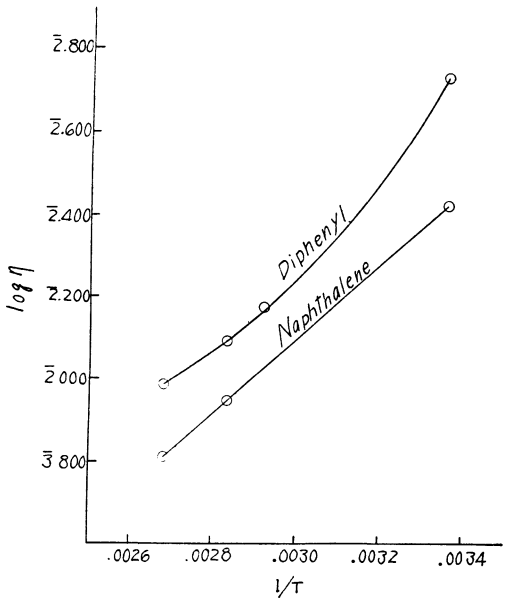


Table 2.

Naphthalene. Melting point: 80.1°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
25	0.02653	$\bar{2}.4237$	0.00336	0.02656
80	0.00886	$\bar{3}.9474$	0.00283	0.00886
100	0.00649	$\bar{3}.8125$	0.00268	0.00649

$$\log \eta_T = -4.8986 + 899.7\frac{1}{T}$$

Table 3.

Diphenyl. Melting point: 70.5°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
25	0.05413	$\bar{2}.7334$	0.00336	0.05413
70	0.01488	$\bar{2}.1727$	0.00292	0.01454
80	0.01243	$\bar{2}.0944$	0.00283	0.01243
100	0.00971	$\bar{3}.9872$	0.00268	0.00971

$$\log \eta_T = -2.6512 + \frac{88.85}{T-233.84}$$

(2) C. V. Raman, *Nature*, **111** (1923), 532.
(3) E. N. Da C. Andrade, *Nature*, **125** (1930), 309.
(4) B. Prasad, *Phil. Mag.*, **16** (1933), 263.

Fortunately the viscosity measurements of molten naphthalene at different temperatures were done by Kurnakow[5] and by Scheuer,[6] from their data the values at regular intervals of temperature being recalculated by Bingham and Spooner,[7] and those of diphenyl by these authors.[7] Taking logarithms of the viscosities against $1/T$ of each substance, we find that in the former case the points with our value at 25°C. strictly lie on a straight line, and in the latter case on a curve on which our value at 25°C. also lies as seen from the figure. Tables 2 and 3 show how the calculated values by the formulae and the observed compare numerically.

As to the viscosity of molten inorganic salts, there have been known, except the salts above cited, the measurements by Lorenz[8] on KCl, KBr, NaCl, and NaBr. Among them KCl only is available for the present purpose. So that, in the following we will consider the solutional viscosity of KCl. For the viscosity of the molten KCl, formula (1) is valid:

$$\log \eta_T = -3.4530 + 1705\frac{1}{T},$$

and the calculated values are in good agreement with the observed as readily seen from Table 4.

Table 4.

Potassium chloride. Melting point: 768°C.

t°C.	$\eta_{obs.}$	$\log \eta$	$1/T$	$\eta_{calc.}$
790	0.0142	$\bar{2}.1523$	0.000941	0.0142
835	0.0121	$\bar{2}.0828$	0.000907	0.0124
920	0.0099	$\bar{3}.9956$	0.000838	0.0095
1035	0.0071	$\bar{3}.8513$	0.000765	0.0071

By the use of the equation, the extrapolated values at 25° and 18°C. are estimated thus:

$$\eta_{25} = 1.89 \times 10^2 \quad \text{and} \quad \eta_{18} = 2.55 \times 10^2,$$

respectively. These show too much higher values than would be expected from the consideration just made on organic non-electrolytes. And if we take the ratios at respective temperatures, they are respectively

$$\text{ratio at } 25° = 2.16 \times 10^4 \quad \text{and} \quad \text{ratio at } 18° = 2.53 \times 10^4.$$

The recent conception on the physics of solids[9] shall be introduced here.

---

(5) N. S. Kurnakow, *Z anorg. allg. Chem.*, **135** (1924), 84, 89.
(6) O. Scheuer, *Z. physik. Chem.*, **72** (1910), 553.
(7) E. C. Bingham and L. W. Spooner, *Physics*, **4** (1933), 393, 394.
(8) R. Lorenz, *Z. physik. Chem.*, **79** (1912), 65.
(9) "Handbuch der Physik", XXIV (Berlin, 1933), 803; F. Zwicky, *Rev. Mod. Physics*, **6** (1934), 193; A. Goetz, *Phys. Rev.*, **45** (1934), 138.

The existence of a crystalline state attributes mainly to the cooperative actions between many elementary particles such as atoms, ions, etc. These interactions extend over distances which are enormously greater than usual action radii of elementary particles, and the cooperative actions, in general, necessitate the introduction of a secondary structure of crystals, or without such conception real crystals which display structure sensitive properties such as the elastic limit, the breaking strength, the thermal and the electrical conductivity, etc. cannot satisfactorily be described by the theory of ideal lattices. By this theory the energetic aspects of the ideal states are already roughly realized in a statistical manner in the melt. It follows that the heat of fusion of the crystal is roughly the same as the gain in energy by a variation leading from the ideal state to the secondary structure, and that an aggregation of groups of approximately equal size which is essential for the formation of a solid crystal takes place during an interval of temperature of a few degrees above the melting point, and that if their formation is prevented, undercooling results down to a temperature at which the group formation is more probable. As regards the dimension of the secondary structure, the theory tells us that a secondary structure superposes on top of the ordinary primary structure, showing perfect regularity also, or in other words the surface density of the plane of it is the same as the planes of free ionic lattices, and its dimension is for most of the crystals found in the region between 100 and 10000 Å, e.g. the plane of a secondary structure of NaCl is divided into 35 primary lattice spacings of cubic block of equal size or in a block of a secondary structure there are 2×10^4 ionic pairs in round number.

Now, the extrapolation of the Raman-Andrade formula far below the melting point as above treated simply means a supposed continuation of the molten state as in like manner as above the melting point, indifferent to the actual phenomenon whether or not the formation of the secondary structure occurs. But, so far as the formula is valid at or about the melting point, its employment far below the melting point should be based on the assumption that although the secondary structure already forms yet the solidification does not appear even at that temperature. This assumption is allowable also from the viscosity theory of simple liquids recently developed by Andrade,[10] who assumes that when a solid is melted it still retains in the liquid form sufficient of its crystalline character for the atoms or the molecules to possess a frequency of atomic or molecular vibration which is practically the same as that of the solid

(10) E. N. Da C. Andrade, *Nature*, **128** (1931), 835; *Phil. Mag.*, **17** (1934), 497.

form at the melting point, and derives a theoretical equation $\eta = \frac{4}{3}\frac{m\nu}{\sigma}$, m being the mass of an atom or a molecule, σ the average distance between the centers of atoms or molecules, and ν the frequency of vibration nearly concordant with the Lindemann formula.[11] Thus, for KCl ν(obs.) $= 4.74 \times 10^{12}$, $m = \frac{74.56}{6.06 \times 10^{23}}$, $\sigma = \left(\frac{74.56}{1.97 \times 6.06 \times 10^{23}}\right)^{1/3}$ and, therefore, the calculated viscosity at the melting point $\eta = 0.0196$, which gives a fair agreement with the extrapolated value 0.0153 from the exponential formula now in question.

From the above considerations together with the fact that the crystal structure of KCl is quite similar to that of NaCl, the ratios above obtained 2.16×10^4 and 2.53×10^4 at 25° and 18°C. respectively may undoubtedly correspond to the number of ionic pairs in a block of the secondary structure, taking for granted that the solutional viscosity of this salt is the viscosity due to its ionic pair.

Hence the following conclusion may be drawn: The solutional viscosity derived from the Ishikawa formula is the viscosity due to the block of a secondary structure in accordance with the secondary structure theory on crystals when the substance is an organic non-electrolyte, or is the viscosity due to the ionic pair when the substance is an ionic salt.

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

(11) F. A. Lindemann, *Physik. Z.*, **11** (1910), 609.

ÜBER (+)- UND (−)-BIS-1,1′-β-TETRAHYDRO-DESOXY-CODEIN.[1]

Von **Kakuji GOTO** und **Hideo SHISHIDO.**

Eingegangen am 2. April, 1935. Ausgegeben am 28. Juni, 1935.

In der XXXIX. Mitteilung[2] haben wir berichtet, dass (+)- bzw. (−)-Dihydro-thebainon mittels $AgNO_3$ ins (+)- bzw. (−)-Bis-1,1′-dihydro-thebainon verknüpft werden kann. Nun wurde dieser Versuch auf

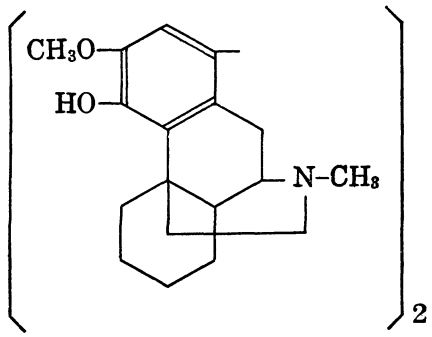
(1) XLI. Mitteilung über Sinomenin.
(2) *Ann.*, **511** (1934), 207.

Demethoxy-desoxo-dihydro-sinomenin ((+)-β-Tetrahydro-desoxy-codein) und (−)-β-Tetrahydro-desoxy-codein ausgedehnt und die entstandenen bimolekularen Basen wurden wohl racemisiert.

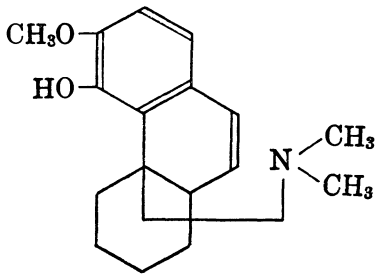
Betreffs des Hofmannschen Abbaues dieser Bis-1,1′-Base, gewinnt man bisher nur die Des-N-methyl-base und die N-freie Substanz, deren Analyse nicht genau mit der berechneten Wert übereinstimmt. So haben wir zurzeit verzichtet diesen Abbau weiter zu verfolgen.

Über den Hofmannschen Abbau von dem monomolekularen Demethoxy-desoxo-dihydrosinomenin haben wir schon früher berichtet.[3] Derselbe Abbau von β-Tetrahydro-desoxy-codein wurde hierbei unternommen und die betreffenden Zwischenprodukten aus Sinomenin und Thebain wurden racemisiert.

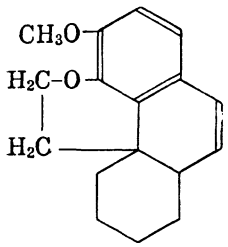
Das racemische Thebenan, aber, leider krystallisiert nicht in der gewöhnlichen Bedingungen des Laboratoriums.



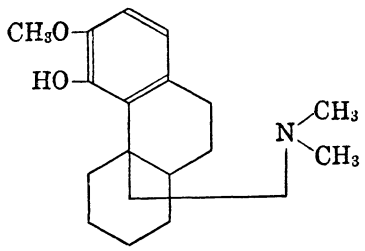
I



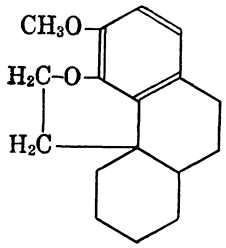
II



III



IV



V

Versuche.

Bis-1, 1′-demethoxy-desoxo-dihydrosinomenin (I). Demethoxy-desoxo-dihydro-sinomenin (1 g.) wurde in 10 c.c. Methanol gelöst und in 50 c.c. Wasser unter

Umrührung eingegossen. Zu dieser Aufschwemmung wurde 0.5 g. $AgNO_3$, gelöst in 50 c.c. Wasser, zugegeben. Nach halber Stunde wurde das Reaktionsgemisch mit NaCl von Silberion befreit. Das Filtrat wurde mit Na_2CO_3 stark alkalisiert und mit Chloroform geschüttelt. Der Chloroform-Rückstand ergab, beim Umkrystallisieren aus Benzol, feine Prismen, welche nach nochmaliger Umkrystallisation bei 230–237° schmolzen. Ausbeute 0.6 g. Es zeigt die Diazo-reaktion nur bis auf 10^4-fache Verdünnung. (Gef.: C, 75.64; H, 8.22; N, 4.87; M. Gew. (Kampfer), 559; Ber. für $C_{36}H_{48}O_4N_2$ (572): C, 75.52; H, 8.39; N, 4.90%; M. Gew., 572. Spez. Drehung (0.1365 g. Subst. in 10 c.c. Äthanol): $[\alpha]_D^{20°} = +91.57°$.)

Jodmethylat. Bereitet durch Vereinigen beider Komponenten in Methanol. Aus Wasser umkrystallisiert, stellt es schöne, oktaedrische Prismen. Schmp. 275–279° (u. Zers.). (Gef.: I, 29.65. Ber. für $C_{38}H_{54}O_4N_2I_2$(856): I, 29.67%.)

Chlorhydrat. Krystallisiert aus 10-proz. Salzsäure. Auch umkrystallisierbar aus Wasser. Schmp. 293–297° (u. Zers.) (Gef.: Cl, 10.72. Ber. für $C_{36}H_{48}N_2O_4 \cdot 2HCl$: Cl, 11.01%.)

Bis-1, 1′-β-tetrahydro-desoxy-codein (I). Darstellung wie bei der (+)-Substanz. Ausbeute 0.2 g. aus 0.55 g. monomolekularer Substanz. Lange Prismen aus Benzol. Schmp. 230–238°. Diazoreaktion ebenso schwach wie bei (+)-Substanz. (Gef.: C, 75.40; H, 8.23; N, 4.79; M. Gew. (Kampfer), 569. Ber. für $C_{36}H_{48}O_4N_2$(572): C, 75.52; H, 8.39; N, 4.90%; M. Gew. 572. Spez. Drehung (0.0876 g. Subst. in 10 c.c. Äthanol): $[\alpha]_D^{20°} = -91.32°$. *Jodmethylat.* Dargestellt wie bei (+)-Substanz. Schmp. 276–279°. (Gef.: I, 29.50. Ber. für $C_{38}H_{54}O_4N_2I_2$(856): I, 29.67%.)

***d, l*-Bis-1, 1′-β-tetrahydro-desoxy-codein.** Je 50 mg. (+)- und (−)-Substanz wurden in Benzollösung vereinigt. Beim Verdünsten des Benzols krystallisierte die racemische Substanz in langen Prismen. Ausbeute 60 mg. Schmp. 255–260°. Kein Drehungsvermögen (0.0545 g. Subst. in 10 c.c. Äthanol und in 1 dm. Rohr, $\alpha = 0$).

Des-N-methyl-β-tetrahydro-desoxy-codein (II). Bereitet wie bei Des-N-methyl-demethoxy-desoxo-dihydro-sinomenin[3]. Schmp. 145–148°. Diazoreaktion positiv noch bei 2,000,000-facher Verdünnung. Rote Halochromie in konz. Schwefelsäure. (Gef.: C, 75.77; H, 9.06; N, 4.56. Ber. für $C_{19}H_{27}O_2N$ (301): C, 75.75; H, 8.97; N, 4.65%. Spez. Drehung (0.1314 g. Subst. in 10 c.c. Methanol): $[\alpha]_D^{22.5°} = +65.45°$).

***d, l*-Des-N-methyl-β-tetrahydro-desoxy-codein.** Je 0.2 g. (+)- und (−)-Des-N-methyl-β-tetrahydro-desoxy-codein wurden gesondert in Äther gelöst und vereinigt. Wurde der Äther verdampft, krystallisierte sich die racemische Substanz (0.25 g.) in schönen Prismen aus. Schmp. 133–136°. Die Substanz drehte die Polarisationsebene nicht (0.1827 g. Subst. in 10 c.c. Methanol und in 1 dm. Rohr, $\alpha = 0$).

(+)-Dehydro-thebenan (III) aus Codein. Darstellung wie bei (−)-Substanz aus Sinomenin.[3] Prismen. Schmp. 107–112°. Halochromie in konz. Schwefelsäure rot. (Gef.: C, 79.52; H, 8.04. Ber. für $C_{17}H_{20}O_2$(256): C, 79.69; H, 7.81%. Spez. Drehung (0.1766 g. Subst. in 10 c.c. Methanol): $[\alpha]_D^{22.5°} = +175.54$).

---

(3) Dieses Bulletin, **6** (1931), 38, 205. Vgl. Small und Cohen, *J. Am. Chem. Soc.*, **54** (1932), 808.

***d, l*-Dehydro-thebenan.** Je 0.2 g. (+)- und (−)-Dehydro-thebenan wurde in Ätherlösung vereinigt. Daraus krystallisierte die racemische Substanz (0.22 g.) in Prismen aus. Schmp. 90–92°. $\alpha = 0$ (0.1810 g. Subst. in 10 c.c. Methanol und in 1 dm. Rohr).

Dihydro-des-N-methyl-β-tetrahydro-desoxy-codein (IV). Bedingung der katalytischen Reduktion wie bei der Darstellung von Dihydro-des-N-methyl-demethoxy-desoxo-dihydro-sinomenin.[3] Schmp. 161°. Diazo-reaktion bemerklich in 2,000,000-facher Verdünnung. Keine Halochromie in konz. Schwefelsäure. (Gef.: C, 75.32; H, 9.91; N, 4.52. Ber. für $C_{19}H_{29}O_2N$ (303): C, 75.25; H, 9.57; N, 4.61%. Spez. Drehung (0.1339 g. Subst. in 10 c.c. Methanol-Chloroform):[4] $[\alpha]_D^{22.5°} = -78.42°$).

***d, l*-Dihydro-des-N-methyl-β-tetrahydro-desoxy-codein.** Je 0.2 g. (−)- und (+)-Substanz wurde in Äther-methanollösung racemisiert. Ausbeute 0.24 g. Prismen, gesammelt in Rosetten. Schmp. 135–140°. $\alpha = 0$ (0.1775 g. Subst. in 10 c.c. Methanol-Chloroform und in 1 dm. Rohr).

(+)-Thebenan aus Codein (V). Dargestellt wie bei (−)-Thebenan[5] aus Sinomenin. Schmp. 48–54°. Zeigt keine Halochromie in konz. Schwefelsäure. (Gef.: C, 78.93; H, 8.82. Ber. für $C_{17}H_{22}O_2$ (258): C, 79.07; H, 8.53%. Spez. Drehung (0.2156 g. Subst. in 10 c.c. Methanol): $[\alpha]_D^{22.5°} = +3.25°$).

d, l-Thebenan konnte nicht bisher in Krystallen erhalten worden.

Chemisches Laboratorium, Kitasato-Institut,
Shiba, Tokyo.

---

(4) Small u. Cohen geben einen niedrigeren Wert an (*loc. cit.*).
(5) (−)-Thebenan aus Sinomenin schmilzt auch bei 48–54°.

ACETON-*d*-WEINSÄUREDIÄTHYLESTER UND SEINE OPTISCHE AKTIVITÄT.

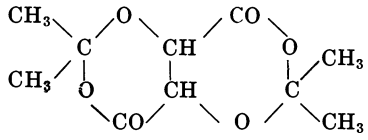
Von Yojiro TSUZUKI.

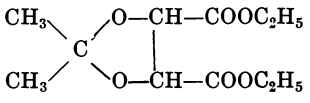
Eingegangen am 6. Juni, 1935. Ausgegeben am 28. Juni, 1935.

Über die Acetonverbindung der *d*-Weinsäure ist bisher nur eine Diacetonverbindung (I) bekannt,[1] und die Verbindung, welche den gleichen Acetonrest an den beiden alkoholischen Hydroxylen trägt, ist noch nicht erhalten. In der Absicht eine solche Verbindung zu gewinnen, habe ich versucht, *d*-Weinsäureester zu acetonieren. Fischer und Appel[2]

(1) H. O. L. Fischer und C. Traube, *Ber.*, **60** (1927), 485.
(2) H. O. L. Fischer und H. Appel, *Helvetica Chim. Acta*, **17** (1934), 1574.

haben vor einiger Zeit ausgesprochen, dass ihnen die Acetonierung von Weinsäuredimethylester bisher nach keiner der bekannten Methoden gelungen war; ich konnte aber ziemlich leicht die erzielte Acetonverbindung (II) synthetisieren, indem ich als Kondensationsmittel wasserfreies Kupfersulfat benutzte.

I 

II 

Diese Verbindung ist, wie erwartet, stark linksdrehend.[3] Die spezifische Drehung ist konzentrations-unabhängig und die Rotationsdispersion ist einfach.[4] Über diese optische Versuche soll später ausführlich mitgeteilt werden.

Zur Darstellung wurden 30 g. Weinsäurediäthylester mit 50 g. wasserfreiem Kupfersulfat und 200 g. Aceton auf dem Wasserbad 36 Stunden gekocht. Nach Abfiltrieren von Kupfersulfat und Abdestillieren von Aceton wurde der dickflüssige Rückstand in Äther aufgenommen, und zur Entfernung unverändertes Esters mit gesättigter Borax-lösung zweimal geschüttelt. Die Ätherlösung wurde mit Natriumsulfat getrocknet, Äther verdampft, und der Rückstand in Vakuum destilliert. Farblose dicke Flüssigkeit. Ausbeute an reiner Substanz 20 g. Leicht löslich in meisten organischen Lösungsmitteln, unlöslich in Wasser. Siedep. 150° (korr., 19 mm.), d_4^{15} 1.1213, n_D^{20} 1.4334, $[\alpha]_D^{15}$ −51.19°. Gefunden: C, 53.17; H, 7.38; Aceton (nach Ripper),[5] 23.43. Berechnet für $C_{11}H_{18}O_6$ (246.14): C, 53.63; H, 7.37; Aceton, 23.58%.

Musashi Hochschule,
Tokio-Nakaarai.

(3) Analog gebaute Brückenderivate der *d*-Weinsäure sind alle stark linksdrehbar, wie z.B. Methylen-Weinsäure (Austin und Carpenter, *J. Chem. Soc.*, **125** (1924), 1943), Benzal-Weinsäuredimethylester (Fischer und Appel, *loc. cit.*).

(4) Über die Beziehung zwischen Konstitution und optischer Aktivität der Weinsäure und ihrer Derivate siehe z.B. T. M. Lowry, *Nature*, **117** (1926), 271, Austin und Carpenter, *loc. cit.*

(5) *Monatsh.* **21** (1900), 740, Vgl. H. Meyer, "Nachweis und Bestimmung org. Verbindungen", (1933), S. 60.

ERZEUGUNG DES LEICHTEN WASSERS UND DIE BESTIMMUNG DER DEUTERIUM-KONZENTRATION IM NORMALEN WASSER.

(Vorläufige Mitteilung.)

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 24. Mai, 1935. Ausgegeben am 28. Juni, 1935.

Eine der zuverlässigen Methoden, die uns die Konzentration des Deuteriums im normalen Wasser bestimmen lassen, besteht darin, dass man das Wasser auf irgendeine Weise vom Deuterium befreit, und das spezifische Gewicht des so erzeugten leichten Wassers im Verhältnis zu dem normalen Wasser bestimmt. Nach dieser Richtung sind schon einige Versuche ausgeführt worden.(1) Die vorliegende Arbeit betrifft die Erzeugung des leichten Wassers aus Osaka Leitungswasser durch die fraktionierte Elektrolyse und die Bestimmung der Deuterium-Konzentration in demselben.

Das Leitungswasser wurde mit NaOH 0.5N gemacht und zwischen Nickel-Elektroden elektrolysiert. Der Knallgasstrom aus dem Elektrolysiergefäss wurde sorgfältig getrocknet und ebensogut getrocknete Luft zugesetzt. Das gemischte Gas wurde dann über das bis auf 300°C. erhitzte Kupferoxyd geleitet und katalytisch zu Wasser rekombiniert. Auf der ersten Stufe der Elektrolyse wurde nur 1/10 Volumen des originalen Wassers zersetzt und rekombiniert. Dem rekombinierten Wasser wurde wieder NaOH zugesetzt und dann wurde es der zweiten Stufe der Elektrolyse unterworfen. Aber auf dieser Stufe wurde 1/2 Volumen des Elektrolysierwassers zersetzt und rekombiniert. Das rekombinierte Wasser wurde für die dritte Stufe der Elektrolyse reserviert. Die dritte und die darauf folgenden Elektrolysen wurden auf ähnliche Weise wie die zweite Stufe durchgeführt. Nach jeder Stufe der Elektrolyse wurde das rekombinierte Wasser sorgfältig gereinigt und dessen spezifisches Gewicht im Verhältnis zu dem ebensogut gereinigten Osaka Leitungswasser bei 18.9°C. bestimmt. Die Dichtmessungen führten wir

(1) E. H. Ingold, C. K. Ingold, H. Whitaker, und R. Whytlaw-Gray, *Nature*, **134** (1934), 661; H. L. Johnston, *J. Am. Chem. Soc.*, **57** (1935), 484; Vgl. auch L. A. Webster, M. H. Wahl, und H. C. Urey, *J. Chem. Phys.*, **3** (1935), 129.

mittels eines Quarzschwimmers durch. Die Messgenauigkeit dürfte $\pm 0.5\ \gamma$ sein.

Wir haben zwei Reihen von fraktionierten Elektrolysen durchgeführt. Bei der ersten, ausgegangen von 10 l. Osaka Leitungswasser, wiederholten wir die Elektrolyse dreimal und bei der anderen, angefangen mit 5 l. originalem Wasser, wurden die sukzessiven Elektrolysen fünfmal nacheinander durchgeführt. Aus diesen Versuchen hat sich ergeben, dass das spezifische Gewicht des rekombinierten Wassers nach der dritten Stufe der Elektrolyse unabhängig von der Zahl der Elektrolysen fast konstant geworden ist.[2] Das spezifische Gewicht des rekombinierten Wassers nach der dritten Stufe der Elektrolyse erwies sich durchschnittlich um 19.3 γ leichter als das des Osaka Leitungswassers. Nimmt man an, dass diese Differenz im spezifischen Gewicht allein von der Befreiung vom Deuterium herkommt, dann ergibt sich aus dem bekannten spezifischen Gewicht des reinen schweren Wassers, dass D/H Verhältnis im Osaka Leitungswasser $1 : 5500 \pm 200$ ist.

Die ausführliche Mitteilung der vorliegenden Arbeit wird später in diesem Bulletin erfolgen.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

(2) Neuerdings hat Johnston (*loc. cit.*) ein leichtes Wasser durch sukzessive Elektrolysen des Columbus City Wasser hergestellt. Aber dabei hat er gefunden, dass die Dichte des rekombinierten Wassers immer wieder abnahm, sogar nach vermuteter vollkommenen Befreiung vom Deuterium. Dies hat er auf die elektrolytische Trennung der Sauerstoffisotope zurückgeführt. In unserem Fall haben wir keine solche stetige Abnahme der Dichte des rekombinierten Wassers gefunden. Die Erklärung für diese Diskrepanz kann man vielleicht in der Verschiedenheit der Versuchsbedingungen besonders der Rekombinationsanordnungen finden.

ISOTOPENZUSAMMENSETZUNG DES WASSERS AUS PETROLEUMQUELLEN.

(Vorläufige Mitteilung.)

Von **Kenzo OKABE** und **Toshizo TITANI.**

Eingegangen am 24. Mai, 1935. Ausgegeben am 28. Juni, 1935.

Bei dem Versuch von A. F. Scott[1] wurde gefunden, dass das Wasser aus zwei amerikanischen Petroleumquellen von 5000 Fuss Tiefe innerhalb der Messgenauigkeit ($\pm 2\,\gamma$) dieselbe Dichte wie gewöhnliches Wasser der Erdoberfläche besitzt.

Wir haben das Wasser aus zehn japanischen Petroleumquellen, deren Tiefe zwischen 30 m. und 1500 m. lag, geprüft. Das Wasser wurde sorgfältig gereinigt und dessen spezifisches Gewicht im Verhältnis zu ebensogut gereinigtem Osaka Leitungswasser bei 21.0°C. mittels eines Quarzschwimmers gemessen. Die Messgenauigkeit war $\pm 0.5\,\gamma$. Aus dem Versuch ergab sich, dass das Wasser aus Petroleumquellen innerhalb der Messgenauigkeit meistens dieselbe Dichte wie gewöhnliches Wasser besitzt. Aber in einigen Fällen fanden wir einen kleinen aber untrüglichen Unterschied zwischen beiden Dichten. Zwei Proben aus Petroleumquellen, die je 833 m. und 754 m. Tiefe besitzen und zu derselben Erdschicht gehören, erwiesen sich um $1.6\,\gamma$ bzw. $1.9\,\gamma$ schwerer als Normalwasser. Eine andere Probe aus einer 30 m. tiefen Bohrung erwies sich dagegen um $1.5\,\gamma$ leichter als gewöhnliches Wasser. Daher liegt die Vermutung nahe, dass nicht die Tiefe der Bohrungen sondern die Erdbeschaffenheit dabei eine Rolle spielte.

Die ausführliche Publikation wird später in diesem Bulletin erfolgen.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

---

(1) A. F. Scott, *Science*, **79** (1934), 565; vgl. auch H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell and H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1948.

DIE WIRKUNG DES VERDÜNNTEN SCHWEREN WASSERS AUF DIE TUBERKELBAZILLEN.[1]

Von M. ITOH, K. INOSHITA und T. TITANI.

Eingegangen am 24. Mai, 1935. Ausgegeben am 28. Juni, 1935.

Über die biologische Wirkung des schweren Wassers in grossen Verdünnungen sind schon viele Versuche ausgeführt worden. Dabei hat sich in einigen Fällen ergeben,[2] dass das verdünnte schwere Wasser auf kleine Lebewesen günstig wirkte. Angeregt durch diese Entdeckungen untersuchten wir die Wirkung des verdünnten schweren Wassers auf das Wachstum der Tuberkelbazillen.

Zwei Stämme von Tuberkelbazillen, einer vom Typus bobinus und der andere vom Typus humanus Kamiike, wurden auf dem Longschen Nährboden kultiviert. Der Nährboden wurde auf die übliche Weise aus gewöhnlichem sowie verdünntem schweren Wasser, das je 0.08, 0.37 und 2.24 atomprozentiges Deuterium enthielt, dargestellt. Ausserdem liessen wir auch die Wasserstoffionenkonzentration der Nährlösung von *p*H 7.25 bis 5.83 varieren. Auf diese Weise wurden die Bakterien auf eine Serie von Nährböden, die in bezug auf Deuterium- sowie Wasserstoffionenkonzentration untereinander verschieden waren, schwimmkultiviert. Nach bestimmten Tagen verglichen wir den Grad des Wachstums der Bakterien auf jedem Nährboden durch die Grösse der Kolonie untereinander. Aus diesem Versuch ging ziemlich eindeutig hervor, dass die Zunahme der Wasserstoffionenkonzentration hemmend, dagegen die Zunahme der Konzentration des Deuteriums fördernd auf das Wachstum der beiden genannten Bakterien wirkte.

Herrn Prof. Dr. Imamura als Direktor des Takeo Instituts sind wir zum besten Dank verpflichtet.

Takeo Institut für Tuberkulosenforschung,
Schiomi Institut für Physikalische
und Chemische Forschungen
und
Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka.

---

(1) Auszug aus der deutschen Mitteilung im "*Osaka Ijishinshi*", **6** (1935), Juni.

(2) S. L. Meyer, *Science*, **79** (1934), 210; T. C. Barnes, *J. Am. Chem. Soc.*, **55** (1933), 4332, *Science*, **79** (1934), 370; E. J. Larson und T. C. Barnes, *Nature*, **133** (1934), 873; T. C. Barnes und E. J. Larson, *Protoplasma*, **22** (1934), 431; G. Lockmann und H. Leunig, *Ber.*, **67** (1934), 1299; O. W. Richards, *J. Bact.*, **28** (1934), 289.

DIE KONZENTRATION DER SCHWEREN ISOTOPE IN KOHLENHYDRATEN.*

Von **Toshizo TITANI** und **Masao HARADA.**

Eingegangen am 29. März, 1935. Ausgegeben am 28. Juli, 1935.

Früher haben wir[1] gefunden, dass das Wasser aus der Rohrzucker-Melasse um 2.8 γ ($\gamma = 10^{-6}$) schwerer als das gewöhnliche Wasser ist; aber fast in derselben Zeit wurde von Briscoe und seinen Mitarbeitern[2] in ihren umfangreichen Arbeiten berichtet, dass das durch Verbrennung von Zucker erhaltene Wasser sogar um 8.6 γ schwerer als Normalwasser ist. Doch weil die von dem eben genannten Verfasser untersuchte Probe aus einem Gemisch von Rohr- und Rübenzucker bestand, wiederholten wir dieselben Messungen mit gut definierbaren Substanzen. Die eine war roher, schwarzer Rohzucker, der direkt aus der Melasse abgeschieden wurde. Die zweite war gereinigter, schön kristallisierter, weisser Rohrzucker, sogenannter raffinierter Zucker und die letzte ebenfalls gut gereinigter und schön kristallisierter, weisser Rübenzucker.

Jede Substanz wurde separat im Luftstrom verbrannt und das erhaltene, abdestillierte Wasser wurde sorgfältig nach folgender Weise gereinigt: Zuerst wurde es zweimal in Dampfform über bis zur Rotglut erhitztes Kupferoxyd geleitet und dann noch viermal nacheinander mit folgenden Zusätzen destilliert:

1. Destillation bei Zugabe von Natronlauge und Kaliumpermanganat,
2. Destillation bei Zugabe von Schwefelsäure und Kaliumpermanganat,
3. Destillation bei Zugabe von Bariumhydroxyd,
4. Destillation ohne Zusatz durch Quarzkühler.

Die drei letztgenannten Destillationen wurden im kohlensäurefreiem Luftstrom durchgeführt. Die Reinheit des letzten Produktes wurde durch Messungen der elektrischen Leitfähigkeit geprüft. Das spezifische Gewicht des

Tabelle 1.

Rohrzucker, roh	+7.8 γ
Rohrzucker, gereinigt	+7.4 γ
Rübenzucker, gereinigt	+6.5 γ

* Kürzlich vorläufig mitgeteilt, dies Bulletin, **10** (1935), 205.

(1) T. Titani und M. Harada, dies Bulletin, **10** (1935), 41.

(2) H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207.

so gereinigten Wassers verglichen wir mit nach gleicher Weise gereinigtem Osaka-Leitungswasser bei 8°C. durch die Schwebemethode mittels eines Quarzschwimmers. Tabelle 1 zeigt die gefundenen Differenzen in γ Einheiten im Vergleich mit gewöhnlichem Wasser.

Diese Ergebnisse stimmen mit denen von Briscoe und seinen Mitarbeitern gut überein. Es liegt nun die Vermutung nahe, dass eine Anreicherung schwerer Isotope in allen Kohlenhydraten allgemein vorhanden ist. Um die Richtigkeit dieser Ansicht zu prüfen, versuchten wir möglichst viele Sorten von Kohlenhydraten nach ihren Gehalt an schweren Isotopen zu untersuchen. Da es aber viel Zeit in Anspruch nehmen würde um chemisch reines Kohlenhydrat in reichlicher Menge herzustellen, untersuchten wir vorläufig hauptsächlich solche Substanzen, welche Kohlenhydrat als Hauptbestandteil enthalten. Die Versuchsordnung ist genau dieselbe wie oben. Die Proben waren meist Handelsprodukte in Pulverform. Je 300 g. davon, weder besonders getrocknet noch gereinigt, wurden direkt im Luftstrom verbrannt. Das dabei erhaltene Wasser war durchschnittlich 70% der theoretisch berechneten Menge. Dieses wurde sorgfältig nach oben erwähnter Weise gereinigt und sein spezifisches Gewicht bei 8°C. mit dem ebenso gereinigtem Osaka-Leitungswasser verglichen. Die Versuchsergebnisse sind in Tabelle 2 zusammengestellt. Erwähnt sind die Handelsnamen der untersuchten Substanzen, ihr Hauptbestandteil, sowie der gefundene Unterschied des spezifischen Gewichtes gegen Normalwasser.

Tabelle 2.

Substanz	Hauptbestandteil	Differenz
Traubenzucker	Glukose	+6.4 γ
Milchzucker	Laktose	+5.9 γ
Lösliche Stärke	Stärke	+3.9 γ
Reismehl	,,	+6.0 γ
Weizenmehl	,,	+6.0 γ
Kartoffelstärke	,,	+5.9 γ
Dextrin	Dextrin	+5.4 γ
Agar-Agar	Galaktan	+4.8 γ
Konjakpulver	Mannan	+5.8 γ

Aus diesen Ergebnissen darf man wohl schliessen, dass mindestens in den oben genannten Kohlenhydraten schwere Isotope, entweder Wasserstoff- oder Sauerstoffisotope höherer Konzentration reichlich vorhanden sind. Nimmt man an, dass der in Tabelle 2 genannte Überschuss an spezifischem Gewicht auf höhere Konzentration von Deuterium zurückzuführen ist, was viel wahrscheinlicher ist als Sauerstoffisotop, dann konnte man sich zwei Möglichkeiten für den Sitz des Deuteriums denken, nämlich entweder in den OH- oder CH-Gruppen der Kohlenhydrate. Nach Versuchen von Bawn[3] wurde gefunden, dass sich

(3) Die mündliche Mitteilung von Dr. J. Horiuti.

die Konzentrationsverteilung des Deuteriums zwischen Amylalkohol und Wasser zugunsten der OH-Gruppe des Alkohols verschiebt. Doch kann die zweite Möglichkeit, dass sich das Deuterium in den CH-Gruppen in höherer Konzentration angesammelt hat, nicht ganz ausgeschlossen werden; denn Reitz und Bonhoeffer[4] haben gezeigt, dass Deuterium ebenso gut wie Protium von Pflanzen assimiliert werden kann. Jedenfalls dürfte es sehr interessant sein andere Kohlenhydrate, z.B. Zellulose oder dergleichen nach ihren Gehalt an schweren Isotopen zu untersuchen.

Für die finanzielle Unterstützung dieser Arbeit danken wir herzlichst der Gakujutsu-Shinkokai (der Notgemeinschaft der Japanischen Wissenschaft).

Physikalisch-Chemisches Laboratorium
der Kaiserliche Universität zu Osaka
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

(4) O. Reitz und K. F. Bonhoeffer, *Naturwissenschaften*, **22** (1934), 744.

ISOTOPENZUSAMMENSETZUNG DES REGEN- UND SCHNEEWASSERS.*

Von Masao HARADA und Toshizo TITANI.

Eingegangen am 15. April, 1935. Ausgegeben am 28. Juli, 1935.

Während des Versuchs über den Deuterium-Gehalt von Wasserproben in verschiedenen natürlichen Vorkommen durch die Messungen ihrer spezifischen Gewichte, fanden wir zufällig kleine aber untrügliche Schwankungen in der Dichte des Regenwassers.

Das Osaka-Regenwasser wurde zunächst von Stäubchen abfiltriert und dann sorgfältig in derselben Weise wie früher[1] gereinigt. Das spezifische Gewicht bei 8°C. der so gereinigten Proben verglichen wir

---

* Kürzlich vorläufig mitgeteilt, dies Bulletin, **10** (1935), 206.

(1) T. Titani und M. Harada, dies Bulletin, **10** (1935), 261.

mit dem Osaka-Leitungswasser durch die Schwebemethode mittels eines Quarzschwimmers. Der Schwimmer war schon ein Jahr lang im Gebrauch und sein Volumen war fast konstant geworden. Die Messgenauigkeit dürfte mindestens ± 0.2 pro Million sein. Die Schwankungen in der Dichte des Regenwassers lagen sicherlich ausserhalb der Fehlergrenze. Bemerkenswert war dabei, dass die Schwankungen der Dichte stark von den Bedingungen, unter denen die Probe gesammelt wurde, abhängen. Einige Beispiele der Messungen sind in der Tabelle 1 zusammengestellt.

Tabelle 1. Überschuss im sp. Gewicht des Regenwassers gegen Osaka-Leitungswasser.

Probennr.	Δs	Bemerkungen
1	$+1.2\gamma$	Am Anfang eines Regenfalls gesammelt
2	-0.8γ	Gegen Ende eines anderen Regenfalls gesammelt
3	$+1.6\gamma$	Anfangsmenge eines Regens
4	-1.3γ	Mittlere Menge desselben Regens wie Nr. 3
5	-1.9γ	Letztere Menge desselben Regens wie Nr. 3 und 4

Die Probe Nr. 1, die am Anfang eines Regenfalls angesammelt wurde, erwies sich etwas schwerer als das Standardwasser. Dagegen war die Probe Nr. 2, die gegen Ende eines anderen Regenfalls aufgefangen wurde, klein bisschen leichter. Diese Verhältniss kann man bei den Proben von Nr. 3 bis 5 noch klarer sehen.

Diese drei Proben von Nr. 3 bis 5 kamen von einem einmaligen Regenfall her. Um diese Proben aufzufangen, stellten wir einen grossen Glastrichter auf, dessen weitere Öffnung, die 30 cm. l. W. besass, nach oben gerichtet war. Das Regenwasser, das auf diesen Trichter fiel, floss in ein Becherglas, das sich dicht unter dem Trichter befand, zusammen. Während desselben Regens wechselten wir das Becherglas dreimal nacheinander und auf diese Weise sammelten wir das gesamte Wasser gesondert in drei Mengen. Die Anfangsmenge, die in der Tabelle 1 mit Nr. 3 bezeichnet ist, wurde vom Anfang (ca. 10 Uhr) bis 11 Uhr angesammelt und betrug 340 c.c. Die mittlere Menge, d.h. die Probe Nr. 4, bestand aus dem Wasser, das von 12 bis 18 Uhr aufgefangen wurde und betrug 1180 c.c. Das Volumen der Endmenge, die Probe Nr. 5, die von

18 Uhr bis zum Ende des Regenfalls (ca. 19½ Uhr) angesammelt wurde, wog 80 c.c. Diese drei Proben wurden separat gereinigt und deren spezifische Gewichte mit dem Standardwasser verglichen.

Die Anfangsmenge Nr. 3 erwies sich um 1.6 γ schwerer, dagegen die Endmenge Nr. 5 um 1.9 γ leichter als das Standardwasser. Das spezifische Gewicht der mittleren Menge war zwischen den beiden oben genannten, aber noch um 1.3 γ leichter als das Standardwasser. Aus diesem Resultat kann man ziemlich sicher schliessen, dass das Regenwasser am Anfang des Regenfalls spezifisch schwerer als gewöhnliches Wasser ist, aber gegen Ende allmählich leichter wird. Es liegt nun die Vermutung nahe, dass entweder die fraktionierte Kondensation bei der Tropfenbildung oder die fraktionierte Verdampfung beim Fallen des Regentropfens durch die atmosphärische Luft eine wichtige Rolle spielt.

Angeregt durch diese Ergebnissen, untersuchten wir dann das Schneewasser. Aber weil es sich in diesem Fall als ziemlich schwer erwies, die Anfangsmenge oder Endmenge, wie beim Regeswasser, separat anzusammeln, prüften wir nur einige einzelne Proben. Beim Sammeln der Proben gaben wir jedoch immer darauf acht, dass der nicht direkt den Boden berührende, sondern auf irgendeinem Gegenstand liegende Schnee angesammelt wurde, da sonst die Isotopenzusammensetzung des Schnees durch die Austauschreaktionen mit dem Bodenwasser etwas geändert werden könnte. Die Messresultate sind in der Tabelle 2 zusammengestellt.

Tabelle 2. Überschuss im sp. Gewicht des Schneewassers gegen Osaka-Leitungswasser.

Probennr.	Δs	Bemerkungen
1	-1.5γ	In Osaka im letzten Winter von Dr. Yamasaki gesammelt
2	-0.5γ	In der Okayama-Provinz in diesem Winter von Herrn Gotoh gesammelt
3	-3.3γ	Wie oben
4	-1.9γ	Auf dem Rokkogebirge in diesem Winter von Dr. Okabe gesammelt

In diesem Fall sieht man schon, dass das Schneewasser fast ausnahmslos spezifisch leichter als das Standardwasser ist. Eine Erklärungsmöglichkeit für diese Ergebnisse kann man vielleicht darin finden, dass die Feuchtigkeit in der Atmosphäre sich unter der Wirkung der Gravitationskraft von unten nach oben verteilt und atmosphärischer Wasser-

dampf mit zunehmender Höhe spezifisch leichter wird. Denn es ist allgemein anerkannt, dass die Schneewolken sich sehr hoch in der Atmosphäre befinden. Wir glauben, dass ein weiterer Versuch über die vorliegende Materie besonders vom meteorologischen Gesichtspunkt verdienstvoll sein würde.

Mit der oben geschilderten Tatsache scheint die folgende Beobachtung im Zusammenhang zu stehen. Dr. Nishibori stellte uns von einer Forschungsreise nach dem Hakutosan (Weisskopfberg) an der Grenze von Korea und Mantschuko eine Probe von natürlichem Eis zur Verfügung. Es wurde aus einem Teich auf einem 2257 m. hohen Berge angesammelt. Solch ein Eis soll, wie Briscoe und seine Mitarbeiter[2] hindeuteten, durch die fraktionierte Krystallisation ein bisschen schwerer als gewöhnliches Wasser sein. Aber gerade das Gegenteil war der Fall mit der obengenannten Prob, weil Dr. Okabe in unseren Laboratorium fand, dass es um 2.2 γ leichter als das Normalwasser war. Diese Diskrepanz kann man vielleicht dadurch erklären, dass der Oberflächenteil des Eises vom Teich nicht eigentlich aus dem Teichwasser ausgefroren, sondern aus dem darauf liegenden Schnee durch Zusammenschmelzen oder Sublimation entstanden ist. Diese Vermutung liegt sehr nahe, weil, wie Dr. Nishibori uns mitteilte, die Oberfläche des Teiches immer fast ganz mit reichlich Schnee bedeckt ist und es sehr schwer ist, eine freie Eisoberfläche aufzufinden.

Für die Unterstützung dieser Arbeit danken wir herzlichst Herrn Dr. Nishibori von der kaiserlichen Universität zu Kioto, der Gakujutsu-Shinkokai (der Notgemeinschaft der Japanischen Wissenschaft), sowie der Hattori-Hohkohkai (der Hattori-Stiftung).

Physikalisch-Chemisches Laboratorium
der Kaiserliche Universität zu Osaka
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

---

(2) H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207.

RECHERCHES SUR LA CONCENTRATION DES IONS D'HYDROGÈNE CONTENUS DANS LES SOLUTIONS AQUEUSES DES AMMINES-CHROMIQUES COMPLEXES ET SUR LEURS SPECTRES D'ABSORPTION. I.[1]

Par Taku UÉMURA et Hidéo SUÉDA.

Reçu le 1 avril 1935. Publié le 28 juillet 1935.

Nous avons déjà publié deux mémoires sur le changement de position subi par les bandes des spectres d'absorption des solutions aqueuses d'une vingtaine d'ammines-cobaltiques complexes[2], et maintenant nous allons aussi étudier systématiquement, avec le même but, la variation des courbes d'absorption des sels chromiques complexes, mis sous forme de solutions aqueuses, en faisant varier de la concentration des ions d'hydrogène (pH) pour déterminer la constitution chimique de ces complexes en solution.

Corps étudiés et procédé expérimental. Les quatorze sels chromiques suivants ont été préparés pour traiter la question précédemment discutée des complexes cobaltiques:

(1) $[Cr(NH_3)_6]Cl_3$
(2) $[Cr(NH_3)_5(H_2O)]Cl_3$
(3) $[Cr(NH_3)_5(OH)]Cl_2$
(4) $[Cr(NH_3)_5Cl]Cl_2$
(5) $[Cr(NH_3)_4(H_2O)_2]Cl_3$
(6) $[Cr(NH_3)_4(OH)_2]Cl$
(7) $[Cr(NH_3)_4(H_2O)Cl]Cl_2$
(8) $[Cr(NH_3)_3(H_2O)_3]Cl_3$
(9) $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$
(10) $[Cr(NH_3)_3(H_2O)Cl_2]Cl$(noir et gris)
(11) $[Cr(NH_3)_2(H_2O)_4]Cl_3$
(12) $[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl$
(13) $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$

Les procédés que nous avons adoptés pour les présentes expériences sont absolument semblables à ceux qui ont été précédemment appliqués aux sels cobaltiques. La valeur du pH a été électriquement mesurée en employant l'électrode d'antimoine[3] dont nous avons déjà parlé. Nous

(1) Traduction du mémoire original publié dans le Bulletin de la Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku Gakuhô), **4** (1935), 29. Exposé fait lors de la Séance de la Société chimique du Japon, le 13 octobre 1934.

(2) Ce bulletin, **10** (1935), 50, 85.

(3) Ce bulletin, **8** (1933), 1.

avons déterminé, comme dans nos expériences précédentes, les coefficients d'extinction au moyen du spectrographe en quartz construit par Jobin et Yvon en utilisant comme source lumineuse une lampe à mercure en quartz. Nous avons relevé les variations des coefficients d'extinction (Colog I/I_0) s'échelonnant entre 230 mμ et 450 mμ de longueur d'onde, sur une plaque photographique "extra rapide" Lumière (marque française). La prise de la photographie d'absorption a été rapidement faite, et des points de densité égale ont été exactement trouvés sur la plaque photographique en nous servant de l'équidensimètre Georges et Bayle construit par Jobin et Yvon.

Relation entre le coefficient d'extinction et la longueur d'onde des solutions des sels complexes. (1) $[Cr(NH_3)_6]Cl_3$, *Chlorure hexammine chromique* (*sel lutéo*). Après avoir synthétisé ce corps d'après la méthode proposée par Jörgensen[4], en faisant varier la valeur du *p*H, nous avons déterminé les coefficients d'extinction au moyen d'une solution aqueuse du sel à 1/200 mol, d'une épaisseur de 50 mm. La relation entre la longueur d'onde et le coefficient d'extinction suivant diverses valeurs du *p*H a été représentée dans le tableau 1.

Tableau 1.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_6]Cl_3$ à même concentration (1/200 mol), pour des *p*H divers (cuve 50 mm.).

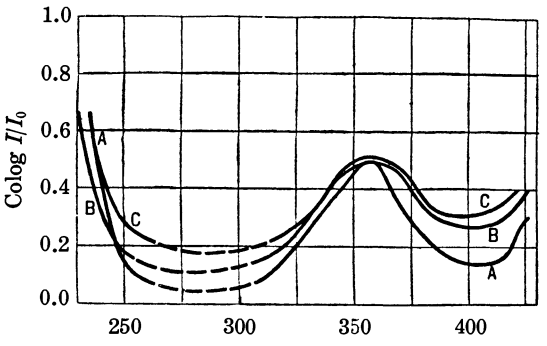
*p*H / λ(mμ)	2.0	2.9	3.7	6.7	7.6	9.2	12.0
230	—	—	1.00	—	—	—	—
235	1.00	—	0.70	1.00	—	—	—
236	0 90	1.00	0.60	—	1.00	—	—
237	0.80	0.90	0.50	0.90	—	1.00	—
238	—	0.80	—	0.80	0.90	—	—
239	0.70	—	—	—	—	—	—
240	0.60	0.70	0.45	0.70	0.80	0.90	—
242	0.50	0.60	0.40	0.60	0.70	—	—
243	0.45	—	0.35	—	—	0.80	1.00
244	0.40	0.45	—	0.50	0.60	—	—
246	0.35	—	—	—	0.50	—	0.90
248	0.25	0.30	—	—	—	—	—

(4) S. M. Jörgensen, *J. prakt. Chem.*, **30** (1884), 1.

Tableau 1. (*fin*)

λ (mμ) \ pH	2.0	2.9	3.7	6.7	7.6	9.2	12.0
251	—	—	—	—	—	—	0.80
252	0.20	0.25	0.25	0.40	0.40	—	—
257	0.15	—	—	—	—	—	0.70 (256)
260	—	0.20 (259)	—	—	0.35 (261)	0.50 (259)	—
263	0.10	0.15 (264)	—	0.35	—	—	—
272	—	—	—	—	—	—	0.60
273	—	—	—	—	—	—	0.45
308	0.10 (307)	—	—	—	0.25	—	—
314	—	0.10	—	0.35	0.35	—	—
319	0.15 (318)	0.15	—	—	—	0.45 (320)	—
322	0.25	0.20 (321)	—	—	0.40	—	—
325	0.30 (324)	0.25 (326)	0.35 (324)	0.40 (324)	0.45 (326)	0.50	0.50
333	0.45	0.40 (334)	0.50 (332)	0.50 (334)	—	0.60 (334)	0.60
338	—	0.45	0.60	0.60 (339)	—	—	—
345	0.60 (346)	0.60	—	0.70 (346)	0.70 (344)	0.70 (346)	0.70 (344)
350	0.70	—	0.70	—	—	—	—
366	0.60	0.60	—	—	—	—	—
368	—	—	0.70	—	—	—	—
372	0.50	—	—	0.70	0.70 (373)	—	0.70
374	0.45	0.45	—	—	—	—	—
377	—	—	—	—	0.60	0.60 (376)	0.60
380	0.40	0.40 (379)	0.50 (381)	—	—	—	—
383	0.35	0.30	—	0.50	0.50 (382)	0.50	—
415	—	0.30	0.45	—	—	0.40 (416)	—
422	0.40	—	—	0.60	0.60	0.50	—
425	0.45 (426)	0.40	0.60 (426)	—	—	—	0.60
430	—	—	—	0.70	0.70	—	—
445	—	0.60	0.70	—	—	0.60	0.70

Parmi les données numériques exposées dans le tableau 1, puisque deux valeurs du pH 2.0 et 2.9 ont produit les mêmes courbes, nous en avons pris une des deux comme courbe A, et la courbe B vient quand le pH est à 3.7, puis la courbe C quand le pH est à 6.7 (fig. 1).



$[Cr(NH_3)_6]Cl_3$ (1/300 mol)
A : pH = 2.0 B : pH = 3.7 C : pH = 6.7

Fig. 1.

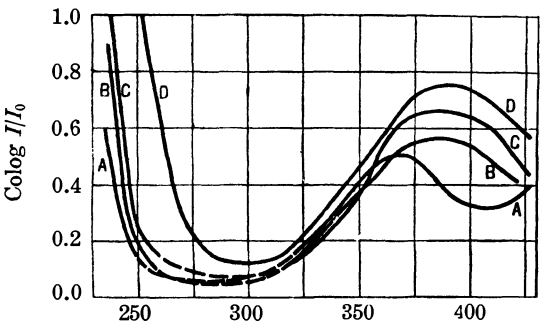
Comme nous avon trouvé une légère quantité du produit de décomposition lorsque le pH est supérieur à 6.7, il semble que la décomposition ayant une vitesse graduelle se produise au voisinage du pH 6, et intensifie le pouvoir absorbant. Les trois courbes A, B et C de la figure 1 ont une position semblable sur la bande d'absorption quand le pouvoir absorbant est à peu près le même. Cela vient probablement de ce que le lutéo ne se transforme pas en autres corps complexes, jusqu'à ce que la décomposition en $Cr(OH)_3$ se produise dans la solution.

Tableau 2.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_5(H_2O)]Cl_3$ à même concentration (1/300 mol), pour des pH divers (cuve 50 mm.).

Colog I/I_0 \ pH	3.5	4.4	5.0	7.7	11.1	Colog I/I_0 \ pH	3.5	4.4	5.0	7.7	11.1
1.00	—	—	—	239	252	0.30	338	340	340	345	331
0.90	—	237	238	241	254	0.35	343	347	348	348	336
0.80	—	238	239	242	257	0.40	349	352	353	352	342
0.70	—	238	240	243	260	0.45	354	361	359	355	350
0.60	235	239	241	243	262	0.50	364	—	365	358	356
0.50	237	240	242	244	265	0.60	—	—	—	367	366
0.45	238	241	242	244	267	0.70	—	—	—	—	373
0.40	239	242	243	245	269	0.70	—	—	—	—	409
0.35	240	242	244	247	270	0.60	—	—	—	410	423
0.30	242	243	245	249	274	0.50	372	—	408	420	—
0.25	244	246	247	250	276	0.45	377	376	—	—	—
0.20	247	248	249	255	277	0.40	387	415	—	—	—
0.15	249	252	254	259	283	0.35	396	—	—	—	—
0.10	—	—	258	—	—	0.35	420	—	—	—	—
0.10	—	—	315	—	—	0.40	428	430	—	—	—
0.15	321	320	321	326	315	0.45	436	450	—	—	—
0.20	327	329	328	332	322	0.50	—	—	466	468	—
0.25	334	335	335	338	326	0.60	—	—	—	—	463

(2) $[Cr(NH_3)_5(H_2O)]Cl_3$, *Chlorure d'aquopentammine chromique* (*sel roséo*). Nous avons préparé ce composé en appliquant la méthode proposée par King[5], et cherché la relation qui existe entre le coefficient d'extinction et la longueur d'onde, en faisant varier cinq fois la valeur du *p*H, comme il est indiqué dans le tableau 2.



$[Cr(NH_3)_5(H_2O)]Cl_3$ (1/300 mol)

A : *p*H = 3.5 B : *p*H = 5.0 C : *p*H = 7.7 D : *p*H = 11.1

Fig. 2.

Ce complexe est dissous dans l'eau et donne une solution acide dont la concentration est 1/300 mol et la valeur du *p*H 3.5. Il se produit une coloration orange, mais la valeur du *p*H monte à 5 et la coloration devient rouge-violette lorsque cette solution est alcaline avec la concentration 1/500 normal. Quand le *p*H atteint 11.1, sa solution aqueuse se décompose au cours de l'expérience, et un précipité se produit.

Comme la position de la bande d'absorption produite par la solution au *p*H 4.4 est semblable à celle montrée par la solution au *p*H 3.5 (courbe A), la courbe donnée par la solution au *p*H 4.4 a été éliminée dans la figure 2. En comparant les deux courbes A (*p*H = 3.5) et B (*p*H = 5.0) représentées dans la figure 2, on en déduit un déplacement du centre de bande d'absorption de 370 mμ à 390 mμ, valeurs approximatives. Cette translation d'environ 20 mμ en une longueur d'onde plus élevée montre aussi l'accroissement graduel du pouvoir absorbant. La fin d'absorption dans la région ultra-violette donne lieu à longueur d'onde légèrement plus grande lorsque le *p*H augmente, et on observe une variation sensible quand il est à 11.1.

D'après la figure 2, le sel roséo amène un déplacement du centre de la bande d'absorption entre la valeur du *p*H 4.4 et 5.0 et il se transforme en un autre complexe $[Cr(NH_3)_5(OH)]Cl_2$ qui présente son centre de bande d'absorption sous une longueur d'onde de 390 mμ, puis ne varie plus jusqu'à ce qu'il se produise un précipité amené par la décomposition. On a trouvé un précipité en déterminant l'absorption de la solution au *p*H 11.1 et l'augmentation considérable du absorbant.

(3) $[Cr(NH_3)_5(OH)]Cl_2$, *Chlorure hydroxopentammine chromique.* Ce corps, comme le précédent, a été préparé d'après les indications

(5) H. J. S. King, *J. Chem. Soc.*, **127** (1925), 2100.

fournies par King[6] et l'absorption a été déterminée en faisant varier quatre fois la valeur du *p*H.

Ce complexe est lui-même dissous en représentant l'alcalinité du *p*H 8.5 pour 1/300 mol de la concentration. Nous avons préparé la solution au *p*H 3.2 un jour après la purification du sel synthétisé. Les deux solutions qui ont respectivement leur *p*H 3.2 et 2.9 sont de coloration orange, tandis que celles qui ont comme *p*H 5.0 ou 8.5 sont rouge-violettes. Ce corps solide a une odeur d'ammoniaque assez forte, et il semble que ce composé commence déjà à se décomposer à l'état solide, par conséquent il est utile de l'employer rapidement après la purification du sel préparé.

La figure 3 montre que le centre de la bande d'absorption se trouve environ à 370 mμ de longueur d'onde, lorsque la valeur du *p*H est de 2.9 ou de 3.2, et que cette longueur d'onde est presque identique à celle que montre le centre d'absorption observé dans le complexe roséo

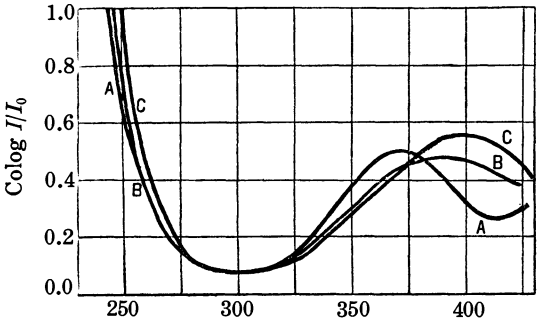
Tableau 3.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_5(OH)]Cl_2$ à même concentration (1/300 mol), pour des *p*H divers (cuve 50 mm.).

Colog I/I_0 \ *p*H	2.9	3.2	5.0	8.5	Colog I/I_0 \ *p*H	2.9	3.2	5.0	8.5
1.00	243	248	245	249	0.20	332	330	336	337
0.90	245	250	247	250	0.25	336	340	343	344
0.80	247	252	249	251	0.30	341	346	351	352
0.70	249	254	250	252	0.35	345	350	356	359
0.60	251	257	252	260	0.40	354	356	362	369
0.50	254	259	254	261	0.45	359	—	375	375
0.45	256	262	257	262	0.50	—	—	—	380
0.40	259	263	259	263	0.50	—	—	—	418
0.35	262	267	261	266	0.45	375	—	406	430
0.30	263	270	263	268	0.40	381	380	420	—
0.25	266	274	266	271	0.35	386	389	—	—
0.20	269	277	271	274	0.30	393	—	—	—
0.15	277	282	274	277	0.30	425	—	—	—
0.10	286	—	282	284	0.35	432	420	—	—
0.10	318	—	317	321	0.40	442	430	—	—
0.15	325	319	328	324	0.45	450	463	—	—

(6) H. J. S. King, *loc. cit.*

$[Cr(NH_3)_5(H_2O)]Cl_3$, le *p*H ayant une valeur de 3.5 (courbe A – fig. 2). Il est également évident, d'après la courbe A de la figure 3, que la solution se laisse le mieux traverser par la lumière quand la longueur d'onde est de 415 mμ. Quand le *p*H atteint 5.0, le centre d'absorption passe à 390 mμ (courbe B – fig. 3), ce qui est observé dans le cas du complexe roséo (courbe B – fig. 2) au *p*H 5.0. Le centre d'absorption, quand le *p*H est de 8.5, se trouve dans une longueur d'onde légèrement plus élevée, comparé à une solution possédant comme valeur du *p*H 5.0 (fig. 3), puis le pouvoir absorbant en région ultra-violette se différencie faiblement des solutions aqueuses ayant des *p*H plus inférieurs.



$[Cr(NH_3)_5(OH)]Cl_2$ (1/300 mol)
A : *p*H = 2.9 B : *p*H = 5.0 C : *p*H = 8.5

Fig. 3.

La grande différence qui existe entre ce complexe et le sel roséo pour des longueurs d'onde peu élevées peut provenir de la décomposition du $[Cr(NH_3)_5(OH)]Cl_2$, et dès lors la relation $[Cr(NH_3)_5(H_2O)]Cl_3 \underset{pH=4-5}{\rightleftharpoons} [Cr(NH_3)_5(OH)]Cl_2$ se justifie dans l'observation des bandes d'absorption. La molécule d'eau, dans le noyau complexe, est remplacée par le radical OH quand on ajoute l'alcali, et l'existence de la relation inverse par l'acide est aussi constatée dans les comptes-rendus publiés par Pfeiffer et Werner[7]. Cette relation est observée, dans notre présente recherche, entre les limites 4 et 5 de la valeur du *p*H, et nous avons déjà montré un cas identique dans notre mémoire précédent quand il s'agit de la solution du roséo cobaltique qui a son point de transformation au *p*H 7.

(4) $[Cr(NH_3)_5Cl]Cl_2$, *Chlorure de chloropentammine chromique* (*sel purpuréo*). Ce corps est obtenu en appliquant les méthodes proposées par Jörgensen et Christensen[8], et la solution aqueuse du 1/500 mol est fournie comme échantillon expérimental. Les coefficients d'extinction, correspondant aux trois différentes valeurs du *p*H, se trouvent dans le tableau 4 et les courbes d'absorption, dans la figure 4.

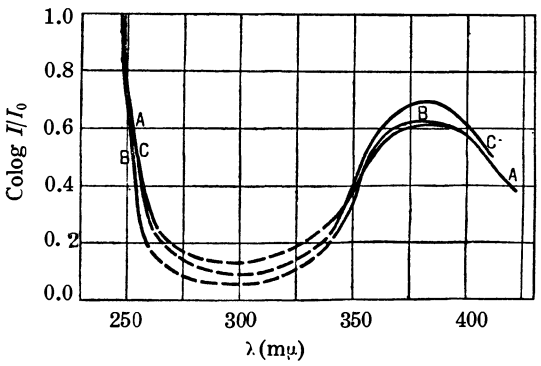
(7) P. Pfeiffer, *Ber.*, **39** (1906), 1864; A. Werner, *Ber.* **40** (1907), 272, 468, 4085.
(8) S. M. Jörgensen, *J. prakt. Chem.*, **20** (1879), 109; O. T. Christensen, *J. prakt. Chem.*, **23** (1881), 54.

Tableau 4.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_5Cl]Cl_2$ à même concentration (1/500 mol), pour des pH divers (cuve 50 mm.).

Colog I/I_0 \ pH	4.0	4.4	8.0	Colog I/I_0 \ pH	4.0	4.4	8.0
1.00	244	—	245	0.10	—	259	—
0.90	245	244	246	0.10	—	340	—
0.80	246	245	247	0.15	337	344	342
0.70	247	246	248	0.20	346	349	344
0.60	248	247	249	0.25	352	352	350
0.50	249	248	250	0.30	357	355	354
0.45	251	249	250	0.35	369	364	362
0.40	252	251	251	0.40	—	—	369
0.35	253	252	253	0.40	—	—	397
0.30	255	254	254	0.35	399	399	402
0.25	257	255	256	0.30	409	410	411
0.20	259	255	259	0.25	416	—	—
0.15	263	258	262				

La solution aqueuse de 1/500 mol de ce complexe est représentée comme faiblement acide et la valeur de son pH est de 4.0. Lorsqu'on rend cette solution alcaline, le pH est supérieur à 8, le précipitation se produit tout de suite après la dissolution. En examinant les courbes d'absorption de trois différents pH, dans la figure 4, on voit que le centre des bandes d'absorption ne varie pas pour ces trois courbes et que le pouvoir absorbant présenté par la solution du pH 8.0 n'est pas très puissant. Dans notre mémoire précédent, dans le cas du sel purpuréo cobaltique, nous avons pu difficilement porter un jugement définitif au sujet du remplacement du radical



$[Cr(NH_3)_5Cl]Cl_2$ (1/300 mol)
A : pH = 4.0 B : pH = 4.4 C : pH = 8.0

Fig. 4.

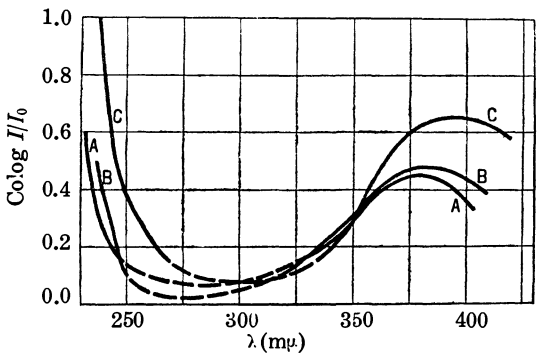
Cl par le radical OH, avec l'addition d'alcali; mais dans le cas présent, la réaction pour le sel purpuréo chromique ne tient pas compte de pareilles conditions. Bref, le purpuréo chromique en solution aqueuse ne se transforme pas en un autre complexe en faisant varier la valeur du *p*H.

(5) $[Cr(NH_3)_4(H_2O)_2]Cl_3$, *Chlorure de diaquotétrammine chromique.* Après avoir préparé ce complexe en appliquant la méthode de Pfeiffer[9], nous avons étudié sa solution aqueuse suivant quatre espèces de *p*H, en mesurant le coefficient d'extinction des solutions.

Tableau 5.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_4(H_2O)_2]Cl_3$ à même concentration (1/300 mol), pour des *p*H divers (cuve 50 mm.).

Colog I/I_0 \ *p*H	3.4	4.1	7.2	8.4	Colog I/I_0 \ *p*H	3.4	4.1	7.2	8.4
1.00	—	—	238	238	0.15	325	326	332	334
0.90	—	—	240	239	0.20	337	334	340	341
0.80	—	—	241	240	0.25	344	341	346	344
0.70	—	—	242	242	0.30	349	248	352	350
0.60	231	—	243	243	0.35	356	453	354	352
0.50	232	237	245	245	0.40	—	360	356	354
0.45	233	238	246	248	0.45	—	370	363	356
0.40	—	240	247	251	0.50	—	—	369	364
0.35	235	241	249	254	0.60	—	—	376	374
0.30	237	243	252	256	0.60	—	—	400	415
0.25	239	244	256	259	0.50	—	—	424	435
0.20	243	245	252	263	0.45	—	397	436	—
0.15	249	246	268	268	0.40	—	409	—	—
0.10	—	250	271	—	0.35	400	—	—	—
0.10	—	320	318	—	0.35	444	—	—	—



$[Cr(NH_3)_4(H_2O)_2]Cl_3$ (1/300 mol)
A : *p*H = 3.4 B : *p*H = 4.1 C : *p*H = 8.4

Fig. 5.

La solution de ce complexe à 1/300 mol de concentration est acide et son *p*H est de 3.4. La position de bande d'absorption donnée par la solution ayant le *p*H 4.1 (courbe B – fig. 5) se trouve sur une longueur d'onde légèrement plus élevée que celle de la solution ayant le *p*H 3.4 (courbe A – fig. 5). Cela montre en même temps un pouvoir absorbant plus

(9) P. Pfeiffer, *Ber.*, **40** (1907), 3126.

grand. Lorsque la valeur du pH atteint 7.2 ou 8.4 (courbe C), cette tendance d'accroissement du pouvoir absorbant devient plus considérable; le centre de la courbe C (pH = 8.4) se trouve à 400 mμ et le pouvoir absorbant sur une longueur d'onde courte montre parallèlement une influence bathochromique. D'après la figure 5, il semble que ce complexe se change en un autre corps $[Cr(NH_3)_4(OH)_2]Cl$ en augmentant d'alcalinité, c'est-à-dire en élevant son pH au-dessus de 4.1.

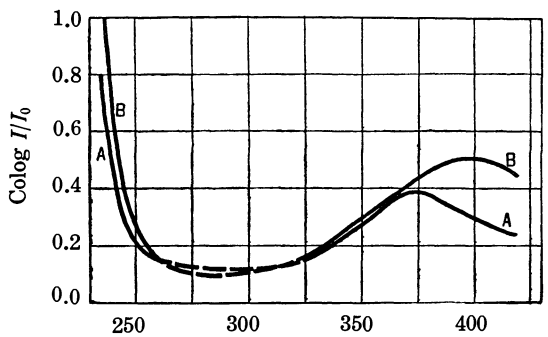
(6) $[Cr(NH_3)_4(OH)_2]Cl$, *Chlorure de dihydroxotétrammine chromique.* En mélangeant et en pétrissant le complexe $[Cr(NH_3)_4(H_2O)(OH)]S_2O_6$ avec le NH_4Cl solide et une légère quantité d'ammoniaque, le composé $[Cr(NH_3)_4(H_2O)(OH)]S_2O_6$ peu soluble disparaît graduellement en se transformant en solution rouge-violette. Après avoir filtré cette solution et éliminé l'excès de NH_4Cl, on obtient un précipité rouge-violet par l'addition d'alcool éthylique et ce corps précipité a été aussi vérifié par l'analyse chimique.

Tableau 6.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_4(OH)_2]Cl$ à même concentration (1/300 mol), pour des pH divers (cuve 50 mm.).

pH / Colog I/I_0	3.0	5.9	pH / Colog I/I_0	3.0	5.9
1.00	—	237	0.20	336	333
0.90	—	238	0.25	345	342
0.80	235	239	0.30	355	355
0.70	237	239	0.35	361	360
0.60	238	241	0.40	—	368
0.50	240	242	0.45	—	379
0.45	241	243	0.45	—	418
0.40	242	245	0.40	—	440
0.35	243	247	0.35	385	—
0.30	245	249	0.30	400	—
0.25	247	251	0.25	413	—
0.20	252	254	0.25	442	—
0.15	265	261	0.30	456	—
0.15	325	322	0.35	470	—

La solution aqueuse du complexe se montre orange quand son pH est de 3.0 et rouge-violette pour le pH 5.9. Le centre d'absorption, pour la concentration 1/300 mol, se trouve à 400 mμ de la longueur d'onde, quand le pH est de 5.9 (courbe B–fig. 6), et en cela il est presque identique à celui que présente le complexe $[Cr(NH_3)_4(H_2O)_2]Cl_3$ au pH 8.4 (courbe C–fig. 5). Mais on ne peut très bien s'expliquer la différence de pouvoir absorbant présentée par ces deux courbes. Le centre de la bande d'absorption du complexe $[Cr(NH_3)_4(H_2O)_2]Cl_3$ au pH 3.4 (courbe A–fig. 5) montre encore une analogie remarquable avec celui du corps $[Cr(NH_3)_4(OH)_2]Cl$ au pH 3.0.



$[Cr(NH_3)_4(OH)_2]Cl$ (1/300 mol)
A : pH = 3.0 B : pH = 5.9

Fig. 6.

D'après cette analogie, la relation $[Cr(NH_3)_4(H_2O)_2]Cl_3 \underset{p\text{H}=4-5}{\rightleftarrows} [Cr(NH_3)_4(OH)_2]Cl$ est donc admise sans aucun doute, tandis que la transformation de $[Co(NH_3)_4(H_2O)_2]Cl_3$ en $[Co(NH_3)_4(OH)_2]Cl$ n'a pas été définitivement constatée dans le cas du complexe cobaltique.

(7) $[Cr(NH_3)_4(H_2O)Cl]Cl_2$, *Chlorure de chlorotétrammoniohydrine chromique.* Ce corps s'obtient d'après la méthode de préparation indiquée par Pfeiffer[10]. Sa solution aqueuse à la concentration de 1/500 mol est acide et son pH de 3.9. Cependant, quand la valeur du pH est de 7.1, la solution du composé est bleuâtre dès après la préparation de la solution, puis elle prend une coloration rouge-violette.

Des cinq pH mesurés, les pH 3.9; 4.4 et 4.9, sont tous les trois presque identiques dans leur courbe de coefficient d'extinction.

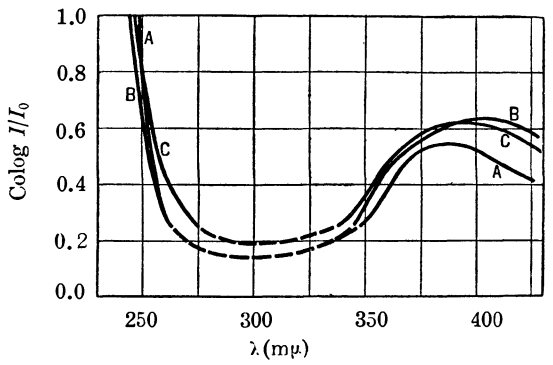
Lorsque le pH atteint 6.0, la bande d'absorption passe vers une longueur d'onde plus élevée et son pouvoir absorbant s'intensifie. Pour le pH 7.1, le centre d'absorption passe légèrement vers une longueur d'onde plus courte, mais une addition d'alcali s'accompagne toujours d'une précipitation par décomposition. Nous pouvons conclure de là à l'existence d'une réaction semblable à celle produite dans les complexes $[Cr(NH_3)_4(H_2O)_2]Cl_3$ et $[Cr(NH_3)_4(OH)_2]Cl$, réaction qui se forme

(10) P. Pfeiffer, *Ber.*, **38** (1905), 3594.

Tableau 7.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ à même concentration (1/500 mol), pour des pH divers (cuve 50 mm.).

Colog I/I_0 \ pH	3.9	4.4	4.9	6.0	7.1	Colog I/I_0 \ pH	3.9	4.4	4.9	6.0	7.1
1.00	245	245	242	239	238	0.20	259	263	262	260	268
0.90	246	246	243	239	239	0.15	263	268	266	264	275
0.80	247	247	244	240	241	0.15	346	348	337	345	338
0.70	248	248	245	242	244	0.20	356	352	349	348	348
0.60	249	249	246	244	246	0.25	362	356	357	357	356
0.50	250	250	248	246	250	0.30	370	370	370	366	360
0.45	251	251	249	247	252	0.35	—	—	—	380	375
0.40	251	253	251	250	253	0.35	—	—	—	426	412
0.35	253	254	252	251	254	0.30	405	400	413	435	435
0.30	254	255	254	254	259	0.25	423	416	—	—	—
0.25	356	258	257	256	262	0.25	465	463	—	—	—



$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ (1/300 mol)
A : pH = 3.9 B : pH = 6.0 C : pH = 7.1

Fig. 7.

comme dans le cas du diaquocomplexe. Cette constatation est aussi applicable au complexe cobaltique.

Comme nous l'avons déjà dit, le radical Cl dans le noyau complexe, comme dans le cas du sel purpuréo $[Cr(NH_3)_5Cl]Cl_2$, n'a pas été influencé par la variation du pH, mais il se transforme, comme le fait la molécule H_2O de constitution, quand il coexiste avec cette molécule d'eau dans le radical complexe.

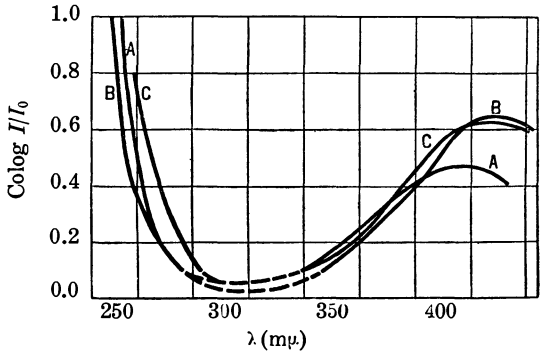
(8) $[Cr(NH_3)_3(H_2O)_3]Cl_3$, *Chlorure de triaquotriammine chromique.* Nous avons obtenu ce corps par la méthode indiquée par Riesenfeld et Seemann[11], et les coefficients d'extinction à 1/300 mol ou 1/500 mol de la solution ont été mesurés en faisant varier le pH.

(11) E. H. Riesenfeld et F. Seemann, *Ber.*, **42** (1909), 4231.

Tableau 8.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_3(H_2O)_3]Cl_3$ à même concentration (1/300 mol), pour des pH divers (cuve 50 mm.).

Colog I/I_0 \ pH	3.3	3.6	6.8	8.9	Colog I/I_0 \ pH	3.3	3.6	6.8	8.9
1.00	243	242	239	—	0.10	—	275	270	278
0.90	—	242	240	—	0.10	—	324	333	324
0.83	244	—	—	—	0.15	—	338	342	337
0.80	—	244	241	249	0.17	338	—	—	—
0.75	245	—	—	—	0.20	—	347	351	348
0.70	—	247	241	252	0.25	351	353	356	355
0.67	247	—	—	—	0.30	—	360	361	359
0.60	—	249	242	254	0.33	361	—	—	—
0.58	249	—	—	—	0.35	—	368	370	362
0.50	250	250	244	258	0.40	—	374	377	369
0.45	—	251	246	260	0.42	378	—	—	—
0.42	252	—	—	—	0.45	—	383	383	375
0.40	—	252	249	261	0.50	—	—	385	377
0.35	—	254	252	262	0.60	—	—	395	394
0.33	254	—	—	—	0.60	—	—	418	415
0.30	—	258	254	263	0.50	—	—	434	435
0.25	258	260	259	264	0.45	—	408	441	440
0.20	—	263	264	274	0.42	414	—	—	—
0.17	263	—	—	—	0.40	—	424	449	444
0.15	—	267	267	276	0.35	—	—	455	—



$[Cr(NH_3)_3(H_2O)_3]Cl_3$ (1/300 mol)
A: pH = 3.3 B: pH = 6.8 C: pH = 8.9

Fig. 8.

La différence entre les pH 3.3 et 3.6 en solution n'a presque pas été observée, tandis que la bande d'absorption passe vers une longueur d'onde plus élevée en intensifiant le pouvoir absorbant, lorsque la valeur du pH atteint 6.8 (courbe B – fig. 8). En augmentant encore le pH jusqu'à 8.9, son influence sur le pouvoir absorbant est très faible dans les régions de

grandes longueurs d'onde, mais assez sensible dans la région ultra-violette. Enfin, la décomposition du corps se produit quand le *p*H atteint 10.1.

(9) $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$, *Chlorure de chlorotriammoniodihydrine chromique;* (10) $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (*noir*), *Chlorure dichlorotriammoniohydrine chromique.* Ces deux complexes ci-dessus nommés sont préparés suivant les indications données par Riesenfeld et Seemann[12].

Tableau 9.

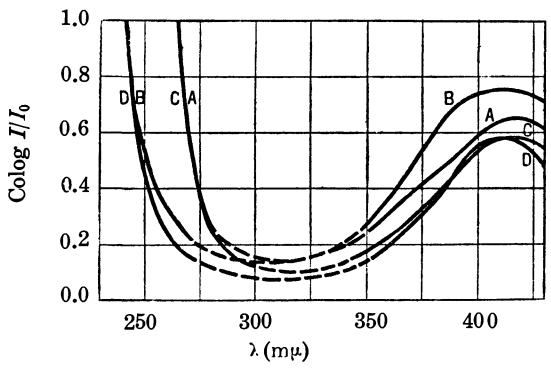
Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ à même concentration (1/500 mol) pour des *p*H divers (cuve 50 mm.).

Colog I/I_0 \ *p*H	3.4	6.7	Colog I/I_0 \ *p*H	3.4	6.7
1.00	261	—	0.15	281	268
0.90	262	—	0.15	351	348
0.80	262	—	0.20	361	356
0.70	264	240	0.25	374	364
0.60	265	241	0.30	389	370
0.50	267	242	0.35	398	380
0.45	268	244	0.40	—	386
0.40	269	247	0.40	—	435
0.35	271	249	0.35	435	459
0.30	274	252	0.30	445	—
0.25	275	254	0.25	454	—
0.20	277	262			

Le complexe $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ dissous en solution aqueuse ayant une concentration de 1/500 mol donne lieu à une solution de coloration rose au commencement, mais quelques minutes après, la solution devient presque incolore quand le *p*H atteint 3.4. Comme on peut l'observer dans la figure 9 (courbes A et B), la courbe du *p*H 6.7 montre un pouvoir absorbant plus faible en région ultra-violette que celle du *p*H 3.4; de plus la bande d'absorption se trouve légèrement dans des longueurs d'onde plus basses dans le premier cas que dans le second.

La concentration à 1/410 mol de la solution du corps $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (noir) présente de l'acidité quand le *p*H est à

(12) E. H. Riesenfeld et F. Seemann, *loc. cit.*



(1/300 mol)

$[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ {A : pH = 3.4 / B : pH = 6.7

$[Cr(NH_3)_3(H_2O)Cl_2]Cl$ {C : pH = 3.8 / D : pH = 6.3

Fig. 9.

3.8, avec une coloration violette-bleuâtre, tandis que la solution aqueuse possédant un pH de 4.7 a une coloration rougeâtre. Lorsque la valeur du pH passe de 3.8 à 4.2, le pouvoir d'absorption s'affaiblit très peu dans la région des longueurs d'onde plus petites, et cette diminution d'absorption devient plus sensible quand le pH atteint 4.7; mais la position d'absorption se modifie légèrement dans les longueurs d'onde plus courtes. Cependant quand le pH passe de 4.7 à 6.3, on n'observe plus de variation sensible, et la précipitation se produit quand le pH est supérieur à 6.3.

De la forme identique des deux courbes A et C, dans la figure 9, nous pouvons induire que les deux complexes $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (pH = 3.8) et $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ (pH = 3.4) prennent une constitution chimique semblable en solution aqueuse, ce qui est probablement le dichloro-complexe comme nous le verrons après.

(10) $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (*noir et gris*), *Chlorure dichloro-triammoniohydrine chromique.* L'autre isomère du complexe

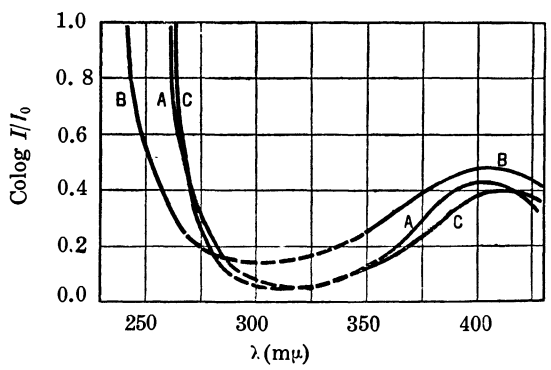
Tableau 10.

Absorption (Colog I/I_0) des solutions de $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (noir et gris), pour des pH divers (cuve 50 mm.).

noir (1/410 mol)					gris (1/820 mol)			
pH / Colog I/I_0	3.8	4.2	4.7	6.3	pH / Colog I/I_0	3.7	4.5	7.0
1.00	263	257	243	—	1.00	256	—	—
0.90	264	258	245	—	0.90	258	—	—
0.80	265	260	247	242	0.80	259	238	—
0.70	266	261	249	242	0.70	259	246	240

Tableau 10. (*fin*)

noir (1/410 mol)					gris (1/820 mol)			
Colog I/I_0 \ pH	3.8	4.2	4.7	6.3	Colog I/I_0 \ pH	3.7	4.5	7.0
0.60	268	262	250	243	0.60	261	242	243
0.50	269	264	252	245	0.50	262	243	245
0.45	270	265	254	246	0.45	262	244	248
0.40	271	266	257	247	0.40	264	246	251
0.35	273	269	260	250	0.35	266	250	255
0.30	275	271	261	252	0.30	268	254	262
0.25	277	273	265	255	0.25	270	260	266
0.20	277	276	269	—	0.20	275	263	273
0.15	282	—	271	262	0.15	278	266	—
0.10	291	—	279	274	0.10	285	—	—
0.10	343	—	321	352	0.10	356	—	—
0.15	358	—	—	360	0.15	371	349	—
0.20	369	356	343	367	0.20	379	363	360
0.25	378	369	357	380	0.25	—	378	384
0.30	387	375	369	386	0.25	—	431	435
0.35	394	388	381	390	0.20	426	443	445
0.40	—	—	391	—	0.15	438	—	—
0.40	—	—	434	—				
0.35	440	—	—	431				
0.30	454	—	—	440				



$[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (1/500 mol)
(gris) A : pH=3.7 B : pH=4.5 (noir) C : pH=3.8

Fig. 10.

$[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (gris) est peu soluble dans l'eau et la solution de 1/820 mol est bleuâtre. Cette solution devient bleue-violette, quand le pH atteint 4.5. Il n'y a presque pas de différence entre les deux courbes d'absorption aux pH 4.5 et 7.0, et la fin de l'absorption de ces deux courbes se trouve dans une région de longueurs d'onde plus basses comparées à celles de la courbe donnée

par la solution ayant le pH 3.7, mais la position de bande de ces trois courbes est semblable.

Quant à la comparaison de deux isomères, noir et gris, nous observons, dans la figure 10, que la courbe du corps gris (courbe A), dans les longueurs d'onde plus courtes, est superposable à celle donnée par le composé noir (courbe C) qui est encore identique dans la région ultra-violette au monochloro-complexe (voir la courbe du $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ de la figure 9). Par conséquent, nous sommes en mesure de conclure à l'identité des courbes de ces trois composés. Nous pouvons observer, dans la figure 10, en comparant les deux courbes A et C, que la bande d'absorption du corps gris se trouve légèrement dans des longueurs d'onde courtes. Nous remarquons encore que l'isomère vert signalé dans certains comptes-rendus n'a pu être obtenu par nous à l'état pur.

Sur les spectres d'absorption des solutions aqueuses des triammines chromiques. Les triammines chromiques que nous avons étudiés ont le centre de bande d'absorption entre 400 mμ et 410 mμ environ de longueurs d'ondes avec des pH élevés. Nous pouvons en conclure que ces corps se transforment en une même matière par addition d'alcali, c'est-à-dire que le radical Cl, dans le noyau complexe, est influencé comme une molécule d'eau de constitution.

Une grande différence, cependant, a été observée en les comparant avec les complexes cobaltiques, et d'après nos recherches[13], ces triammines cobaltiques ont donné lieu à une anomalie d'absorption pour la formation des complexes polynucléaires, et l'absorption ultra-violette de ces complexes a disparu. Les triammines chromiques, au contraire, présentent généralement le même déplacement des bandes d'absorption que les complexes hydrines. On ne peut donc admettre aucun changement dans la constitution du corps dissous, comme cela a été observé dans le cas des complexes cobaltiques. On peut tenir compte de l'existence d'un composé comme $[Cr(NH_3)_3(H_2O)_2(OH)]Cl_2$ qui a remplacé la molécule H_2O dans le noyau complexe par le radical OH, mais un pareil composé a simplement été signalé par Werner[14]. Celui-ci a seulement obtenu l'iodure d'un corps semblable. Il semble donc que la constatation de cette comparaison soit assez difficile à faire.

Les isomères des triammoniodichloro-cobaltiques ont donné une absorption identique, mais les deux isomères chromiques, types noir et gris,

(13) Ce bulletin, **10** (1935), 85.

(14) A. Werner, *Ber.*, **39** (1906), 2663.

ont montré des courbes d'absorption différentes, comme nous l'observons dans la figure 10.

Nous avons admis le changement des complexes triammoniodichloro-cobaltiques en monochloro-complexes dans la solution aqueuse et, maintenant, les complexes chromiques correspondants, même les monochloro-complexes, se transforme en dichloro-complexes . Cela vient de ce que les absorptions dans la région ultra-violette sont identiques (fig. 9) ; ces absorptions sont différentes dans la position du monochloro-complexe, comme $[Cr(NH_3)_4(H_2O)Cl]Cl_2$ (voir la figure 7), mais identiques dans le dichloro-complexe, comme $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$ que nous verrons dans la catégorie suivante. De plus, si ce dichloro-complexe se transforme en monochloro-chromique dans la solution, les isomères que nous avons déjà signalés doivent être exclus. Cependant les deux isomères, types noir et gris, dont nous avons parlé, existent définitivement d'après les bandes d'absorption différentes que nous avons constatées sans aucun doute.

(11) $[Cr(NH_3)_2(H_2O)_4]Cl_3$, *Chlorure de diammoniotétrahydrine chromique;* (12) $[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl$, *Chlorure de dioldiammoniodihydrine chromique;* (13) $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$, *Chlorure de dichlorodiammoniodihydrine chromique.* Les trois complexes ci-dessus

Tableau 11.

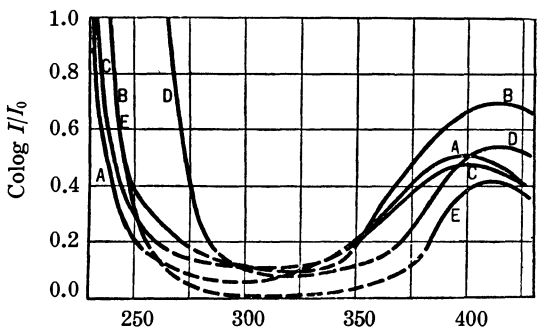
Absorption (Colog I/I_0) des solutions de diammines-chromique complexes à même concentration (1/500 mol), pour des pH divers (cuve 50 mm.).

A : $[Cr(NH_3)_2(H_2O)_4]Cl_3$ B : $[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl$ C : $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$

	A			B	C	
pH / Colog I/I_0	3.1	4.8	5.2	3.4	3.6	6.0
1.00	—	—	236	—	260	235
0.90	—	—	237	—	262	237
0.80	230	—	238	230	263	237
0.70	231	238	239	231	264	239
0.60	232	241	241	233	266	239
0.50	233	241	242	235	268	242
0.45	234	242	242	236	269	243
0.40	236	244	—	237	270	243
0.35	236	246	243	238	272	244

Tableau 11. (*fin*)

	A			B	C	
*p*H / Colog I/I_0	3.1	4.8	5.2	3.4	3.6	6.0
0.30	238	253	244	240	273	245
0.25	240	259	249	243	276	247
0.20	243	266	258	249	278	250
0.15	247	273	268	254	279	251
0.10	254	—	275	266	287	257
0.10	345	—	350	346	367	381
0.15	355	350	353	357	378	386
0.20	365	360	359	361	382	390
0.25	376	370	368	381	388	—
0.30	—	380	378	—	400	—
0.35	—	390	387	—	—	—
0.35	—	440	456	—	—	—
0.30	—	465	472	—	430	—
0.25	424	—	—	425	453	—
0.20	444	—	—	—	484	435
0.15	—	—	—	—	—	455
0.10	—	—	—	—	—	466



(1/300 mol)

$[Cr(NH_3)_2(H_2O)_4]Cl_3$ { A : *p*H = 3.1, B : *p*H = 5.2

$[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl$ C : *p*H = 3.4

$[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$ { D : *p*H = 3.6, E : *p*H = 6.0

Fig. 11.

nommés ont été synthétiquement formés suivant la méthode préconisée par Werner et Klien[15], et le complexe $[Cr(NH_3)_2(H_2O)_4]Cl_3$ d'après Bancelin[16] a donné un corps qui présente une coloration différente de celui obtenu par la méthode de Werner et Klien.

La solution du $[Cr(NH_3)_2(H_2O)_4]Cl_3$ de concentration 1/500 mol donne une valeur de *p*H 3.1. Quand son *p*H passe de 4.8 à 5.2, la solution devient brune.

(15) A. Werner et J. Klien, *Ber.*, **35** (1902), 237.
(16) M. J. Bancelin, *Compt. rend.*, **193** (1931), 597.

D'après la courbe des coefficients d'extinction (courbes A et B – fig. 11) lorsque le pH est de 5.2, l'absorption ultra-violette est moindre que dans le cas où le pH est de 3.1, et la position de la bande d'absorption passe vers des longueurs d'onde plus élevées en intensifiant le pouvoir absorbant.

Le complexe $[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl$ est difficilement soluble dans l'eau, mais il se dissout dans l'acide peu concentré (acide hydrochlorique de 4/100 normal) en donnant un pH de 3.4, et cette solution acide produit une courbe d'absorption superposable à celle du tétraquo-complexe au pH 3.1 (courbes A et C – fig. 11). On peut observer donc la réaction $[Cr(NH_3)_2(H_2O)_2(OH)_2]Cl \rightarrow [Cr(NH_3)_2(H_2O)_4]Cl_3$ à l'état acide.

Le composé $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$ a été mesuré aux pH 3.6 et 6.0 à une concentration d' 1/500 mol. L'absorption dans la région ultra-violette est faible au cas où le pH est élevé, et elle est semblable à celle donnée par la solution du tétraquo-complexe à grand pH, dans la région ultra-violette, et la position du centre d'absorption ne se différencie pas non plus entre ces deux complexes (courbes B et E – fig. 11) ; ce tétraquo-complexe a seulement un pouvoir absorbant plus grand que le dichloro-complexe. Le radical Cl se comporte, dans le noyau complexe de ce diammine chromique, exactement comme la molécule d'eau de constitution.

Comparaison des aquo-complexes chromiques. La figure 12 met en comparaison les courbes d'absorption des aquo-complexes à un pH d'environ 3.0. L'absorption dans la région des longueurs d'onde plus basses est à peu près identique excepté chez le triaquo-complexe. Le centre de la bande d'absorption passe approximativement de 10 à 14 mμ aux longueurs d'onde plus grandes, en remplaçant une molécule de NH_3 par une de H_2O dans le radical complexe, mais son pouvoir absorbant ne montre pas une grande différence. La comparaison de la bande d'absorption, dans la région visible, a été récemment étudiée par

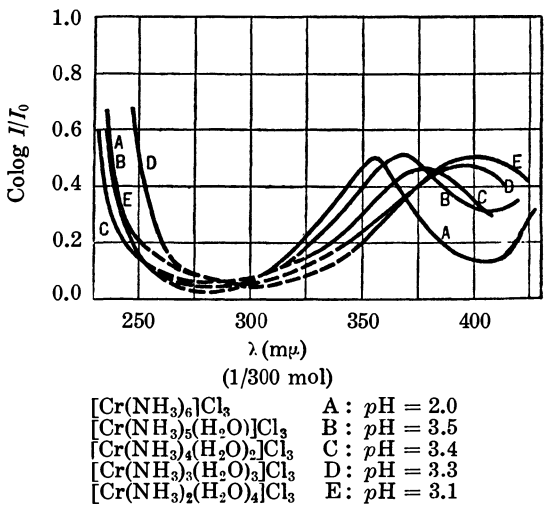
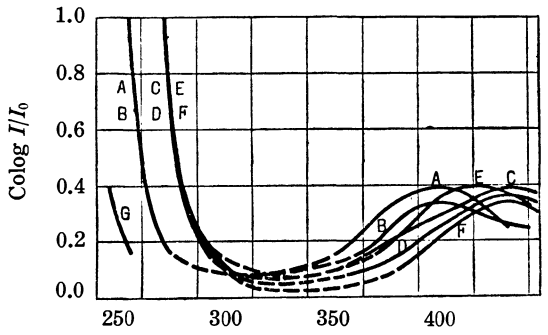


Fig. 12.

Colmar et Schwartz[17], et leurs résultats s'accordent à peu près avec les nôtres.

Nous avons déjà observé le déplacement des bandes d'absorption aux longueurs d'onde plus grandes par comparaison avec les complexes cobaltiques ayant une concentration chimique semblable, mais le changement du pouvoir absorbant a été aussi signalé dans la région ultra-violette.

Comparaison des chloroaquo-complexes chromiques. En prenant plusieurs complexes chromiques qui ont le radical Cl avec la molécule d'eau dans leur noyau complexe, les courbes des coefficients d'extinction au voisinage du *p*H 4.0 ont été comparées dans la figure 13. Les deux courbes d'absorption A et B présentées par le monochloro-complexe sont identiques dans la région ultra-violette et la position des bandes d'absorption occupe à peu près la même position; seulement la courbe B absorbe une partie de la lumière ayant des longueurs d'onde un peu plus grandes, mais son pouvoir absorbant est aussi plus faible.



(1/500 mol)

$[Cr(NH_3)_5Cl]Cl_2$ A : *p*H = 4.0
$[Cr(NH_3)_4(H_2O)Cl]Cl_2$ B : *p*H = 3.9
$[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ C : *p*H = 3.4
$[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (noir) D : *p*H = 3.8
$[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (gris) E : *p*H = 3.7
$[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$ F : *p*H = 3.6
$[Cr(NH_3)_6]Cl_3$ G : *p*H = 2.0

Fig. 13.

Par la comparaison des solutions aqueuses des trois dichloro-complexes, c'est-à-dire le premier $[Cr(NH_3)_3(H_2O)_2Cl]Cl_2$ (courbe C) qui, nous l'avons vu, a pris la constitution du dichloro en solution, le deuxième $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (noir) (courbe D), et le troisième $[Cr(NH_3)_2(H_2O)_2Cl_2]Cl$ (courbe F), la similitude du phénomène d'absorption dans la région ultra-violette a été nettement observée et la variation des bandes d'absorption n'est presque pas perceptible.

Seulement, le complexe $[Cr(NH_3)_3(H_2O)Cl_2]Cl$ (gris) (courbe E), dans la région ultra-violette, a une absorption analogue aux trois corps ci-dessus décrits, mais sa bande d'absorption dans les longueurs d'onde plus élevées se trouve entre celle du monochloro et des dichloros.

(17) R. I. Colmar et F. W. Schwartz, *J. Am. Chem. Soc.*, **54** (1932), 3204.

Comme nous venons de le montrer, l'absorption dans la région ultra-violette des monochloro- et dichloro-complexes présente une grande analogie, et l'influence exercée par la présence d'une molécule d'eau de constitution n'est pas aussi considérable que dans le cas des aquo-complexes.

La position des bandes d'absorption se déplace graduellement vers des longueurs d'onde un peu plus grandes, par suite de l'augmentation des molécules d'eau qui existent dans le noyau complexe. Cependant, contrairement au cas des aquo-complexes, on n'a pu remarquer aucune relation précise, comme nous pouvons l'observer dans la figure 13.

La position de la courbe, à la fin de l'absorption, se déplace vers 18 mμ environ, dans les longueurs d'onde plus élevées, en augmentant le nombre des radicaux Cl dans le noyau complexe, et les aquo-complexes, dans le même cas, présentent une position de courbe assez ressemblante à celle du lutéo qui, lui, n'a pas de radical Cl.

Résumé.

(1) Les solutions aqueuses des ammines-chromiques complexes étudiées n'ayant pas de radical OH dans le noyau complexe sont acides et donnent des valeurs de pH 3–4 aux concentrations 1/300–1/500 mol.

(2) Lorsque quelques changements se produisent quand on augmente la valeur du pH dans les courbes des coefficients d'extinction au voisinage du pH 4.5 (inférieur à 7), nous avons constaté que le radical OH entre dans le noyau complexe, excepté les deux complexes: le lutéo et le purpuréo.

(3) La molécule d'eau de constitution est facilement remplaçable par le radical OH, et le radical Cl montre la même tendance quand il est coexistant avec la molécule d'eau dans le noyau complexe.

(4) Lorsque la molécule d'eau de constitution des complexes étudiés est remplacée par le radical OH, la bande d'absorption donnée par le composé se déplace vers des longueurs d'onde plus élevées.

(5) Quand on fait graduellement augmenter le nombre des molécules d'eau contenues dans le noyau complexe des sels hydrines, la bande d'absorption se déplace au fur et à mesure vers de longueurs d'onde de plus en plus grandes, tandis que la position de la fin d'absorption dans la région ultra-violette reste la même.

(6) Dans le cas des chloroaquo-complexes, la position de la bande d'absorption ultra-violette n'est presque pas en relation avec le nombre

des molécules d'eau de constitution, et la fin d'absorption se déplace régulièrement vers des longueurs d'onde plus élevées tout en étant proportionelle au nombre du radical Cl qui se trouve dans le noyau complexe.

En terminant cette publication, nous tenons à remercier la Société "Téjima Kogyô-Shikindan" qui a bien voulu se charger d'une partie des frais de nos présentes études.

Laboratoire de Chimie minérale, Faculté des Arts et Métiers de Tokyo (Tokyo Kogyô-Daigaku).

ON THE PRESENCE OF INERT GASES IN SOME MINERAL SPRING GASES IN JAPAN.

By I. SUGANUMA and K. KITAOKA.

Received April 25th, 1935. Published July 28th, 1935.

Introduction. One of the authors, I. Suganuma, who has long been studying mineral springs and their products in Japan[1] from chemical points of view expected the presence of helium in the natural gases from Masutomi Springs in Yamanashi Prefecture, from the fact that the springs contain radon in a very high quantity, the highest among the springs in Japan.

Gases of Masutomi Springs, gushing out with water, generally contain carbonic acid gas to the extent of 98–99%, oxygen to 0.2–0.8%, and the rest is almost entirely nitrogen. We collected the spring gases from two sources, one of which is Kumitoriyu Spring of Tuganerô Hotel and the other is the left side spring of Fujimotorô Hotel in order to determine helium contents. The water of the former contains radon to 266 mache per liter at 22°C., and the latter to 965 mache at 19°C.[2].

The Procedure and the Apparatus. According to F. Paneth and his collaborators[3] the methods of isolating inert gases can be divided into

(1) I. Suganuma, this Bulletin, **3** (1928), 69, 73, 87.

(2) The figures of radon contents in "The Mineral Springs of Japan", by R. Ishizu (1915), are somewhat different from ours.

(3) F. Paneth, H. Gehlen, and K. Peters, *Z. anorg. allgem. Chem.*, **75** (1928), 383.

two classes, one may be called a chemical method, fixing nitrogen by calcium or magnesium metal or by electric discharge with oxygen, and the other is to be called an adsorption method, fixing nitrogen by active charcoal cooled in liquid air. The treatment carried out by the present authors is as follows.

The gases collected at Masutomi Springs or later at other places were first freed from their active constituents, i.e. carbonic acid gas by means of concentrated caustic alkali, oxygen by alkaline pyrogallol solu-

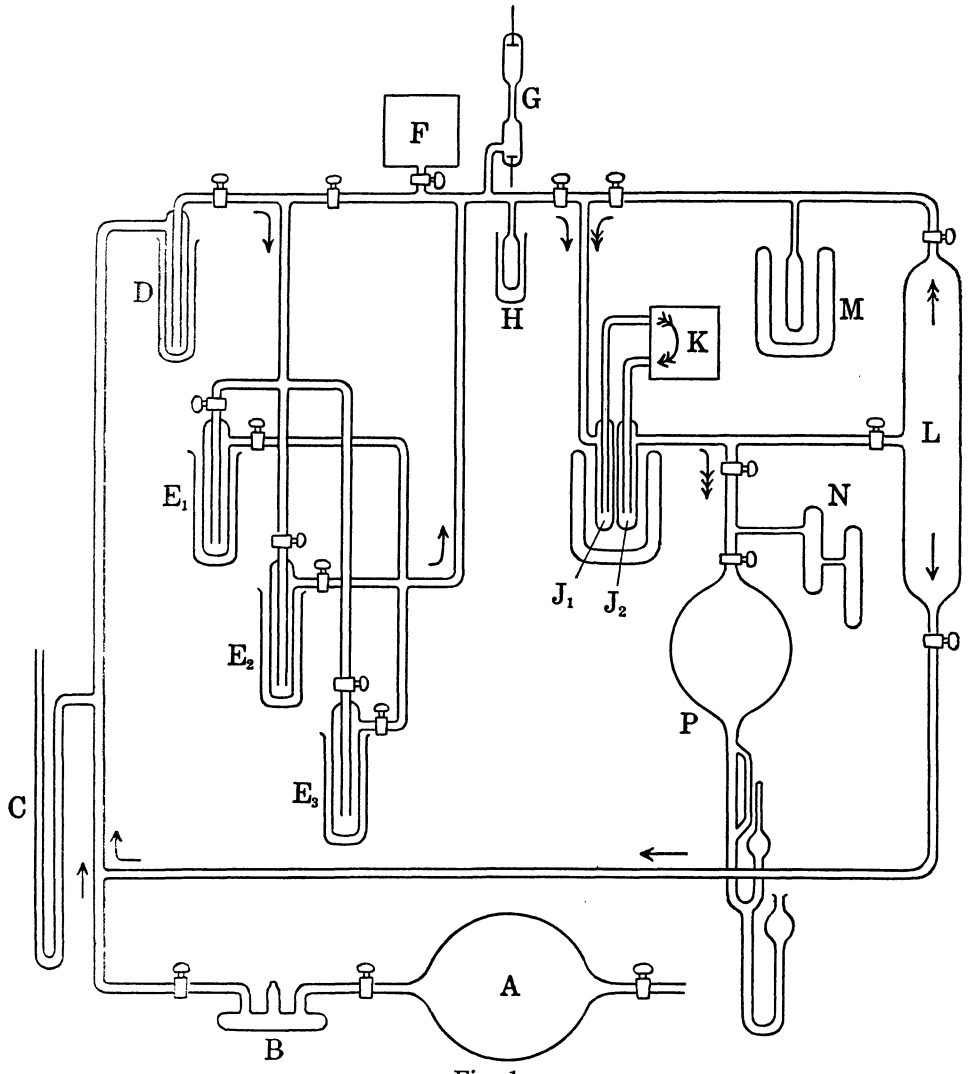


Fig. 1.

tion, heavy hydrocarbons by fuming sulphuric acid, and methane by explosion with oxygen, and the crude nitrogen, which contains probably the inert gases were studied.

The apparatus devised to detect helium in the crude nitrogen is shown in Fig. 1. A is a glass bulb of about one liter capacity, B a tube containing phosphorus pentoxide, C a mercury manometer, D a Pyrex-glass tube containing some copper filings with an electric furnace attached, E_1, E_2, and E_3 three Pyrex-glass tubes, each provided with an electric furnace and containing a mixture of metallic calcium and magnesium oxide prepared from quick lime and metallic magnesium powder, in the proportion of five parts of the former and three parts of the latter, by heating at about 550°C. in vacuum, one of the three tubes being used at a time while the others serving as reliefs, F a Langmuir mercury condensation pump, accompanied by an oil pump serving as a fore-pump, G a Geisler tube for measuring the pressure of nitrogen in the tubes above described, H a Pyrex-glass tube containing palladium powder, previously heated at red heat in vacuum, J_1 and J_2 two traps placed in a Dewar vessel for condensing mercury vapour from another Langmuir condensation pump K working in three steps and carrying the gases in one direction only, i.e. from J_1 to J_2, L a glass bulb of one liter capacity, all the gases under experiment being able to be confined in this bulb if desired, M a glass side tube placed in a Dewar vessel and containing about one c.c. of cocoanut charcoal, previously heated at about 250°C. in vacuum, N a Geisler tube for detecting helium and other inert gases, and P a McLeod manometer provided with a large glass bulb, its capacity, together with that of N, being 1100 c.c.

The whole apparatus is first evacuated with pump F, while D,E's,H, and M are heated until no more gas evolves there. About 750 c.c. of crude nitrogen under experiment, already freed from the active constituents as mentioned above, are introduced and confined into bulb A from the reservoir by the method of water substitution. Dried on passing through B, the gas proceeds to D,E,G,H,J_1,J_2,K, and L, returning to D as shown by the arrows in the figure.

During the circulation, the gas is first freed from all traces of oxygen by copper filings in D heated at about 400°C. Then nitrogen is removed by metallic calcium in one of E's heated at about 500°C., and hydrogen is removed with metallic palladium in H heated at about 250°C.

When the pressure is gradually lowered and no trace of nitrogen cocks, the gas is circulated in the order of J_1,K,J_2,L,M, and J_1 as shown can be seen any longer at G, by an appropriate management of the stop-

by double arrows in the figure, during which time the condensable inert gases are adsorbed by the charcoal in M cooled in liquid air, and almost all of helium is left behind.

Finally the gas is collected in N as shown by the triple arrow in the figure, where the spectra of the gas are photographed and the pressure of the gas in P is also measured by the manometer attached.

In the earlier stages of the investigation, the magnesium arc method was applied instead of calcium powder method for fixing nitrogen, but in the former method the time required for the purpose was much longer than in the latter.[4]

The Comparison of Inert Gases Obtained from the Springs Masutomi, Nozawa, etc., with those of the Ordinary Atmospheric Nitrogen. It has been found by the spectral observation, that the crude nitrogen from Masutomi Springs contains a little helium and the spectra of the sample from Kumitoriyu Spring of Tuganerô Hotel are shown on plate Ia, Fig. 2, where the spectral lines of not only helium but also neon can be seen. If the spectra of the gas are examined without the complete treatment of charcoal adsorption, some spectral lines of argon, say 6677 and 7067 Å, can also be seen. It may therefore be suspected that the gas has been contaminated with the atmospheric nitrogen either on the earth or underground. It was therefore necessary to compare these inert gases from the springs with those in the air.

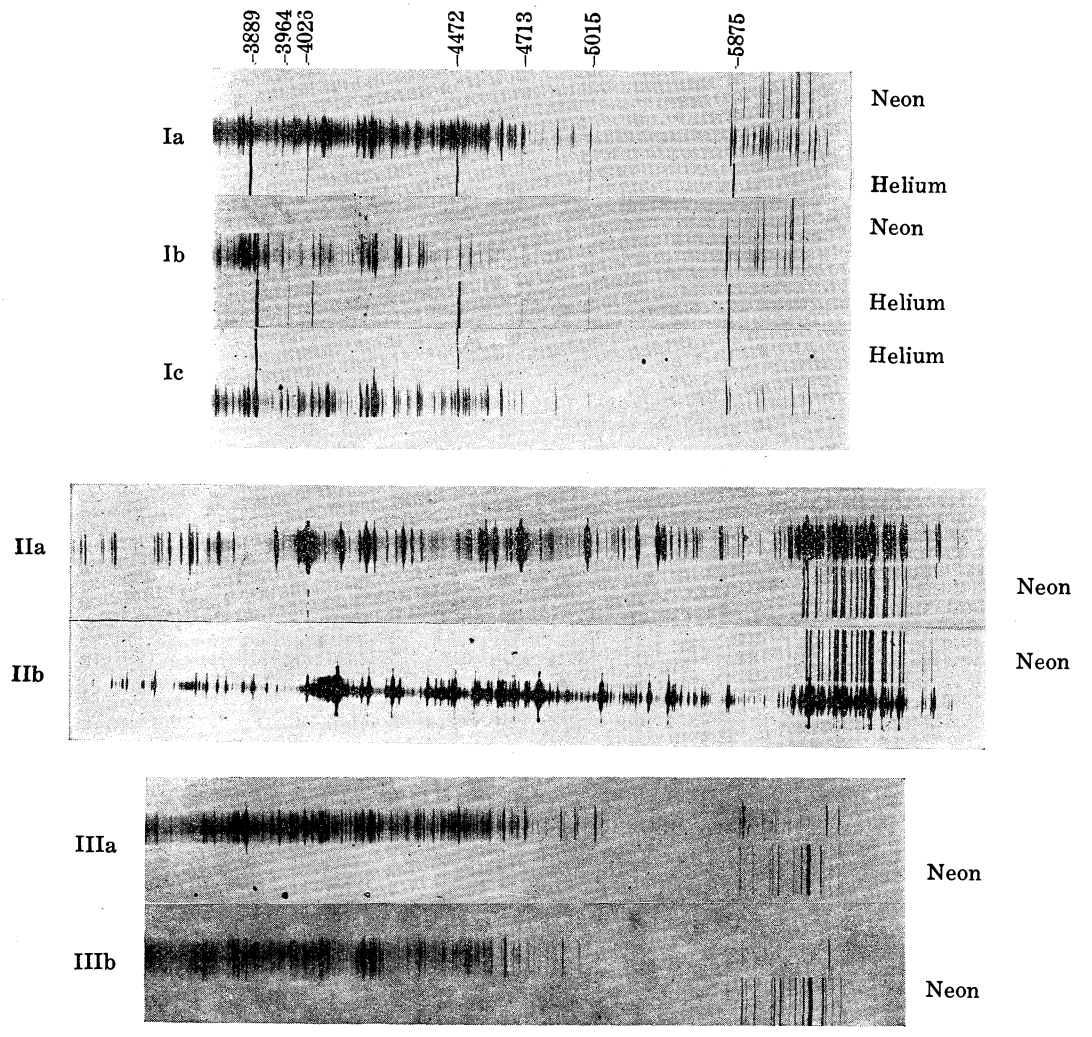
Then, 750 c.c. of the atmospheric nitrogen prepared from air, the volume of which is almost the same as that taken in the preceding experiment, was subjected to the spectral examination as before with the same apparatus. The spectra of the remaining inert gases are shown on plate Ib, Fig. 2. By comparing the two plates Ia and Ib, it can be easily seen that the characteristic lines of helium, especially the line 5015 Å, on the former plate are more intense than those on the latter. It can be supposed that the gas from Masutomi Springs originally contained helium and other inert gases.

Now arises a question whether the presence of helium in the gas from Masutomi Springs is due to the radioactivity product or the primordial atmosphere underground. It has long been questioned why certain natural gases are rich in helium,[5] but the question has not yet been satisfactorily answered.

---

(4) Paneth and his collaborators (*loc. cit.*) preferred metallic calcium for fixing hydrocarbons as well when crude nitrogen contains them.

(5) A. Holms, "The Age of the Earth", 1931, 396, where the literature concerning this point of the question is abundantly cited.



Time of exposure 5 minutes.

Fig. 2.

It has been repeatedly ascertained that as experimental facts the origin of helium in natural gases is not directly related to the radioactivity.(6) We feel, on the other hand, a temptation to consider the richness of helium be somehow connected with the radioactivity, for an

(6) Jeffreys, "The Earth", 1929, 310. Kano and Yamaguchi, *Rep. Aeronaut. Res. Inst. Imp. Univ. Tokyo*, Vol. **13** (1926). Paneth and others, *loc. cit.*

easy liberation of helium may be caused by the cracking[7] and the diffusion of helium through rocks or glasses has been observed.[8]

However the fact that we have found the presence of neon and argon, accompanied with helium, does not favour that temptation. The authors compared the experimental results of the gas from Masutomi Springs with those of the other spring gases which are not or almost not radioactive. For this comparison the gas from Nozawa Springs in Nagano Prefecture was first taken.

The water of the springs is slightly alkaline, containing some quantity of calcium sulphate and calcium bicarbonate. The gas from the springs is combustible, chiefly consisting of methane but mixed with only a little nitrogen. On treating the gas in the same way as mentioned above, the spectral lines of helium and neon were observed, as shown on plate Ic, to be nearly as intense as those in the case of Masutomi Spring gases.

The authors now put importance on the fact that the helium in both cases is accompanied by neon and probably also by the other inert gases of argon, etc. Yamaguchi and Kano, in their studies on natural gases in our country, proved in their plates the presence of helium but none of other inert gases. They adopted exclusively charcoal adsorption method by which neon and argon were probably adsorbed. So it was thought worth while by us to repeat some researches of the inert gases in the same natural gases as studied by them.

The results of our experiments on the inert gases from the springs of Katayamazu and Wakura in Ishikawa Prefecture are shown on plates IIa and IIb, Fig. 2, respectively, where the distinctness of spectral lines has fully convinced us of the presence of the larger contents of helium and neon.

The two other spring gases of Futai near Yusawa Station and of Hirota near Kashiwazaki City, both of which are situated in Niigata Prefecture, were collected and studied by us. The gas of Futai Spring resembles that of Masutomi mentioned above in being rich in carbonic acid gas, but it is different in having almost no radioactivity. The gas of Hirota Spring is combustible owing to its petroleum nature and is slightly radioactive.[9] About 120 c.c. of crude nitrogen obtained from those spring gases was put under the spectral examination as before, and

(7) R. J. Strutt, *Proc. Roy. Soc.*, A, **82** (1909), 166. J. A. Gray, *ibid.*, 391. D. O. Wood, *ibid.*, **84** (1911), 70.

(8) Williams and Ferguson, *J. Am. Chem. Soc.*, **44** (1922), 2160.

(9) N. Yamada, *J. Chem. Soc. Japan*, **44** (1923), 1018.

the spectra of both helium and neon were photographed, plates IIIa and IIIb, Fig. 2.

As for the quantitative estimation it was found that 0.02 for Futai Spring, and 0.2 for Katayamazu Spring, is roughly the volume percentage of helium mixed with a portion of neon to the crude nitrogen.

An Interpretation of the Presence of the Inert Gases in Spring Gases. As to the origin of helium underground Paneth and his collaborators supposed the socalled "fossil helium", which, during a long course of time, had come out of some radioactive minerals in deep places and been accumulated underground under some geological conditions.

The present authors consider that the origin of helium underground has almost no relation to the radioactivity but it is primordial, i.e., helium was contained in the ancient air which was enclosed in the internal parts of the earth, and its richness in the spring gases is due to its inertness and diffusibility causing natural accumulation underground. Oxygen and nitrogen in the ancient air were gradually lost owing to their chemical activity, leaving the inert gases behind.

These arguments are supported by the following facts: (1) So far as the present experiments have been carried out, the spring gases from different districts in Japan, contain helium accompanied by neon and most probably by argon besides. The coexistence of these inert gases has been found by Paneth and his collaborators as well as by Moureu and Lepage.[10] (2) Inert gases are always found with nitrogen in spring gases. (3) So far as the authors have observed, more or less nitrogen has always been found in spring gases, some of which consist of carbonic acid gas and some of the natural gas of petroleum nature. (4) The percentages of helium and neon in the crude nitrogen from spring gases are larger than that in ordinary atmospheric nitrogen. (5) The spring gases of Katayamazu and Wakura are comparatively rich in neon as well as in helium (cf. plates IIa and IIb).

Summary.

Researches of inert gases in some mineral spring gases in Japan have been carried out with the conclusion that the primordial inert gases were contained in the ancient air which was enclosed in the internal parts of the earth, and in the long course of time the oxygen and nitrogen were gradually lost owing to their chemical activity leaving behind inert

(10) *J. chim. phys.*, **11** (1913), 63.

gases such as helium, neon, and argon. When the spring gases are produced largely underground and gush out of the earth they are accompanied generally by the primordial gases, that is to say, they come out upwards together with the inert gases.

The authors wish to express best thanks to Dr. Y. Isida and Mr. M. Fukusima of the Institute of Physical and Chemical Research in Tokyo for their kindness and labour taken in the spectrographical part of the work and also wish to acknowledge with thanks that a part of the expense of this study was defrayed from a grant given by the Educational Department.

The First Higher School, Tokyo.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. V. THE CONSTITUTION OF EICOSATETRAENOIC ACID $C_{20}H_{32}O_2$.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received May 7th, 1935. Published July 28th, 1935.

As described in the 4th report of this series,[1] the highly unsaturated C_{20}-acids were separated from sardine oil. On further fractionation of these acids into individual components, an eicosatetraenoic acid $C_{20}H_{32}O_2$ was isolated, and also the presence of an eicosapentenoic acid $C_{20}H_{30}O_2$ was confirmed by separating a concentrated fraction of this acid. The present paper deals with the constitution of the eicosatetraenoic acid thus obtained. For the determination of its constitution, its amyl ester was subjected to ozonolysis. Among the products of ozonolysis, butyric acid $CH_3 \cdot (CH_2)_2 \cdot COOH$, butyric aldehyde $CH_3 \cdot (CH_2)_2 \cdot COH$, succinic acid $HOOC \cdot (CH_2)_2 \cdot COOH$, and amyl hydrogen succinate $HOOC \cdot (CH_2)_2 \cdot COOC_5H_{11}$ were identified, and also the presence of succinic semi-aldehyde, succinic aldehyde and amyl ester of succinic semi-aldehyde was indicated. Besides these compounds, minor amounts of carbon dioxide and acetaldehyde were found; these compounds, however, are

(1) This Bulletin, **10** (1935), 241.

believed to be derived from a minor ingredient (probably amyl eicosapentenoate) which contaminates the amyl ester used for this experiment. It is seen from these results that amyl eicosatetraenoate has the following groups: $CH_3\cdot(CH_2)_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot COOC_5H_{11}$, of which it must contain three of the group $=CH\cdot(CH_2)_2\cdot CH=$, since it has four ethylenic linkings. Although in the case of moroctic acid described in a previous paper,[2] the positions of three groups which lied between CH_3- and -COOH were determined from the experimental results found by examining the products of ozonolysis of methyl ester of tetrathiocyano-moroctate prepared by the selective addition of thiocyanogen to methyl moroctate, the positions of the respective groups in amyl eicosatetraenoate were confirmed without further proof, since all the products of ozonolysis consisted of C_4-compounds. The constitution of eicosatetraenoic acid is thus established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 16:17}$-acid which is expressed by the following formula:

$$CH_3\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

In comparing the constitution of eicosatetraenoic acid with that of gadoleic acid ($\Delta^{9:10}$-eicosenoic acid)[3] which is a constituent distributed widely in marine animal oils, it should be noted here that eicosatetraenoic acid has no ethylenic linking in 9:10-position. As stated in previous papers,[4] similar relations were found to exist between the polyethylenic and monoethylenic acids having sixteen and eighteen carbon atoms respectively. Thus hiragonic acid ($\Delta^{6:7,\ 10:11,\ 14:15}$) has no ethylenic linking in the same position as zoomaric acid ($\Delta^{9:10}$), likewise moroctic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$) has no ethylenic linking in the same position as oleic acid ($\Delta^{9:10}$).

Experimental.

The methods of isolation of eicosatetraenoic acid from sardine oil have already been described in the previous paper.[5] The same acid as described in the previous paper was used for this experiment. It showed d_4^{15} 0.9300, n_D^{15} 1.4935, neutralisation value 184.3 (calc. for $C_{20}H_{32}O_2$: 184.4), iodine value by the Wijs method 334.0 (calc. 333.7). It was heated with an equal amount of amyl alcohol containing 2.5% of hydrogen chloride on the water-bath under a reflux condenser for one hour, and the resulting amyl ester was separated from the excess of amyl alcohol and some unchanged free acid. The amyl ester (5 g.) was dissolved in 50 c.c. of chloroform

(2) This Bulletin, **10** (1935), 232.
(3) Toyama and Tsuchiya, *J. Soc. Chem. Ind. Japan*, **37** (1934), 31, 34.
(4) This Bulletin, **10** (1935), 192, 232.
(5) This Bulletin, **10** (1935), 241.

ozonised oxygen was passed into the solution under cooling with ice-salt until it became saturated, and on distilling off chloroform under reduced pressure, the ozonide remained as a light yellow viscous oil. Fifteen g. of the amyl ester yielded 24 g. (or 160%) of ozonide which was not thoroughly freed from chloroform. The calculated yields for normal ozonide $C_{25}H_{42}O_{14}$ and ozonide peroxide $C_{25}H_{42}O_{15}$ are 151.3 and 155.6% respectively. Water (150 c.c.) was added to the ozonide, and the liquid was heated in a flask on the water-bath for about 30 minutes. During the heating, a current of hydrogen was passed into the flask, and the volatile decomposition products (**A**) carried over with hydrogen were collected in other three flasks (**a**, **b** and **c**) which were connected in succession to the initial flask by a delivery tube; the first (**a**) was filled with 200 c.c. of water under cooling with ice, the second (**b**) and the third (**c**) with 400 c.c. of approximately 1/3N barium hydroxide solution. The decomposition products remaining in the initial flask partly dissolved in water, and partly separated as an oily substance (**C**) under the aqueous solution (**B**), which was separated by means of filtration. By these treatments the decomposition products of ozonide were separated into three portions (**A**, **B** and **C**).

1. **Volatile Decomposition Products (A).** The aqueous solution in the flask (**a**) produced a pink colouration with Schiff's reagent. On adding *p*-nitrophenylhydrazine and hydrochloric acid, there was formed a precipitate of *p*-nitrophenylhydrazone which on recrystallisation from 50% alcohol yielded *p*-nitrophenylhydrazone of butyric aldehyde in yellow needles of m.p. 86.5–87° (Found: N, 20.29. Calc. for $C_{10}H_{13}O_2N_3$: N, 20.29%). Harries[6] gives m.p. 87° for the same compound. The solution in the flask (**a**) showed also the presence of acetaldehyde by a deep blue colouration produced with diethylamine and sodium nitroprusside. The quantity of acetaldehyde must, however, be small, since *p*-nitrophenylhydrazone prepared from this solution, as stated above, yielded *p*-nitrophenylhydrazone of butyric aldehyde by a single recrystallisation. The solution in the flask (**a**) contained also acidic substances which were not further examined. The barium hydroxide solution in the flask (**b**) was found to contain a small amount of precipitate of barium carbonate, from which the amount of carbon dioxide formed by ozonolysis was calculated as being 1.02% of the amyl ester used for ozonolysis. Should amyl eicosatetraenoate contain the group $=CH\cdot CH_2\cdot CH=$, there would be a formation of carbon dioxide by the secondary decomposition of the products of ozonolysis, such as malonic acid and the corresponding aldehyde derived from that group, and the yield of carbon dioxide would be 11.75% of amyl eicosatetraenoate, provided that the secondary decomposition proceeds to a quantitative extent. As is seen from the results obtained with methyl moroctate in the third report and also with amyl esters of highly unsaturated C_{22}-acids which will be reported elsewhere, the secondary decomposition due to the presence of the group $=CH\cdot CH_2\cdot CH=$ takes place to a considerable extent, though not to a quantitative extent, and it never gives such a minor yield of carbon dioxide as in the present experiment. The formation of carbon dioxide in the present experiment is most likely to be due to contamination of the amyl ester used for ozonolysis with a minor ingredient having the group $=CH\cdot CH_2\cdot CH=$, such as amyl eicosapentenoate. Also the possibility is not excluded that a small portion of the ozonide of amyl eicosatetraenoate undergoes abnormal

(6) "Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen", p. 185.

decomposition with the formation of carbon dioxide. The presence of a minor amount of acetaldehyde in the solution of the flask (a) as stated above is also explainable by the same reason.

2. **Aqueous Solution (B).** This was neutralised with sodium carbonate and then extracted with ether in order to separate the neutral substances. The aqueous solution separated from ethereal extract was acidified with hydrochloric acid, and the acidic substances liberated were extracted with a large quantity of ether. By these treatments the substances dissolved in the aqueous solution (**B**) were separated into (i) neutral substances and (ii) acidic substances.

(i) *Neutral Substances.* Yield 0.6 g. These substances consisted of an orange yellow liquid and showed aldehyde reaction. They were oxidised with an alkaline solution of potassium permanganate, the products obtained after acidification were taken up with ether, and on removal of ether, there remained a mixture consisting of solid and liquid, of which the greater part of liquid was removed by absorption when the mixture was poured on a sheet of filter paper. The remaining solid showed m.p. 175–176° after being washed with a little cold ether and was considered to be an impure succinic acid. From these results, the presence of succinic aldehyde in the initial neutral substances is postulated.

(ii) *Acidic Substances.* Yield 11.2 g. These substances consisted of a reddish orange liquid. They were extracted three times with petroleum ether by using 150 c.c. each time, and the petroleum ether solution was separated from the residual insoluble portion.

The petroleum ether solution was heated on the water-bath until the solvent has distilled off, the residue was then heated in an oil-bath, and there was obtained about 1 g. of colourless distillate between 180–200° (temperature of bath). The silver salt prepared from this distillate was found to be silver butyrate (Found: Ag, 55.41. Calc. for $C_4H_7O_2Ag$: Ag, 55.34%). The final residue of distillation showed aldehyde reaction. Oxidation with alkaline permanganate followed by acidification gave a mixture of liquid and solid, from which the liquid portion was removed by absorption when the mixture was poured on a sheet of filter paper. The remaining crystalline solid showed m.p. 175–176° after being washed with a little cold ether; this was considered to be an impure succinic acid.

The petroleum ether insoluble portion (7.4 g.) consisted of a liquid which deposited crystalline solid on keeping at room temperature. The product obtained by oxidation with alkaline permanganate followed by acidification had neutralisation value 946.5 (calc. for $C_4H_6O_4$: 950.6) and m.p. 182–183°, after being washed with a little cold ether. The melting point was unaltered when the substance was admixed with a pure specimen of succinic acid. When the liquid portion was separated from the initial petroleum ether insoluble portion and kept at room temperature, there was formed a deposit of crystalline solid which was separated from the liquid portion. Further standing of the liquid portion gave another quantity of crystalline solid. Both deposits of crystalline solid thus obtained were considered to be succinic acid as they melted at about 180°. Hence the liquid portion is believed to contain semi-aldehyde of succinic acid which gives crystalline succinic acid by the oxidation in air.

3. **Oily Substances (C).** These were neutralised with sodium carbonate solution, and the neutral substances were removed by extraction with ether. The acidic substances liberated from their sodium salts on acidification were taken up with ether.

The neutral substances (3.1 g.), when oxidised with alkaline permanganate and then acidified, yielded an oily product which proved to be amyl hydrogen succinate having neutralisation value 296.3 and saponification value 592.1 (calc. for $C_9H_{16}O_4$: neutr. value 298.2 and saponif. value 596.5). On recrystallising from ethyl acetate, the free acid liberated from this ester in the usual way yielded succinic acid; neutr. value 945.2, m.p. 182–183°.

The acidic substances (3.4 g.) showed neutr. value 286.5 and saponif. value 590.1, and seemed to consist principally of amyl hydrogen succinate. The free acid liberated from this ester yielded succinic acid which had neutr. value 947.2 and m.p. 180–181° after recrystallisation from ethyl acetate.

Summary.

The eicosatetraenoic acid separated from sardine oil was converted into the amyl ester, and the latter was subjected to ozonolysis. Among the products of ozonolysis were found: butyric acid, butyric aldehyde, succinic acid and amyl hydrogen succinate. The presence of succinic semi-aldehyde, succinic aldehyde and amyl ester of succinic semi-aldehyde was also indicated. Accordingly the constitution of the eicosatetraenoic acid is shown to be $\Delta^{4:5,\ 8:9,\ 12:13,\ 16:17}$-eicosatetraenoic acid as expressed by the following formula:

$$CH_3\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. VI. THE CONSTITUTION OF EICOSAPENTENOIC ACIDS $C_{20}H_{30}O_2$.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received May 7th, 1935. Published July 28th, 1935.

On examining the highly unsaturated C_{20}-acids in sardine oil, we separated an eicosatetraenoic acid and a concentrated fraction of eicosapentenoic acid as described in the 4th report of this series.(1) In the 5th report,(2) the constitution of the eicosatetraenoic acid was established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 16:17}$-acoid. The present paper deals with the determination of the constitution of the eicosapentenoic acid by examining the products of the ozonolysis of the amyl ester prepared from the concentrated fraction of eicosapentenoic acid which had been obtained in the previous study. The concentrated fraction of eicosapentenoic acid used for this experiment, however, contained a considerable amount of eicosatetraenoic acid. It was, therefore, expected from the beginning that the result of the present experiments would not bring sufficient data to establish the constitution of the eicosapentenoic acid. A further experiment will be carried out when the pure eicosapentenoic acid is separated in sufficient quantity.

Among the products obtained by the ozonolysis of the concentrated fraction of amyl eicosapentenoate were found: succinic acid $HOOC\cdot(CH_2)_2\cdot COOH$, amyl ester of succinic semi-aldehyde $HOC\cdot(CH_2)_2\cdot COOC_5H_{11}$, amyl hydrogen succinate $HOOC\cdot(CH_2)_2\cdot COOC_5H_{11}$, carbon dioxide CO_2, acetic acid $CH_3\cdot COOH$ and acetaldehyde $CH_3\cdot COH$. A higher aldehyde in addition to acetaldehyde seemed to be present. Of these compounds a portion of succinic acid, amyl hydrogen succinate and the corresponding semi-aldehyde must have been derived from amyl eicosatetraenote which contaminated the amyl ester fraction used for the ozonolysis, but it was ascertained from the yields of these compounds that not only amyl eicosatetraenoate but also amyl eicosapentenoate itself yielded these compounds, and accordingly eicosapentenoic acid has the groups $=CH\cdot(CH_2)_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot COOH$. Carbon dioxide was formed obviously by the secondary decomposition of the products of ozonolysis

(1) This Bulletin, **10** (1935), 241.
(2) This Bulletin, **10** (1935), 296.

derived from the group $=CH\cdot CH_2\cdot CH=$, and since amyl eicosatetraenoate does not contain the group $=CH\cdot CH_2\cdot CH=$, carbon dioxide obtained in the present experiment must have been derived exclusively from amyl eicosapentenoate; a comparatively large yield of carbon dioxide indicates that amyl eicosapentenoate has more than one of the group $=CH\cdot CH_2\cdot CH=$. Although acetic acid and acetaldehyde are formed together with carbon dioxide by the secondary decomposition of the products of ozonolysis derived from the group $=CH\cdot CH_2\cdot CH=$, it should be taken into consideration that when amyl eicosapentenoate has the group $CH_3\cdot CH=$, it yields acetic acid and acetaldehyde on ozonolysis. A higher aldehyde which seemed to be present in addition to acetaldehyde could not be identified, but it was supposed to be butyric aldehyde derived from the contaminating eicosatetraenoate. From these results, eicosapentenoic acid is shown to contain the following groups: $=CH\cdot(CH_2)_2\cdot COOH$, $=CH\cdot(CH_2)_2\cdot CH=$ and $=CH\cdot CH_2\cdot CH=$, of which eicosapentenoic acid contains more than one of the group $=CH\cdot CH_2\cdot CH=$. The group at the CH_3-side was left undetermined, and consequently the constitution of eicosapentenoic acid could not be definitely established. If, however, eicosapentenoic acid is assumed to have ethylenic linkings at 4:5-, 8:9- and 12:13-positions as in the case of moroctic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$) and eicosatetraenoic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 16:17}$), we can ascribe from the results of the present experiment the following constitution ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 18:19}$) to eicosapentenoic acid.

$$CH_3\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

Experimental.

The concentrated fraction of eicosapentenoic acid used for this experiment was the same sample as described in the 4th report, and had d_4^{15} 0.9399, n_D^{15} 1.5109, neutralisation value 185.1, iodine value by the Wijs method 392.7. As is seen from the iodine value, this fraction still contained a considerable amount of eicosatetraenoic acid (iodine value 333.7) in addition to eicosapentenoic acid (iodine value 419.9). Assuming that this fraction consists exclusively of the two acids, the percentage of eicosapentenoic acid is found to be 68.44%. The above fraction was refluxed with an equal amount of amyl alcohol containing 2.5% of hydrogen chloride for one hour, and the resulting amyl ester was freed from unchanged free acids and the excess of amyl alcohol. The amyl ester (5.5 g.) thus obtained was dissolved in chloroform (50 c.c.), the solution was cooled with ice-salt, and a current of ozonised oxygen was passed through the solution until it became saturated. On distilling off chloroform under reduced pressure, the ozonide was obtained as an orange yellow syrup. As the ozonide was extremely unstable, the last traces of chloroform were not removed. Water (50 c.c.) was added to the ozonide in a flask, and the liquid was heated on

the water-bath for 30 minutes, a current of hydrogen being passed into the flask. The volatile substances (**A**) carried over with hydrogen were collected in three flasks (**a**, **b** and **c**) as in the case of previous experiments of ozonolysis; the first (**a**) was filled with 50 c.c. of water under cooling, the second (**b**) and the third (**c**) with 200 c.c. of approximately 1/3N solution of barium hydroxide. The products remained in the initial flask were separated into aqueous solution (**B**) and oily substances (**C**).

1. **Volatile Substances (A).** These substances were collected in the three flasks (**a**, **b** and **c**). The aqueous solution in the flask (**a**) produced a pink colouration with Schiff's reagent, and a deep blue colouration with diethylamine and sodium nitroprusside, indicating the presence of acetaldehyde in the solution. The *p*-nitrophenylhydrazone prepared from this solution showed m.p. 118–119° after recrystallisation from 50% alcohol (Found: N, 22.61. Calc. for $C_8H_9O_2N_3$: N, 23.46%). The N-content is lower than the calculated value for *p*-nitrophenylhydrazone of acetaldehyde, indicating the presence of higher aldehyde besides acetaldehyde. Although this higher aldehyde was not identified, it should be noted here that the aqueous solution in the flask (**a**) should contain a higher aldehyde such as butyric aldehyde besides acetaldehyde since the amyl ester used for ozonolysis was contaminated with amyl eicosatetraenoate which on ozonolysis yielded butyric aldehyde. The aqueous solution in the flask (**a**) showed also acid reaction and produced a deep red colouration on addition of ferric chloride after neutralisation, from which the presence of acetic acid was inferred.

The barium hydroxide solution in the flask (**b**) was found to contain a considerable amount of a precipitate of barium carbonate which was also found in a minor amount in the barium hydroxide solution in the flask (**c**), and consequently carbon dioxide must have been formed by the ozonolysis. The formation of carbon dioxide is to be attributed to the secondary decomposition of the products of ozonolysis derived from the group $=CH\cdot CH_2\cdot CH=$, and since amyl eicosatetraenoate contaminated the amyl ester used for ozonolysis has no such group, amyl eicosapentenoate must have that group. Calculating from the iodine value 392.7, the total quantity of amyl eicosapentenoate contained in 5.5 g. of the amyl ester used for ozonolysis was found to be 3.77 g. Calculating from the quantity of the precipitate of barium carbonate, on the other hand, the quantity of carbon dioxide formed by the ozonolysis was found to be 0.69 g. or 18.3% of the quantity (3.77 g.) of amyl eicosapentenoate. This is considerably higher than the calculated yield 11.8% which is obtainable on assumption that amyl eicosapentenoate has only one of the group $=CH\cdot CH_2\cdot CH=$ and that the secondary decomposition of the products of ozonolysis derived from that group takes place to a quantitative extent. Consequently amyl eicosapentenoate must contain more than one of the group $=CH\cdot CH_2\cdot CH=$.

2. **Aqueous Solution (B).** The substances dissolved in aqueous solution (**B**) were extracted with ether (500 c.c.), and on distilling off ether from the ethereal solution, there was obtained 4 g. of a reddish orange liquid which was treated with 50 c.c. of petroleum ether in order to effect a separation into petroleum ether insoluble portion and petroleum ether solution.

Petroleum ether insoluble portion (3 g.) was oxidised with alkaline permanganate, and the product, after being acidified and washed with a little ether, was recrystallised from ethyl acetate, yielding impure succinic acid; neutralisation value 945.9 (calc. for $C_4H_6O_4$: 950.6), m.p. 179–180°. Hence, this portion is believed to consist of

succinic acid and the corresponding aldehyde. Although these C_4-compounds may partly be derived from amyl eicosatetraenoate contaminating the amyl ester used for ozonolysis, the yield of this portion indicates that these compounds have been derived also from amyl eicosapentenoate. On distilling off the petroleum ether solution, the distillate of petroleum ether showed acid reaction, and the residue had a smell of acetic acid.

3. **Oily Substances (C).** This portion (2.1 g.) was neutralised with sodium carbonate solution, and the neutral substances were extracted with ether.

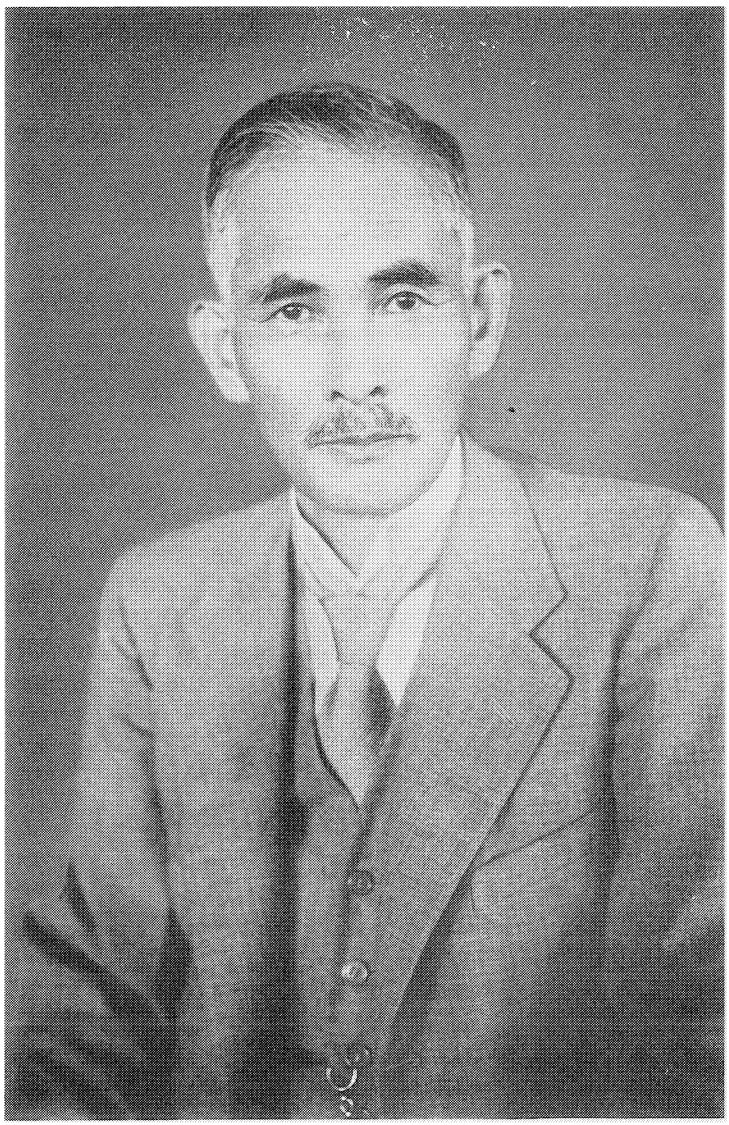
The acidic substances, obtained from the neutralised solution on acidification, had neutralisation value 295.3 and saponification value 594.1, indicating that they consisted principally of amyl hydrogen succinate $C_9H_{16}O_4$ (neutralisation value 298.2, saponification value 596.5). The free acid obtained from this mono-amyl ester yielded, on recrystallisation from ethyl acetate, succinic acid; neutralisation value 947.1, m.p. 182–183°. Oxidation of the neutral substances with alkaline permanganate gave an acid ester having neutralisation value 295.1 and saponification value 592.1. The free acid obtained from the acid ester yielded impure succinic acid melting at 179–180° after recrystallisation from ethyl acetate. From these results, the oily substances (**C**) were found to consist mainly of amyl hydrogen succinate and the corresponding semi-aldehyde.

Summary.

A concentrated fraction of eicosapentenoic acid containing an appreciable amount of eicosatetraenoic acid was converted into amyl ester and the latter was subjected to ozonolysis. Among the products of ozonolysis were found: succinic acid, amyl hydrogen succinate, amyl ester of succinic semi-aldehyde, carbon dioxide, acetic acid, acetaldehyde and a higher aldehyde (probably butyric aldehyde). The yield of these compounds and also the constitution of eicosatetraenoic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 16:17}$) being taken into consideration, it was concluded that the eicosapentenoic acid had the following groups: $=CH\cdot CH_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot COOH$, of which it contained more than one of the group $=CH\cdot CH_2\cdot CH=$. As the group at the CH_3-side was left undetermined in these experiments, the constitution of the eicosapentenoic acid was not established with certainty. If, however, it is assumed that there are ethylenic linkings in 4:5-, 8:9- and 12:13-positions like in the eicosatetraenoic acid, the constitution must be $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 18:19}$-eicosapentenoic acid as expressed by the following formula:

$$CH_3\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.



Motooki Matsuo

PRESIDENT MOTOOKI MATSUI.

Dr. Motooki Matsui was born on December 25th, 1873, at Uchinomura in Sawara-gun of Fukuoka Prefecture, as the second son of Motosuke Hiroba of a samurai family in the clan of Kuroda. In 1889 he was adopted as heir by Tsukuda Matsui. After finishing the elementary and middle school education in the native province, he proceeded through the Fifth Higher School at Kumamoto to the Imperial University of Tokyo where he graduated in 1898 from the Chemical Department of the College of Science. He was conferred the degree of Doctor of Science in 1911.

For seven years after graduating from the Imperial University of Tokyo, he taught in local higher schools and was invited in 1905 to the Imperial University of Kyoto as Assistant Professor in the College of Science and Engineering. In 1911 he was sent by the Government to Germany and England for a further study of analytical chemistry. In Germany he worked at first on electrolytic analysis under Prof. Classen of the Technische Hochschule of Aachen, and then moved to Giessen where he studied chiefly organic electro-chemistry in Prof. Elbs's laboratory. On returning to Japan in 1914, he was appointed Professor in the Imperial University of Kyoto and held the chair of analytical chemistry for nineteen years since then. During these years he was elected the Dean of the Faculty of Science for 1921–1923. He served as the President of the Chemical Society of Japan for the term 1932–1933. In July, 1933, he was elected the President of the Imperial University of Kyoto.

During the earlier days of assistant-professorship in Kyoto Dr. Matsui made investigations in the field of organic chemistry and he was much interested in organic sulphur compounds. A general mode of formation for thio-acids R–CSOH and their esters R–CSOR′ was established for the first time, and was subsequently published in his doctral thesis entitled "Action of Hydrogen Sulphide upon Imido-esters". Since returning from study abroad, his researches were done chiefly in the fields of organic electro-chemistry and analytical chemistry where many important contributions were made to promoting these branches of science in Japan. Among them, especially the research on the mechanism of Kolbe's reaction is, it is presumed, the one that filled his heart with the greatest eagerness and hope.

Dr. Matsui was endowed from the boyhood with a rare intellectuality and grew up as a gentleman of many noble characters and of warm sympathy which filled his laboratory with the atmosphere of admiration and congeniality. At the same time, Dr. Matsui possesses a superb poetical talent and has composed numerous exquisite pieces in the branch of "haiku".

As the President of the Imperial University of Kyoto, the ancient capital city of legends and traditions of hundreds and thousands of years, Dr. Matsui bears on his shoulders the heavy but delightful burden of rearing select thousands of the nation's youths for building up the Japan of to-morrow. Let us all unite in wishing him health and prosperity.

The following is a list of the published scientific papers of Dr. Matsui and those of his pupils under his direct guidance, arranged in the chronological order, and also excellent books written by him during his tenure of the professorship.

Masayoshi ISHIBASHI.

Mitsuru KUHARA and Motooki MATSUI: The Formation of Amines from Halogeniminoesters, *J. Tokyo Chem. Soc.*, **29** (1908), 12.

Motooki MATSUI: Action of Hydrogen Sulphide upon Imidoesters, *Memoirs Coll. Sci. & Eng., Kyoto Imp. Univ.*, **1** (1903–8), 285.

Motooki MATSUI: Oxidation of Hydroquinone by the Catalysis of Carbon, *ibid.*, **1** (1903–8), 386.

Motooki MATSUI: Formation of Iminoesters by Direct Alkylation of Acid Amides with Dimethyl Sulphate, *ibid.*, **2** (1909–10), 37.

Motooki MATSUI: Acyl Derivatives of Thiamides, *ibid.*, **2** (1909–10), 241.

Motooki MATSUI: On Alkylation of Acid Amides, *ibid.*, **2** (1909–10), 397.

Motooki MATSUI: Iminosulphides. Part I. Condensation of Benzonitrile with Thiobenzamide, *ibid.*, **2** (1909–10), 401.

Motooki MATSUI: Action of Hydrogen Sulphide upon Iminoesters. Part II. Formation of Thion-esters and Acids, *ibid.*, **3** (1911–12), 247.

Motooki MATSUI and Shiu SHIMIZU: Electrolytic Reduction of Menthone, *Memoirs Coll. Sci., Kyoto Imp. Univ.*, **4** (1919–21), 245.

Motooki MATSUI and Tadasu NAKAZAWA: The Qualitative and Quantitative Determination of Nickel and Cobalt, *ibid.*, **4** (1919–21), 265.

Kashichi ONO: Electrolytic Reactions of Naphthalene and its Derivatives. Part I. Electrolytic Oxidation of Naphthalene, *ibid.*, **5** (1921–22), 111.

Seiichi ISHIKAWA: Condensation of Nitriles with Thiamides. I. Benzonitrile and Thiobenzamide, *ibid.*, **5** (1921–22), 179.

Kashichi ONO: Electrolytic Reactions of Naphthalene and its Derivatives. Part II. Electrolytic Oxidation of α-Naphthol, *ibid.*, **5** (1921–22), 263.

Kashichi ONO: Electrolytic Reactions of Naphthalene and its Derivatives. Part III. Electrolytic Oxidation of α-Naphthylamine and ar-Tetrahydro-α-Naphthylamine, *ibid.*, **5** (1921–22), 345.

Shunzo KOIZUMI: Electrolytic Oxidation of Alcohols. I. Isoamyl-alcohol, *ibid.*, **5** (1921–22), 359.

Kashichi ONO: The Reaction between α-Pinene and Acids. I. α-Pinene and Sulphuric Acid, *ibid.*, **6** (1922–23), 305.

Masayoshi ISHIBASHI: Electrolytic Reduction of Oximes. I. Benzoinoxime, *ibid.*, **7** (1924), 39.

Seiichi ISHIKAWA: Condensation of Nitriles with Thiamides. II. Acetonitrile with Thiobenzamide; and Benzonitrile with Thioacetamide, *ibid.*, **7** (1924), 93.

Kashichi ONO: Studies on Camphor Oils. Part I. On the Reaction between Camphor Red Oil and Sulphuric Acid, *ibid.*, **7** (1924), 99.

Kashichi ONO: Studies on Camphor Oils. Part II. On the Reaction of Japanese Acid Clay to Camphor White Oil, *ibid.*, **7** (1924), 349.

Kashichi ONO: Studies on Camphor Oils. Part V. On the Sesquiterpenes and Sesquiterpenalcohols of the Japanese Camphor Oil, *ibid.*, **8** (1925), 1.

Shunzo KOIZUMI: The Electrolytic Oxidation of Alcohols. II. Electrolytic Chlorination of Ethyl-alcohol, *ibid.*, **8** (1925), 155.

Masayoshi ISHIBASHI: Electrolytic Reduction of Oximes. III. Benzildioxime, *ibid.*, **8** (1925), 383.

Masayoshi ISHIBASHI: Electrolytic Reduction of Oximes. II. γ-Isonitrosovaleric Acid and α-Isonitrosopropionic Acid, *ibid.*, **9** (1925–26), 37.

Kashichi ONO: Studies on Camphor Oils. III. Action of Oxalic Acid upon Terpinhydrate, *ibid.*, **9** (1925–26), 75.

Kashichi ONO: Studies on Camphor Oils. IV. On the Reaction of Japanese Acid Clay to Terpinhydrate and Terpineol, *ibid.*, **9** (1925–26), 153.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part I. Formaldehyde and Acetaldehyde, *ibid.*, **9** (1925–26), 183.

Yoshihito SAKURADA: On Carbolthionic Acids and their Esters. Part I, *ibid.*, **9** (1925–26), 237.

Yoshihito SAKURADA: On Carbolthionic Acids and their Esters. Part II, *ibid.*, **10** (1926–27), 67.

Yoshihito SAKURADA: On Carbolthionic Acids and their Esters. Part III. Carbithioic Acids and Esters, *ibid.*, **10** (1926–27), 79.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part II. Metanitrosobenzaldehyde, *ibid.*, **11** (1928), 1.

Shunzo KOIZUMI: The Electrolytic Oxidation of Alcohols. III. Electrolytic Oxidation of Benzyl-alcohol, *ibid.*, **11** (1928), 383.

Shunzo KOIZUMI: The Electrolytic Oxidation of Alcohols. IV. Electrolytic Oxidation of Propyl-alcohol in Alkaline Solutions, *ibid.*, **11** (1928), 391.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part III. Ortho- and Para-Oxybenzaldehydes, *ibid.*, **11** (1928), 407.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part IV. Vanillin and Piperonal, *ibid.*, **11** (1928), 419.

Masayoshi ISHIBASHI: Quantitative Analysis of Phosphoric Acid. Part I. Determination as Magnesium Pyrophosphate, *ibid.*, **12** (1929), 23.

Masayoshi ISHIBASHI: Quantitative Analysis of Phosphoric Acid. Part II. New Gravimetric and Volumetric Methods, *ibid.*, **12** (1929), 39.

Masayoshi ISHIBASHI: Quantitative Analysis of Phosphoric Acid. Part III. Determination as Zinc Ammonium Phosphate, *ibid.*, **12** (1929), 49.

Hatsumi KATAGISHI, Yoshinobu GIMBAYASHI, and Motooki MATSUI: The Anodic Behaviour of Substituted Acetic Acid. Part I. Diphenylacetic Acid, *ibid.*, **12** (1929), 57.

Kaoru MATSUMIYA and Hisakazu NAKATA: Organic Compounds of Arsenic. VI. Electrolytic Reduction of some Aryl-Arsinic Acids, *ibid.*, **12** (1929), 63.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part V. Cinnamic Aldehyde, *ibid.*, **12** (1929), 69.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part VI. Complete Reduction of the Carbonyl Group, *ibid.*, **12** (1929), 73.

Masayoshi ISHIBASHI: Quantitative Analysis of Phosphoric Acid. Part IV. Gravimetric and Volumetric Determination as Ammonium Phosphomolybdate, *ibid.*, **12** (1929), 135.

Otozo FUNAKOSHI: A Sensitive Reaction of Cuprous Ion, *ibid.*, **12** (1929), 155.

Goro SHIMA: On the Electrolytic Reduction of Ketones. Part I. Reduction of α, β-Unsaturated Ketones, *ibid.*, **12** (1929), 327.

Koichiro OGURA: Electrolytic Reduction of Nitriles. Part I, *ibid.*, **12** (1929), 339.

Hidemaru ITOMI: The Electrolytic Reduction of *o*-Nitrobenzene Azophenol, *ibid.*, **12** (1929), 343.

Masayoshi ISHIBASHI: Quantitative Analysis of Phosphoric Acid. Part V. New Colorimetric Determination, *Anniversary Volume dedicated to Prof. M. CHIKASHIGE* (1930), 1.

Goro SHIMA: On the Electrolytic Reduction of Aldehydes. Part VII. Crotonaldehyde, *Memoirs Coll. Sci., Kyoto Imp. Univ.*, A, **13** (1930), 86.

Masayoshi ISHIBASHI: Quantitative Analysis of Phosphoric Acid. Part VI. Determination of Phosphoric Acid in a Phosphate Fertilizer, *ibid.*, **13** (1930), 291.

Hidemaru ITOMI: On the Electrolytic Reduction of 3-N-Phenyl-4-Ketodihydroquinazoline, *ibid.*, **13** (1930), 311.

Goro SHIMA: On the Electrolytic Reduction of Ketones. Part II. The Formation of Hydrocarbons, *ibid.*, **13** (1930), 315.

Arata IWAMURA: Quantitative Spectrum Analysis. Part I. On the Electrodes used in Quantitative Emission-Spectrum Analysis. Part II. Quantitative Emission-Spectrum Analysis of Lead in Zinc Oxide, *ibid.*, **14** (1931), 43.

Gisho SAKURADA: A new Method of Determining Tin and Antimony in their Mixture, *ibid.*, **14** (1931), 73.

Arata IWAMURA: Quantitative Spectrum Analysis. Part III. Quantitative Emission-Spectrum Analysis of Cadmium in Zinc Oxide. Part IV. Quantitative Emission-Spectrum Analysis of Copper contained in Lead, *ibid.*, **14** (1931), 327.

Motooki MATSUI, Tetsunosuke SAWAMURA, and Teruzo ADACHI: Electrolytic Reduction of Saccharin. Part I. Electrolysis in Acid and Alkaline Solutions, *ibid.*, **15** (1932), 151.

Motooki MATSUI and Gisho SAKURADA: On the Splitting of the Sulphonic Group from the Aromatic Ring by Electrolytic Reduction, *ibid.*, **15** (1932), 181.

Motooki MATSUI and Shingo ARAKAWA: Electrolysis of a Mixture of Two Fatty Acids, *ibid.*, **15** (1932), 189.

Hisashi KIYOTA: Electrolytic Deposition of Zinc from Acid Solutions, *ibid.*, **15** (1932), 301.

Arata IWAMURA: Quantitative Spectrum Analysis. Part V. Determination of Rubidium Chloride contained in an Artificial Carnallite, *ibid.*, **15** (1932), 355.

Arata IWAMURA: Quantitative Spectrum Analysis. Part VI. An Attempt to determine the Amount of Gold contained in Natural Ores, *ibid.*, **15** (1932), 359.

Arata IWAMURA: Quantitative Spectrum Analysis. Part VII. Determination of the Ratio of the Concentrations of Gold and Silver contained in a Sample, *ibid.*, **15** (1932), 365.

Arata IWAMURA: Quantitative Spectrum Analysis. Part VIII. Determination of Each Salt in a Mixture of Two Salts with the same Anion or a Two Oxide Mixture of Different Elements contained in a Sample by the Spectrographical Determination of the Ratio of the Concentrations of the Two Elements in Question, *ibid.*, **15** (1932), 371.

Motooki MATSUI and Kenichi KIZAKI: On the Mechanism of Kolbe's Reaction, Part I. Electrolysis of Free Acetic Acid, *ibid.*, **16** (1933), 297.

Toshio KOZU: Precipitation of Aluminium with Hydrogen Ammonium Carbonate, *ibid.*, **17** (1934), 17.

Yoshihito SAKURADA: On Carbolthionic Acids and their Esters. Part IV. A new Method of Formation for Thiamides and Thiohydrazides, *Bull. Chem. Soc. Japan*, **2** (1927), 307.

Buhei SAKURAI: Electrolytic Reduction of Phthalimides. Part I, *ibid.*, **5** (1930), 184.

Buhei SAKURAI: Electrolytic Reduction of Alkylphthalimides. Part II. Phthalic Anhydride, *ibid.*, **7** (1932), 127.

Buhei SAKURAI: Electrolytic Reduction of Alkylphthalimides. Part III. Reduction of Phthalic Anhydride, *ibid.*, **7** (1932), 130.

Buhei SAKURAI: Electrolytic Reduction of Alkylphthalimides. Part IV. Complete Reduction, *ibid.*, **7** (1932), 155.

Hamilton Ryoichi MATSUDA: The Relation between Kolbe's Reaction and Hydrogen Ion Concentration. The Mechanism of Kolbe's Reaction, *ibid.*, **7** (1932), 18.

Hamilton Ryoichi MATSUDA: The Relation between Kolbe's Reaction and Hydrogen Ion Concentration. VII. The Mechanism of Kolbe's Reaction, *ibid.*, **7** (1932), 297.

Ctozo FUNAKOSHI: Qualitive and Quantitative Determination of Bismuth by Means of Selenious Acid, *J. Chem. Soc. Japan*, **53** (1932), 433.

Otozo FUNAKOSHI: On a Method for the Separation of Alkaline Earths, *ibid.*, **54** (1933), 1215.

Toshio KOZU: On the various Methods of Determination of Aluminium as its Oxide, *ibid.*, **54** (1933), 653.

Toshio KOZU: Determination of Aluminium by Hydrazine Carbonate, *ibid.*, **54** (1933), 682.

Toshio KOZU: Determination of Aluminium by Ethylamine and its Carbonate., *ibid.*, **55** (1934), 437.

Toshio KOZU: Determination of Aluminium by Methylamine and its Carbonate, *ibid.*, **55** (1934), 447.

Toshio KOZU: Determination of Aluminium by Means of Hexamethylene-tetramine, *ibid.*, **55** (1934), 1295.

Shunzo KOIZUMI: The Anodic Behaviour of Alcohols in Alkaline Solutions, *Memoirs Coll. Sci., Kyoto Imp. Univ.*, **A, 17** (1934), 329.

Books in Japanese written by Dr. Motooki MATSUI:
The Analytical Chemistry,
The Electro-Analysis,
The Organic Electro-Chemistry,
The Organic Chemistry.

ELECTROLYTIC OXIDATION OF ANILINE OIL.

By Toyokichi YASUI.

Received April 2nd, 1935. Published August 28th, 1935.

In 1856, Perkin discovered the first coal-tar dye, mauve; various oxidizing agents were used by different investigators for producing the red dyes from the crude aniline. It is well known that by the strong oxidizing agents mauve is produced, and by the weak oxidizing agents fuchsine is produced.

The author has intended to ascertain what kind of the red dye is produced by the electrolytic oxidation of the crude aniline.

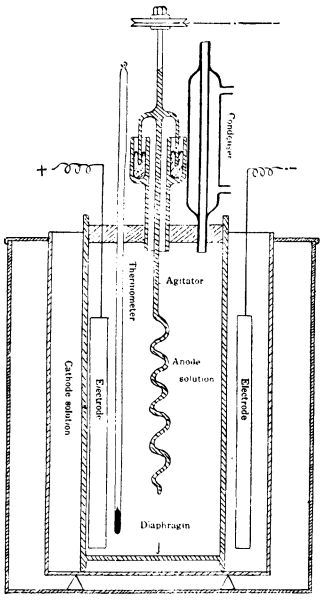


Fig. 1.

The experimental apparatus is shown in Fig. 1. Experimental conditions were as follows: Reagents taken, aniline 15.5 g., *o*-toluidine 17.7 g., and *p*-toluidine 17.7 g. Anode solution, aqueous solution of mineral acid salts of the reagents. Cathode solution, aqueous solution of mineral acid. Electrode, carbon plate. Diaphragm, cylindrical porous cell. Current density, 2 amp./100 sq. cm. Temperature, 80°–90°C. Voltage, 5–6 volts.

I. Quantity of Electricity and Depth of Colour. Under the above conditions, the electrolytic oxidation was applied to aniline oil with a constant agitation of the anode solution. The anode solution became red in short time and by continued treatment it passed into yellow, and finally lost the dying property.

This red dye is difficultly soluble in cold water, fairly soluble in hot water; with alkali it yields a brown precipitate. Its solubility in acid is proportional to the acid concentration, and it becomes colourless by reduction and is gradually recoloured in the air. From these properties it does not belong to triphenylmethane dyes and we may suppose it belongs to the azine group.

At the beginning of the electrolysis, the yield of the dye is proportional to the quantity of electricity; by a further passage of the electrical current the concentration is rather decreased and it is decomposed into foreign substances.

II. Investigation of Absorption Spectrum. It is well known that mauve, safranine, and fuchsine are produced by the oxidation of aniline oil. By comparing the absorption spectra of these dyes with that of the dye which is produced by the electrolytic oxidation, it may be ascertained that the new dye belongs to the series of these dyes, and it is recognized as an intermediate product from the spectra taken at intervals during the oxidation. The absorption curves are shown in Fig. 2. From these curves the dye produced by the electrolytic oxidation is none of mauve, safranine, and fuchsine, but it is situated between mauve and safranine or fuchsine.

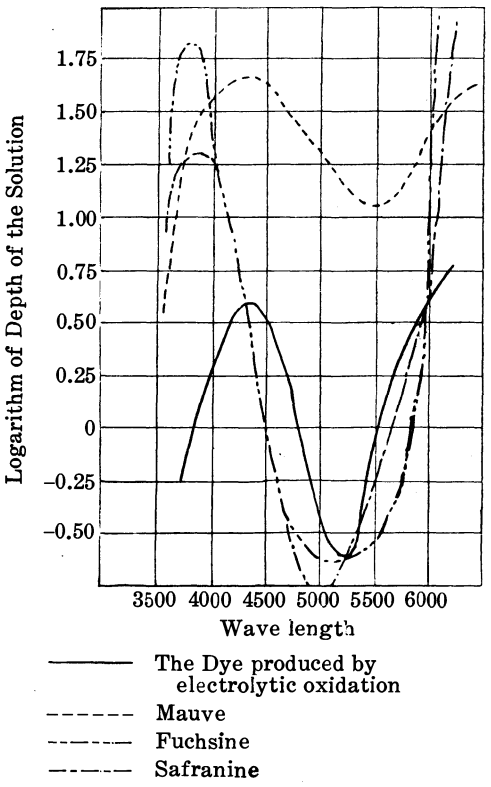


Fig. 2.

At the beginning of the oxidation the absorption takes place at the indigo part and it moves to the purple part, but no definite intermediate product can be recognized by the curves.

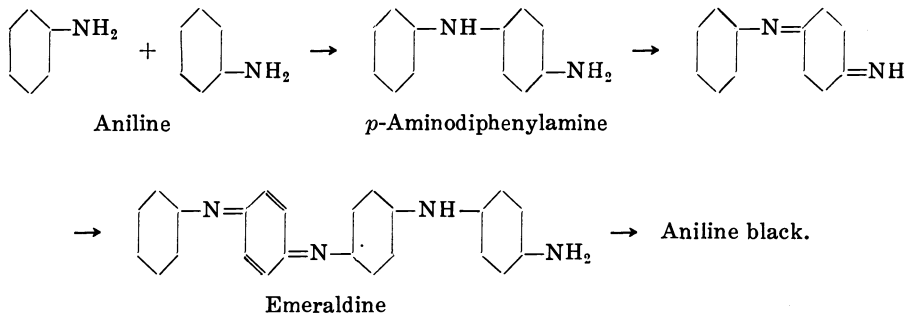
III. The Intermediate Product. From the absorption curves no definite intermediate product can be recognized even though the curves move with progressing oxidation.

By the electrolytic oxidation in the cold, say below 10°C., a blue precipitate is produced, which is scarcely soluble in cold water, fairly soluble in hot water, and easily soluble in alcohol.

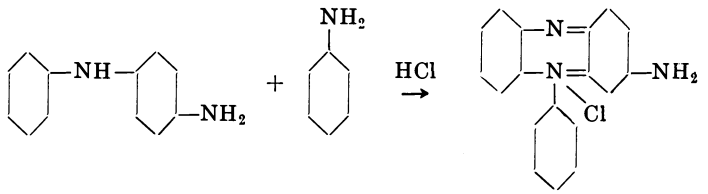
To ascertain the composition of the blue precipitate aniline was first subjected to the electrolytic oxidation at 5–7°C.; the blue precipitate which was soon formed was drawn out from the solution and purified by washing. This blue substance is the same as quinonanil (emeraldine) in all behaviours, which is produced by the ordinary oxidation of aniline.

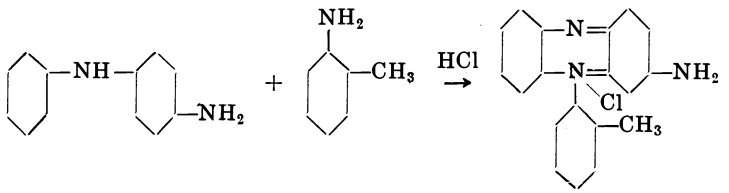
Examination of the properties of the ether soluble substance leaves no doubt that it is *p*-aminodiphenylamine, but the quantity was too small for crystallization.

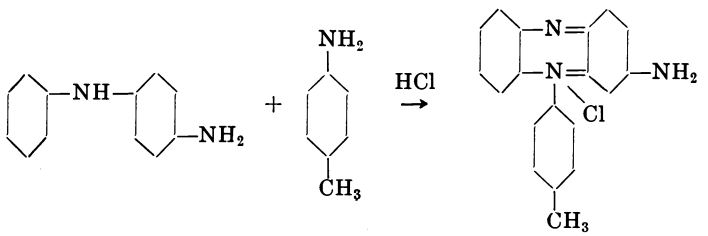
The following equations show the process of the electrolytic oxidation of aniline:



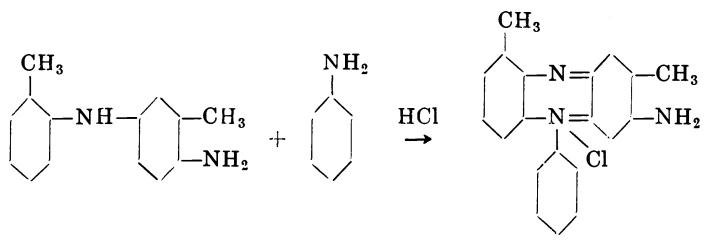
p-Aminodiphenylamine reacts with anilines and produces the red dye, apo-safranine:



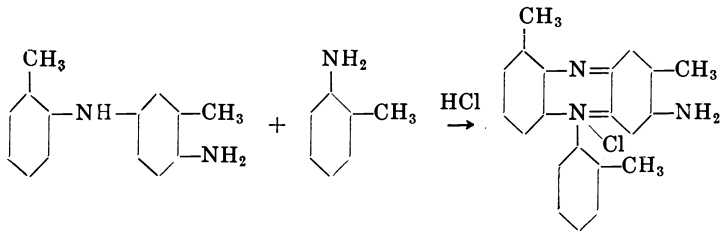




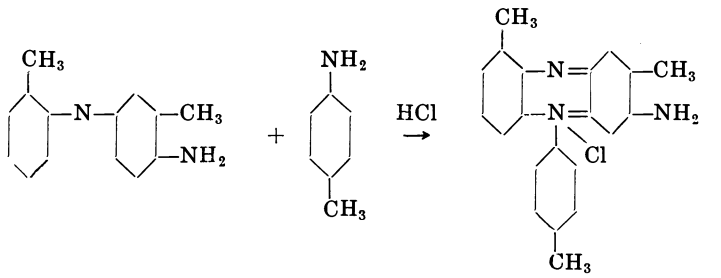
The *p*-aminodiphenylamine produced from *o*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine in the following manner:



(IV)



(V)

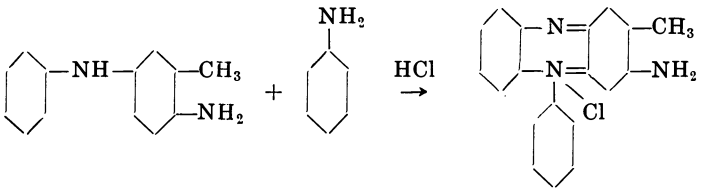


(VI)

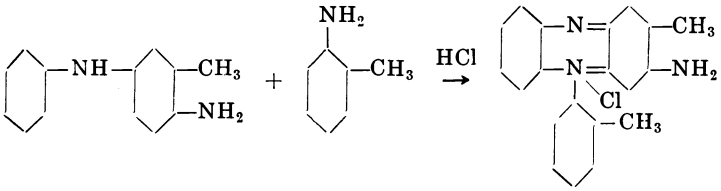
From *p*-toluidine no blue precipitate can be produced. In this case, the basic dyes of reddish-violet are Barsilowsky's and Perkin's bases.

$(C_7H_7N)_3$ (VII) $(C_7H_7N)_3$ (VIII)

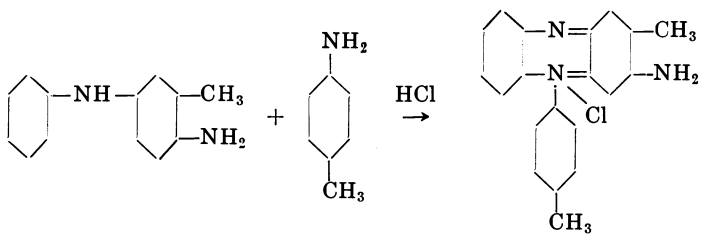
The *p*-aminodiphenylamines from aniline and *o*-toluidine react with aniline, *o*-toluidine, and *p*-toluidine in the following manner:



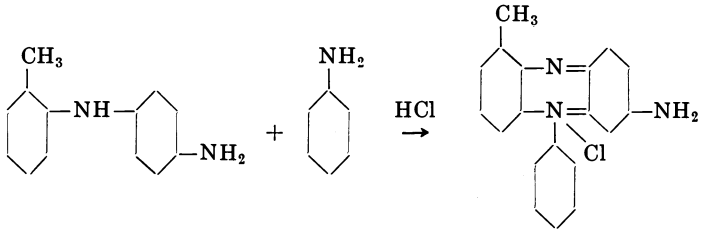
(IX)



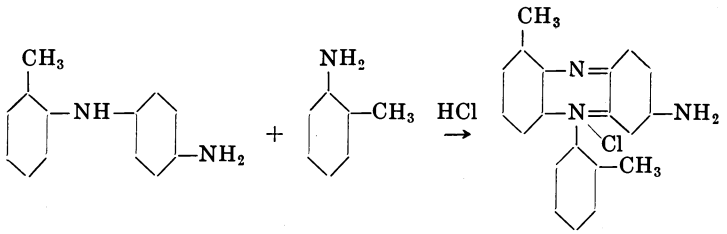
(X)



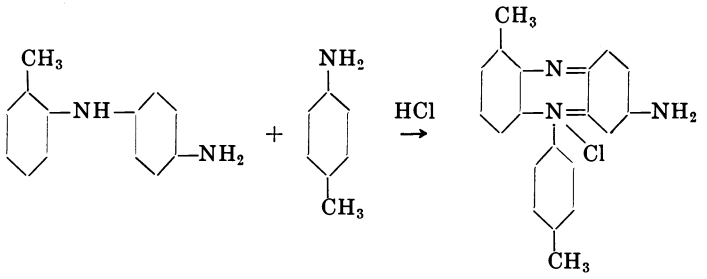
(XI)



(XII)

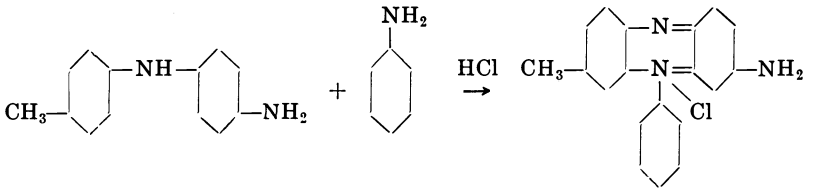


(XIII)

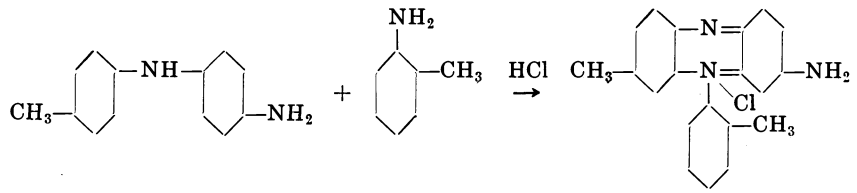


(XIV)

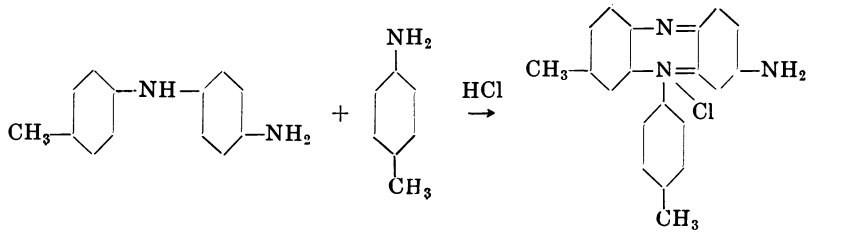
The *p*-aminodiphenylamine from aniline and *p*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine as follows:



(XV)

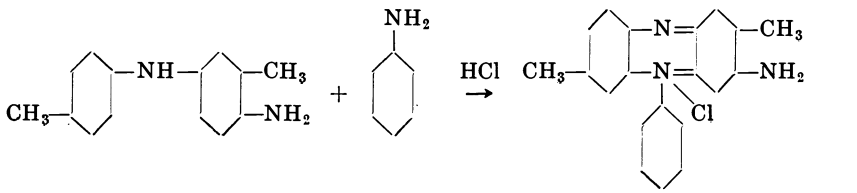


(XVI)

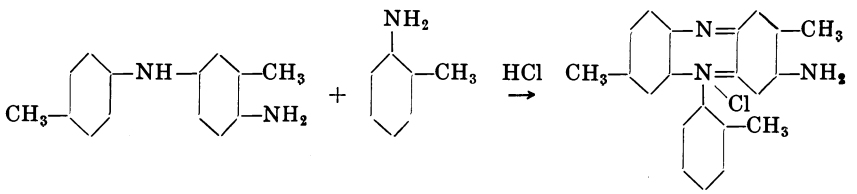


(XVII)

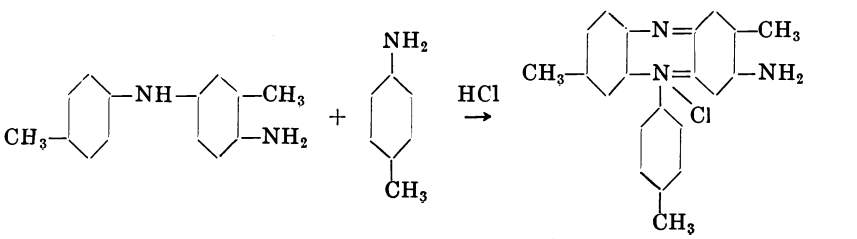
The *p*-aminodiphenylamine from *o*-toluidine and *p*-toluidine reacts with aniline, *o*-toluidine, and *p*-toluidine as follows:



(XVIII)



(XIX)



(XX)

As described above, there are produced 20 kinds of the red dyes by the electrolytic oxidation of aniline oil. Among them (II), (III), (IX), (XII), and (XV) form one group of isomers, (IV), (X), (XI), (XIII), (XIV), (XVI), (XVII), and (XVIII) another group and (V), (VI), (VII), (XIX), and (XX) a third group.

Summary.

(1) By the electrolytic oxidation of aniline oil in acid solution neither safranine nor fuchsine is produced.

(2) *p*-Aminodiphenylamine is first produced, it passes into emeraldine and finally into aniline black.

(3) *p*-Aminodiphenylamine reacts with aniline and homologues producing aposafranine.

The author wishes to express his sincere thanks to Dr. M. Matsui, President of the Imperial University of Kyoto, for his kind encouragement and valuable advices given in the course of these studies.

(October 30th, 1933)

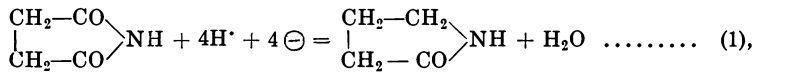
Chemical Laboratory,
Fukui College of Technology.

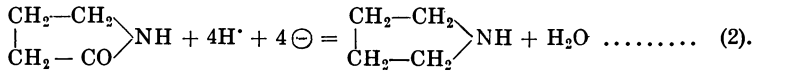
ELECTROLYTIC REDUCTION OF SUCCINIMIDE.

By **Buhei SAKURAI.**

Received April 2nd, 1935. Published August 28th, 1935.

When succinimide is subjected to reduction, it is supposed, in the first stage one of its carbonyl groups undergoes reduction giving rise to the formation of pyrrolidone, and then, by further strong reduction, the other carbonyl group is reduced, pyrrolidine being produced as the complete reduction product:





Many researches have already been reported on the reduction of succinimide, both chemical and electrolytical, with a view to obtain pyrrolidine.

For instance, A. Ladenberg[1] reduced succinimide chemically with metallic sodium in a solution of pure ethyl alcohol, and obtained a small quantity of pyrrolidine. J. Schnick[2] used amyl alcohol in place of ethyl alcohol with a little increase in the yield of pyrrolidine.

J. Tafel[3] attempted an electrolytic reduction with lead cathode of strong reducing ability in solution of 50% sulphuric acid and with very high current density, and obtained pyrrolidone, the product formed by the reduction of only one of the two carbonyl groups. E. Späth[4] also tried a similar electrolysis with derivatives of succinimide and obtained a fair yield of reduction products corresponding to pyrrolidine. Thus the reduction of succinimide itself has been considered more difficult than that of its derivatives.

As the present writer previously recognized the stronger reducing power in zinc amalgam cathode than in lead cathode, he applied it to the projected reduction of succinimide and succeeded in obtaining a pretty good result with a greater yield than in any foregoing experiments.

The cathode for the reduction of such a difficultly reducible substance must be made with an extremely pure material in order to acquire a high reducing power, and, therefore, metals with impurities and consequently with lower overvoltage must not be used. The cathode of zinc amalgam used was made as pure as possible in the following manner. An unglazed cylindrical cell 5 cm. in diametre and 15 cm. in height, which had been prepared with special care as to material, was treated with hot dilute hydrochloric acid for several days until it had no colour. Thus all impurities were dissolved away. Then 250 g. of redistilled pure mercury from E. Merck was introduced into the cylinder and a saturated aqueous solution of pure zinc sulphate also from E. Merck was poured on it. This cell was put in a glass vessel containing pure dilute sulphuric acid and a lead electrode. Zinc was produced by electrolysis on the surface of the mercury as cathode and the lead as anode. When the electrolysis went far enough and the mercury solidified into a sponge-like substance, it was stopped. Zinc amalgam thus prepared was used in the experiments.

The conditions of electrolysis were as follows: Cathode, zinc amalgam, 15 sq. cm.; cathodic solution, 100 c.c. of 50% H_2SO_4 from E. Merck; anode, cylindrical lead; anodic solution, pure 50% H_2SO_4; current density, 100 amperes for 100 sq. cm.; temperature, 38°–40°; time of electrolysis, 6 hours.

Succinimide (10 g.) was introduced into the cathodic solution and the solution was electrolysed with vigorous agitation. The cathodic solution was

(1) *Ber.*, **20** (1887), 2215.
(2) *Ber.*, **32** (1899), 952.
(3) *Ber.*, **33** (1900), 2224; *Z. physik. Chem.*, **35** (1905), 433.
(4) *Mona sh.*, **50** (1928), 349.

cooled during electrolysis by passing cold water through a lead tube inserted in the porcelain cylinder, and the vessel was placed in circulating cold water. The imide dissolved after a little while into a transparent solution. For about half an hour from the beginning the evolution of hydrogen gas was very slight, indicating a smooth reduction. Then the evolution of hydrogen gas increased gradually. When the electrolysis was over, the cathodic solution was taken out and made weakly alkaline with caustic soda solution under cooling in cold water. The characteristic odour of pyrrolidine, the complete reduction product, was set free, and red litmus paper brought near turned blue at once, indicating the presence of a volatile base.

Then the solution was subjected to steam distillation and pyrrolidine distilled off easily with steam. The distillation was continued until red litmus paper changed its colour no more. As pyrrolidine is easily soluble in water, the distillate was a dilute aqueous solution of it. After neutralization of this solution with hydrochloric acid and evaporation on a water bath there remained 1.5 g. of the hydrochloride of pyrrolidine, which corresponded to 14% of the theoretical yield. The gold salt of pyrrolidine which was precipitated on addition of gold chloride melted at 205°. Found : Au, 47.85. Calc. for $C_4H_9N \cdot HCl \cdot AuCl_3$; Au, 47.95%.

The residual solution in the distilling flask was precisely neutralized with sulphuric acid, and after sodium sulphate, which crystallized on cooling the solution, was removed, pyrrolidone, the partial reduction product, remained as an oily substance. It was extracted with ether and 5 g. of crude pyrrolidone was obtained after the removal of the ether. When it was distilled, pure pyrrolidone distilled over at 250°. In a cold place it became crystals melting at 25°.

When succinimide was electrolysed for 12 hours, other conditions being the same as before, the yield of pyrrolidine increased to 28%. If the electrolysis takes place at above 60° and the concentration of sulphuric acid is 50%, succinimide decomposes into succinic acid and ammonia.[5] If sulphuric acid of 65% or over be used, the decomposition happens more easily. If the sulphuric acid is 30% or under, the decomposition does not happen even at 80°, while no reduction takes place.

The writer expresses his sincere thanks to Dr. Motooki Matsui, President of the Imperial University of Kyoto, at whose suggestion this work has been carried out.

(February 17th, 1934)

Chemical Institute, Osaka Women's College,
Sumiyoshi, Osaka.

(5) Pannain, *Gazz. chim. ital.*, **35**, II, 94.

ON THE INDUCED REACTION.

By Riki HORIUCHI.

Received April 2nd, 1935. Published August 28th, 1935.

Since an observation regarding the induced reaction appeared in Mohr's text-book (1855), many chemists have treated it, but its theory still remains unknown. Further, the induced reactions so far described appear to be limited to oxidation reactions, and they are called induced oxidation in other words.

The writer, in the course of a study of isomerization of eugenol and safrol, has discovered an induced reaction, which differs in its nature from any known before, and he has shown it to be a kind of catalytic action.[1]

For the isomerization of safrol into isosafrol, caustic potash is usually used as catalyst, heat being applied at the same time. But, eugenol is difficulty isomerized by the same treatment and gives sometimes a resinous matter, but the reaction generally does not take place. On the other hand, if, eugenol is mixed with safrol and treated with caustic potash as in the case of safrol transformation, eugenol is smoothly isomerized into isoeugenol, safrol being transformed into isosafrol at the same time. Further, experiments have shown that when eugenol and safrol are mixed together, not only eugenol but also safrol are completely isomerized at such a low temperature as would not cause the formation of isosafrol if safrol exists alone. The isomerization of eugenol may be considered to become easy owing to any one of the three following causes: (1) either safrol or isosafrol is a suitable solvent for eugenol; (2) either safrol or isosafrol catalytically accelerates the isomerization of eugenol; (3) the isomerization of safrol induces the isomerization of eugenol.

In order to ascertain which one of these was the real cause, the writer used various solvents as substitutes for safrol, but no positive result was obtained. Even if isosafrol was used as the solvent, the result was negative. It could not be considered that eugenol isomerization was due to the catalytic action of safrol, because safrol becomes isosafrol promptly. Therefore, for the explanation of eugenol isomerization it must be considered that the isomerization of eugenol is accelerated by the isomerization of safrol in the presence of caustic potash; in other words this phenomenon is an induced reaction, where the primary reaction with safrol as inducer and caustic potash as actor accelerates the reaction of caustic potash and eugenol as

(1) *J. Chem. Soc. Japan*, **45** (1924), 209.

acceptor. This view has naturally extended the induced reaction to isomerization beyond oxidation.

A very interesting fact is that, irrespective of the quantity of safrol, and thus in spite of much smaller quantity of safrol compared with that of eugenol, the latter isomerizes vigorously. Not a few authors have explained the mechanism of the induced reaction as consecutive reaction; but, taking into account such views as that of Mellor[2] represented by the formula

$$\text{Induction factor} = \frac{\text{Amount of acceptor transformed}}{\text{Amount of inducer transformed}},$$

it is possible to increase the induction factor to a very large quantity, and the experimental results of the writer have evidently verified that this induced reaction is a catalysis.

The writer, desiring further to extend the above theory to general reactions, has obtained another example.[3] Diphenyl oxide is formed in the reaction expressed by the following equation, copper powder being used as a catalyst:

$$C_6H_5OK + C_6H_5Br = C_6H_5OC_6H_5 + KBr.$$

In case sodium phenolate is used instead of potassium phenolate, the reaction velocity is extremely reduced, but if potassium phenolate and sodium phenolate are mixed together, the reaction proceeds more rapidly than when they are used separately, just in the same manner as the mixture of safrol and eugenol is isomerized by caustic potash.

For such an induced reaction, the writer proposes the name "mutually induced reaction". He considers that, in this case, the relation of the primary reaction to the secondary will be just the same as the relation of the secondary to the primary, each accelerating and promoting the other.

Besides, the writer has given elsewhere many examples of induced reactions and verified that they are all mutually induced reactions.[4] A list of examples including the above-mentioned is given in Table 1.

Table 1.

Primary reaction	Secondary reaction	Actor	Inducer	Acceptor
Safrol+KOH	Eugenol+KOH	KOH	Safrol	Eugenol
Eugenol+KOH	Safrol+KOH	KOH	Eugenol	Safrol
KOH+Eugenol	NaOH+Eugenol	Eugenol	KOH	NaOH
KOH+Safrol	NaOH+Safrol	Safrol	KOH	NaOH
$C_6H_5OK+C_6H_5Br$	$C_6H_5ONa+C_6H_5Br$	C_6H_5Br	C_6H_5OK	C_6H_5ONa

(2) "Chemical Statics and Dynamics", (1904), 333.
(3) *J. Chem. Soc. Japan*, **47** (1926), 368.
(4) *J. Chem. Soc. Japan*, **47** (1926), 357; *ibid.*, **48** (1927), 171.

As given in the table, in these induced reactions, the constitutions and chemical properties of the inducer and the acceptor resemble each other. In view of these facts, the writer has made further experiments by mixing substances of similar constitutions and has obtained an unexpected result of an induced reaction.[5] By the action of dilute sulphuric acid citronellal produces a large quantity of isopulegol, while citral, a minute quantity of dehydroisopulegol. The writer has, therefore, treated the mixture of these two substances in the same way with the expectation that, by induction, these two alcohols might be formed in larger quantities; but, on the contrary the reaction proceeded to an entirely different direction, and each formed a pinacone. These pinacones have not yet been recorded and the writer named them dicitronellal pinacone, $(C_{10}H_{17})_2(OH)_2$, and dicitral pinacone, $(C_{10}H_{15})_2(OH)_2$, respectively. They are formed in large quantities in the above reaction, which affords a good example of the formation of two similar substances from two other similar substances.

To sum up, the induced reaction is explained by the writer in the following manner. When two homologous substances or substances of similar structures are mixed, they catalyze each other, and similar reactions always take place. If one of the two substances reacts with a third substance, they act as inducer and acceptor to each other, and this action accelerates the reaction to a further extent and thus causes induction. In other words, in these induced reactions, the fundamental condition is that the inducer and the acceptor must have a resemblance in chemical structure and properties.

Having found such a fundamental feature of the induced reaction, the writer has made an observation in some usual catalytic actions. As shown in Table 1 the isomerization of eugenol is an induced reaction, in which caustic potash and caustic soda mutually act as inducer and acceptor, but this induced reaction may be described as a catalytic action with caustic soda as catalyst and caustic potash as promotor. Consequently, an induced reaction of this kind is nothing but a catalysis with a promotor. With this view, the writer has investigated the reactions formerly considered mere promotor reactions and found an interesting fact. For instance, it is known that in the ammonia synthesis catalyzed by iron, if molybdenum, tungsten, uranium, etc. are used as promotor, the catalystic activity of iron increases, thus accelerating the velocity of the formation of ammonia. In the case of formation of hydrogen from water gas, $CO+H_2O = CO_2+H_2$, the velocity of formation is said to be greater if the oxides of nickel, chromium, etc. are used as promotor with iron catalyst than if iron alone is used. Further, in the case of producing aniline black from aniline, *p*-diamine or *p*-aminophenol is

(5) *Ibid.*, **47** (1926), 417.

used with vanadium salt as catalyst. In the two former instances, the resemblance in the properties between the catalyst and the promotor is quite clear from the periodic system. In the last instance, although the promotor does not resemble the catalyst, it possesses properties similar to those of aniline, the subject of the reaction.

If the above examples are considered in the light of the writer's opinion that two similar substances mutually act as inducer and acceptor on each other and can cause an induced reaction, it is conceivable that these promotor reactions can also be described as induced reactions.

The writer wishes to extend the observation to catalytic actions in general. The above-described induced formation of diphenyl oxide is conceivable as a reaction of sodium phenolate and bromobenzene catalyzed by potassium phenolate. Or again, the isomerization of eugenol, if this be described as a reaction of eugenol and sodium hydroxide, may be said to be a catalysis by potassium hydroxide. Thus, these induced reactions may be considered as ordinary catalytic actions.

The formation of dicitronellal pinacone appears to be slightly different from the above. As a rule, citronellal yields isopulegol in the reaction with sulphuric acid, but, when it is mixed with citral, the formation of isopulegol is retarded exceedingly, and on the other hand, the reaction is directed toward the formation of dicitronellal pinacone which induces the formation of dicitral pinacone. If this induced reaction is considered a catalytic action by citral, then citral acts poisonously on the formation of isopulegol, that is to say, as a negative catalyst. Consequently, the induced reaction given above involves not only positive but also negative catalysis.

These explanations will show that many examples of catalytic actions, whether positive or negative, and of promotor actions can be described as induced reactions in the sense defined by the writer, that is, reactions taking place when two similar substances are mixed together.

How can the mechanism of this new and particular induced reaction be explained? The radiation theory of reactions proposed by Perrin or C. W. Lewis was once valued as an interesting hypothesis, but the experiments do not support it. If the radiation theory is applied to the present case, it appears that the explanation may be given easily on the basis that the particular radiation emitted by the primary reaction has induced the secondary reaction. However, in this case also, there is no experimental fact to support the hypothesis. Furthermore, the fact that the induction factor can be enlarged to infinity brings about the difficulty that the induced reaction must be considered as a photo-chemical chain reaction. These facts lead the writer to the consideration that this catalytic action may be solved by the

collision theory with the special steric factor taken into account. The writer will further make quantitative experiments and desires to study carefully the mechanism.

At any rate, in view of chemical synthesis, this induction may be utilized to accelerate the reaction velocity; or in the absence of any known standard for the choice of a catalyst, a consideration of the induction may now give some suggestions for this purpose.

Summary.

(1) The induced reaction, which was formerly limited to oxidation reaction, has been extended to reactions in general, and many examples have been given.

(2) All these induced reactions have been proved to be catalytic actions.

(3) Evidences have been given to show that among catalytic actions, positive or negative, and promotor actions, there are many instances which can be described as induced reactions.

(4) It has been shown that these induced reactions must always have two similar substances as inducer and acceptor.

The above thesis is based upon many experiments made since 1924 under the guidance of Dr. Matui, President of the Imperial University of Kyoto. The writer has also been given many valuable advices by Prof. Horiba. He wishes to express his hearty thanks to them.

(April 20th, 1934)

Takasago Perfumery Company, Ltd.,
Kamata, Tokyo.

ON THE STRUCTURE OF NAPHTHALENE NUCLEUS.

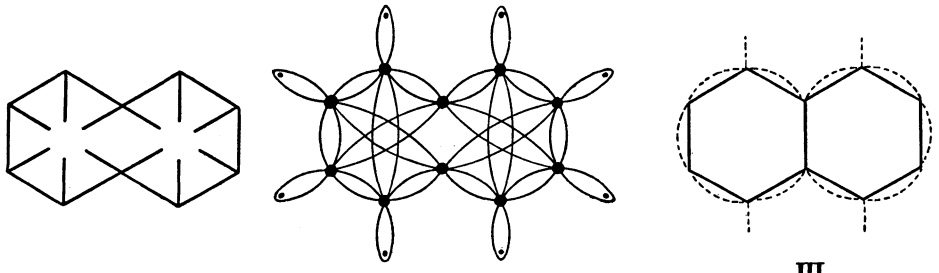
By Nobuo NAKATA.

Received April 2nd, 1935. Published August 28th, 1935.

Although many attempts were made to assign a structural formula to naphthalene, there is much uncertainty in this problem. As an introduction to my own experiments,[1] on which I will report shortly, I have tried to obtain a clear notion on the status of the problem.

(1) *Ber.*, **64** (1931), 2059.

The structural arrangement of the carbon atoms is proved by many syntheses, but the distribution of the five double bonds is very doubtful. This question is identical with the problem of the aromatic nature of the naphthalene system. Bamberger,[2] signifying the analogy between benzene and naphthalene, proposed formula (I) with centric valencies, which in terms of the modern electronic theory of valency is the renewed formula by L. Pauling (II).[3] But these formulæ give no account of the well-known fact that naphthalene does not possess the same degree of aromatic nature as benzene. By the usual substitution reagents naphthalene is very easily attacked, and our model must explain such irregularities.



I II III

The application of Thiele's theory of partial valencies to naphthalene formula (III) can doubtlessly account for the unusual reactivity of the α-positions. But, since the properties of anthracene are not explained by Thiele's theory without the hypothesis that the meso-carbon-atoms are ter-valent, it seems also uncertain to work with Thiele's theory in the naphthalene series. Furthermore, formula (III), cannot account for the very surprising fact that the 3-position is not an ortho-position to the 2-position. For instance, 2,3-dihydroxy-naphthalene cannot be converted into a quinone, while the 1,2-compound can and, on coupling with diazonium-compounds, β-naphthol reacts at an α-position, but by no means at any of the β-positions. The very profound spectrochemical data, collected on naphthalene compounds by K. v. Auwers and his collaborators,[4] lead to the conclusion that the physical and chemical properties of this hydrocarbon are explained by Erlenmeyer's formula (IV) with nuclei, one aromatic and the other partly hydroaromatic. The investigation by Bhatnagar and Singh[5] on the parachor value of

(2) *Ann.*, **257** (1890), 1.

(3) *J. Am. Chem. Soc.*, **48** (1926), 1140.

(4) Auwers and Frühling, *Ann.*, **422** (1920), 192; Auwers and Krollpfeiffer, *ibid.*, **430** (1923), 230.

(5) *J. Indian Chem. Soc.*, **6** (1929), 263.

IV V VI a VI b

naphthalene seems also to demonstrate that it is not a homogeneously aromatic system, but really consists of two different rings. However, formula IV is interpreted by Auwers as not representing a rigid system, but as being in a mobile equilibrium with formula V, in which the ring on the right is aromatic, whereas in the system IV the left ring has a benzenoid character. This interpretation corresponds to the oscillation hypothesis for explaining the fact that only one *o*-dichloro-benzene exists (VI a, VI b). The generalization proposed by Auwers is by no means a progress in the naphthalene chemistry. The previously mentioned fact that the 1,2-, but not the 2,3- positions are really ortho-positions cannot be understood if we assume the equilibrium between IV and V. Only when we make the special assumption that those exclusively combined by a double linkage are ortho-positions and when we, in the second place, attribute the rigid formula IV to naphthalene, we can explain the anomaly in question, an anomaly, indeed, which induced Obermiller[6] to deny the existence of a real bond between the carbon atoms 2 and 3 and between carbon atoms 6 and 7. The difficulty is deepened by the observation of H. de Làszlò[7] that the carbon atoms 2 and 6 are not wholly identical with the carbon atoms 3 and 7 respectively.

There is another question concerning the stereochemical behaviour of naphthalene. Are all the carbon atoms of each ring placed on one plane or are the two rings in our system on the same plane? The observation of Bragg[8] that naphthalene has only one center of symmetry in its crystal is interpreted by E. Bergmann and Mark[9] on the basis of the fact that benzene in its crystalline state is represented by a puckered ring, in which carbon atoms lie alternatingly in two planes. The same assumption for the naphthalene nucleus gives really a centrosymmetrical model. But we must add that the carbon atoms can vibrate between the two possible extreme positions.[10] This statement is confirmed by Mack[11] on measurements of

(6) *J. prak. Chem.*, (2), **126** (1930), 257.
(7) *J. Am. Chem. Soc.*, **50** (1928), 892.
(8) W. H. and W. L. Bragg, " X-Rays and Crystal Structure ", p. 230.
(9) *Ber.*, **62** (1929), 750.
(10) Cf. Richard Kuhn, *Ann.*, **475** (1929), 13.
(11) *J. Am. Chem. Soc.*, **47** (1925), 2468.

the area of the gaseous naphthalene molecule. The centrosymmetry of naphthalene excludes also the possibility that the two rings do not lie in the same plane, an assumption made by Kaufler[12] many years ago. But we must remember the possibility that not all naphthalene derivatives have the same structure, a supposition already expressed by Willstätter.[13]

It seems desirable to make new experiments for elucidating the state of affairs. The method applied by me to the problems in question is the measurement of dipole moments, which has led to very interesting results in the field of organic chemistry.[14]

The moments measured are given in Table 1. The experimental details will be published elsewhere. The comparison between the α-substituted naphthalenes and the corresponding benzene derivatives (nitrobenzene 3.96, fluorobenzene 1.45, chlorobenzene 1.56, bromobenzene 1.49[15]) leads to the very surprising conclusion that only the α-positions of the naphthalene nucleus have an aromatic character. The moments of the isomeric β-compounds are higher, and since the aliphatic halogen atoms have higher moments than the aromatic, we must conclude that the β-positions of naphthalene have aliphatic character. The carbon atoms 2 and 3 are ethanoid, and here is the explanation for the mentioned anomaly of the 2,3-compounds, an explanation which demonstrates, I believe, the correctness of formula IV.

Table 1.

Substance	Dipole moment in 10^{18} electrostatic units	Substance	Dipole moment in 10^{18} electrostatic units
α-Nitronaphthalene	3.88	1,4-Dichloronaphthalene	0
α-Fluoronaphthalene	1.42	1,5-Difluoronaphthalene	~0
α-Chloronaphthalene	1.50	1-Bromo-5-nitronaphthalene	2.49
α-Bromonaphthalene	1.48	2,8-Dichloronaphthalene	2.58
β-Fluoronaphthalene	1.49	2,6-Dichloronaphthalene	0.60
β-Chloronaphthalene	1.57	1-Bromo-2-fluoronaphthalene	2.34
β-Bromonaphthalene	1.69	1-Bromo-2-iodonaphthalene	1.80

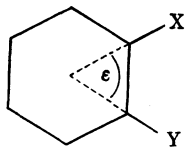
The centrosymmetry of naphthalene is demonstrated by the moments of 1,4-dichloronaphthalene, 1,5-difluoronaphthalene and 1-bromo-5-nitronaphthalene. In a centrosymmetrical model the partial moments of the

(12) *Ann.*, **351** (1907), 151; *Ber.*, **40** (1907), 3250.
(13) *Ber.*, **56** (1923), 1407.
(14) Cf. E. Bergmann and L. Engel, *Z. physik. Chem.*, (B), **8** (1930), 111.
(15) Bergmann, Engel, and Sándor, *Z. physik. Chem.*, (B), **10** (1930), 106, 397.

substituents in the α-positions must be additive, and in the former two compounds they compensate one another; the moments of the latter substance must be equal to the difference of the nitro-group and bromine, namely $3.98-1.49=2.49$, what comes true indeed. The moment of 2,8-dichloronaphthalene has also the expected value. It results from the moments of chlorine in α- and β-positions, respectively, by vectorial addition in an angle of 60°, postulated by the model.

Therefore, it is very surprising that 2,6-dichloronaphthalene has not a zero moment.[16] If other compounds of the same type, which are under investigation, have also a definite moment, we must conclude that in these compounds the naphthalene system is not "uniplanar", but folded.

The investigation of naphthalene derivatives must be pursued. I believe that the most interesting question is the relation between neighbouring atoms and their mutual influence. Therefore, I have measured also the moments of 1-bromo-2-fluoro- and 1-bromo-2-iodo-naphthalene. Bergmann, Engel, and Sándor have exactly proved that the neighbouring atoms in *o*-dihalogenobenzenes repel one another on account of their "Raumbeanspruchung", which increases in the order $F<Cl<Br<I$. The angle between the ortho-valencies, which is normally 60°, increases, and the dipole moment of the compound therefore decreases. The dipole moment of the compound is calculated by the equation

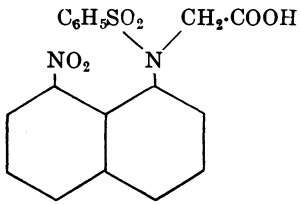


$$\mu^2=\xi^2+\eta^2-2\xi\eta\cos(180-\varepsilon);$$

hence

$$\varepsilon=\arccos\frac{\mu^2-\xi^2-\eta^2}{2\xi\eta}.$$

It is very interesting that on comparison of the two di-halogenated naphthalene derivatives mentioned, with *o*-bromo-fluoro-benzene and *o*-bromo-iodobenzene the angles between the ortho-valencies are almost same (80 and 97° in the benzene series, 76 and 105° in the naphthalene compounds).



It is a well-known fact that also the 1,8-positions in naphthalene are in a certain measure ortho-positions; the very great influence between them is best demonstrated by the resolution of the compound:[17] Höjendahl[18] has measured the moment of 1,8-dinitronaphthalene. If we assume the found value (7.1) to be correct, we must

(16) *Loc. cit.*
(17) Mills and Elliot, *J. Chem. Soc.*, **1928**, 1291.
(18) *Physik. Z.*, **30** (1929), 391.

conclude that the valencies are not parallel to one another, but make—on account of the "Raumbeanspruchung" of the nitro-groups—an angle of ca. 50°. In this question further investigations will bring many interesting informations.

(June 15th, 1934)

SOME NEW DERIVATIVES OF PROTOCATECHUIC ACID FORMED FROM SAFROL AND TWO EXAMPLES OF THE REARRANGEMENT OF THE ACYL GROUP.

By **Kashichi ONO** and **Minoru IMOTO.**

Received May 10th, 1935. Published August 28th, 1935.

Many investigations have already been made on treating safrol (I) with methanol and caustic alkali for splitting off the methylene-dioxy group and thus obtaining methoxy-isoeugenol (II) and methoxy-isochavibetol (III).[1] On protocatechuic acid derivatives (X) formed from them, some detailed work has been published by Hirao[2] of our laboratory of the Nippon Koryo Yakuhin Kaisha, Ltd., Kobe. The commercial production of vanillin from safrol is practiced by our company by this method on a large scale. The present paper deals with the synthesis of new acids by acetylation, benzoylation, and oxidation of a mixture of phenolic compounds of II and III.

The mixed phenolic compounds II and III are obtained from safrol by treatment with methanol and caustic alkali under pressure. If acetic anhydride alone is used for acetylation, diacetate is formed, while, if anhydrous sodium acetate is also added to a large excess of acetic anhydride, the monoacetates alone are formed. When benzene was used as solvent, there was no reaction observed to take place, while, by taking xylene as the solvent, monoacetate was the principal product. By addition of a drop of concentrated sulphuric acid, diacetate alone is produced.

The authors have succeeded easily in crystallizing out methoxy-isochavibetol benzoate (XIV) by employing the method used by Hirao, namely,

(1) G. Ciamician and P. Silber, *Ber.*, **23** (1890), 1162; S. Nagai, *J. Soc. Chem. Ind., Japan*, **27** (1924), 631; N. Hirao, *J. Chem. Soc. Japan*, **51** (1930), 441; T. Hiraizumi, *J. Soc. Chem. Ind., Japan*, **34** (1931), 584; T. Kuwata, *ibid.*, **34** (1931), 590.

(2) *J. Chem. Soc. Japan*, **51** (1930), 713; *ibid.*, **54** (1933), 194, 992; etc.

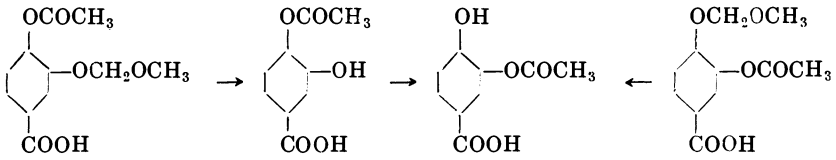
by dissolving the decomposition products of safrol with potassium hydroxide, shaking the solution with benzoyl chloride, treating the soft lump of mixed benzoates with alcohol, and crystallizing out methoxy-isoeugenol benzoate (XIII). The mother liquor contains the compound XIV, which crystallizes out on allowing the mother liquor to stand for about three days. Its m.p. is 55°.

The filtrate from XIII and XIV deposits, when concentrated on the water bath and allowed to stand, propenyl-pyrocatechin benzoate (XV).

When the diacetate of propenyl-pyrocatechin was oxidized with neutral or alkaline potassium permanganate, a resinous product alone was obtained. Both monoacetates (V and VI) could also be oxidized only in acid solution. The monobenzoates XIII and XIV could, however, be oxidized in neutral medium showing that benzoyloxy group is not so easily saponified as acetoxyl group. In this manner, besides the previously known diacetoxy-benzoic acid (VII) the following four new acids were obtained:

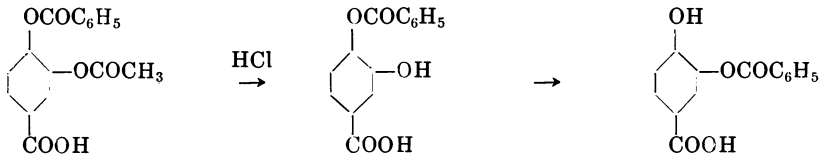
VIII 4-Acetoxy-3-(methoxy-methoxy)-benzoic acid, m.p. 112–113°;
IX 3-Acetoxy-4-(methoxy-methoxy)-benzoic acid, m.p. 150–152°;
XVI 4-Benzoyloxy-3-(methoxy-methoxy)-benzoic acid, m.p. 127°;
XVII 3-Benzoyloxy-4-(methoxy-methoxy)-benzoic acid, m.p. 117–118°.

Diacetoxy-benzoic acid was saponified by concentrated hydrochloric acid into protocatechuic acid (X) and the latter was changed by benzoylation by the Schotten-Baumann method into a new compound, dibenzoyloxy-benzoic acid benzoylester (XII). The compounds VIII and IX were changed by splitting off the methoxy-methoxy group by treating with acids into a compound melting at 198° corresponding to 3-acetyl-protocatechuic acid (XI) synthesized by Ciamician and Silber,[1] and E. Fischer, M. Bergmann, and W. Lipschilz,[3] and melting at 197–199°. Evidently a rearrangement of the acyl group has taken place:

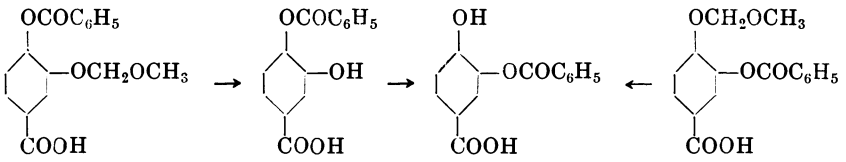


Such a rearrangement of the acyl group has been observed already by various workers, and the present authors have also obtained, by a similar splitting of the methoxy-methoxy group from XVI and XVII, the same compound with melting points 224° and 225°, corresponding to 3-benzoyl-protocatechuic acid (XVIII) obtained by E. Fischer by the following rearrangement:

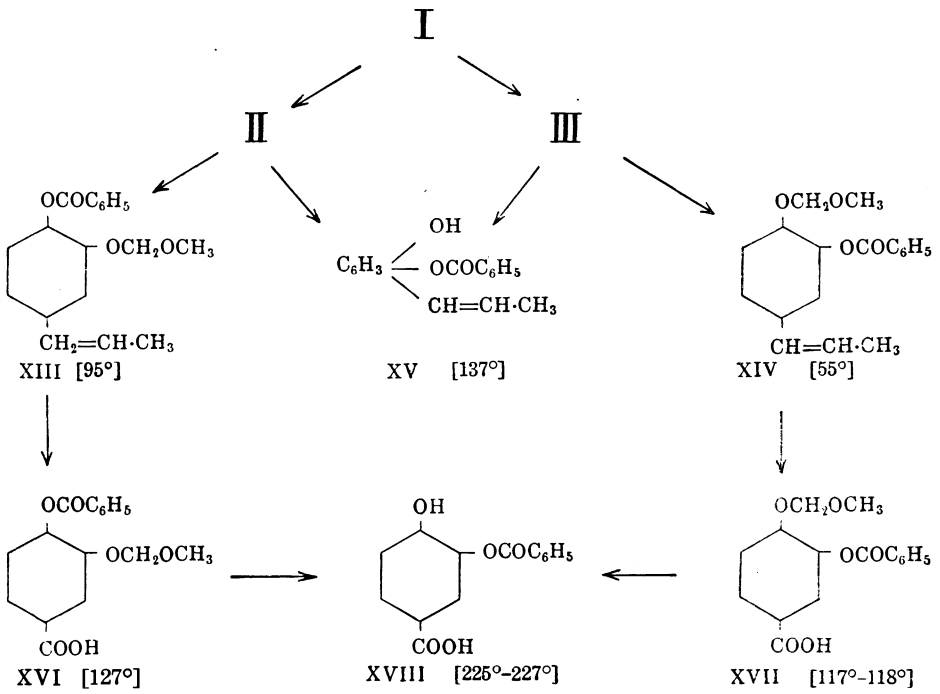
(3) *Ber.*, **51** (1918), 45.

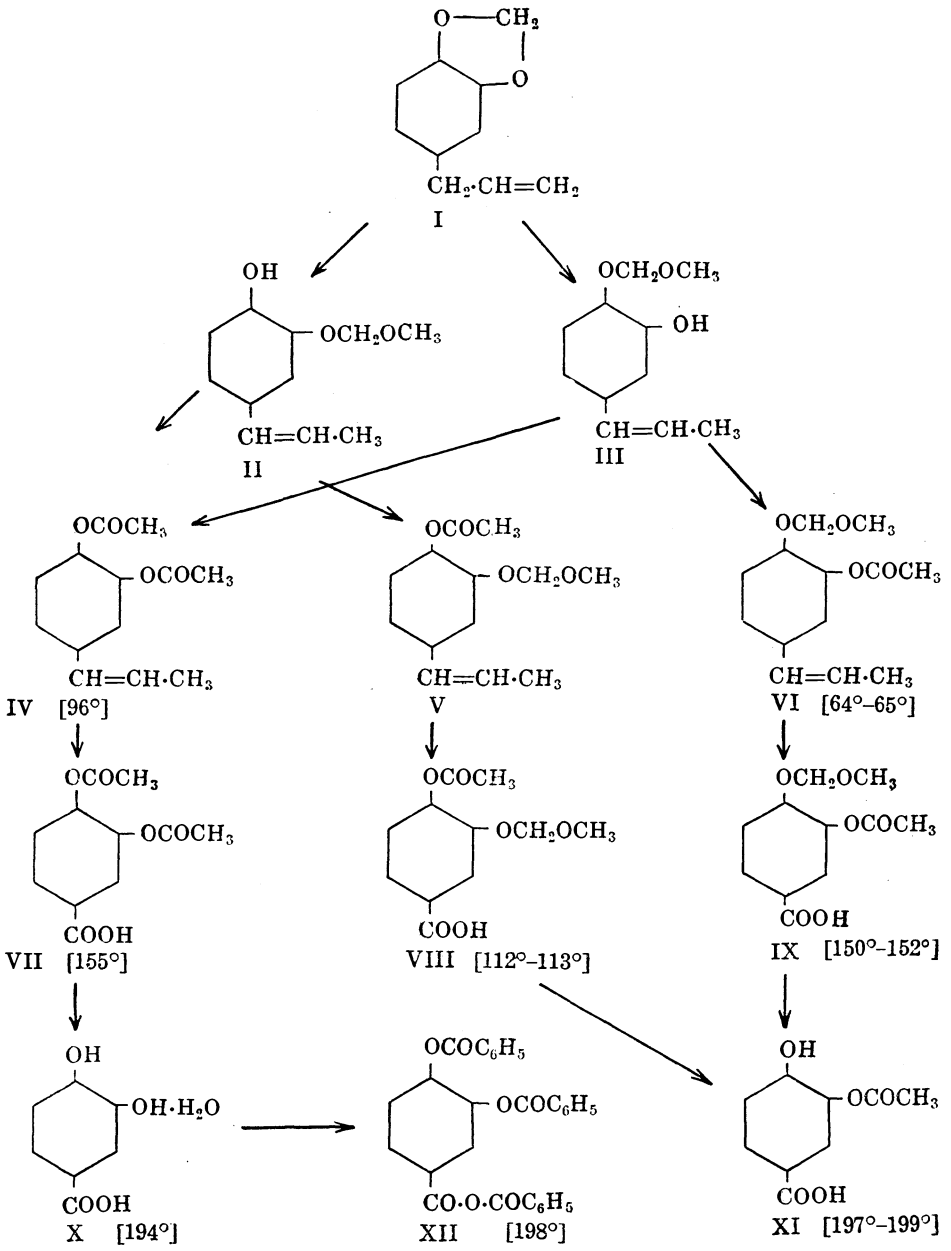


It is evident, therefore, that we have reached the same object of rearrangement by a method different from that of E. Fischer.



The above results are summarized as follows:




O—CH2
O
CH2·CH=CH2
I
OH
OCH2OCH3
CH=CH·CH3
II
OCH2OCH3
OH
CH=CH·CH3
III
OCOCH3
OCOCH3
CH=CH·CH3
IV [96°]
OCOCH3
OCH2OCH3
CH=CH·CH3
V
OCH2OCH3
OCOCH3
CH=CH·CH3
VI [64°–65°]
OCOCH3
OCOCH3
COOH
VII [155°]
OCOCH3
OCH2OCH3
COOH
VIII [112°–113°]
OCH2OCH3
OCOCH3
COOH
IX [150°–152°]
OH
OH·H2O
COOH
X [194°]
OCOC6H5
OCOC6H5
CO·O·COC6H5
XII [198°]
OH
OCOCH3
COOH
XI [197°–199°]

Experimental Part.

(1) **Decomposition of Safrol.** Potassium hydroxide (17 g.) was dissolved in 30 g. of methanol and transferred to the autoclave with 30 g. of safrol, and the mixture was kept at 200°–208° for three hours in an oil bath and then allowed to cool. The contents were poured out into water and the isomerized product, isosafrol, was extracted with ether. On distilling off the ether, 3 g. of isosafrol was obtained. The aqueous layer was cooled with ice and acidified with 110% of the theoretical amount of dilute sulphuric acid. The phenolic substance which floated out was extracted with ether. By distilling off the ether, 31 g. of the raw product was obtained which gave by redistillation 27 g. of the mixture of II and III.

(2) **Acetylation.** (A) *Preparation of the di-acetate.* (a) The decomposition product (100 g.) of safrol and acetic anhydride (105 g.) were kept at 140–145° on an oil bath for 3 hours. Water (150 c.c.) was added and the whole was warmed for 30 minutes on the water bath. On cooling, di-acetate separated out in crystals.

(b) The decomposed phenolic substance (40 g.) was dissolved in 40 g. of xylene, 24 g. of acetic anhydride and one drop of concentrated sulphuric acid were added, and the whole was heated under reflux condenser for two hours. The contents were poured into water, warmed on the water bath for 30 minutes, and cooled. The crystals thus separated were recrystallized from alcohol and showed the m.p. 95°. Yield was 24 g.

(B) *Preparation of the mono-acetates.* (a) The decomposed phenolic substance (100 g.), anhydrous sodium acetate (100 g.), and acetic anhydride (400 g.) were heated under a reflux condenser for 3.5 hours. The contents were poured into a double volume of water, warmed for one hour on the water bath, and then extracted with benzene. On distilling off the benzene, an oily substance was obtained which was subjected to fractional distillation under a reduced pressure of 14 mm.

Fraction	Temperature	Quantity distilled	d_{18}	n_{15}
1	-170°	5 g.		
2	170–172°	105 g.	1.1114	1.5383
3	172–176°	12 g.		

Molecular refraction of fraction 2 was found 66.0, the calculated value for $C_{13}H_{16}O_4$ being 63.05, and hence $\Delta = 3.05$. As the similar derivatives of propenyl-benzene always show $\Delta = 2-3$, the figures thus obtained seem to correspond to those of monoacetyl compound. Fraction 2 (90 g.) was changed to a soft lump by treating with the freezing mixture according to Kuwata.

On filtration by suction, it was separated into 25 g. (27.8%) of crystals (VI) and 65 g. (71.2%) of an oily matter (V). The crystals melted, after washed with cooled alcohol, at 64°.

Fraction	Temperature	Quantity
1	xylene	
2	-165°	2g.
3	165–167°	23.5 g.
4	167–170°	0.5 g.
5	170–171°	13.2 g.

(b) The decomposed phenolic substance (50 g.), xylene (50 g.), and acetic anhydride (28 g.) were heated under a reflux condenser for 1.5 hours. The product was warmed with water for 30 minutes. The floating oily matter was fractionated under 13 mm. pressure. The fraction 2 gave a beautiful green coloration with $FeCl_3$ and proved to be the unchanged phenolic substance. The fraction 5 was the product aimed at and gave by freezing crystals melting at 64°.

(3) **Benzoylation.** The decomposition product of safrol (50 g.) was dissolved in KOH solution (15 g. in 250 c.c. of water); after adding benzoyl chloride (35 g.), the mixture was well stoppered and shaken for 3 hours. The soft lump formed was separated and treated with 150 c.c. of alcohol, from which 20 g. of crystals melting at 95° separated out. From the mother liquor allowed to stand for 3 days, there separated out 12 g. of crystals melting at 52°. The last filtrate was concentrated on the water bath to about 40 c.c. and allowed to stand when a third crop of crystals came out, which on recrystallization from alcohol melted at 137°.

(4) **Oxidation.** (a) *Protocatechuic acid di-acetate* (VII). Six grams of IV was mixed with 500 c.c. of water and 30 c.c. of 10% sulphuric acid and the mixture was subjected to oxidation by treating it on the water bath with a 2 per cent. solution of 20 g. of $KMnO_4$. The filtrate was salted out and then extracted with ether. After evaporation of ether 1.1 g. of white crystals were left behind, m.p. 142–150°. By repeating this process, 1.5 g. of crystals melting at 149° were obtained.

(b) *Methoxy-vanillic acid acetate* (VIII). Three grams of the oily part of the monoacetate described above was mixed with 300 c.c. of water and 20 c.c. of 10% sulphuric acid and the mixture was subjected to oxidation by adding 500 c.c. of water containing 10 g. of $KMnO_4$ on the water bath. After filtering and cooling, the product was treated exactly the same as in the case of the di-acetate mentioned above. The crystals obtained by recrystallizing twice from water melted at 112–113°. (Found: C, 54.7; H, 4.9; molecular weight (in camphor), 249.3. Calc. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0%; mol. wt., 240.)

(c) *Methoxy-isovanillic acid acetate* (IX). With the compound VI melting at 64°, the same treatment was repeated as in the case (b). The pure white crystalline product, after recrystallized three times from water, melted at 150–152°. (Found: C, 54.8; H, 5.1. Calc. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0%.)

(d) *Methoxy-isovanillic acid benzoate* (XVII). Two grams of the substance XIV melting at 55° was treated with 5 g.of $KMnO_4$ in 500 c.c. of water on the water bath as usual. Sulphuric acid was not added in this case, and the oxidation was found to be very slow. After warming for three hours on the water bath, a small quantity of methanol was added to reduce the remaining $KMnO_4$. The product was then filtered, acidified with acetic acid, and extracted with ether. The pure white needle crystals obtained by recrystallizing twice melted at 117–118°. (Found: C, 62.9; H, 5.1. Calc. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.6%.)

(e) *Methoxy-vanillic acid benzoate* (XVI). With the compound XIII melting at 95°, exactly the same treatment as in the case (d) was carried out. The pure white crystals obtained by recrystallizing twice melted at 127°. (Found; C, 63.3; H, 4.8. Calc. for $C_{16}H_{14}O_6$: C, 63.6; H, 4.6%.)

(5) **Saponification and the Rearrangement of Acyl Group.** (a) *Protocatechuic acid* (X). The substance VII (1 g.) was heated with 10 c.c. of methanol and 1 c.c. of concentrated hydrochloric acid under the reflux condenser for 1.5 hours. Water (30 c.c.) was then added, methanol was distilled off, and the residue was extracted with ether. The solid matter left on evaporating off ether was recrystallized from water. It melted now at 195° and weighed 0.5 g. When mixed with a pure sample of protocatechuic acid there was no change of m.p., showing the completeness of saponification.

(b) *Rearrangement of the acyl group from VIII to XI.* The substance VIII (0.2 g.) melting at 112–113° was warmed with 3 c.c. of glacial acetic acid and one drop of concentrated hydrochloric acid on the water bath for an hour. Water is then added and the product was extracted with ether. The ethereal extract was washed with water; on evaporation of ether, the residue was twice recrystallized from water, yield 0.05 g. The substance melted at 198° and when mixed with protocatechuic acid, depression of the melting point resulted.

(c) *Partial saponification from IX to XI.* The substance IX (0.1 g.) was warmed with 3 c.c. of 30% alcohol and 2 drops of 10% sulphuric acid on the water bath for 3 hours. The reaction product was extracted with ether as usual. A small quantity of a substance melting at 198°

was obtained which did not lower the m.p. when mixed with the substance obtained in (b).

(d) *Rearrangement from XVI to XVIII and from XVII to XVIII.* The substance XVI (0.5 g.) was warmed with 5 c.c. of glacial acetic acid and 1 c.c. of concentrated hydrochloric acid on the water bath for 1.5 hours, when a rather strong resinification took place. The product was extracted as usual with ether and a small amount of a substance melting at 224° after recrystallized from water was obtained. Another substance with m.p. 225° was obtained from XVII on treating it exactly in the same manner. The two substances did not show any lowering of melting point when mixed together, showing that they are the same compound.

Addendum. *Dibenzoyloxy-benzoic acid benzoylester* (XII). Protocatechuic acid (1 g.) and NaOH (4 g.) were dissolved in 36 g. of water. Under ice cooling, 9.1 g. of benzoyl chloride was added and the whole was shaken, when a white substance separated copiously. It was collected with suction, and recrystallized four times with use of activated charcoal, m.p. 198°. (Found: C, 71.7; H, 3.4, molecular weight (in camphor), 449. Calc. for $C_{28}H_{18}O_7$: C, 72.1; H, 3.8%, mol. wt., 466.)

Research Laboratory of
Nippon Koryo Yakuhin Kaisha, Ltd., Kobe.

ON THE CATALYTIC ACTION OF ACTIVE CARBON UPON TERPENES AND THE RELATED COMPOUNDS.

By Seizo KIMURA.

Received May 14th, 1935. Published August 28th, 1935.

The investigations of Ruzicka and his co-workers[1] on the compounds of the higher terpene series with use of the dehydrogenation reaction of sulphur are too well known to need detailed statements. The present author has used active carbon together with sulphur in his studies and found that cyclic compounds of the terpene series can, in liquid phase, easily be transformed into aromatic compounds. This fact made him interested in the catalytic action of active carbon upon terpenes and the related compounds, so as to start an investigation on this reaction especially in the liquid phase.

(1) *Helvetica Chim. Acta*, **4** (1921), 505.

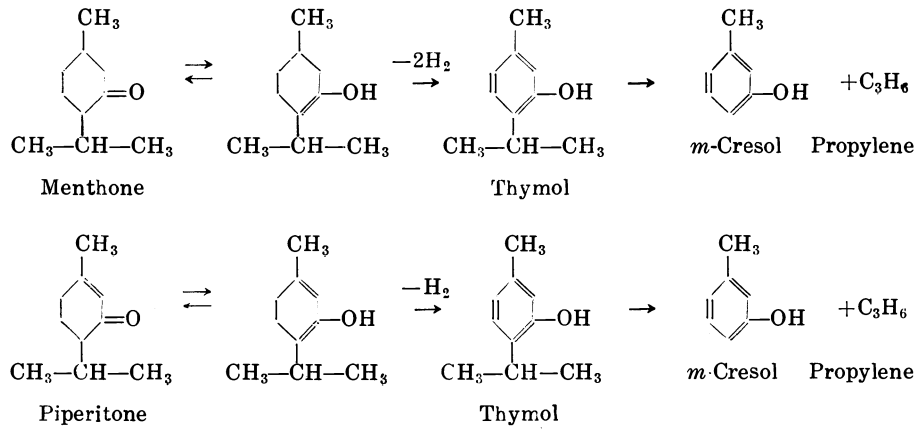
The studies of catalytic action of active carbon have been made by various workers and some of the results have been already applied in industry. Most of them were, however, made by the reaction in the gaseous phase and up to 1932 there was none made upon the compounds of terpene series, except that of Asahina and Nakanishi[2] who reported the fact that cineol is converted to *p*-cymene by the action of palladium-charcoal or charcoal for bleaching purpose. The present author has also made investigations, in relation to the dehydrogenation reaction of sulphur, upon the action of active carbon alone on cineol. He then found a small quantity of *p*-cymene as the dehydration and dehydrogenation product of cineol.

(I) Catalytic Action upon Menthone and Piperitone. As active carbon exerts dehydrogenation action, it is expected to cause upon the terpene-ketones capable of existing in the enol form, such as menthone and piperitone, simultaneously a dehydrogenation action and a keto-enol metamerization. *l*-Menthone (b.p. 72°C./6 mm., $d_4^{25.5}$ 0.8905, n_D^{20} 1.4513, $[\alpha]_D^{30}$ −24.75) (50 g.) made by oxidation of menthol by Beckmann's method was heated with 25 g. of active carbon under a reflux condenser for 20 hours, the internal temperature being kept at 220°C. From the resulting oily material, about 2.7–3.4 g. of a phenolic substance was extracted with 5% NaOH solution. In this latter substance *m*-cresol was identified by elementary analysis and also by conversion into trinitro-*m*-cresol (m.p. 105–106°C.). A small quantity of thymol was also identified as thymol phenylurethane (m.p. 106–107°C.). The residue after the removal of the phenolic substance consisted of unacted menthone and it was noticed that during this reaction there was an optical transformation of *l*-menthone into *d*-menthone.

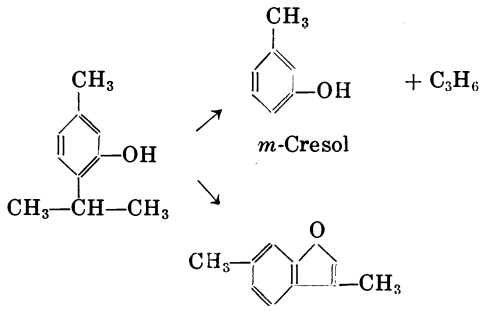
Piperitone (b.p. 90.5–92°C./5 mm., d_4^{24} 0.9305, $n_D^{26.8}$ 1.4831, $[\alpha]_D$ −48.22) (50 g.) prepared by refining oil of *Eucalyptus dives* of Australian origin was heated with 25 g. of active carbon for 20 hours, the internal temperature being kept at 200–240°. About 13.4 g. of a phenolic substance was extracted from the reaction product by treating it with 5% NaOH solution. As before, in this phenolic substance, *m*-cresol was identified by the elementary analysis and conversion into trinitro-*m*-cresol (m.p. 105–106°C.), and a small quantity of thymol was recognized by the elementary analysis and conversion into thymol phenylurethane (m.p. 106–107°C.). The residue after separating the phenolic substance consisted chiefly of the unacted piperitone which was identified by preparing α- and β-semicarbazones (m.p. 226–227° and 174–176° respectively). As expected, the keto-enol metamerization took place by which the enol form of menthone or piperitone was first formed. By their

(2) *J. Pharm. Soc. Japan*, **52** (1928), 1.

dehydrogenation, thymol was then produced from which the isopropyl group was split off to form *m*-cresol as represented in the following scheme :



In order to make the final mechanism clear, 50 g. of thymol (m.p. 50–51°C.) was mixed with 25 g. of active carbon and subjected to the same treatment as before by which about 7.3 g. of a phenolic substance was obtained. This latter substance was proved by elementary analysis and by the formation of trinitro-*m*-cresol to be chiefly *m*-cresol itself. It was interesting here to find that about 5.4 g. of a neutral substance was obtained which was identified as 2,5-dimethylcumarone by the physical constants of its principal distillate (b.p. 212–217°C., $d_4^{25.5}$ 1.0352, $n_D^{22.5}$ 1.5521), molecular refraction (found : 44.66–44.99, theoretical : 43.76 for $C_{10}H_{10}O$), colour reaction, elementary analysis, and the formation of its picrate (m.p. 75–76°C.). In this way, thymol is changed to *m*-cresol by splitting off of the isopropyl group by the action of active carbon. At the same time it undergoes dehydrogenation and is changed into a compound of cumarone series. This is represented by the following scheme :



This formation of dimethylcumarone is presumed to take place also when menthone or piperitone is acted upon by active carbon ; though its identification is expected to be impossible on account of a too small trace of it present.

(II) Catalytic Action upon Cyclic Terpene Alcohols. From the resemblance of the properties of active carbon with those of acid clay, Florida earth, etc., it is inferred that it will also exert a dehydration action upon terpene alcohols. For examining the action of active carbon, *d*- and *l*-terpineol were taken as representative members of cyclic tertiary terpenealcohols. *d*-*α*-Terpineol (m.p. 35°C., d_4^{15} 0.9390, n_D^{14} 1.4843, $[\alpha]_D^{25}$ +9.85) (100 g.) made by refining pine oil of the American origin was heated with 20 g. of active carbon for 5 hours at about 200°C. About 67.9 g. of an oily product and 9.8 g. of water were obtained. By repeated refining of the oil, it was proved by the physical constants, molecular refraction, elementary analysis, and by the formation of dipentene-tetrabromide (m.p. 124°C.) that it consisted almost entirely of dipentene.

By the action of boric acid upon brown comphor oil, after the removal of safrol, an alcoholic substance was obtained which was separated as boric acid ester. By refining the latter product, *l*-*α*-terpineol (m.p. 35°C., $d_4^{24.8}$ 0.9323, n_D^{25} 1.4802, $[\alpha]_D^{25}$ −13.70) was prepared. This substance (25 g.) was mixed with 5 g. of active carbon and heated for 6 hours at about 200°C. About 19.6 g. of an oily product and 4.3 g. of water were obtained. In this oil, dipentene was also identified.

Active carbon was also made to act upon *l*-menthol and *d*-borneol as representative of cyclic secondary terpene alcohols.

l-Menthol (m.p. 42–43°C., $[\alpha]_D^{12}$ −49.07 in alcoholic solution) (50 g.) was heated with 10 g. of active carbon for 5 hours at 200°C. An oily distillate (16.9 g.) and 3.6 g. of water were obtained. The principal distillate was shown to be Δ^3-*p*-menthene by its physical constants (b.p. 166-167°C., d_4^{12} 0.8108, n_D^{22} 1.4532, $[\alpha]_D^{21}$ +15.22), molecular refraction (Found: 45.958, theoretical: 45.713 for $C_{10}H_{18}$), and elementary analysis. The dextro-rotatory property of this substance is especially to be noted. The residual part in the flask was extracted with ether and proved to be unchanged *l*-menthol.

d-Borneol (m.p. 203–204°C.) (50 g.) was heated with active carbon (50 g.) for 4 hours over direct flame. On distilling, 31.4 g. of an oil and 6 g. of water were obtained. By repeated distillation, the principal distillate was found to correspond well to camphene in its physical constants (b.p. 158–161°C., d_4^{15} 0.8651, $n_D^{22.5}$ 1.4685), molecular refraction (found: 44.025, calculated for $C_{10}H_{16}$: 43.513), and the results of elementary analysis. The trial to separate a crystalline sample of camphene from this material by cooling was rewarded only with a minimum quantity of crystals melting at 49°C. and with a camphor-like odour.

Judging from these experimental results, the dehydration activity of active carbon resembles that of acid clay though it is not so violent as

the latter. With acid clay, the action is quickly completed in 20–30 minutes, while with active carbon it proceeds slowly and at a rather high temperature.

(III) Catalytic Action upon Acyclic Terpene Alcohols. Upon the presumption that the action of active carbon must be the same on acyclic compounds as on cyclic compounds, its reaction was studied upon geraniol and linalool representing cyclic terpene-alcohol compounds.

Geraniol to be used was separated and refined from citronella oil of the Javanese origin and had d_4^{15} 0.8807, n_D^{17} 1.4769, and $[\alpha]_D^{15}$ ±0. It (200 g.) was heated with 40 g. of active carbon for 21 hours at 225°C. About 130 g. of an oily matter and 16.1 g. of water were obtained. By repeated distillation, the lower boiling portion (b.p. below 70°C./8 mm.) yielded myrcene which was identified by its physical constants (b.p. 47–49°C./7.5 mm., d_4^{15} 0.8062–0.8081, n_D^{15} 1.4667–1.4692, $[\alpha]_D^{16}$ ±0), molecular refraction (found: 46.846–46.982, calculated for $C_{10}H_{16}\overline{3}$: 46.979), and the results of elementary analysis. Besides myrcene thus identified, there was also found dipentene recognizable by conversion into its tetrabromide. The portion of the intermediate boiling points (b.p. 100–110°C./8 mm.) consisted chiefly of the unchanged geraniol. When the latter was removed, the residue showed physical constants well approaching those of linalool. The higher boiling portion (b.p. above 110°C./8 mm.) was repeatedly distilled, but it gave nothing worth of being considered as the chief constituent. However, it is presumed to have been oxides of the diterpene series.

Linalool prepared by refining the linalool of bois de rose, had the constants: b.p. 74°C./5.5 mm., d_4^{23} 0.8687, $n_D^{23.5}$ 1.4590, $[\alpha]_D^{24}$ −14.18. It (300 g.) was mixed with 60 g. of active carbon and subjected to the same procedure as before. An oily product weighing 159.7 g. was obtained together with 29.6 g. of water. The oily matter gave by repeated fractional distillation a lower boiling portion (b.p. below 70°C./7 mm.) which yielded as the chief constituent dipentene (tetrabromide m.p. 124°C.) besides a small quantity of a substance corresponding to myrcene (b.p. 43–44°C./5.5 mm., d_4^{20} 0.8087, n_D^{20} 1.4671). The portion of the intermediate boiling points (b.p. 70–85°C./7 mm.) consisted chiefly of the unchanged linalool. The higher boiling portion (b.p. above 85°C./7 mm.) gave a compound showing physical constants (b.p. 150–155°C./5 mm., d_4^{18} 0.8858, n_D^{17} 1.5014), molecular refraction (found: 90.467, calculated for $C_{20}H_{32}\overline{4}$: 90.484), and the results of elementary analysis well agreeing with those of α-camphorene, which was synthesized by Semmler and Jonas[3] from myrcene and had the constants: b.p. 178–180°C./8.5 mm.,

(3) *Ber.*, **46** (1913), 1566.

d_{18} 0.8844, n_D 1.50199, $[\alpha]_D$ ±0. This must have been formed by polymerization of myrcene produced by dehydration of linalool.

The attempt to detect geraniol in the distillates was made in vain.

From the above-given results, it is positively ascertained that active carbon exerts a power of dehydration, of ring formation, and of polymerization upon acyclic terpene alcohol compounds like geraniol and linalool.

(IV) **Catalytic Action upon Acyclic Terpene Aldehydes.** Citral and citronellal were taken as representatives of acyclic terpene aldehydes upon which the action of active carbon was tested.

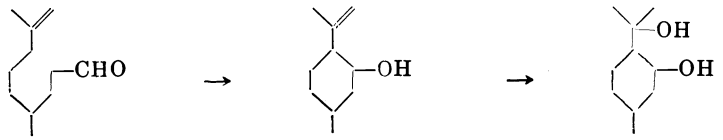
Citral was separated from lemongrass oil of the Indian origin and showed the constants: b.p. 96–97°C./6.5 mm., d_4^{15} 0.8918, n_D^{20} 1.4872, $[\alpha]_D^{10}$ ±0. It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an oil-bath with constant stirring. At about 135°C. the reaction became very brisk. The yield of the oily reaction product was about 50% of the citral used. By repeated fractional distillation a lower fraction was obtained which proved to be *p*-cymene by its physical constants (b.p. 174–177°C., d_4^{15} 0.8593–0.8624, n_D^{20} 1.4912–1.4940), molecular refraction (found: 45.390–45.445, calculated for $C_{10}H_{14}$: 44.845), the results of elementary analysis, and the property of forming *p*-oxyisopropyl-benzoic acid (m.p. 155–156°C.). The higher boiling fraction (b.p. 160–165°C./4 mm., d_4^{15} 0.9379, n_D^{20} 1.5251) showed in elementary analysis the presence of a hydrocarbon of the molecular formula $C_{20}H_{28}$. Besides, the presence of a small quantity of a terpene was inferred, which resembled citral-terpene detected by Horiuchi[4] among the reaction products obtained by the action of 20% sulphuric acid upon citral.

Citronellal (b.p. 69–71°C./5 mm., d_4^{15} 0.8553, n_D^{20} 1.4467, $[\alpha]_D^{10}$ +11.02) was obtained by refining citronella oil of the Javanese origin. It (300 g.) was mixed with 60 g. of active carbon and subjected to the treatment as before. When the temperature of the oil bath reached about 99°C., a brisk reaction commenced, and the yield of the oily reaction product was about 57% of the citronellal taken. Upon fractional distillation, about 45 g. of a distillate having properties of isopulegol was obtained. After repeated purification by distillation, it showed physical constants (b.p. 66-68°C./4 mm., d_4^{15} 0.9148, n_D^{20} 1.4704, $[\alpha]_D$ +2.15), molecular refraction (found: 47.209, calculated for $C_{10}H_{18}O$: 47.238), and the results of elementary analysis proving it was isopulegol. By oxidation with the chromic acid mixture, it formed isopulegone which was converted to the oxime (m.p. 122–123°C.).

(4) *Mem. Coll. Sci., Kyoto Imp. Univ.*, **11** (1928), 190.

The higher boiling fraction had as the chief constituent di-isopulegol ether (b.p. 160–170°C./4 mm.) showing upon a further purification the physical constants (b.p. 157–158°C./4 mm., d_4^{15} 0.9188, n_D^{20} 1.4819, $[\alpha]_D^{13}$ −0.87), and the results of elementary analysis corresponding to the formula $C_2H_{34}O$. Besides this, a very small quantity of a terpene hydrocarbon was detected with the constants: b.p. 47–55°C./4 mm., d_4^{15} 0.8594, n_D^{20} 1.4826, $[\alpha]_D$ +39.92.

It was thus recognized that active carbon possesses dehydration activity as well as the action of ring formation and polymerization upon acyclic terpenealdehyde compounds. Especially interesting was the fact that isopulegol was very easily formed from citronellal without use of any solvent. This fact makes the present author concur to the view[5] that isopulegol is formed by the direct ring formation of citronellal:



In order to corroborate this view, the temperature of the oil bath was kept comparatively low at about 70°C. to avoid the formation of water by the decomposition of citronellal. After a slow reaction taking place during three hours, there was found a large quantity (about 22%) of isopulegol formed which could not be thought as having come through the stage of menthoglycol.

(V) **Catalytic Action upon Safrol and Isosafrol.** Under the expectation that safrol and isosafrol would undergo the opening of their methylene-dioxy ring by active carbon, the reaction was tried under pressure, as it was known by experiments not to take place under ordinary pressure.

Safrol was prepared by separation and purification from brown camphor oil (b.p. 232.5–233°C., d_{15} 1.1050, n_D^{20} 1.5378, $[\alpha]_D$ ±0). It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an autoclave. At about 190°C., a brisk reaction commenced to taken place showing a pressure of 40 atmospheres and rising in temperature to 265°C. The reaction product was extracted with ether and the dark brownish oily matter was subjected to distillation under reduced pressure, when 40.3 g. of an oil was obtained. At the same time an increase of coaly matter was noted. The chief constituent consisting of about 22 g. of phenolic material had the properties (b.p. 118–130°C./4 mm., d_4^{15} 1.0942–1.0946, n_D^{20} 1.5441–1.5444), from

(5) *Loc. cit.*; *J. Soc. Chem. Ind., Japan*, **34** (1931), 161.

which and from the result of elementary analysis there was attributed to it a formula $C_9H_{12}O_2$ containing two hydroxyl groups and no methoxyl group. To prove the constitution of the product, it was methylated in usual way when it showed physical constants: b.p. 95–100°C./4 mm. d_4^{15} 1.0167, n_D^{20} 1.5164. From this and from the results of elementary analysis and determination of methoxyl groups, the methylated oil was proved to have the molecular formula $C_{11}H_{16}O_2$ containing two methoxyl groups. It is clear then that the phenolic substance corresponding to it contains two hydroxyl groups.

The methylated oil gave on oxidation with potassium permanganate veratric acid (m.p. 179–181°C.). By nitration, it gave 6-nitro-3,4-dimethoxy-1-propyl-benzene (m.p. 80.5–81°C.).[6] These results show that the methylated oil is 3,4-dimethoxy-1-propyl-benzene and that the chief constituent of the higher boiling fraction of the phenolic matter produced from safrol is 3,4-dihydroxy-1-propyl-benzene. The 3,4-dihydroxy-1-propyl-benzene obtained by the present author was an difficultly crystallizable oil, so that it perhaps contained some impurities.

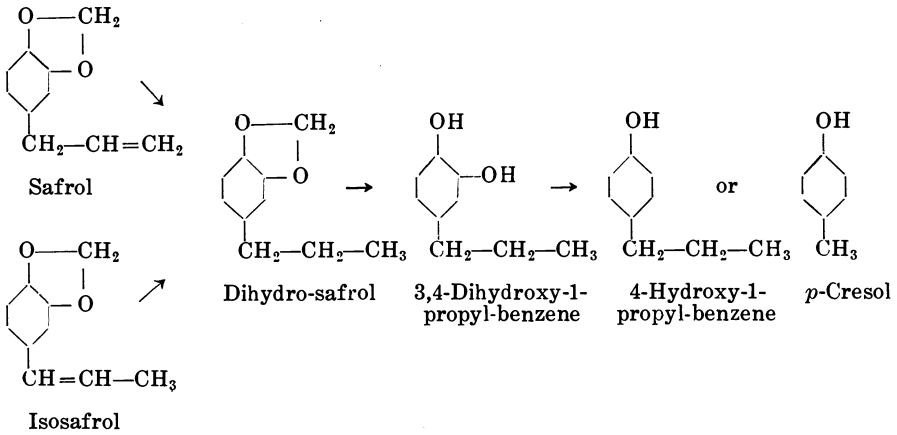
Another sample of 3,4-dimethoxy-1-propyl-benzene (b.p. 110–115°C./3 mm., d_4^{15} 1.0569, n_D^{20} 1.5652) was prepared by reduction of methyl-iso-eugenol with absolute alcohol and metallic sodium. The 6-nitro-3,4-dimethoxy-1-propyl-benzene (m.p. 80.5–81°C.) prepared by its nitration showed no change of melting point when mixed with the nitration product mentioned above. From the phenolic matter obtained as above, a small quantity of a substance of comparatively low boiling point (b.p. 85–115°C./5 mm., d_4^{26} 1.0266–1.0340, n_D^{26} 1.5291–1.5285) was obtained. When methylated, it gave an oil having physical constants: b.p. 65–70°C./4.8 mm., d_4^{15} 0.9809, n_D^{20} 1.5129. From the results of elementary analysis and from the fact that by oxidation it gave anisic acid (m.p. 179–181.5°C.), the methylated oil was found to be *p*-cresol-methyl-ether and the original phenolic matter was inferred to be *p*-cresol, although the formation of 4-hydroxy-1-propyl-benzene is not precluded. The material was too small in quantity to decide the question definitely.

The neutral material obtained had physical constants: b.p. 80–84°C./3.5 mm., d_4^{28} 1.0786–1.0768, n_D^{28} 1.5282–1.5255. It is quite different from safrol or isosafrol. From the fact that the phenolic substance contained a propyl group and that dihydro-safrol can be obtained in a large quantity from isosafrol, the formation of dihydrosafrol from safrol can be easily imagined, and the neutral substance mentioned above is safely presumed to be a mixture of safrol and dihydro-safrol.

A sample of isosafrol (b.p. 114–117°C./7 mm., d_{15} 1.1247, n_D^{20} 1.5757, $[\alpha]_D$ ±0) was obtained by isomerization of safrol in the usual way. It (200 g.)

(6) H. Thoms, *Ber.*, **36** (1903), 860.

was heated with 40 g. of active carbon as before under pressure. At 198°C. the reaction began to take place very briskly and the pressure rose to 33 atmospheres with the rise of temperature to 284°C. At the completion of the reaction, 37.8 g. of an oily matter was distilled off at 61–125°C. under 4 mm. In about 10 g. of phenolic substance from the oily reaction product, 3,4-dihydroxy-1-propyl-benzene was identified as in the case of the experiment with safrol. The neutral substance was identified as almost pure dihydro-safrol from the physical constants (b.p. 80–83°C./4 mm., d_4^{29} 1.0626, n_D^{30} 1.5151), and the molecular refraction (found : 46.54, calculated for $C_{10}H_{12}O_2$: 45.87), and the results of elementary analysis. From these results it is inferred that, by heating safrol and isosafrol with active carbon, the reaction runs in such a way that a portion is decomposed and carbonised producing hydrogen which is added to the double bonds of the allyl or propenyl group, changing it to a propyl group. At the same time the methylene-dioxy ring is split, chiefly to produce dihydroxy compounds, a small fraction of which is converted to hydroxy compounds by the loss of one hydroxyl group. This is made clear by the following scheme :



While in the experiments with safrol the neutral substance consists of a mixture of unchanged safrol and dihydro-safrol, in the case of isosafrol it consists almost wholly of dihydro-safrol. This is easily understood from the consideration that, generally in the reduction with metallic sodium and alcohol, the propenyl group is more easily hydrogenated than the allyl group.(7) The fact that carbon is liberated at the same time with the liberation of hydrogen

(7) G. Ciamician and P. Silber, *Ber.*, **23** (1890), 1162; A. Klages, *Ber.*, **32** (1899), 1439.

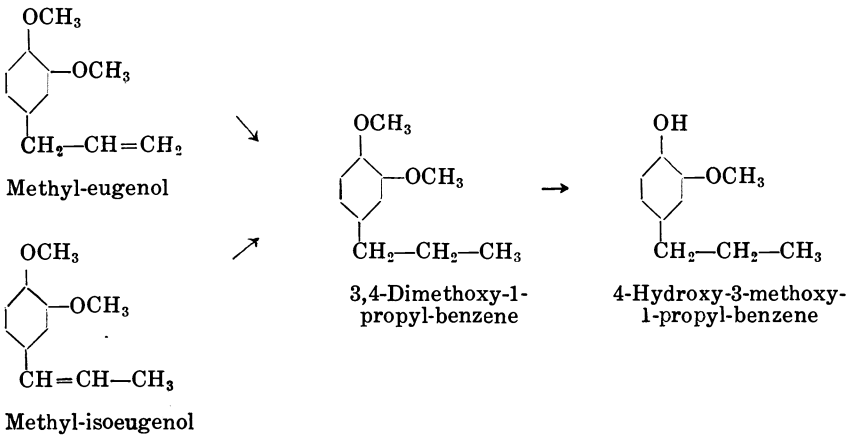
by the decomposition of the material, is made clear by the existence of a much larger quantity of carbon at the end of reaction than at the beginning.

From the results reported here it is concluded that active carbon exerts a splitting action upon the methylene-dioxy ring of safrol and isosafrol as well as the catalytic hydrogenation action.

VI. Catalytic Action upon Methyl-eugenol and Methyl-isoeugenol. From the above-mentioned experiments it was expected that active carbon may have a de-methylating action upon the methoxyl group. As it was also desired to extend the catalytic hydrogenation experiment to other kinds of compounds, the present author tested the activity of active carbon upon methyl-eugenol and methyl-isoeugenol. A sample of methyl-isoeugenol (b.p. 125–131°C./6 mm., $d_4^{18.8}$ 1.0590, $n_D^{18.5}$ 1.5707) was obtained by methylating isochavibetol and purifying the product in the usual way. It (200 g.) was mixed with 40 g. of active carbon and slowly heated in an autoclave up to 247°C., when a brisk reaction commenced raising the pressure to 24 atmospheres. At the completion of the reaction, the product was extracted with ether. The small quantity of the phenolic substance contained in the oily product showed physical constants (b.p. 90–93°C./4.5 mm., $d_4^{21.5}$ 1.0487, $n_D^{22.2}$ 1.5239), colour reactions, and results of elementary analysis proving that it consisted of 4-hydroxy-3-methoxy-1-propyl-benzene. The main fraction (about 20 g.) of the neutral matter was subjected to repeated fractionation and showed the physical constants: b.p. 108–110°C./6 mm., $d_4^{19.2}$ 1.0140, n_D^{21} 1.5159. From these figures and from the results of elementary analysis, it was identified as 3,4-dimethoxy-1-propyl-benzene. This conclusion was corroborated by further facts that it produces by oxidation with potassium permanganate veratric acid (m.p. 179–181°C.) and that it yields by nitration 6-nitro-3,4-dimethoxy-1-propyl-benzene.

A sample of methyl-eugenol (b.p. 123°C./9 mm., d_4^{17} 1.0372, $n_D^{17.8}$ 1.5337) was prepared by methylation of eugenol. It (200 g.) was heated with 40 g. of active carbon under pressure as before. From the reaction product, a small quantity of phenolic substance and a large amount of neutral substance were obtained. The main fraction of the neutral material was shown by the elementary analysis and by the nitration to 6-nitro-3,4-dimethoxy-1-propyl-benzene to consist chiefly of 3,4-dimethoxy-1-propyl-benzene. The physical constants (b.p. 110-112°C./6 mm., $d_4^{16.4}$ 1.0184, n_D^{6} 1.5208) did not, however, agree with those obtained before for the product from methyl-isoeugenol: this is due perhaps to the admixture of the unchanged material. This is again due to the different susceptibilities to hydrogenation of allyl group and propenyl group, endorsing the conclusion already drawn by the author in the case of safrol and isosafrol.

The reaction mechanism inferred from the above results is as follows. The hydrogen produced by thermal decomposition under pressure is added to the double bonds of allyl and propenyl groups by the catalytic action of active carbon to change them to a propyl group. The hydroxy compounds are then formed by de-methylation. Active carbon thus exerts a catalytic hydrogenation as well as de-methylation as in the previous instances. This is schematized as follows:



Cantelo[8] has made investigations of catalysis by animal charcoal, silica gel, etc., upon the thermal decomposition of methane. Kusama and Uno[9] have subjected methane to thermal decomposition under the catalysis of nickel with the formation of carbon and hydrogen. The latter concluded that the relation between the quantity of the catalyser and the percentage of the hydrogen formed depended upon the catalytic activity of carbon which accumulated in the reaction. In the experiments reported here, active carbon is considered to have exerted some catalytic activity of thermal decomposition.

The investigation here described was performed under the kind guidance of Dr. Kashichi Ono to whom a sincere acknowledgment is herewith rendered by the author.

Research Laboratory of
Nippon Koryo Yakuhin Kaisha, Ltd.,
Kobe.

(8) *J. Phys. Chem.*, **28** (1924), 1036.
(9) *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **8** (1929), 1.

DETERMINATION OF SILICIC ACID BY VOLUMETRIC METHOD.

By Sansei KITAJIMA.

Received April 2nd, 1935. Published August 28th, 1935.

Determination of silicic acid has hitherto been executed by making in usual ways a solution of the sample to be analysed, by evaporating the solution with hydrochloric or nitric acid, and by weighing the resulting silicon dioxide. In the determination of a minute quantity of the same, the yellow colour of ammonium silicomolybdate is conveniently utilized by comparing it with the colour of a standard solution having the same constituents and containing a known quantity of silicon.[1] Ammonium silicomolybdate can be prepared from an acetic or a sulphuric acid solution of silicate and a solution of ammonium molybdate. In case the comparison of the two colours is unfavourable and does not give accurate results, a solution of benzidine or stannous chloride is added to the yellow solution of the ammonium silicomolybdate and the resulting colour of benzidine blue or molybdenum blue is used for the comparison, so that the determination of a very minute quantity of silicic acid can be made readily.

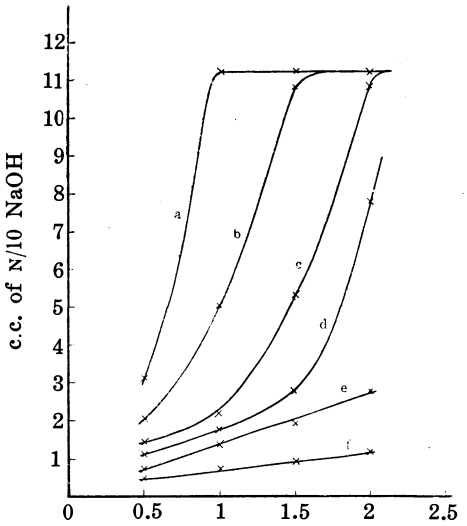
The yellow compound described above appears usually in solution when acid solutions of ammonium molybdate and silicate are mixed together. With a view to arriving at an easy and accurate method of determination of silicic acid, experiments have been made by the present author to see whether or not this compound can be separated in the form of a precipitate containing all of silicic acid present in the original solution. They have shown that silicic acid can be separated in the form of precipitate by a method which has not been used up to now, and that the same acid can be determined by a volumetric method. A detailed account on this subject being expected to be issued from The Institute of Physical and Chemical Research, Tokyo, outlines only are here presented.

(1) F. Diénert and F. Wandenbulcke, *Compt. rend.*, **176** (1923), 1478; *Bull. soc. chim.*, [4], **34** (1923), 1131. Atkins and Wilson, *Biochem. J.*, **20** (1923), 1223. Isaac, *Bull. soc. chim. biol.*, **6** (1924), 157. Foulger, *J. Am. Chem. Soc.*, **49** (1927), 429. F. J. King and C. C. Lucas, *J. Am. Chem. Soc.*, **50** (1928), 2395. Oberhanser and Schormüller, *Z. anorg. allgem. Chem.*, **178** (1929), 381. F. Feigl und P. Krumholz, *Ber.*, **62** (1929), 1138. F. Feigl, *Z. anal. Chem.*, **77** (1929), 299. W. F. Hillebrand and G. E. F. Lundall, "Applied Inorg. Analysis," (1929), 540. F. Feigl, "Qualitative Analyse mit Hilfe von Tüpfelreaktion," (1931), 310.

The present author has once made studies on the suitable conditions for the complete precipitation of ammonium phosphomolybdate, and found that the concentration of nitric acid, ammonium nitrate, and ammonium molybdate had important effects on the precipitation.[2] In the same manner, he has

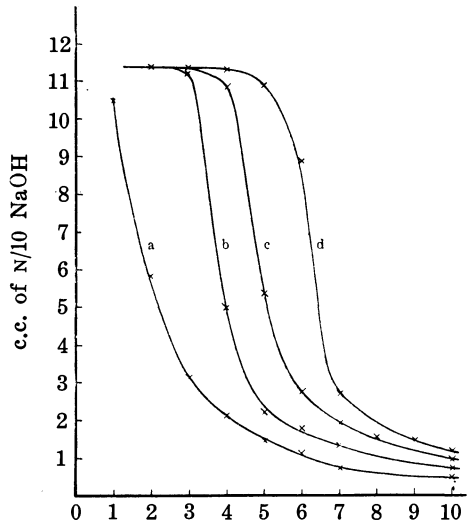
Table 1.

Quantity (g.) of ammonium nitrate added	Quantity (c.c.) of N/10 NaOH solution required for the titration of the yellow precipitate		
	When 3 c.c. of HNO_3 and 1 c.c. of the ammonium molybdate solution were used	When 4 c.c. of HNO_3 and 1 c.c. of the ammonium molybdate solution were used	When 5 c.c. of HNO_3 and 1.5 c.c. of the ammonium molybdate solution were used
0	0	0	0
1	0	0	0
3	10.15	4.48	4.36
5	11.31	5.05	6.37



a: NH_4NO_3 5 g., HNO_3 3 c.c.
b: ,, ,, ,, 4 ,,
c: ,, ,, ,, 5 ,,
d: ,, ,, ,, 6 ,,
e: ,, ,, ,, 7 ,,
f: ,, ,, ,, 10 ,,

Fig. 1.



a: NH_4NO_3 5 g., Ammonium molybdate sol., 0.5 c.c.
b: ,, ,, ,, 1.0 ,,
c: ,, ,, ,, 1.5 ,,
d: ,, ,, ,, 2.0 ,,

Fig. 2.

(2) S. Kitajima, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **16** (1931) 285; *Bull. Inst. Phys. Chem. Research, Japan*, **10** (1931), 65.

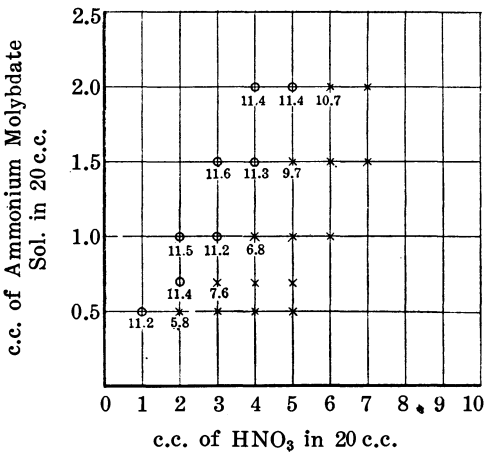
recently found that the increase in the concentration of ammonium nitrate and molybdate decreases the solubility of the yellow precipitate of ammonium silicomolybdate, and that when the concentration of nitric acid is increased within a certain limit, the solubility of the yellow precipitate is increased, but when the concentration of the same is increased beyond the same limit, silicic acid tends to separate itself and not to form the yellow precipitate, so that the determination of silicic acid becomes impossible. An example showing the conditions for the precipitation is given in Table 1 and Figs. 1 and 2.

Reagents employed in the experiments were as follows: nitric acid sp. gr. 1.379, about 13.4 N; ammonium nitrate solution contained 1 g. of the repeatedly recrystallized salt in 1.5 c.c. of the solution; ammonium molybdate solution contained 0.232 g. of molybdenum in 1 c.c. and was made by dissolving 50 g. of the salt in 100 c.c. of dilute ammonia solution obtained from 1 volume of concentrated ammonia (sp. gr. 0.9) and 3 volumes of water. The sodium silicate solution was made by dissolving about 1% anhydrous sodium silicate and confirmed by gravimetric method to contain 0.0622 g. of SiO_2 in 10 c.c.

Various quantities of the sodium silicate solution, water, the ammonium molybdate solution, the nitric acid, and the ammonium nitrate solution were taken in succession into an Erlenmeyer flask having a glass stopper, so as to make the total volume of the mixture just 20 c.c. The mixture was shaken and allowed to stand in a bath of about 70° for one hour. The yellow precipitate was collected, washed, and titrated with N/10 NaOH solution, phenolphthalein being employed as indicator. In the filtration and washing, various sorts of filters were employed, and the precipitate was found to be liable to come more or less into the washings, in every case where filter paper was used. Glass filters having fine pores were found to be most suitable for washing. Aqueous solutions of nitric acid, potassium nitrate, ammonium nitrate, and other salts in varying concentrations were separately employed in washing the precipitate in order to avoid its passing through the filter without success. A solution of 15% NH_4NO_3 and 0.02% HNO_3 (about 0.00027 N in HNO_3) was finally found to be most suitable for the washing purpose.

Various known quantities of the sodium silicate solution were taken, and silicic acid was precipitated as yellow ammonium silicomolybdate by the method described above by using varying quantities of the reagents. The precipitates were titrated with a standard NaOH solution. Among various values obtained by the titration, there were found a number of the largest

and identical ones. Out of these values and those showing the concentrations of the reagents in the solutions, in which the yellow precipitates formed, a diagram shown in Fig. 3 has been made, which shows the interdependence of the reagents in the complete precipitation of silicic acid.



The diagram in Fig. 3 shows perfect and imperfect precipitation of ammonium silicomolybdate in the mixed solutions containing 0.1 c.c. of the sodium silicate solution, 5 g. of NH_4NO_3, and the varying quantities of HNO_3 and ammonium molybdate given in the diagram. Here, the mark ○ indicates complete, and × incomplete, precipitation. Figures given below the marks show the number of c.c. of N/10 NaOH solution required for the titration of the precipitates.

Fig. 3.

That the largest and identical value described above corresponds to the correct value of silicic acid has been confirmed as follows. The mixture resulting from the titration was transferred to a casserole, evaporated to a volume of about 10 c.c., and then heated with 6–10 c.c. of concentrated sulphuric acid until white fume of the acid was vigorously given off. The residual solution was diluted with 50 c.c. of water. The insoluble silicic acid was collected, washed thoroughly, transferred to a crucible, ignited, and weighed, the weight of silica being found to correspond to the quantity of the silicate contained in the original solution.

The quantity of silicic acid present in the yellow precipitate being considered by the author to be determinable also by reducing the molybdic acid present in the same precipitate to a lower compound and by titrating the latter with an oxidizing agent, experiments have been made as follows. The final solution of the titration was evaporated in a casserole to a volume of about 10 c.c., and heated with 6–10 c.c. of concentrated sulphuric acid until white fume was given off and the liquid became blue. The residual solution was diluted with 50 c.c. of water, shaken with zinc amalgam, and titrated with N/10 $KMnO_4$ solution. The experiments have shown that this method gives accurate results more readily than that of the titration with sodium hydroxide.

A few examples of the determination of silicic acid actually made by gravimetric method and by volumetric method using both NaOH and $KMnO_4$ are given in Table 2.

Table 2.

I	II	III	IV	V	VI	VII
Quantity of the sodium silicate solution taken (c.c.)	Quantity of SiO_2 contained in the sodium silicate solution (g.)	Quantity of the N/10 NaOH solution used in the titration (c.c.)	Number obtained by dividing the number under II by the corresponding number under III	Quantity of SiO_2 determined by gravimetric method (g.)	Quantity of the N/10 $KMnO_4$ solution used in the titration (c.c.)	Number obtained by dividing the number under II by the corresponding number under VII
5	0.03106	112.60	0.000275			
3	0.01863	68.73	0.000271			
2	0.01242	45.90	0.000270			
1	0.00621	22.59	0.000274			
1	0.00621	22.54	0.000275			
2.5	0.01553	56.53	0.000274	0.01616	103.2	0.000166
0.5	0.00310	11.50	0.000270	0.00338	18.5	0.000167
0.5	0.00310	11.31	0.000274	0.00302	18.6	0.000166
			0.000273			0.000166

As shown in column IV in Table 2, the mean was found to be 0.000273. This number is justified to be a factor, by which the numbers given in column III showing the quantities of the NaOH solution in c.c. are multiplied in order to find the quantities of SiO_2; namely, c.c. of N/10 NaOH $\times$ 0.000273 = g. of SiO_2. Just in the same way the numbers in column VI are multiplied by the mean, 0.000166, in order to obtain the quantities of SiO_2; namely c.c. of N/10 $KMnO_4 \times 0.000166$ = g. of SiO_2.

The following conclusions have thus been obtained: (1) From a solution of silicate, silicic acid can be completely precipitated as ammonium silicomolybdate of yellow colour. (2) Concentration of each of nitric acid, ammonium nitrate, and ammonium molybdate suitable for complete precipitation of the yellow compound has been found experimentally. (3) The quantity of silicic acid present in the yellow precipitate can be determined either by titrating the precipitate with sodium hydroxide, or by reducing molybdic acid present in the precipitate to a lower compound and by titrating the latter with potassium permanganate. (4) Silicic acid can also be determined by gravimetric method, from the yellow precipitate or from the solution resulting from the titration with sodium hydroxide or potassium permanganate.

The author wishes to acknowledge his indebtedness to Prof. I. Wada, under whose direction this work has been carried out, and who has aided in the preparation of the manuscript for publication.

(September 10th, 1933)

QUANTITATIVE EMISSION SPECTRUM ANALYSIS OF LEAD AND CADMIUM CONTAINED IN ZINC OXIDE.

By Arata IWAMURA.

Received April 2nd, 1935. Published August 28th, 1935.

(1) **Sample Electrodes.** For the purpose of spectrographically determining very small quantities of lead and cadmium contained in zinc oxide, the oxide was first transformed into a solid conducting mass by treating merely with hydrochloric acid and then dried. A most suitable electrode was prepared in the following way:

Zinc oxide (30 g.) was gradually added to 35 c.c. of 6N HCl in a porcelain mortar and the mixture was constantly agitated, kneaded, and then moulded in a wooden mould before it was quite set, and the product was dried in an air-oven. The solid mass thus prepared was a round tablet, 3 cm. in diameter and 3 mm. thick, a round hole being made at its centre. Two such tablets containing zinc oxide with no foreign impurities except lead and cadmium were employed as the electrodes; the hydrochloric acid also contained no foreign impurities.

(2) **The Apparatus Used and the Method of Experiment.** To excite sparks between a pair of such electrodes, a transformer giving 10 kilovolts in the secondary was used. Self-inductance of a magnitude of about 62,000 cm. was always inserted in the secondary circuit. The light from an uncondensed spark between the electrodes was focused by means of a quartz lens on the slit of a small Hilger quartz spectrograph and spectrograms were thus obtained. When the sample contains a trace of lead and cadmium, the lead lines at λ 4058, 3684 Å and the cadmium line at λ 2288 Å were always detected on the plate. The photographic density of a line was recorded by means of Moll's recording microphotometer and for practical purposes the maximum heights of the curve for these lines measured from the neighbouring background were taken as a measure of the practical intensities of these lines.

The so-called "comparison method" was tried in analysing lead or cadmium in zinc oxide. Another method of analysing cadmium was to draw a density concentration curve in connection with the line at λ 4201.8 Å and to determine graphically the content of cadmium from the density of the cadmium line in the spectrum of the sample of unknown cadmium content.

(3) **Reproducibility of the Spectrograms of Zinc Oxide Containing Lead and Cadmium and the Sensitivity of the Analysis.** Reproducibility of the spectrograms of zinc oxide electrodes containing lead was studied and it was observed that the result was reproducible within a range of $+6.5--6.1\%$. The microphotometer record proved to be sensitive within a range of $\pm 1\%$ of error. Sensitivity of the spectrographic analysis of lead or cadmium in zinc oxide was graphically determined from the density concentration relation in the following way: A series of spectrograms were taken of sparks emitted from electrodes containing varying amounts of lead or cadmium, and the practical intensities of the line were measured on microphotometer curves for various contents of lead or cadmium, and a curve connecting intensity of the line and the corresponding amount of lead or cadmium was drawn. The extrapolation of this curve gave the minimum detectable limit in the present method, i.e. the sensitivity of the method. The sensitivity of the analysis of lead in zinc oxide was thus found to be 1×10^{-6} under the conditions of the present experiment. In the case of cadmium in zinc oxide, the sensitivity was found to be 1.5×10^{-6} under the conditions of the experiment.

(4) **Influence of Acids Used for Cementing Zinc Oxide.** The influence of hydrochloric, sulphuric, and nitric acids used in cementing the zinc oxide containing 0.010% of lead or 0.050% of cadmium was determined by using the lead line at λ 4058 Å, or the cadmium line at λ 2288 A, and the densities (d_{mm}) given by the microphotometer were found as shown in Table 1.

Table 1.

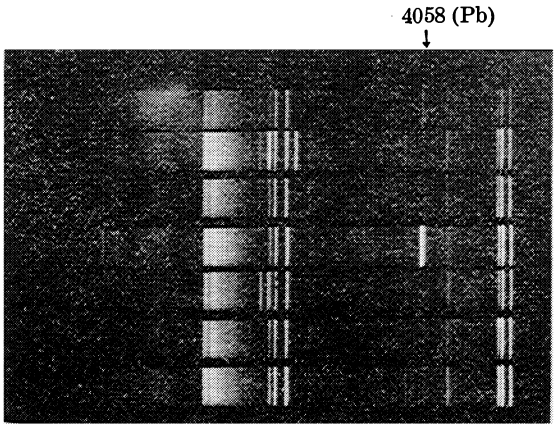
d_{mm} \ Acids	Hydrochloric acid	Sulphuric acid	Nitric acid
d_{mm} $\lambda = 4058$ Å	23.2	22.3	$17.5+\alpha$
d_{mm} $\lambda = 2288$ Å	15.3	9.3	9.1

It will be seen that though the densities are of the same order of magnitude, hydrochloric acid gave the most sensitive result. The sample of zinc oxide containing much carbonate was not suitable to be cemented into the electrodes for the purpose of analysing lead, because the lead lines at λ 4058 Å and 3683 Å were masked by the cyanogen bands. Such a sample containing carbonate should be heated in a porcelain dish for the purpose of decomposing carbonate and then be prepared into electrodes as described above.

(5) **Influence of Cations.** Those elements which have some spectral lines in the vicinity of the lead line at λ 4058 Å are shown in Table 2.

Table 2.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
4077.7	Sr II	10 R	4045.8	Fe I	8 R
4066.4	Co I	7 R	4045.4	Co I	8 R
4063.6	Fe I	8 R	4044.2	K I	10 R
4056.6	Cu	2 R	4041.4	Mn I	8 R
4055.3	Ag I	8 R	4035.7	Mn I	5 R
4047.2	K I	10 R	4034.5	Mn I	8 R



Fe : Zn

Fe : Zn = 1 : 1000

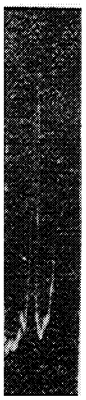
Co : Zn ,,

Mn : Zn ,,

K : Zn ,,

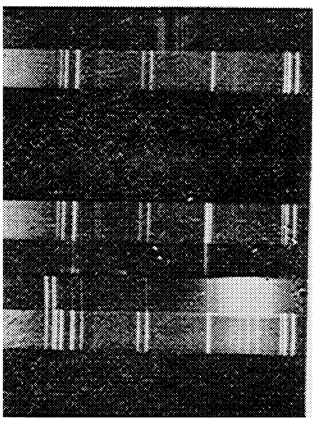
Cu : Zn ,,

Ag : Zn ,,



a

c Fe+Pb



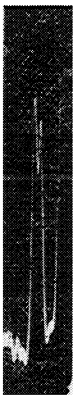
Fe : Zn = 5 : 1000

Mn : Zn ,,

,, ,,

Cu : Zn ,,

Co : Zn ,,



b

d Mn+Pb

Plate I.

Now, each of the above-mentioned elements was added in small varying amounts to a definite quantity of zinc oxide sample containing a definite amount of lead till the concentration of the added element became 0.5 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked, and spectrographed as usual. It was observed that the elements iron and manganese had marked influence upon the densities of the line at λ 4058 Å (Plate I, **a** and **b**, and the corresponding microphotometer records **c** and **d**). Hence these two elements should be avoided in preparing the electrodes for a given sample of zinc oxide. If such elements are unavoidably present, then observe the lead line at λ 3684 Å.

Now, the common elements which have some spectral lines in the vicinity of the lead line at λ 3684 Å are shown in Table 3.

Table 3.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
3705.6	Fe I	6 R	3682.2	Fe	6
3700.3	Co	7	3679.9	Fe I	5
3687.5	Fe I	6 R	3677.6	Fe	6
3685.2	Ti II	10 R	3676.6	Co	8
3683.5	Pb	3 R	3674.2	Ni I	6
3683.1	Co	8	3669.5	Fe	6
			3669.0	Ti I	6

Iron and cobalt lines will practically coincide with the lead line at λ 3684 Å. But, it is practically very rare that cobalt occurs in zinc oxide, but iron does frequently as one of the impurities. If iron is present in zinc oxide in an appreciable quantity, then the spectrograph of higher dispersion should be employed.

With regard to the estimation of cadmium in zinc oxide, similar attention was paid. Those elements which have some spectral lines in the vicinity of the cadmium line at λ 2288 Å are shown in Table 4.

Table 4.

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
2298.2	Fe	I	2293.85 2294.30	Cu	5
2297.8	Fe	—	2292.5	Fe	—
2294.7	Cd	4	2291.1	Fe	—

Table 4. (*Concluded*)

λ in Å	Origin	Intensity	λ in Å	Origin	Intensity
2290.6	Fe	—	2286.7	Sn	3
2290.0	Ni	—	2280.2	Fe	—
2289.0	Fe	—	2279.9		
2288.1	As	3	2279.6	Ni	—
2287.6	Fe	—	2276.6	Bi	2
2287.3					

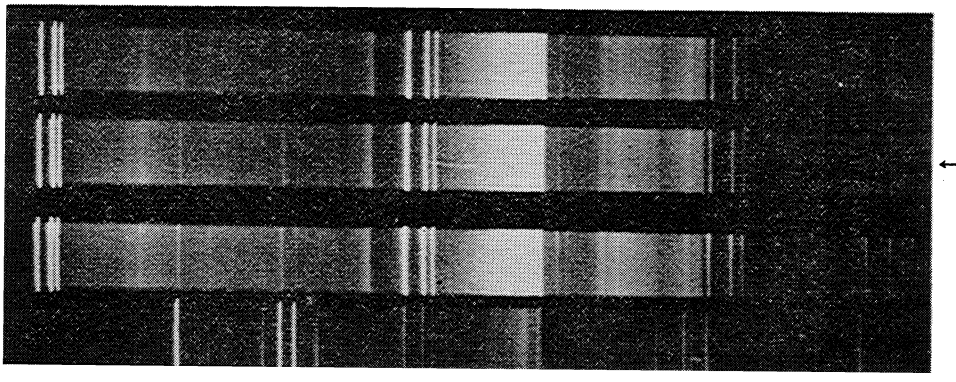
Now, each of the above-mentioned elements was added in small varying amounts, to a definite quantity of a zinc oxide sample containing a definite amount of cadmium till the concentration of the added element became 3 mol in 1000 mol of zinc oxide, and the mixture was cemented into electrodes, sparked, and spectrographed as usual. The above-mentioned elements were observed to give no detectable lines interfering with the cadmium line, λ 2288 Å, and, therefore, it became evident that the addition of these elements in the concentration mentioned above would influence neither the background nor the cadmium line.

(6) **Influence of Capacity and the Self-inductance.** When condensed discharge was effected between the electrodes consisting of zinc oxide, they were easily broken and no desirable exposure could be made. The present writer was forced to use uncondensed spark discharge throughout the experiment and was unable to study the influence of capacity systematically. The introduction of capacity into the secondary circuit of the transformer was possible after the uncondensed spark discharge was continued for a few minutes, but then, there appeared air-lines which masked the lead lines in question.

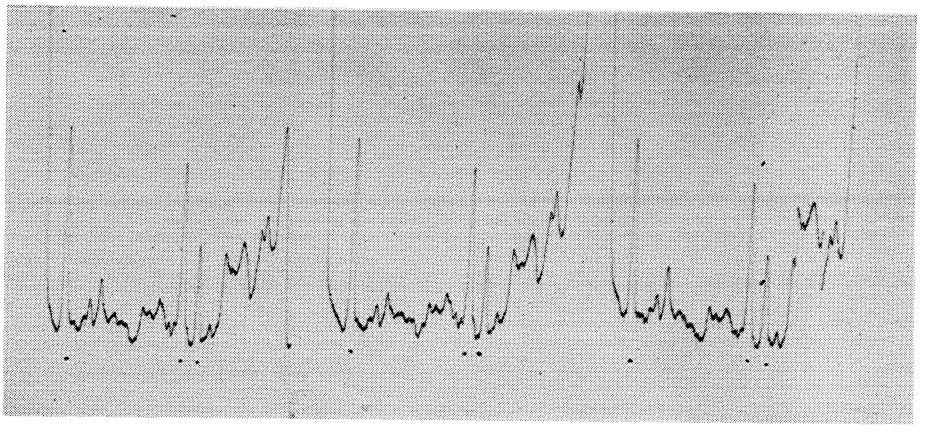
The introduction and increase of self-inductance in the secondary circuit of the transformer cleared up those air-lines and gave a clear back ground in the spectrogram. In analysing cadmium by uncondensed spark discharge nothing particular was observed.

(7) **Influence of Developers upon the Fogging of the Background of the Plate.** During the course of the experiment, the present writer has found that the hydroquinone developer which gives a strong contrast is one of the most satisfactory developers in order to make the background clear in contrast to the blackening of the lines. The use of pyrogallol developer or metol hydroquinone developer seems to be less satisfactory.

(8) **Comparison of the Results of Spectrographical Analysis of Lead or Cadmium with those of Chemical Analysis or with Theoretical Values.** Let S denote the value of lead or cadmium spectrographically obtained, C that chemically found, T the theoretical value, and Δ the divergency from the chemical or theoretical values. (See Plate II, a and b.)



a



b

Plate II.

As is shown in Table 5 the spectrographical results are generally somewhat higher than the chemical or theoretical ones, but they are of the same order of magnitude in case of lead and cadmium, the divergency being always within the limit of the permissible error.

Table 5.

	Pb %			Cd %			
	I	II	III	I	II	III	IV
S	0.0007	0.00137	0.00289	0.00137	0.01640	0.02012	0.01135
C	0.0006	0.00133	0.00270	—	—	—	—
T	—	—	—	0.00136	0.01536	0.01921	0.01082
Δ	0.0001	0.00004	0.00019	0.00001	0.00104	0.00091	0.00053
$\Delta\%$	+14+	+3-	+7-	+0.7-	+6.8-	+4.7-	4.9-

Summary.

(1) Electrodes consisting of a zinc oxide sample containing lead or cadmium, were prepared for the purpose of quantitative emission-spectrum analysis.

(2) The reproducibility of the spectrograms of the electrodes was tested, and was shown to be within -4.8 to $+6.5\%$, under the conditions of the experiment.

(3) The sensitivity of this method for estimating lead and cadmium contained in zinc oxide was determined to be 1×10^{-6} and 1.5×10^{-6} respectively under the conditions of the experiment.

(4) Influence of acids used for cementing zinc oxide, influence of the presence of carbonate and that of some metallic salts added to zinc oxide were tested. Some remarks on capacity and on the developing of the plate were described.

(5) The values obtained by emission-spectrum analysis were compared with those found by chemical analysis or with theoretical values.

The above experiment was conducted during the years 1929–1931, under the financial support by Dr. M. Momotani of Osaka, to whom the writer's most heartfelt thanks are due.

(January 5th, 1934)

Faculty of Science,
Imperial University of Kyoto.

THE ELECTROLYTIC DEPOSITION OF ZINC FROM ACID SOLUTIONS.

By Hisashi KIYOTA.

Received April 2nd, 1935. Published August 28th, 1935.

There have been a great many works dealing with the electrolytic deposition of zinc from the various acid solutions, but none of the methods hitherto proposed can be regarded as perfect. The chief difficulty in zinc electrolysis was thought to lie in a property of zinc, which forms a spongy deposit, and an attempt was made, in this investigation, to ascertain how far this difficulty might be overcome and to establish a convenient method for the quantitative analysis of zinc.

Throughout all the experiments, a platinum basin of about 150 c.c. capacity previously plated with copper was employed as the cathode, and a platinum disk which could be rotated as the anode.

In order to find out what results were attainable when the methods previously known were followed with this apparatus, a series of experiments was performed according to the methods given by F. Spitzer,[1] A. Fischer and R. J. Boddaert,[2] F. F. Exner,[3] and L. H. Ingham.[4] None of these methods, however, gave satisfactory results, all producing the deposit in spongy form, and some giving a deposit adhering to the cathode so loosely that even washing could not be effected.

The best results were obtained by the present author with an acetic acid solution containing some sodium acetate. An outline of the experiment follows.

The sample of zinc was taken below 0.5 g. from the analytical standpoint. The suitable volume of the electrolyte was found to be about 125 c.c. To see the effects of many important factors they were fixed in a range suitable for the analytical purpose and the electrolysis was carried out, changing at a time one factor only to be tested. The following results were obtained: (A) Zinc tended to deposit in a fine crystalline form with a metallic lustre giving a negative error in the cases where (1) the concentration of the acetic acid

(1) F. Spitzer, *Z. Elektrochem.*, **11** (1905), 404.

(2) A. Fischer and R. J. Boddaert, *Z. Elektrochem.*, **10** (1904), 946.

(3) F. F. Exner, *J. Am. Chem. Soc.*, **25** (1903), 899; *Chem. Zentr.*, **74** (1903), (2), 1210.

(4) L. H. Ingham, *J. Am. Chem. Soc.*, **26** (1904), 1270; *Chem. Zentr.*, **75** (1904), (2), 1758.

was comparatively great, (2) the quantity of the sodium acetate was comparatively small, (3) the current density was comparatively small, (4) the temperature of the electrolyte was comparatively high, and (5) the rotation of the anode was comparatively quick. (B) In the cases reverse to the above, zinc tended to deposit in a spongy form giving a positive error.

The author investigated further by adjusting the factors and found out a method for the electrolytic determination of zinc. This method is very convenient and give very accurate results. It is carried out as shown below.

(1) The sample was used in the form of zinc sulphate, 6 g. of crystalline sodium acetate and various amounts of acetic acid being added. Water was added up to 125 c.c., and the solution was electrolyzed. (2) The concentration of the acetic acid was adjusted according to the amount of zinc present: for 0.5 g. of zinc, 0.15–0.21 normal; for 0.3 g., 0.21–0.27 normal; and for 0.1 g., 0.27–0.33 normal. (3) The electrolysis was begun at room temperature. The regulation of the temperature of the electrolyte was unnecessary. (4) The anode was rotated at the rate of 1500–1700 turns per minute. (5) The current density was maintained at 0.5–0.6 amp./dm^2, till the potassium ferrocyanide reagent ceased to give the reaction of zinc—the main electrolysis—and it was then raised to 3–4 amp. and continued for about 10 minutes. (6) The duration of the main electrolysis varied from about 35 minutes to about 80 minutes according to the amounts of zinc: for 0.5 g. zinc, 65–80 min.; for 0.3 g., 50–60 min.; for 0.1 g., 35–40 min.; and for 0.001 g., 0 min. (7) At the end of the electrolysis, the cathode was washed with water without stopping the current and the rotation of the anode, then washed with alcohol, and ether, dried, and weighed. (8) In these experiments, the errors were always within 0.1 mg.

The influences of such substances as sodium sulphate, ammonium sulphate, ammonium acetate, sodium chloride, and sodium nitrate on the zinc deposition was investigated. The presence of sodium sulphate, ammonium sulphate, and ammonium acetate had no significantly harmful influence, when their concentration was lower than 0.15 normal. The nitrate greatly retarded the deposition of zinc and tended to deposit the metal in a spongy form. The effect of the chloride was not nearly so bad as that of the nitrate, and still it was often a cause of negative error.

The author wishes to express his sincere thanks to Prof. Motooki Matsui, under whose guidance and encouragement this work was carried out.

Kyoto Women's College,
Katsura, Kyoto.

ON THE ELECTROLYTIC DEPOSITION OF METALS FROM THEIR PYROPHOSPHATE SOLUTIONS.

By Shiro KOYANAGI.

Received April 2nd, 1935. Published August 28th, 1935.

Pyrophosphates of various metals dissolve in alkali pyrophosphate solutions to form complex salts which are generally thought to have such compositions as represented by $Na_2[M^{II}P_2O_7]\cdot xH_2O$ or $Na[M^{III}P_2O_7]\cdot xH_2O$. As to the electrolytic deposition of metals from these complex pyrophosphate solutions A. Brand[1] conducted some experiments long ago. The present author has studied the electrolytic deposition of nickel, cobalt, copper, zinc, and cadmium from their complex pyrophosphate solutions with Classen's electrode in order to find best conditions for the analysis of these metals. Iron was found not to be deposited completely from the pyrophosphate solution. For the other metals, especially for zinc and cadminum which were hitherto known to give no satisfactory deposit, the method was found to give very trustworthy result.

Nickel. Nickel sulphate was taken as the sample, and its pyrophosphate solution mixed with some ammonium carbonate was used as the electrolyte.

Ni (as $NiSO_4\cdot 7H_2O$)	$Na_4P_2O_7\cdot 10H_2O$	$(NH_4)_2CO_3$	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.3 g.	3.0–5.0 g.	3.0–4.0 g.	120 c.c.	1.0–2.0	6.0–7.0	ord. temp.	800 per min.	90–120 min.

Cobalt. Cobalt sulphate was used for analysis. The amount of cobalt taken for analysis should be kept below 0.2 g.; otherwise the deposit acquires somewhat dark appearance.

Co (as $CoSO_4\cdot 7H_2O$)	$Na_4P_2O_7\cdot 10H_2O$	$(NH_4)_2CO_3$	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.2 g.	4.0–5.0 g.	1.0–2.0 g.	125 c.c.	1.0–1.5	6.0–7.0	ord. temp.	800 per min.	70–100 min.

Copper. The pyrophosphate solution mixed with some ammonium nitrate was found to give the best result.

(1) *Z. anal. Chem.*, **28** (1889), 581.

Cu (as $CuSO_4 \cdot 5H_2O$)	$Na_4P_2O_7 \cdot 10H_2O$	NH_4NO_3	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.3 g.	7.0–8.0 g.	3.0–5.0 g.	120 c.c.	1.0–1.5	4.0–5.0	ord. temp.	800 per min.	90–120 min.

Zinc. Zinc pyrophosphate solution with the addition of ammonium nitrate was taken as the electrolyte, and electrolysis was conducted with the cathode previously electroplated with copper.

Zn (as $ZnSO_4 \cdot 7H_2O$)	$Na_4P_2O_7 \cdot 10H_2O$	NH_4NO_3	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.2 g.	7.0 g.	0.5–1.0 g.	125 c.c.	1.0–1.5	6.0–7.0	ord. temp.	500 per min.	120 min.

Cadmium. The conditions for its analysis were very similar to those for zinc determination.

Cd (as $3CdSO_4 \cdot 8H_2O$)	$Na_4P_2O_7 \cdot 10H_2O$	NH_4NO_3	Volume	Amp.	Volt	Temp.	No. of rotation	Time
0.1–0.2 g.	9.0 g.	1.0 g.	125 c.c.	2.0–2.5	5.5–6.0	ord. temp.	500–600 per min.	120 min.

In conclusion the author wishes to express his thanks to Prof. M. Matsui for his kind advices.

(April 15th, 1934)

PRECIPITATION OF ALUMINIUM WITH HYDROGEN AMMONIUM CARBONATE.[1]

By Toshio KOZU.

Received April 2nd, 1935. Published August 28th, 1935.

In the previous communication[2] it was reported that aluminium is precipitated with a hydrazine solution saturated with carbon dioxide. If, by a similar treatment, ammonia might be made equally suitable for aluminium analysis it would be a very useful precipitant of aluminium, perhaps surpas-

(1) An abstract from the original, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, 1934, 17.
(2) *J. Chem. Soc. Japan*, **54** (1933), 682.

sing all others. It was for the hope of accomplishing this purpose that the present work was undertaken.

The *p*H value of a solution of commercial ammonium carbonate having the concentration of about one molar, is 8.70 at 21°. When this solution is cooled with ice and saturated with carbon dioxide, hydrogen ammonium carbonate begins to crystallize out on the bottom of the vessel, the *p*H value of the solution at this instant being lowered to 7.6. The molar solution of hydrogen ammonium carbonate thus separated was found to have *p*H 7.5 at 20°, which changed to 7.8 after three weeks. To prepare a reagent suitable for aluminium analysis, it is not necessary to isolate hydrogen ammonium carbonate in solid form; we have only to saturate a molar solution of commercial ammonium carbonate with carbon dioxide till hydrogen ammonium carbonate begins to separate out, and then to expel the excess of carbon dioxide dissolved in it by exposing the solution to a reduced pressure of about 15 mm.

Gravimetric Analysis. To determine aluminium gravimetrically, a potassium alum solution containing 0.1446 g. Al_2O_3 in about 30 c.c. with two drops of bromo-thymol blue was slowly treated with hydrogen ammonium carbonate under constant agitation, till the indicator exhibited blue colour. The precipitation of aluminium was always accompanied by the evolution of carbon dioxide. After standing for 20 minutes the vessel containing the precipitate was warmed on a water bath for 40–60 minutes with occasional shaking. The heating should be continued till ammonia gas, recognizable by its odour, ceases to evolve. The *p*H value of the mother liquor at this instant was observed to be 7.45 at 21°. The precipitate was then filtered and washed with water warmed to 50–60°, till the filtrate no longer showed the reaction of SO_4''. It was first dried at 100°and then ignited at 1100°. The results of analysis are shown in Table 1. Even a trace of aluminium was never found in the filtrate.

Table 1. Al_2O_3(taken): 0.1446 g.

Al_2O_3 found (g.)	Error (g.)	Al_2O_3 found (g.)	Error (g.)
0.1445	−0.0001	0.1446	−0.0000
0.1448	+0.0002	0.1442	−0.0004
0.1442	−0.0004	0.1444	−0.0002
0.1443	−0.0003	0.1451	+0.0005
0.1447	+0.0001	0.1444	−0.0002

To determine the composition of the aluminium compound precipitated by hydrogen ammonium carbonate the precipitate formed at room tempera-

ture was left to stand for a night, filtered with a glass filter, and well washed with water. After water was removed by suction as completely as possible, the precipitate was placed over calcium chloride in a vacuum desiccator. The precipitate, which had a powdery amorphous form, gave the following results on analysis: Al_2O_3, 47.71; H_2O, 35.01; CO_2, 17.28. Calc. for $4Al(OH)CO_3 \cdot 6Al(OH)_3 \cdot 9H_2O$: Al_2O_3, 48.72; H_2O, 34.44; CO_2, 16.82%.

The formulas hitherto given by several authors for basic aluminium carbonate differ from one another and also from that of the present author, perhaps owing to divergence in the conditions under which the precipitate was prepared.

The solubility of the basic aluminium carbonate in water was found to be 0.00242 at 20.5°, and 0.00307 at 21.5° per 1000 c.c.

When precipitated from a very dilute solution, basic aluminium carbonate takes the form of very fine particles which when warmed with mother liquor, become unsuitable for analytical treatment, being changed thereby into a colloidal form.

The most suitable concentration was found to be 47.4–23.7 millimol solution of potassium alum, that is, the solution containing 1.3459 g. of potassium alum in 30–70 c.c.

Procedure. The procedure of the new method for analysing aluminium as its oxide may be stated as follows: To a solution containing 0.05–0.1 g of aluminium in the form of potassium alum in 30 c.c.–40 c.c. about one molar hydrogen ammonium carbonate solution is slowly added with stirring, till bromo-thymol blue, added beforehand, turns blue. As the evolution of carbon dioxide ceases at this stage the end point of the reaction is easily recognized without the use of an indicator. After standing for 20–30 minutes the precipitate is warmed on a water bath, whereupon carbon dioxide accompanied by some ammonia is again evolved. Heating is continued for 40–60 minutes till the odour of ammonia becomes unrecognizable. Add some water, if necessary, taking care to keep the total volume of the mother liquor always less than 50 c.c. The precipitate is then filtered and washed with warm water of about 60° till the filtrate shows no reaction of SO_4''. After drying at about 100° the precipitate together with the filter paper is placed in a crucible and ignited at about 1100°. When the crucible is weighed, it must be enclosed tightly in a well-stoppered weighing tube.

Summary.

(1) Hydrogen ammonium carbonate prepared by saturating the solution of commercial ammonium carbonate with carbon dioxide may conveniently be used for quantitative precipitation of aluminium.

(2) The precipitate formed with hydrogen ammonium carbonate at ordinary temperature is fairly stable in a solution having the *p*H value of 7.6, and its composition is represented by $4Al(OH)CO_3 \cdot 6Al(OH)_3 \cdot 9H_2O$.

(3) The solubility of the basic carbonate in water is found to be 0.00242 g. per 1000 c.c. at 20–21°.

(4) The analytical procedure for gravimetric determination of aluminium with hydrogen ammonium carbonate is given.

(5) Several precautions which are to be taken in the analytical treatment of basic aluminium carbonate are fully described.

In conclusion the author wishes to express his warm thanks to Prof. Motooki Matsui for his kind guidance and valuable suggestions.

(June 10th, 1934)

ON THE ANALYSIS OF BISMUTH BY MEANS OF SELENIOUS ACID.

By Otozo FUNAKOSHI.

Received April 2nd, 1935. Published August 28th, 1935.

Berg and Teitelbaum[1] measured the sensitivity of formation of bismuth selenite precipitate in 1/3 and 1/4 normal nitric acid, and they fixed the limit of detectability of bismuth at 0.000016 g. in 5 ml., i.e. 1:300000. They state that an accurate gravimetric analysis can be made by making the precipitate, having the composition $Bi_2(SeO_3)_3 \cdot H_2O$, anhydrous by boiling in the mother liquor and then by properly drying and weighing.

For satisfactorily accomplishing the analysis of bismuth by the use of selenious acid as the precipitant, it is important to have a clear knowledge of the relation of the acid concentration to the formation of the precipitate, and of the behaviour of other metals upon selenious acid. The present investigation was started for clarifying these points.

The Material and Reagents. The material for the experiments was prepared from the selenium of the Hitachi Mine by heating it in the stream of oxygen, purifying the selenium oxide by repeated resublimation, adding a

(1) *Z. anorg. allgem. Chem.*, **189** (1930), 101.

small quantity of freshly boiled water, and evaporating on the water-bath. For oxidizing any liberated selenium, the evaporation was continued with the addition of 3–4 ml. of concentrated nitric acid, and the residue was finally heated over direct flame until white fumes were developed. The selenious acid thus prepared was used as a 5 per cent. aqueous solution.

Kahlbaum's bismuth nitrate of the superior quality and Merck's nitric acid of sp. gr. 1.4 for analytical use were employed for making 1% solution of the former and 0.5 N solution of the latter.

The Sharpness of the Reaction leading to the Formation of Bismuth Selenite Precipitate. For the purpose of ascertaining the limits of formation of bismuth selenite precipitate, observations were made under the conditions of reaction detailed in Table 1.

Table 1.

Bi taken (g.)	Selenious acid solution (ml.)	Total volume (ml.)	Nitric acid normality	Limit of formation of ppt.	Remarks
0.000043	1.3	4.3	1/3.3	1×10^{-5}	Immediate white turbidity; crystalline particles on heating. Clear supernatant liquid.
,,	1.6	8.6	1/4.3	2×10^{-5}	Fine cryst. particles on heating 1 minute.
,,	1.9	12.9	1/3.9	3×10^{-5}	Fine cryst. particles on heating 2 minutes.
,,	2.05	15.05	1/3.8	3.5×10^{-5}	Fine cryst. particles on heating 2 minutes.
,,	2.0	17.2	1/3.7	4.0×10^{-5}	A few fine cryst. particles on heating 2 minutes.
,,	2.5	21.5	1/3.6	5.0×10^{-5}	A few fine cryst. particles on heating 2–3 minutes. Clearly distinct from the blank test.
0.000086	1.5	4.5	1/3.4	5.0×10^{-5}	The same as above.

From the above-given results, it is seen that 0.00001 g. of Bi in 5 ml. can be detected when the final acid normality is 1/4. The sensitiveness is 1:500000.

The Influence of Acid Strength on the Sensitivity of Precipitation. If the acidity is above 0.86 N in nitric acid, the precipitation of bismuth selenite is incomplete even when 0.00086 g. of Bi is contained in 6 ml. of the solution. Beyond 1 N in acidity, there is no precipitation at all. It is found that, for the complete precipitation, the acidity must be below 0.5 N. The influence of hydrochloric acid is about the same as that of nitric acid. Sulphuric acid is, however, very much weaker in this respect, for up to 1.4 N it does not hinder the precipitation of a solution of 0.00086 g. Bi in 5–6 ml., while nitric acid completely prevents the precipitation already at 0.9 N. When heated, nitric acid prevents the precipitation at 0.6 N while with sulphuric acid the limit is reached only at 0.9 N.

The Action of Selenious Acid upon the Salts of other Metals. Such metals as Cu, Cd, Fe$^{\cdot\cdot}$, Al, Ni, Co, Mn, Zn, Ca, Li, Na, and K are not precipitated by selenious acid and can be separated from bismuth by its use. Iron and chromium in the trivalent state are precipitated within 15 minutes by heating at the concentration of 4.5×10^{-5} and 5×10^{-4} respectively. The iron precipitate is dissolved by 1/6 N HNO_2, 2/7 N HCl, and 1/3 N H_2SO_4. The chromium precipitate is dissolved by 1.7 N HNO_3, 0.7 N HCl, and 1.2 N H_2SO_4.

Solution of such metals as Hg, Pb, Sn$^{\cdot\cdot}$, Sb, and Ag are precipitated by selenious acid at the concentration of 7.5×10^{-4} to 1.5×10^{-5}. The lead precipitate is readily soluble in HNO_3 or HCl. Solutions of Ba, Sr, Mg, Ti, and Th are precipitated at the concentration of 5×10^{-4} to 2×10^{-5}, and the precipitates of Ba, Sr, and Th are dissolved in the presence of 1.1–2 N HCl, or 0.7–1.2 N HNO_3. Among the twelve elements mentioned above which are precipitable with selenious acid, silver, ferric iron, barium, titanium, and thorium are more sensitive than the rest, and consequently their presence makes the qualitative detection of bismuth somewhat uncertain. As bismuth, mercury, and lead have the common properties of being precipitated by H_2S and of not dissolving in ammonium sulphides, their detection will have nothing to gain by the use of selenious acid reagent.

The Quantitative Determination of Bismuth with Selenious Acid. Fifty ml. of 1% solution of bismuth nitrate are diluted to 80–90 ml. and nitric acid is added to the resultant strength of 0.35–0.38 N. The solution is heated to boiling and the selenious acid reagent is added slowly with stirring. After the completion of precipitation, an excess of a few ml. of the reagent is added while still keeping the solution boiling for some time. After cooling the precipitate is filtered and washed with cold water until there is no selenious acid remaining in the filtrate. The precipitate is well dried in the air and is then ignited rather strongly from the outset over the Bunsen burner for an hour (If the heating is begun slowly with a small flame, there is

a danger of a loss of bismuth in the stream of subliming SeO_2 formed by the decomposition of the precipitate). After cooling it is weighed in the usual manner.

It is to be noted here that if the heating is done, as suggested by Berg and Teitelbaum, at first for an hour at 50° and for another hour at 105°–115°, and the precipitate is weighed as $Bi_2(SeO_3)_3$, it is rather difficult to attain a constant result (Table 2).

Table 2.

Product finally weighed	Theoretical value (g.)	Values found (g.)		
		1	2	3
$Bi_2(SeO_3)_3$	0.4031	0.3948	0.4029	0.3979
Bi_2O_3	0.2349	0.2348	0.2349	0.2347

It is seen from the Table that a more accurate and constant result is obtained by strongly igniting the bismuth selenite precipitate and weighing the product as Bi_2O_3, than by drying is at 105°–115° and weighing as $Bi_2(SeO_3)_3$.

The author wishes to express his deep gratitude to Professor Matsui for his valuable guidance.

(August 5th, 1934)

A NEW GRAVIMETRIC METHOD FOR THE DETERMINATION OF LEAD AS LEAD SALICYLALDOXIME AND ITS SOLUBILITY MEASUREMENT BY USING Th B AS RADIOACTIVE INDICATOR.

By Masayoshi ISHIBASHI and Haruo KISHI.

Received May 10th, 1935. Published August 28th, 1935.

I. Gravimetric Determination of Lead as Salicylaldoxime Compound.

An excellent method of quantitatively determining copper as a salicylaldoxime compound has been proposed by F. Ephraim.[1] The present authors

(1) F. Ephraim, *Ber*, **63** (1930), 1928.

have now found a new gravimetric method for the analysis of lead using salicylaldoxime.

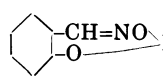
Material Used. The sample used was Kahlbaum's lead acetate for analysis, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, the composition of which was proved to be quite exact by the gravimetric determination of lead as the chromate. Of this substance, 7.3228 g. was dissolved in 1 liter; and this solution contains 0.0400 g. of lead in 10 ml.

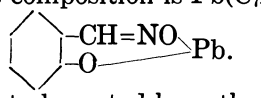
Salicylaldoxime was prepared from salicylaldehyde and hydroxylamine hydrochloride and purified by repeated recrystallization from ligroin. The colourless crystals thus obtained had the melting point 63°C. The substance had some tendency to get somewhat coloured when stored. One gram of it is dissolved at room temperature in 5 ml. of alcohol and the solution is slowly poured into 95 ml. of pure water warmed to about 80°C. A little of the oxime which may remain at first as a turbid suspension is gradually dissolved away. The solution is now filtered after a thorough stirring and the 1% solution of the oxime thus prepared is used for precipitating the lead salt.

Procedure. Twenty-five ml. of the lead acetate solution is diluted with pure water to about 50 ml. and treated with a slight excess of salicylaldoxime. Ten per cent. ammonia water is then slowly added so as to make the *p*H of the solution greater than 6.5. For this purpose, neutral red (*p*H = 6.8—8.0) or phenolphthalein (*p*H = 8.2—10.0) is used as a convenient indicator. After clarifying the turbid mother liquor by stirring, it is allowed to stand about an hour. The easily filtrable precipitate of slightly yellow colour is transferred to a glass filter, washed with 20% alcohol, and filtered by suction. It is thoroughly dried at about 105°C., cooled, and weighed as usual. The result is shown in Table 1.

Table 1.

No.	Salicylaldoxime added (g.)	Pb-Salicylaldoxime found (g.)	Pb		Difference (g.)
			added (g.)	found (g.)	
1	0.08	0.1648	0.1000	0.1000	0.0000
2	0.08	0.1647	0.1000	0.0997	—0.0003
3	0.08	0.1646	0.1000	0.0996	—0.0004
4	0.08	0.1647	0.1000	0.0997	—0.0003
5	0.08	0.1645	0.1000	0.0996	—0.0004

Pb:  Pb = 0.6054.

For deciding upon the composition of lead salicyladoxime, the quantitative determination of lead and nitrogen in it was made. Lead in a weighed quantity of the substance dried at 105°C. was precipitated in acetic acid solution as lead chromate and weighed. Nitrogen was determined as ammonia by the Kjeldahl method. As shown in Table 2 the results prove that the probable composition is $Pb(C_7H_5O_2N)$ and suggest that the allowable constitution is  .

It is to be noted here that, in copper salicylaldoxime, one atom of copper is combined with two molecules of salicylaldoxime, while, in lead salicylaldoxime, one atom of lead is combined with only one molecule of the aldoxime. Similar examples are found among other oxime compounds of metals, which we intend to report in another connection.

Table 2.

Pb-Salicylaldoxime taken (g.)	$PbCrO_4$ found (g.)	Pb			Difference %
		g.	%	as $Pb(C_7H_5O_2N)$ %	
0.1640	0.1558	0.09988	60.81	60.54	+0.27
Pb-Salicylaldoxime taken (g.)	NH_3 found (g.)	N			Difference %
		g.	%	as $Pb(C_7H_5O_2N)$ %	
0.1642	0.007627	0.006272	3.82	4.09	−0.27

The hydrogen ion concentration of the precipitating solution, from which lead salicylaldoxime was completely precipitated, was determined with indicators in the following way. A strong acetic acid solution of lead acetate was first prepared, in which the addition of an excess of the salicylaldoxime solution formed no precipitate. This acid mixture was divided into several portions, to each of which a separate indicator was added and ammonia water was poured drop by drop so as to produce a definite colour grade showing a definite *p*H value. The reaction mixtures were allowed to stand for an hour, and then filtered. Each of the filtrates was now tested for lead with sodium sulphide solution to ascertain the degree of completeness of precipitation. Indicators used for this purpose were tropeolin 00 ($pH = 1.3-3.0$), methyl orange ($pH = 3.1-4.4$), methyl red ($pH = 4.2-6.3$), neutral red ($pH = 6.8-8.0$), and phenolphthalein ($pH = 8.2-10.0$). It was found that, at $pH \leqq 6.5$, the filtrate formed no precipitation of lead sulphide showing that the pre-

ceding precipitation of lead salicylaldoxime was complete. By utilizing the differences of *p*H values produced in this way, the authors[2] succeeded in separating and determining copper and lead in a mixture.

II. Solubility Determination of Lead Salicylaldoxime by Using Th B as the Radioactive Indicator. There are four methods used ordinarily in determining solubilities of difficultly soluble compounds; namely, (1) a definite quantity of the saturated solution is evaporated to dryness and the dry residue weighed; (2) the electrical conductivity of the saturated solution is determined and the solubility calculated; (3) the single potential between the electrode and ions of the dissolved salt is measured and the solubility calculated; (4) the solubility product is first found from the equilibrium constant and the solubility calculated.

Each of these methods is accompanied by a theoretical limitation and consequently the result gives only a conditional value. The fifth method described below is free from this defect. (5) G. v. Hevesy and F. Paneth[3] first used in the determination of the solubility of lead chromate Ra D as indicator. Generally, when a radioactive isotope of the metal, whose salt is to be measured, is used as an indicator, the solubility found represents the total quantity of the dissolved part no matter whether that part is ionized or hydrolyzed or not. Moreover, the manipulation of this method is not complex at all and the result is believed to be far more rational than that obtained with the four ordinary methods.

The solubilities of some of difficultly soluble organo-metallic complex salts are known, but, as they were determined by the first method cited above, there is no safeguard as to their exactness. The present authors have succeeded in obtaining exact solubility of lead salicylaldoxime in water with the use of Th B ($T = 10.6$ h.), the radioactive isotope of lead.

Radio-thorium was taken as the mother substance of Th B. In the upper part of the receptacle for radio-thorium, a small plate of platinum, which is easily inserted or removed, is suspended. Between the receptacle (+) and the platinum plate (−) a pure water resistance is inserted and a potential of 200 volts is applied with both the terminals connected with the earth. As soon as thorium-emanation is evolved from radio-thorium through the step of Th X, it is caught on the platinum plate and Th A, Th B, Th C, etc. are caused to deposit on it. On taking off the platinum plate, Th A ($T = 0.14$ sec.) is rapidly disintegrated and leaves Th B, Th C, etc. behind. It is to be

(2) M. Ishibashi and H. Kishi, *J. Chem. Soc. Japan*, **55** (1934), 1067.
(3) G. v. Hevesy and F. Paneth, *Z. anorg. allgem. Chem.*, **82** (1913), 223.

noted here that the radio-activity (β-ray) of Th B is too weak and insufficient, so that what we measure practically is the intensity of α- and β-rays evolved from Th C produced from Th B. For this reason, it is necessary that Th B and Th C are in transient equilibrium ; if the radio-activity of radio-thorium is strong and the duration of exposure of the platinum plate short, an allowance of a certain period of time will be necessary before the attainment of this transient equilibrium. In our case, however, the quantity of radio-thorium was small and the radio-activity weak, so that about one week's exposure of the platinum plate was necessary for performing one experiment. In such a case, it is to be easily presumed, and is also proved, that the transient equilibrium is practically attained at the moment of the removal of the platinum plate.

The measuring apparatuses used were the radioscope of the Rikagaku-kenkyujo, an accurate watch, and a stop-watch. According to the theoretical formula expressing the decline of radioactivity, $I_t = I_0 e^{-\lambda t}$, the value for a definite instant was calculated from the experimental values at various instants. I_0 is the radioactivity at the start, I_t that at the end of a period t, λ the disintegration coefficient, which is 0.0654 ($h.^{-1}$) for Th B.

Procedure. The platinum plate suspended above radio-thorium for about one week was treated with about 5 ml. of hot concentrated acetic acid to dissolve the deposited Th B, Th C, etc. The solution was diluted to about 50 ml. with pure water and exactly one ml. of it was taken from a burette on a watch glass. It was now evaporated up on the water bath and dried in the air bath at about 120°C. The radioactivity was measured with the residue after its complete cooling (Table 3). Radioactivity measurements made later on were calculated back to that of this first instant.

On the other hand, 20 ml. of the same radioactive indicator solution were measured off from the burette and poured into a beaker of 100 ml. capacity ; a weighed quantity of lead acetate was added to it and dissolved by stirring with a glass rod so as to distribute the acetates of Th B and Th C homogeneously in the lead acetate solution. The salicylaldoxime solution was now added in excess. After adding phenolphthalein, ammonia water was slowly added with constant agitation until pink colour was produced. After allowing to stand for about an hour, the precipitate was collected and washed in the usual way.

The wet lead salicylaldoxime thus prepared was placed in an Erlenmeyer flask of about 200 ml. capacity, about 100 ml. of pure water was added to it, and the flask was tightly closed with a rubber stopper and introduced to a thermostat at 25°C. It was kept in rotation for 24 hours for the purpose of the complete saturation. Finally it was taken out from the thermostat and

filtered. About 20 ml. of the first filtrate were thrown away for avoiding the concentration change caused by the adsorption on filter paper. Out of the remaining 80 ml. of the filtrate, 50 ml. are accurately measured out into the evaporating dish, evaporated on the water bath, and dried in the air bath as before. After cooling, the radioactivity was measured (Table 4 and Table 5).

Table 3.

Natural discharge			Radioactivity for 1 ml.			
Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Corrected value (I_0)
0.00	60.0	0.50	0.00	60.0	26.0	26.0–0.5 = 25.5
20.00	50.0		0.77	40.0		

Table 4.

Radioactivity for 20 ml.	$Pb(C_7H_5O_2N)$ equivalent to 0.0318 g. of $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ (g.)	$Pb(C_7H_5O_2N)$ corresponding to radioactivity of one scale division per min. (g.)
Number of scale divisions per min. $25.5 \times 20 = 510$	$\frac{0.0318 \times 0.5463}{0.6054} = 0.0287$ $\begin{cases} Pb/Pb(C_2H_3O_2)\cdot 3H_2O = 0.5463 \\ Pb/Pb(C_7H_5O_2N) = 0.6054 \end{cases}$	$0.0287/510 = 0.0000564$

Table 5.

Natural discharge			Radioactivity for 50 ml.				
Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Measuring time elapsed (min.)	Reading of scale divisions	Number of scale divisions per min.	Corrected value	
						I_t	I_0
0.00	50.0	0.41	0.00	50.0	0.56	0.56–0.41 = 0.15	1.14 (t=31 hs.)
24.39	40.0		17.86	40.0			

It is seen from Table 5 that the radioactivity of the dried material from 50 ml. of the saturated solution of lead salicylaldoxime is 1.14, and hence the radioactivity for one liter of it is $1.14 \times 20 = 22.8$. From Table 4 it is known that the weight of lead salicylaldoxime corresponding to unit radioactivity is 0.0000564 g. and hence the solubility in 1 liter of pure water at 25°C. must be $22.8 \times 0.0000564 = 0.0001287$ g. $\fallingdotseq 1.29 \times 10^{-3}$ g.

In the same way, the result of the second experiment with the saturation time of 15 hours was found to be 1.61×10^{-3} g., and that of the third experiment with the saturation time of 27 hours was found to be 1.22×10^{-3}g. The minimum time necessary for the complete saturation is thus found to be somewhere within 15 hours of rotatory agitation.

Table 6. Solubility per liter at 25°C.

Pb-Salicylaldoxime		Pb
(g.)	(mol)	(g.)
1.29×10^{-3}, 1.61×10^{-3}, 1.22×10^{-3} } mean 1.37×10^{-3}	3.8×10^{-6}, 4.7×10^{-6}, 3.6×10^{-6} } mean 4.0×10^{-6}	7.79×10^{-4}, 9.75×10^{-4}, 7.39×10^{-4} } mean 8.31×10^{-4}

Summary.

(1) Lead is quantitatively precipitated as salicylaldoxime compound from a neutral and a strongly ammoniacal solution of pH $\gtrless$ 6.5.

(2) The composition of the material precipitated and dried at about 105°C. is possibly $Pb(C_7H_5O_2N)$.

(3) The solubility of lead salicylaldoxime in pure water at 25°C., measured by the use of radioactive isotope Th B as indicator, is 1.37×10^{-3} g. per liter, i.e., 4.0×10^{-6} mol/l.

The authors wish to express their gratitude to Professor G. v. Hevesy of the University of Freiburg i.B., Germany, for his generosity to send them the sample of radio-thorium used in this experiment.

THE WATER IN INORGANIC COMPOUNDS. II. THE WATER CONTENT OF ODO ACID CLAY AT VARIOUS TEMPERATURES IN AIR CURRENT OF THE CONSTANT WATER VAPOUR PRESSURE.

By Minoru NAKAMOTO.

Received April 2nd, 1935. Published August 28th, 1935.

Studies on the water in Odo acid clay have been reported by many investigators.[1] The present writer,[2] too, has often done similar researches, one of which will be briefly described below.

The whole apparatus used in our experiment is shown in Fig. 1. The air current was produced and purified in A, B, C, and D, and, after saturated with the water vapour in the thermostat (Fig. 2), was introduced into the reaction furnace in which the platinum crucible containing the sample was hung as shown in Fig. 1. The weight change of the sample was observed by Honda's thermobalance.[3] The temperatures of the thermostat (T_2), connec-

Table 1.

g (g.)	P mm. Hg	T	P'mm. Hg	p mm. Hg	V (c.c.)	$\frac{V}{\text{Time}}$ c.c./min.	π mm. Hg
0.1151	761.5	291.9	771.0	16.0	2000	3.0	54.5
0.1787	763.0	292.6	773.0	17.0	3000	2.1	56.4
0.1806	759.0	292.6	769.0	17.0	3000	2.3	57.0
0.1198	764.0	291.1	772.0	15.5	2000	2.0	56.5
0.1139	763.5	292.1	773.5	16.5	2000	5.3	54.0
0.1173	762.5	292.1	772.5	16.5	2000	16.7	55.5
0.1170	755.0	292.1	764.5	16.5	2000	13.6	55.4
0.1783	765.0	290.1	773.0	14.5	3000	12.9	55.7
0.1183	756.5	289.1	764.5	13.6	2000	14.1	55.3
0.1782	763.0	291.1	771.0	15.5	3000	13.4	56.1
0.1775	758.5	291.6	768.0	16.0	3000	23.4	55.9
0.1782	763.0	290.6	771.0	15.0	3000	23.4	55.9

(1) *J. Soc. Chem. Ind., Japan*, **32** (1929), 997; *ibid.*, **33** (1930), 69, 304, 1040; *ibid.*, **34** (1931), 680; *J. Chem. Soc. Japan*, **51** (1930), 673, 755.
(2) *J. Chem. Soc. Japan*, **50** (1929), 473; *ibid.*, **54** (1933), 717, 772.
(3) *Kinzoku-no-Kenkyu*, **1** (1924), 542.

tion tube E (T_3), and the furnace (T_4) were strictly conditioned as follows: $T_2 < T_3 < T_4$. To confirm the saturation of the air current with the water vapour, the vapour pressure was calculated by the following formula from the experimental data in Table 1, which were determined at the temperatures: $T_2 = 40°C.$, $T_3 = 55°C.$, $T_4 = 65°C.$: $\pi = \dfrac{62370\,gPT}{(P'-p)MV+62370\,gT}$, where π

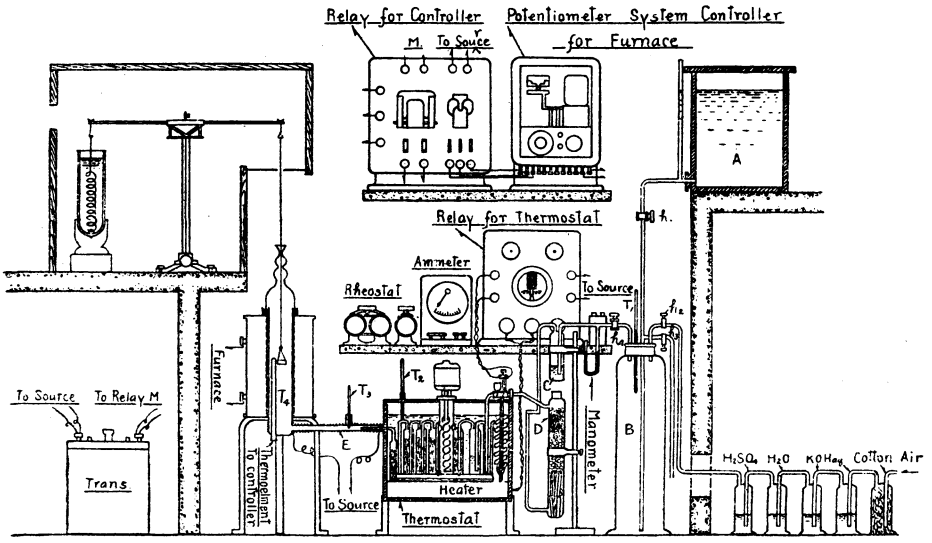


Fig. 1.

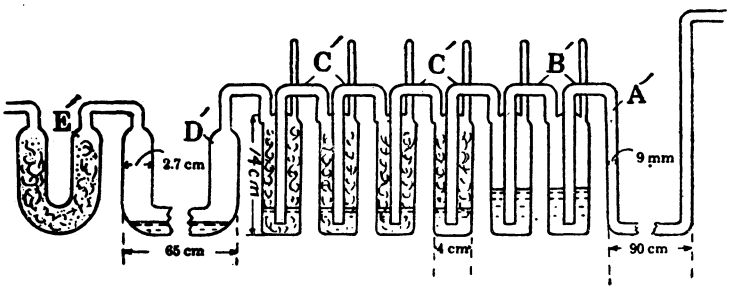


Fig. 2.

is the saturated vapour pressure at 40°C., g weight of the water caught by calcium chloride tubes connected to the furnace, P atmospheric pressure, P' pressure of the introduced air, p saturated vapour pressure at T, T absolute temperature of B in Fig. 1, V volume of the introduced air, and M 18.

Table 1 shows the calculated results, from which it was confirmed that the air current had the saturated vapour pressure at the desired temperature. The experimental results of the dehydration and hydration of Odo acid clay between room temperature and 150°C. are shown in Tables 2–4 and Fig. 3, and those of the dehydration up to 800°C., in Tables 5–7 and Fig. 4.

Table 2.

Dehydration (T_2 = 25°C., 23.8 mm. Hg)			Hydration (T_2 = 25°C., 23.8 mm. Hg)		
T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
35	50	0.80(×)	120	35	11.31
50	30	3.90	100	35	10.25
60	15	6.14	80	40	8.78
80	25	8.46	60	35	6.50
100	15	10.04	50	50	4.39
120	15	11.22	35	60	0.22
150	10	11.40			

Table 3.

Dehydration (T_2 = 40°C., 55.3 mm. Hg)			Hydration (T_2 = 40°C., 55.3 mm. Hg)		
T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_4 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
50	50	0.72	120	35	10.68
,,	50	0.14(×)	,,	35	10.51
60	20	4.04	100	35	9.35
,,	30	3.96	,,	34	9.31
80	35	7.16	80	40	7.59
,,	35	6.96	,,	40	7.61
100	35	9.30	60	35	4.76
,,	25	9.16	,,	35	4.76
120	35	10.60	50	45	1.01
,,	35	10.34	,,	45	1.03
150	38	10.84			
,,	40	10.96			

Table 4.

Dehydration (T_2 = 60°C., 149.4 mm. Hg)			Hydration (T_2 = 60°C., 149.4 mm. Hg)		
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
70	25	1.03(×)	120	70	9.20
,,	35	0.76(×)	,,	90	9.22
80	60	3.24	100	40	9.27
,,	40	3.60	,,	50	7.28
100	20	6.78	80	65	3.62
,,	20	6.52	,,	85	3.81
120	20	8.90	70	70	0.44(×)
,,	40	9.20	,,	90	0.28(×)
150	25	10.11			
,,	25	10.34			

(×) Weight increase in %.

Table 5.

Dehydration (1.5 mm. Hg, Drying bottles ($CaCl_2$, H_2SO_4) instead of thermostat)					
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
35	30	4.50	150	20	11.68
			200	20	11.95
50	20	6.82	300	20	12.18
,,	24	7.10	,,	20	12.32
60	25	8.52	400	20	12.75
80	32	9.70	500	25	14.15
,,	30	9.59	,,	25	14.05
100	30	10.75	600	20	15.60
120	25	11.54	800	10	15.84
,,	25	11.46	,,	10	15.76

Table 6.

Dehydration (T_2 = 25°C., 23.8 mm. Hg)					
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
50	20	3.99	400	15	12.66
100	25	10.12	500	15	13.70
150	15	11.37	600	15	15.24
200	15	11.70	800	15	15.58
300	15	12.24			

Table 7.

Dehydration ($T_2 = 40°C.$, 55.3 mm. Hg)					
T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)	T_1 Heating temp. (°C.)	Heating time (hr.)	Weight decrease (%)
100	20	9.28	400	30	12.39
,,	15	9.31	,,	30	12.51
,,	20	9.11			
150	30	10.78	500	25	13.33
,,	20	10.97	,,	30	13.59
			,,	25	13.23
200	40	11.21	600	25	14.65
,,	30	11.39	,,	25	14.83
,,	35	11.36			
300	45	11.84	800	20	15.36
,,	40	12.03	,,	15	15.34
,,	40	11.90	,,	20	15.45

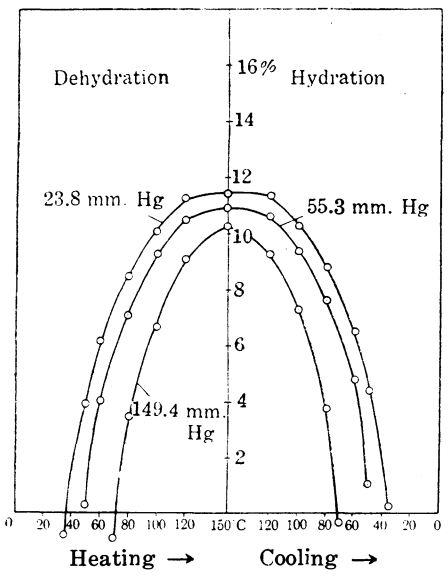


Fig. 3.

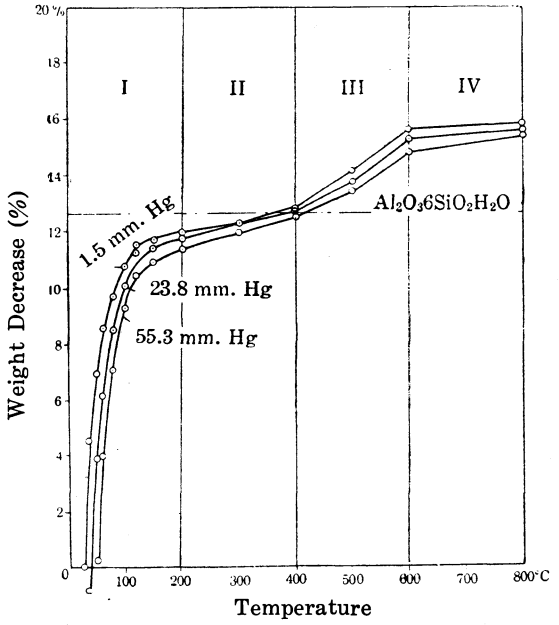


Fig. 4.

From the above investigations, it seems that the following conclusions must be derived: (1) There could not be observed the existence of a polyhydrate. (2) The water evolved on heating up to 300°C. is the adsorbed water and that evolved above 300°C. is the combined water. (3) The amount of the combined water nearly corresponds to one molecule of water, assuming that Odo acid clay has the composition $Al_2O_3 \cdot 6SiO_2$ in the anhydrous state.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Matsui for his invaluable advices and to Prof. N. Sasaki for his kind guidance given throughout this work.

(November 30th, 1933)

Kanazawa Technical College,
Kanazawa, Japan.

ON THE ACTION OF LIGHT UPON THE DISSOLUTION OF AMORPHOUS SELENIUM IN CARBON BISULPHIDE.

By Jitaro SHIDEI, Shogo HASHIZUME, and Saburo KITAHARA.

Received April 2nd, 1935. Published August 28th, 1935.

The solubility of red amorphous selenium in carbon bisulphide and the action of light on it have been measured by several investigators.[1] Their results, however, are qualitative in nature. The present work was undertaken in order to determine these systematically and more accurately, for studies of this sort are valuable for the light they throw upon the dissolution of some materials sensitive to light.

Experimental. Red amorphous selenium was prepared by reducing selenium dioxide with sulphur dioxide in aqueous solution acidified with hydrochloric acid. The selenium dioxide was obtained by dissolving vitrious selenium of Merck in dilute nitric acid and purifying by repeated sublimation at about 300°C. in the atmosphere of nitrogen dioxide in a glass tube. Carbon bisulphide was carefully purified by the ordinary method.

(1) E. Mitscherlich, *Sitzber. Akad. Wien*, **1855**, 409; *J. prak. Chem.*, (1), **66** (1855), 257. C. F. Rammersberg, *Ber.*, **7** (1874), 667. R. Saunders, *J. Phys. Chem.*, **4** (1900), 455. G. Briegleb, *Z. physik. Chem.*, (A), **144** (1929), 340; *Naturwiss.*, **17** (1929), 51.

In every experiment, 250 c.c. of carbon bisulphide and 1 g. of red amorphous selenium were employed. Carbon bisulphide was previously kept in a reaction vessel at the required temperature, with which selenium was then mixed. The time at which the two components were mixed was taken as the initial point of dissolution. After mixing them, portions, each nearly 25 c.c., of the solution were withdrawn at proper time intervals and their compositions were determined.

For the light source, an electric lamp of 100 volts and 400 watts was employed, and the reaction vessel was illuminated from its bottom. The experiments were carried out at 33°, 25°, 0.5°, −9°, and about −60°.

(1) *The results at 33°C.* In the dark, the dissolved amount of selenium first increased rapidly and reached its maximum after about 2 hours. After that time, it decreased slowly, and in about 10 hours it seemed to reach a constant value. Previous to the time when the maximum was observed, a quantity of red monoclinic crystals was found to deposit on the bottom of the vessel, and after that time the residue was observed to consist entirely of red monoclinic crystals.

In the case of exposing to light, similar behaviours as in the dark were observed, but the rate of dissolution increased remarkably. The constant dissolved amount which was to be reached finally, seemed to coincide with that in the dark. The experimental results are shown in Table 1 and Fig. 1. The dissolved amounts are given in mg. Se per 100 g. CS_2.

Table 1.

Temp. °C.		Time (hours)									
		1	2	3	4	5	6	8	10	26	28
33	(D)	67.0	98.1	98.9	93.6	87.4	83.1	72.8	70.0	66.5	69.0
	(L)	99.5	99.2	—	79.4	—	71.6	68.8	67.2	60.5	60.1
25	(D)	17.4	33.8	—	63.9	—	65.9	59.9	56.5	—	48.0
	(L)	50.4	63.2	—	58.4	—	55.2	48.0	44.5	44.9	45.4
0.5	(D)	—	0.9	—	0.7	—	1.0	1.8	4.4	—	—
	(L)	21.6	24.3	—	28.3	—	26.9	26.4	25.5	—	—
−9	(D)	—	0.6	—	0.8	—	1.0	0.8	—	—	—
	(L)	17.4	22.4	—	23.4	—	18.6	18.3	—	—	—

(D) and (L) show the results in the dark and in exposure to light respectively.

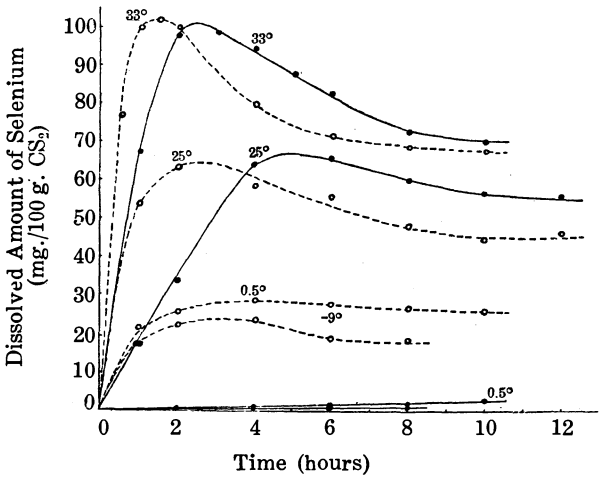


Fig. 1.

(2) *The results at 25°C.* In this case similar behaviours of dissolution were observed; the dissolved amount of selenium had a maximum value, and after a long time it seemed to reach a constant value smaller than that at 33°C. The red monoclinic crystals were also found depositing about the time of the maximum dissolution. However, the dissolved amount at each time was far smaller than that at 33°C., and both the time needed to reach the maximum and that to the final constant value were longer in this case than at 33°C. Light exerted more remarkable influence upon the rate of dissolution.

(3) *The results at 0.5°C. and −9°C.* In the dark, the dissolved amount of selenium was quite small and the rate of dissolution was so slow at these temperatures that the maximum dissolution was not reached within 10 hours. The action of light on the rate of dissolution was found to be very strong as will be seen from Table 1 and Fig. 1. At these temperatures red monoclinic crystals were found only in a trace and barely after exposure to light for about 6 hours, but not in the dark.

(4) *The results at about −60°C.* In the dark, the dissolution of selenium was not observed at all. By exposure to light, it was dissolved slightly.

Discussion of Results. G. Briegleb[1] has confirmed the constitutions of the several modifications of selenium and interpreted their transformation in solution by a diagram for pseudo ternary solution. According to him, the red amorphous selenium is pure Se_2, the monoclinic one is mixed crystals of varying compositions of Se_1 and Se_2, the latter predominating in amount, and the amorphous one is transformed into the monoclinic through the equilibrium $2\,Se_1 \rightleftarrows Se_2$ in solution, after being dissolved in carbon bisulphide.

The results obtained by the present writers seem undoubtedly in some degree to give a strong evidence in favour of the consideration of Briegleb. The above-mentioned fact that the dissolved amount of selenium has a maximum value, is in a good agreement with his view, for, according to it,

the deposition of the monoclinic selenium from the solution and the dissolution of the amorphous one must compensate each other after a certain time, and then, the former would predominate over the latter in rate. When all of amorphous selenium was transformed into the monoclinic one, the dissolved amount would reach a constant value corresponding to the solubility of the latter, as was the case in every experiment mentioned above except those at lower temperatures. In order to ascertain this again, the solubility of monoclinic selenium was measured in the dark. The samples used for this purpose were prepared by deposition from solutions of amorphous selenium in carbon bisulphide at the respective temperatures at which their solubilities were to be measured. The experimental results are given in Table 2 (No. 1 and No. 3).

Table 2.

Temp. °C.	No.		Time (hours)				
			1	2	4	6	8
33	1	(D)	42.6	53.0	62.1	64.4	65.0
	2	(L)	40.5	53.1	61.5	64.9	67.5
25	3	(D)	32.9	42.4	46.1	44.9	45.7
	4	(L)	32.8	41.2	46.2	45.9	45.2

The results indicate that monoclinic selenium has a definite solubility at each temperature and that, in favour of the consideration just mentioned above, the values of it coincide with those of the constant dissolved amounts given in Table 1, which were to be reached after a long time at the respective temperatures.

The transformation between the two modifications may also be considered to be due to some catalytic action of the solvent, but, the evidence of this cannot be shown in the present experiments.

Light seems to cause the increase in the rate of dissolution only. But, it cannot be decided from the results mentioned above, whether light acts on any one or both of the two modifications. In order to determine this, the following experiments were carried out. (1) The dissolved amounts of the samples of the monoclinic selenium the same with those used in No. 1 and No. 3 in Table 2 were measured at 33°C. and 25°C. and in exposure to light. The results obtained indicate no action of light on the monoclinic selenium as is shown in Table 2 (No. 2 and No. 4). (2) The dissolved amounts were measured with the mixtures the same with those employed in the experiment at 0.5°C. in Table 1 in the light and in the dark and at 0.5°C. By these experiments, it was found that the dissolved amount was suddenly decreased when the light was cut off, but increased again on exposure to light so as to reach the value which would be reached if the mixture were exposed to light

Table 3.

No.	Time (hours)										
	1	2	3	4	5	6	7	7.5	8	8.5	10
1	(L)				(D)						
	21.8	25.8	—	27.3	—	21.1	—	—	19.6	—	18.8
2	(L)	(D)									
	23.5	25.9	23.9	—	19.0	—	18.0	—	—	—	—
3		(L)			(D)				(L)		
	23.2	—	—	29.3	24.3	—	—	18.6	—	24.0	27.1

Table 4.

Time (hours)									
0.5	1	1.5	2	3	4	5	6	8	
—	99.5	—	99.2	—	79.4	—	71.6	68.8	[From Table 1, 33°C. (L).]
	(L)			(D)			(L)		
76.8	—	101.6	—	88.4	—	74.5	71.6	69.0	

throughout the time (Table 3). These behaviours can well be interpreted by assuming that light causes an increase in the rate of dissolution of the amorphous selenium alone, for, as has been already mentioned, at such a temperature as low as 0.5°C. some of the amorphous selenium remained unaltered for a fairly long time because of its slow transformation into the monoclinic modification. (3) Similar experiments were made at 33°C. These showed that the dissolved amounts in the light coincide with those in the dark at each time after the illumination of about 2 hours, as seen from Table 4. Since, in this case, the amorphous selenium was all found to transform into the monoclinic modification in a short time, the residue being all the monoclinic, it is a matter of course that the dissolved amount remains the same in the light and in the dark, provided the monoclinic modification does not suffer the action of light.

(December 15th, 1933)

Chemical Institute,
Tokyo University of Literature
and Science.

ON THE ACTION OF CHLORIDE FLUXES ON OXIDES CONTAINED IN ALUMINIUM.

By Takayasu HARADA.

Received April 2nd, 1935. Published August 28th, 1935.

Introduction. The usual trouble experienced with aluminium ingot is the contamination or the formation of oxides. Hanson and Slater[1] attributed the chief cause of the formation of pin-holes in aluminium cast to the action of steam, and it is well known that in corroded parts of aluminium ware oxides are always detected in their centers. This being so, the injurious effect of oxides contained in aluminium is generally even more serious than that of other metals contained as impurities. The oxides in aluminium can not be removed by reducing agents such as carbon or hydrogen which are usually effective in other heavy metals. In the case of aluminium, however, it can only be cleaned or deoxidised by means of fluxes, but the fundamental chemical reactions underlying this action have never been fully elucidated so far.

I found that all the chloride fluxes have a decided cleaning power although in varying degrees, and that this deoxidising action is due chiefly to the chlorine gas liberated from these fluxes in contact with aluminium. Based on this knowledge, I made a systematic study of the action of chlorine gas and also of nitrogen gas on aluminium melt and was able to throw some light on the mechanism of cleaning.

Chloride Fluxing. As chloride fluxes the following chlorides were employed in my experiments: sodium chloride, potassium chloride, ammonium chloride, lithium chloride, calcium chloride, magnesium chloride, barium chloride, nickel chloride, manganese chloride, zinc chloride, aluminium chloride, ferric chloride, cupric chloride, stannous chloride, silicon tetrachloride, titanium tetrachloride, and carbon tetrachloride.

The aluminium ingot, 250 grams for each experiment, was melted at 700°C. in a graphite crucible, and each of the above fluxes in varying quantities packed in thin aluminium plate, was thrown into the melt kept at about 700°C. and pushed down to the bottom of the crucible by means of an iron utensil so that the deoxidising action was as complete as possible. Liquid

(1) *J. Inst. Metals*, **46** (1931), 187.

chlorides were injected to the bottom part of this melt through an iron tube and well agitated.

The molten aluminium acted upon by the fluxes was then cast. The specimen casts so obtained were then subjected to analysis and to metallographic examination.

It is certain, however, that all these chloride fluxes have more or less deoxidising power depending on the kind and quantity used. Moreover, the general effect appears about the same regardless of the kind of metals of the chlorides. The conceivable reactions which may occur between these chlorides and aluminium are discussed below.

Firstly, if the number of chloride molecules which decompose without entering into reaction with aluminium, either by heat, or by catalytic action of aluminium, or by some other causes, is taken as x, then

$$x\mathrm{M}_a\mathrm{Cl}_b = ax\mathrm{M} + bx\mathrm{Cl} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1).$$

where M denotes metal.

Secondly, if the number of chloride molecules which decompose and give off chlorine that combines with aluminium is taken as y, then

$$y\mathrm{M}_a\mathrm{Cl}_b + c\mathrm{Al} = c\mathrm{AlCl}_3 + ay\mathrm{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

where $by = 3c$, hence $c = by/3$.

Lastly, if the number of chloride molecules which remain as such or go out of the sphere of reaction by sublimation or volatilisation, is taken as z, then

$$z\mathrm{M}_a\mathrm{Cl}_b = z\mathrm{M}_a\mathrm{Cl}_b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3).$$

Although it is conceivable that a certain portion of the chloride forms double salts with aluminium or aluminate, such complex cases are not included in the formula (3) for the sake of simplicity. This omission, however, does not interfere much with the main discussion, for, as has been confirmed by experiments, no chloride remains in the cooled cast of aluminium.

From the above three equations we obtain

$$(x+y+z)\mathrm{M}_a\mathrm{Cl}_b + (by/3)\mathrm{Al} = (by/3)\mathrm{AlCl}_3 + (ax+by)\mathrm{M} + bx\mathrm{Cl} + z\mathrm{M}_a\mathrm{Cl}_b \quad . \quad (4).$$

If there is no chloride that has not undergone decomposition, or in the case $z = 0$,

$$(x+y)M_aCl_b+(by/3)Al = (by/3)AlCl_3+(ax+by)M+bxCl \quad \ldots\ldots\ldots\ldots \quad (5).$$

Therefore, if we determine, after the treatment with a chloride, the amounts of M and Cl remaining in the aluminium and that of evolved chlorine, we can conjecture the type of the reactions which actually took place during fluxing.

For this purpose, the amount of chlorine liberated from the chloride thrown into aluminium was first determined, but it was soon discovered that the results obtained were not entirely reliable on account of several factors which made the determination very troublesome. Under the circumstances, the amount of metal remaining in the aluminium specimen was determined on one hand, and on the other hand the amount of chlorine liberated by the decomposition of the chloride alone in a heated tube at 800°C. was estimated. From the combined results of these determinations, the degree of decomposition of the chloride may be more accurately estimated.

A fixed amount of each of the above-mentioned chlorides was thrown into the molten aluminium in a graphite crucibles, and the chlorine gas evolved was absorbed by normal solution of silver nitrate, the amount of chlorine absorbed being determined by titrating the excess of silver nitrate with normal sodium chloride solution.

It must be mentioned that in order to obtain reliable figures in this experiment it is necessary to repeat the experiment at least 6 times—sometimes as often as 9 times—as it is exceedingly difficult to carry out the experiments under the same conditions exactly.

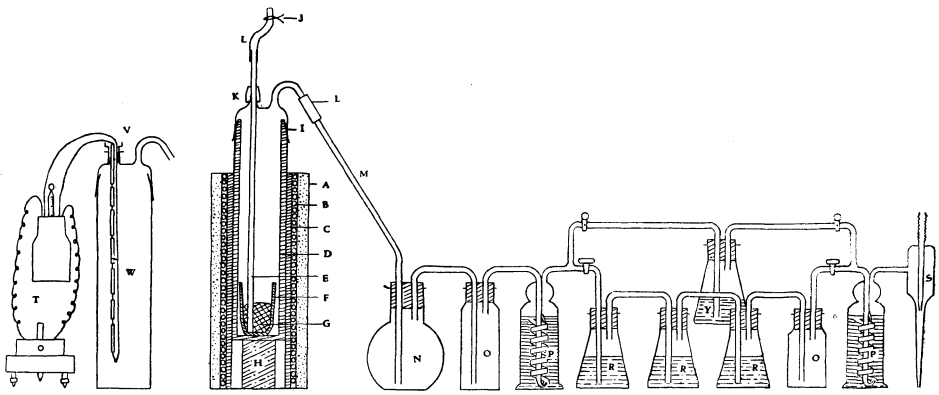


Fig. 1.

The arrangement of the apparatus for the experiment is shown in Fig. 1. A tall refractory cylinder with a closed bottom (D) is placed inside an electric

furnace (ABC) supported on a block (H) and the open end of the cylinder is covered tightly with a glass cap (I) provided with a hole and a branch pipe. The aluminium specimen (G) is melted in a graphite crucible (F) placed on the bottom of the refractory cylinder, and an iron pipe (E) passing through a hard rubber tubing (K), is inserted into the molten aluminium. A thick rubber tube (L) is attached to the top of the iron pipe and is provided with a regulating cock (J). The branch pipe of the glass cap is connected with a cooling tube protruding into a dust-catcher (N), which is followed by an empty bottle (O), a gas drying bottle (P) filled with concentrated sulphuric acid, bottles (R, R, R) containing normal silver nitrate solution, another empty bottle (O), and a washing bottle of sulphuric acid (P) connected with a filter pump (S). An extra bottle (Y) containing a known quantity of normal silver nitrate solution serves for determining the end point of the reaction by sucking a part of the gas through it toward the end of reaction. If no turbidity occurs in this bottle the reaction may be considered as finished. In the case when the degree of decomposition of a chloride alone is to be examined by putting it in a hot place heated at 800°C., a cylinder (W) instead of (D) is used in which a thermo-couple is placed, the other parts being the same as the above-mentioned arrangement.

A fixed amount of a chloride was thrown into the aluminium melt through the iron pipe (E) and the suction pump (S) was set to work, adjusting at the same time the cock (J) so that the absorption of the chlorine would be complete.

A great deal of attention is required for control of suction according to the nature of the chloride—whether it is volatile or fusible. Even volatile chlorides seldom reach as far as bottle (O) or (P) on strong suction, but are generally deposited in the cooling tube (M) and are mostly caught in the bottle (N). Three bottles of silver nitrate solution were found to be sufficient on actual experiment. No accident whatever occurred even in the case of liquid chloride. The results of experiments are given in Table 1.

From these results it will be noticed that the various chlorides differ in their decomposition rates. The following chlorides were found to give off a comparatively large quantity of chlorine: NH_4Cl, LiCl, $MgCl_2$, $ZnCl_2$, $MnCl_2$, $AlCl_3$, $FeCl_3$, $CuCl_2$, $SiCl_4$, and $TiCl_4$. It is interesting to note that the decomposition of LiCl and $FeCl_3$ is very much accelerated in the presence of aluminium. The following chlorides, on the other hand, suffer decomposition to a much less extent: NaCl, KCl, $CaCl_2$, $BaCl_2$, $NiCl_2$, $SnCl_2$, and CCl_4, of which NaCl alone is enhanced in its decomposition rate when it is in contact with molten aluminium.

Table 1.

Chloride		NaCl	KCl	NH_4Cl	LiCl	$CaCl_2$	$MgCl_2$	$ZnCl_2$	$BaCl_2$	$NiCl_2$	$MnCl_2$	$AlCl_3$	$FeCl_3$	$CuCl_2$	$SnCl_2$	$SiCl_4$	$TiCl_4$	CCl_4
Quantity of sample taken (g.)		5	5	5	5	5	5	5	5	5	5	5	5	5	5	10 (6.56 c.c.)	10 (5.69 c.c.)	10 (6.13 c.c.)
Quantity of Cl } in the Quantity of M } sample (g.)		3.033 1.967	2.388 2.621	3.316 1.684	4.181 0.819	3.150 1.850	3.725 1.275	2.686 2.314	1.455 3.545	2.737 2.263	2.878 2.122	3.985 1.015	3.279 1.721	2.629 2.371	1.825 3.175	9.45 0.54	7.498 2.51	9.21 0.79
Analysis	Quantity of Cl evolved (g.) Number of experiments	0.7551 9	0.2282 7	1.0250 6	2.8351 6	0.0825 6	1.5553 6	1.178 6	0.0505 6	0.3703 6	1.0402 6	2.0204 6	1.0950 6	1.0404 6	0.4152 6	4.5704 6	3.5303 7	0.1203 6
	Quantity of M (g.) Number of experiments	0.4547 3	0.5392 3	nil. 2	0.4863 5	trace 3	0.5559 3	0.1240 4	nil. 3	0.4028 3	0.1033 3		0.5092 3	0.8962 4	0 8382 3	0.2360 3	0.1333 3	trace 2
Evolution rate of Cl (%)		15.1	5.8	20.5	56.7	1.7	31.1	23.6	1.0	7.4	20.8	40.4	21.9	20.8	8.3	45.7	35.8	1.2
Decomposition rate of Cl (%)		24.5	12.1	30.9	67.8	6 0	41.8	43.5	3.1	13.7	36.1	50.6	33.4	39.5	22.8	48.7	47.8	1.3
Decomposition rate of M (%)		28.2	20.4		59.3		43.6	53.5		17.8	49.4		46.5	37.8	26.4	43.7	53.0	
When the sample was thrown into an empty cylinder heated at 800°C.																		
Quantity of Cl evolved (g.) Number of experiments		0.3506 3	0.3225 5	1.0023 3	2.1052 5	0.8658 4	1.9401 3	1.4053 3	trace 3	0.5962 3	1.2448 3	2.9558 5	0.3153 5	1.6002 5	0.5303 3	8.3490 3	5.5244 3	0.0363 4
Evolution rate of Cl (%)		7.0	6.5	20.0	42.1	17.3	38.1	28.8	trace	19.9	24.9	59.1	6.3	21.2	10.6	83.5	55.2	0.4
Decomposition rate of Cl (%)		11.2	13.5	30.2	50.4	27.5	52.1	52.3		21.7	43.3	74.2	9.6	60.8	29.6	88.3	73.7	0.4

Decomposition seems to be accelerated by aluminium.
Considerable evolution of chlorine is noticeable. Such a chloride may be used as flux.
Remarkable evolution of chlorine is noted.
Very little evolution of chlorine. Such a chloride is unsuitable for flux.

Quantity of M (metal) = % of metal remaining in aluminium after reaction ÷ 100× Original quantity of aluminium. (It is assumed that the slag contained the same percentage of metal.)
Evolution rate of Cl (chlorine) (%) = Quantity of chlorine evolved ÷ Total weight of sample × 100.
Decomposition rate of Cl (%) = Quantity of chlorine evolved ÷ Total chlorine content in sample × 100.
Decomposition of M (%) = Quantity of metal estimated ÷ Total metal content in sample × 100.

Table 2. Analysis of the Original and Cleaned Aluminium Specimens.
(250 grams aluminium kept at 750C°. for 5–10 minutes after the flux is added.)

(A) Cleaning with Zinc Chloride.

Mark of sample	$ZnCl_2$ added (%)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Zn mean (%)	Zn lost* (%)
0	Original Al ingot	1.010 1.672 1.918 2.589 2.213 3.356	0.73	0.36	0.127	
Z8	8	0.435 0.461 0.714 0.724 0.767	0.76	0.21	3.71	0.53
Z7	5	0.582 0.459 0.468 0.403 0.802	0.75	0.26	2.20	0.16
Z6	3	0.863 0.978 0.854 1.002 1.008	0.75	0.18	1.34	0.13
Z5	2	1.063 0.975 1.065 1.927 0.726	0.77	0.21	0.92	0.10
Z4	1	0.828 0.769 0.584 0.813 0.848	0.71	0.25	0.51	0.07
Z3	0.7	0.844 0.939 0.904 0.794 0.703	0.72	0.24	0.4005	0.005

(A) (*Concluded*)

Mark of sample	$ZnCl_2$ added (%)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Zn mean (%)	Zn lost* (%)
Z2	0.5	0.728 0.659 0.808 0.798 0.798	0.71	0.26	0.294	0.023
Z1	0.3	0.988 0.898 0.924 1.078 0.918	0.69	0.23	0.178	0.050

*Zn in aluminium ingot + Zn in $ZnCl_2$ added −Zn in cleaned aluminium.

(B) Cleaning with Titanium Chloride.

Mark of sample	$TiCl_4$ added (g.)	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Ti mean (%)
T4	10	1.231 1.751 0.945 0.932	0.89	0.37	0.45
T3	5	1.722 2.430 0.752	0.80	0.34	0.26
T2	3	1.636 1.218 0.513 1.556	0.78	0.30	0.14
T1	1	2.165 1.020 2.051 1.644	0.73	0.36	0.06

Taking the rate of chlorine evolution into consideration the following chlorides may be recommended as suitable fluxes for the evolution of chlorine: LiCl, $AlCl_3$, $FeCl_3$, $SiCl_4$, and $TiCl_4$.

Now returning to the subject of the cleaning or deoxidising action of the chloride, it can be supposed that this is attributable to the action of either the chloride, i.e. M_aCl_b itself, or the products of decomposition, i.e. M or Cl, or $AlCl_3$ newly formed.

For example in the case of zinc chloride used as a flux, it is not likely that $ZnCl_2$ itself or $AlCl_3$ formed will reduce Al_2O_3. Besides, in the cleaned aluminium, chlorine is not detected. It is also not expected that the metallic zinc would have a deoxidising action on aluminium. Chlorine, on the other hand, is entirely non-reactive with the oxygen in aluminium, and yet the fact that cleaning has been effected is evident from the analytical results recorded in Table 2 (A). Similarly, titanium tetrachloride has also a cleaning power as shown in Table 2 (B).

Here again, the cleaning action can not be ascribed to any chemical reaction in connection with $TiCl_4$ and aluminium. It is interesting to note that the cleaning action is not necessarily proportional to the amount of the flux added, and that in the case of zinc chloride, about 0.7% of the flux gives the maximum efficiency or the condition approaches the case of equation (5) in which no chloride remains undecomposed. This percentage of flux for the maximum efficiency, however, varies with the nature of chlorides, the quality of the aluminium, and the amount of the melt.

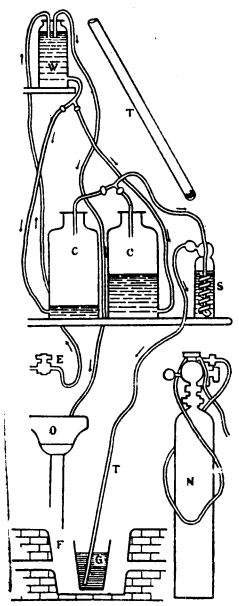


Fig. 2.

Based on the results of the above experiments, that all the chlorides show more or less a similar cleaning effect, the present author was led to think that the chlorine gas set free from the chloride may perhaps be responsible, directly or indirectly, for this deoxidising action. He, therefore, conducted experiments by using chlorine gas alone in an apparatus as shown in Fig. 2.

Chlorine gas, prepared from hydrochloric acid and potassium permanganate, is stored in bottles (C, C). By means of a water flow from a reservoir (W), whose water level is kept constant by an overflow device, the chlorine gas, after being dried over sulphuric acid (S), is bubbled, at a constant rate through an iron pipe (T) having many small holes at one end,

into the molten aluminium in a graphite crucible (G). N in the figure is a nitrogen bomb, and in case nitrogen gas is used instead of chlorine gas for comparison, this bomb is directly connected to the drying bottle (S).

The results of experiments, in which chlorine gas was passed into 250 grams of aluminium melt at 750°C. for varying durations are shown in Table 3.

Table 3. Analysis of Aluminium Treated with Chlorine Gas.
(250 g. Al treated at 750°C., settled for 5–10 min. after the gas passed.)

Mark of sample	Duration of passing of chlorine	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Mark of sample	Duration of passing of chlorine	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)
0	See Table 2 (A)				C5	1 min.	0.987 0.718 0.807 0.908 0.870	0.74	0.11
C1	10 sec.	1.235 1.261 1.088 1.062 0.918	0.65	0.11	C6	1.5 min.	0.707 0.897 0.953 0.938 0.784	0.80	0.11
C2	15 sec.	1.005 1.023 1.215 1.061 0.889	0.68	0.17	C7	2 min.	0.717 0.879 0.824 0.791 0.850	0.96	0.23
C3	20 sec.	1.173 0.708 1.016 0.898 1.036	0.73	0.25	C8	2.5 min.	0.736 0.795 0.838 0.848 0.760	0.89	0.19
C4	40 sec.	0.774 0.671 0.634 0.987 0.870	0.79	0.11					

As obvious from these results, the chlorine gas alone is decidedly effective for the cleaning action, and the Al_2O_3 content approaches the level of what may be called the "limit of dissolved oxygen" with the prolongation of the treatment. By this treatment, aluminium is attacked by chlorine and some portion is lost as aluminium chloride.

Table 4. Ignition Temperatures of Various Metals in Chlorine Gas. (Sample taken, 5 grams.)

Metal	Ignition temp. °C.	Extinction temp. °C.	Duration of burning. (min. per 5 g.)
Aluminium	130	270	10
Iron	215	315	8
Silicon	440	510	22
Copper	370	380	0.5
Zinc	535 (390*)	560	30

*White fume was observed, but no active ignition occurred at this temperature.

Table 4 shows the ignition temperatures of aluminium and other metals generally contained in aluminium as impurities in the atmosphere of chlorine, as determined by the author. The same table also shows the extinction temperatures and the duration of burning when 5 grams of each of the specimens were employed for the experiment. As all the metals, contained as impurities, have a higher ignition and extinction

Table 5. Analysis of Aluminium Treated with N_2 Gas. (250 g. Al treated at 750°C., and settled at the same temperature for 5–10 min. after the passing of the gas.)

Mark of sample	Duration of passing of nitrogen	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)	Mark of sample	Duration of passing of nitrogen	Oxygen as Al_2O_3 (%)	Fe mean (%)	Si mean (%)
0	See the Table 1.				N5	1.5 min.	0.823 0.624 0.775 0.598 0.971	0.50	0.14
N1	10 sec.	1.423 1.388 1.298 0.663 1.617	0.53	0.15	N6	2 min.	0.818 0.633 0.597 0.729 0.659	0.70	0.13
N2	20 sec.	0.938 0.808 0.908 1.834 1.157	0.53	0.14	N7	3 min.	0.838 0.904 0.623 0.728 0.673	0.65	0.13
N3	40 sec.	0.812 0.595 0.588 0.938	0.51	0.15	N8	4 min.	0.938 0.668 0.790 1.099 0.826	0.65	0.12
N4	1 min.	0.838 0.903 0.958 0.724 0.625	0.44	0.14	N9	5 min.	0.893 0.838 0.725 0.753 0.828	0.67	0.12

temperatures than pure aluminium, they are not materially reduced in quantity by the treatment with a chloride.

During this treatment, the formed chlorides, the oxides, and other occluded impurities accumulate on the top of the melt and go into the slag, which amount increases with the duration of the treatment. By analysis, the cleaned aluminium was found to contain almost no detectable chlorine. As has already been confirmed, chlorine gas has no deoxidising action. Hence, the only possible explanation regarding the cleaning effect by chlorine must be sought mainly in its action of mechanical removal of the oxide at the time of its ascension through the molten aluminium. It is also conceivable that the undecomposed chloride or the newly formed aluminium chloride aids the removal of the impurities at the time of their sublimation or volatilisation.

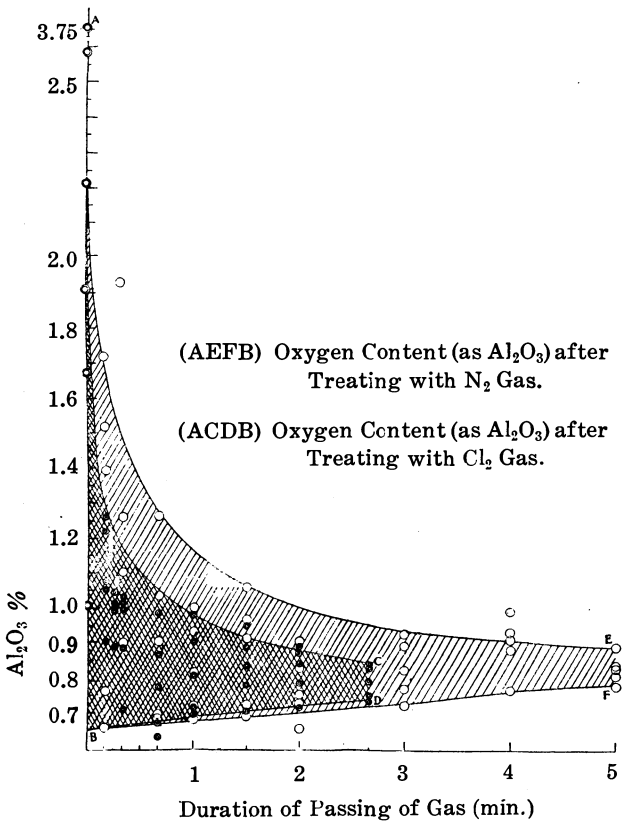
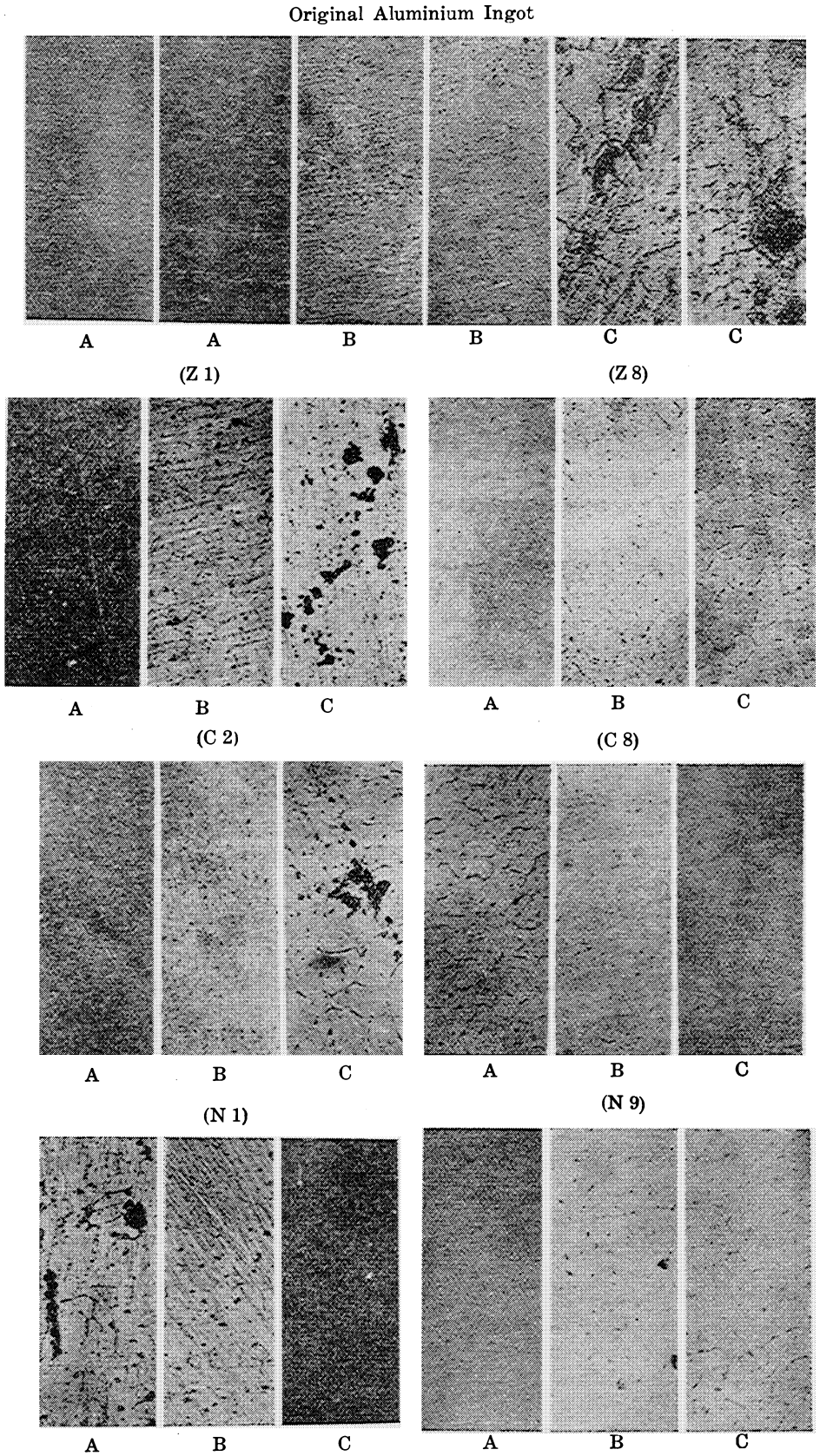


Fig. 3.

If the above reasoning be correct, any kind of gas, which has no tendency to remain in aluminium as chlorine, should act in the same way. In order to test this point, I tried in a similar way with nitrogen gas for comparison, which has been found almost non-reactive with aluminium. The results of experiments with nitrogen gas are given in Table 5, which shows clearly that the above reasoning is justified.

The cleaning effect of chlorine and nitrogen is shown diagrammatically in Fig. 3; this indicates clearly that similar, if not the same, results are obtained with these gases.



A : Macrograph ×7, B : Polished surface ×120, C : Surface etched with NaOH solution.

Fig. 4.

From the above experimental results, the author ventures to propose that any gas that is not likely to be occluded in aluminium or any compound which will liberate such a gas in molten aluminium would act as a cleaning agent. Its cleaning efficiency, however, depends on such properties as viscosity between the gas and the metal, specific gravity of the metal, etc. For a chloride flux, it is, therefore, advisable to select a compound which decomposes easily according to the equation (1) and the liberated metal, when alloyed with aluminium, does not harm the properties of the resulting aluminium.

Microscopical Examination of the Specimens. All the specimens obtained in the present investigation were microscopically examined. In Fig. 4 photographs of some representative specimens are shown.

Conclusion. When aluminium ingot is treated with chloride fluxes, the content of oxygen in the aluminium is decreased. The cleaning action of these chloride fluxes is mainly due to the chlorine gas liberated from the chlorides, which, when escaping from the aluminium melt, conveys and removes the oxide and other impurities contained in the aluminium melt. Any other gas, such as nitrogen, which is not likely to be combined or occluded by aluminium, has also the same cleaning power if used alone or in combination with other gases. When fluxes other than chlorides have to be employed for cleaning purpose, one should select such compounds which do not remain unchanged in the aluminium or as their decomposition products. Or if they remain, they should give no harmful effect to the aluminium. Compounds that give off a comparatively large quantity of harmless gas in aluminium are suitable for cleaning fluxes, and LiCl, $AlCl_3$, $TiCl_4$, and $SiCl_4$ are recommended for this reason.

The author might take this opportunity to say that cleaning by chlorine gas is actually carried out in several aluminium works in this country, and is giving satisfactory results.

(July 20th, 1934)

ON THE ARRANGEMENTS OF THE MICRO-CRYSTALS IN LEAD DEPOSITED BY ELECTROLYSIS.

By Hideki HIRATA, Yoshio TANAKA, and Hisaji KOMATSUBARA.

Received April 2nd, 1935. Published August 28th, 1935.

Introduction. By way of continuity with our previous investigations[1] on the crystalline structure in various electro-deposited metals, essentially the same experiment has been repeated with electrolysed specimens of lead. The heterogeneous X-rays emitted from the molybdenum anticathode were also utilized in the present experiment.

Here it should be stated that the crystal form of lead belongs to I'c of $a_0 = 4{,}983$Å.[2]

Specimens. To prepare the specimens used in this experiment, a platinum wire was steeped by 2 cm. into the electrolyte as the cathode. At a distance of 3–5 cm. from the cathode, a thin plate of lead, 1.5 cm. × 3 cm. in area and serving as anode, was placed. The conditions under which these specimens were obtained, are given in Table 1.

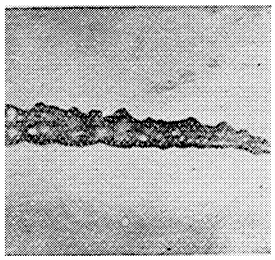
Table 1.

No. of specimens	Composition of electrolyte	Current of electrolysis (amperes)	Potential applied to the electrodes (volts)	Distance between the electrodes (cm.)	Temp. °C.
A	6 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ was dissolved in 200 c.c. H_2O. $C_2H_4O_2$ sufficient for clearing the solution was added.	The current was gradually increased from about 0.1 ampere, with the augment of deposit.	4	5	about 20
B	10 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 5 c.c. $C_2H_4O_2$ 195 c.c. H_2O	0.1	3.5	3	20
C	5 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 2.5 c.c. $C_2H_4O_2$ 197.5 c.c. H_2O	0.1	3.5	3	20
D	2.5 g. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ 1.3 c.c. $C_2H_4O_2$ 198.7 c.c. H_2O.	0.08	4	3	14

(1) For example, H. Hirata and Y. Tanaka; *Mem. Coll. Sci., Kyoto Imp. Univ.*, **A, 17** (1934), 143.

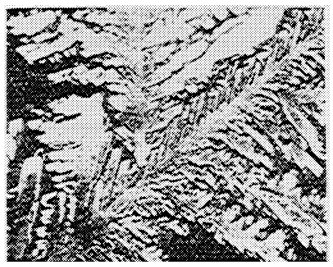
(2) E. A. Owen and G. D. Preston, *Proc. Phys. Soc.*, **35** (1923), 101.

Though powdery or needle-shaped deposits of lead were often detected at the beginning of the electrolysis, the specimens of lead which appeared after several hours, usually had a foliated form with many branchlets. But some of the needle-shaped specimens were observed to remain unaltered, when electrolysis proceeded for a comparatively long time. The micro-structures of these two types of specimens are reproduced in Fig. 1 and 2.



Specimen C (needle-shaped). ×50.

Fig. 1.



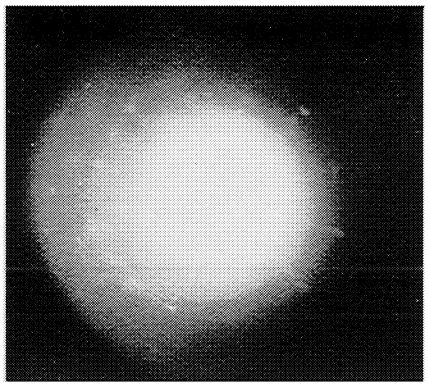
Specimen C (foliated). ×50.

Fig. 2.

Experimental Results. The crystalline structures of the specimens mentioned above were examined by means of Laue's method. To take a diffraction pattern of the foliated specimens, a piece of them was so placed that the foliated surface was perpendicular to the incident X-ray beam, while, with a fragment of the needle-shaped specimens, the interference figure was obtained by setting its longitudinal axis perpendicular to the direction of the incident beam. In doing so, the photographic plate was always placed perpendicularly to the incident beam in a position 3.2 cm. behind the specimen.

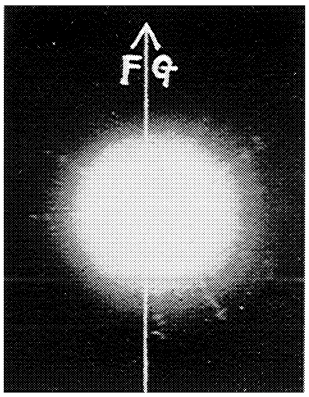
Some of the diffraction patterns thus obtained with the foliated and needle-shaped specimens are reproduced respectively in Fig. 3, 4, 5, 6, and 7. In these figures, the direction of the maximum growth of deposited lead (i.e., the direction of the longitudinal axis or the stem of the foliage) is represented by an arrow G.

Not only the patterns here reproduced, but also most of the diffraction figures given by these specimens, were found to be essentially the same: i.e., all the figures, except Fig. 3 were observed to be made up with a set of radiating bands. On the other hand, Fig. 3 consists of several Debye-Hull rings due to the reflections of the prominent atomic planes of the lead crystal. This shows that a considerable portion of the specimen giving Fig. 3, is composed of an irregular aggregation of microcrystals of lead, but the other specimens are mostly of a fibrous structure.



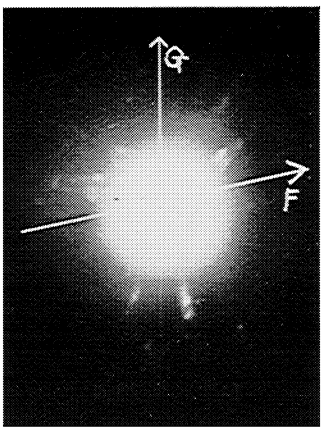
Specimen C (foliated). $\beta = 90°$.

Fig. 3.



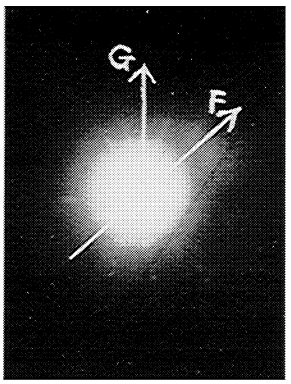
Specimen C (needle-shaped). $\beta = 90°$.

Fig. 4.



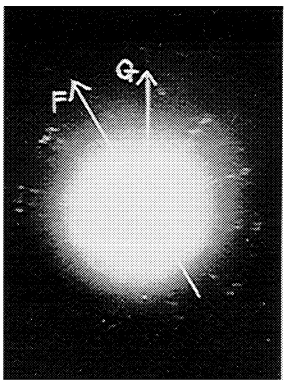
Specimen C (foliated).
$\beta = 90°$.

Fig. 5.



Specimen B (foliated).
$\beta = 90°$.

Fig. 6.



Specimen A (foliated).
$\beta = 90°$.

Fig. 7.

Having thus ascertained these facts, the writers tried to determine the direction of the common axis of the micro-crystals in the fibrous specimens mentioned above. This was done in the same manner as in our previous investigations.[1]

In the annexed figures, Fig. 8, 9, 10, and 11, the full lines represent diagramatically the theoretical positions of the prominent radiating bands, which are expected to appear when a lead crystal is rotated around a direction parallel to one of its [211] axes (represented by an arrow F), and the incident X-ray beam is made to strike this crystal taking the

direction perpendicular to the axis of rotation mentioned above. The shaded parts of the same figures are copies of the original plates of Fig. 4, 5, 6, and 7.(3) To transcribe these copies, the original plates of Fig. 4, 5, 6, and 7 were respectively placed upon Fig. 8, 9, 10, and 11, in such a way that the direction represented by F and the centre of the central spot in both figures coincide with each other. As can be seen from Fig. 8, 9, 10, and 11, the agreement between the calculated curves and those observed is satisfactory. Consequently, we may infer that the specimens giving the diffraction patterns reproduced in Fig. 4, 5, 6, and 7 are, in the main at least, composed of micro-crystals having one of the [211] axes in common.

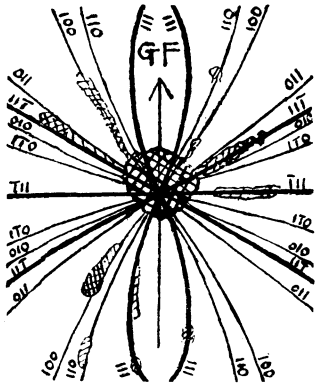


Fig. 8.

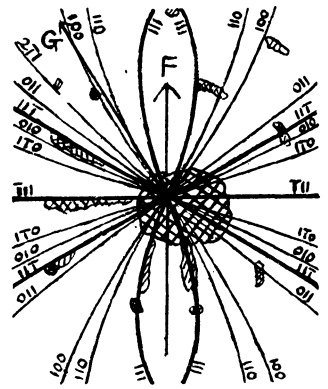


Fig. 9.

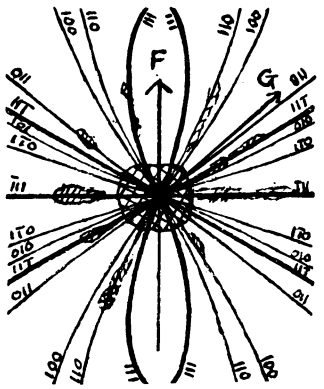


Fig. 10.

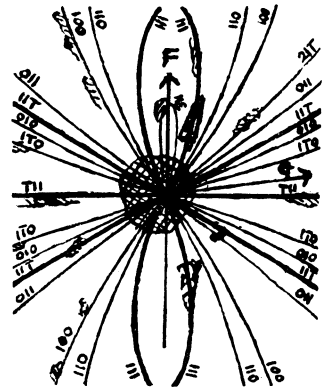
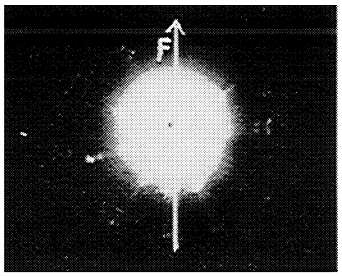


Fig. 11.

(3) It is to be noticed that the diffraction patterns reproduced in Fig. 3–7 and 12 interchange from right to left as compared with those of the original plates.

Next, to confirm the above inference, the writers investigated the interference phenomena due to an oblique incidence of the X-ray beam to the fibrous direction of the same specimen as was used in the case of Fig. 4. Fig. 12 is the diffraction figure taken when the axis of fibre was tilted 45° from its vertical position towards the incident beam. To take this diffraction figure, the photographic plate was also placed 3.2 cm. behind the specimen.



Specimen C (needle-shaped).
$\beta = 45°$.

Fig. 12.

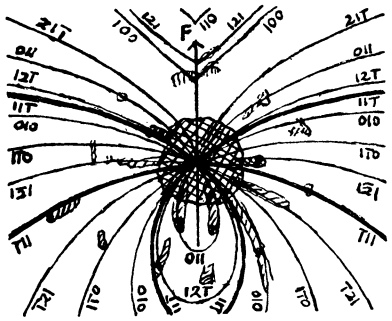


Fig. 13.

In the annexed figure, Fig. 13, the theoretical curves traced out by calculation are compared with Fig. 12. As may be seen from Fig. 13, the agreement between the calculated curves and the observed ones is rather satisfactory. Accordingly, our foregoing inference was confirmed as correct, and we may conclude that the micro-crystals of lead have a tendency to be electrolytically deposited with the normals to their icositetrahedral faces (211) arranged parallel to a definite common direction. This is in no way different from the experimental results given by Frölich, Clark, and Aborn.[4]

But, it is noticed that the direction of fibre thus determined, does not always coincide with the direction of maximum growth of deposited lead. As has already been seen, the diffraction patterns, Fig. 4, 5, 6, and 7, were produced, when the directions, represented respectively by F and G, were parallel to the photographic plate. Consequently we may conclude, on the one hand, that these two directions F and G coincide with each other in the needle-shaped specimen, which produced Fig. 4, while, on the other hand, both directions F and G being situated parallel to the largest surface of the foliated specimen, the angles between them are found by measurement from Fig. 5, 6, and 7 to be about 33°, 48°, and 80° respectively.

(4) *Z. Elektrochem.*, **32** (1926), 295.

The angles between the [211] axes of a crystal belonging to the cubic system, are generally confirmd by calculation to be 33°34′, 48°12′, 60°, and 80°24′. Thus, it may be inferred that the direction of the maximum growth of deposited lead G also coincides roughly with one of the [211] axes of the micro-crystals forming the considerable part of the specimens. This inference may explain why the branchlets of the foliated specimen make angles of about 33°, 48°, and 60° with one another, as shown in Fig. 2.(5)

Summary. The arrangements of the micro-crystals in electrolytic specimens deposited from acetic acid solutions, were examined with X-rays, by the so-called "transmission method". From the diffraction patterns obtained, it was confirmed on the one hand, that the micro-crystals of lead have a tendency to be electrolytically deposited in a fibrous way, with one of the normals to their (211) faces arranged parallel to a definite common direction, as was the case in the experiments of Frölich, Clark, and Aborn. On the other hand, the direction of the growth of deposited lead, was found to coincide roughly with any one of the [211] axes, which make an angle 0°, 33°34′, 48°12′, and 80°24′ respectively with the common axis of the micro-crystals.

In conclusion the writers wish to express their best thanks to Professor D. Uno for the interest he has taken in the experiments. Their thanks are also due to the Imperial Academy of Japan for the fund granted for the investigation.

Institute of Metallography,
Imperial University of Kyoto.

(September 25th, 1934)

(5) As all the branchlets of the foliated specimens were found not to lie in the same plane, the writers were obliged to flatten each specimen by placing it between two glass plates, before its micro-photograph was taken. Thus, the angles between some of the branchlets, especially those between the big branchlets and the stems of the foliage seen in Fig. 2, are different from the actual angles.

DIE DILATOMETRISCHEN UNTERSUCHUNGEN DER GEGOSSENEN KUPFERREICHEN BRONZEN.[1] (UNTERSUCHUNGEN ÜBER DIE FESTELÖSLICHKEIT DER LEGIERUNGEN. II.)

Von Denzo UNO, Saburo KATORI und Masamichi FUJII.

Eingegangen am 10. Mai, 1935. Ausgegeben am 28. August, 1935.

Allgemein ist das Feingefüge kupferreicher Mischkristall-Legierungen im gegossenen Zustand stark ausgeseigert. Insbesondere ist diese Neigung desto grösser, je länger das Erstarrungsintervall ist. In diesem Falle werden die Eigenschaften durch die ganzen Teile der Probe ungleichmässig, und wenn die unter Seigern verursachte zweite Phase spröde wäre, würden die mechanischen Eigenschaften der ganzen Probe verschlechtert. Soweit es möglich ist, muss man dementsprechend das Gefüge der Probe durch die richtigen Wärmebehandlungen homogenisieren.

Beim Homogenisieren wird die Probe oftmal überhitzt, oder sie wird der ungenügenden Erhitzung wegen länger Zeit wärmebehandelt. Es tritt also die Verflüchtigung des Bestandteiles, oder die Oxydation der Probe ein. Es wäre auch ökonomisch nicht wünschenswert.

Wir berichteten schon über die abnormen Dilatationserscheinungen,[2] welche die Gefügeänderungen beim Erhitzen der gegossenen Mischkristall-Legierungen begleitet.

Nun wurden in diesem Versuche die abnormen Dilatationsänderungen unter den verschiedenen Wärmebehandlungen gemessen. Es wurden dann die Beziehungen zwischen dieser Dilatations- und der Gefügeänderung bei den gegossenen kupferreichen Bronzen genau erläutert. Über die abnormen Ausdehnungserscheinungen der sandgegossenen Bronzen sind einige Versuche durch Imai u. Hagitani[3] schon berichtet worden.

Zum Dilatationsversuche benutzten wir die verbesserte Differential-Dilatometer[2] und die Messung wurde um sich vor Oxydation der Probe zu schützen, immer im Vakuum vorgenommen.

(1) Vorgetragen auf der Jahresversammlung der Japanischen Chemischen Gesellschaft, Tokio, April 1933.

(2) D. Uno, S. Yoshida u. S. Katori, vorgetragen auf der Versammlung des Chemischen Instituts kaisl. Universität Osaka, Juni 1931. Vortragssammlung desselben Instituts, **3** (1932), 152.

(3) Imai u. Hagitani, *Mem. Ryojun Coll. Engineering*, **4** (1931), 99.

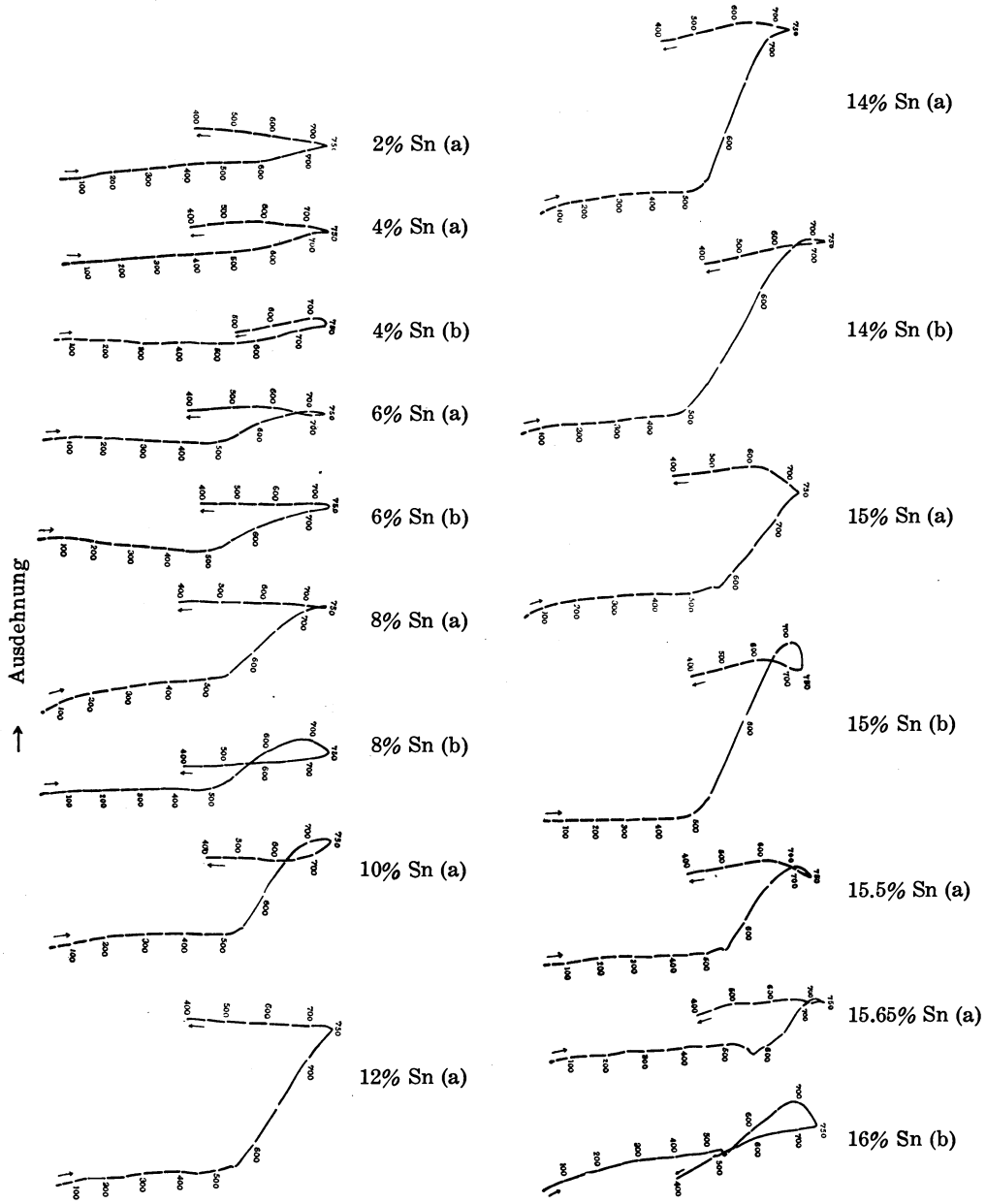


Abb. 1. Differentiale Dilatationskurve der gegossenen Bronzen.
(Gussform a u. b)

Abb. 1 zeigt die Wiedergabe der dilatometrischen Kurve von gegossenen Proben, die 2 bis 10% Zinn enthalten. Beziehungsweise entsprechen die Kurven a und b in Abb. 1 derjenige der im Kokillform a und b gegossenen Proben. Bei etwa 500°C. findet die abnorme Ausdehnung in den Proben statt, die über 4% Zinn enthalten. Je mehr Zinngehalt, desto grösser wird die Ausdehnung. Über 15% Zinn wird sie aber viel kleiner. Dies stimmt hauptsächlich mit den Ergebnissen von Imai u. Hagitani überein.

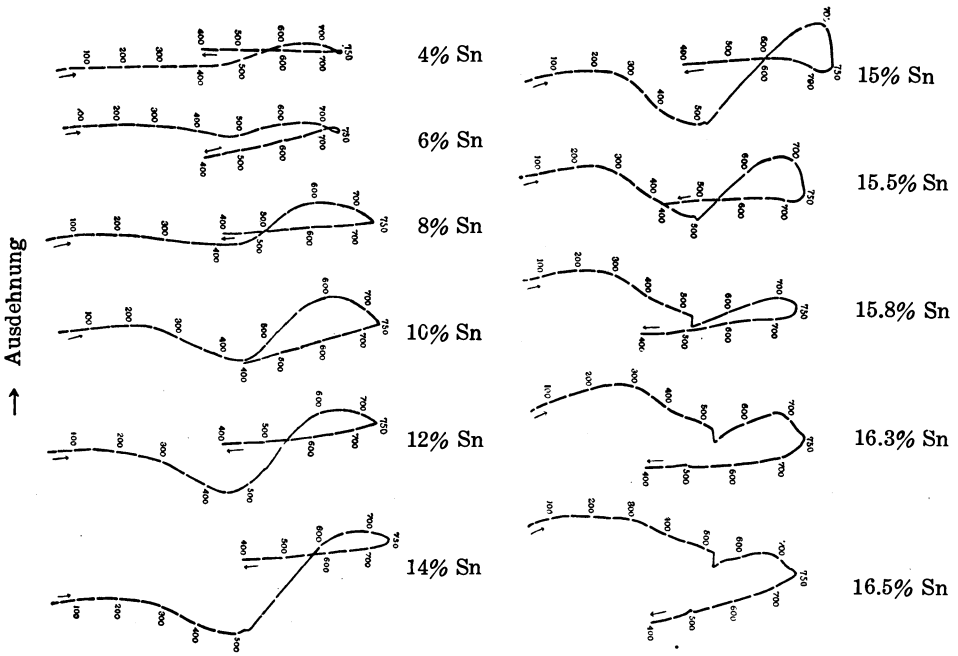
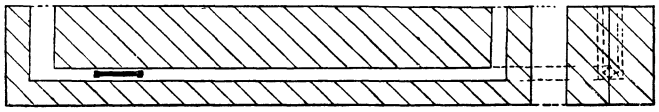
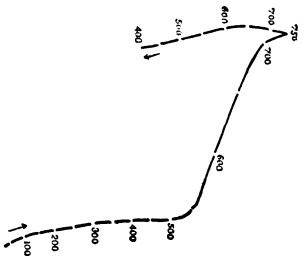


Abb. 2. Differentiale Dilatationskurve der gegossenen Bronzen. (Gussform h)

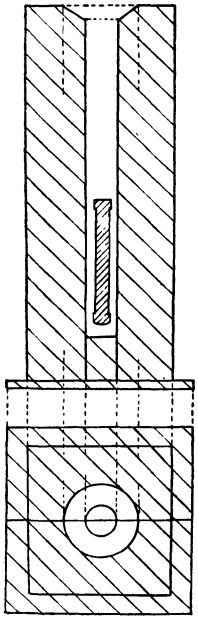
Abb. 2 ist die Wiedergabe der Kurve von den im Kokillform h gegossenen Proben, welche 4 bis 16% Zinn enthalten. Die Kurvengestalt ist etwas anders wie bei Abb. 1. Es zieht sich zum Beispiel von etwa 250°C. allmählich zusammen, und bei etwa 450°C. dehnt es sich aus. Nur findet sich diese Zusammenziehung über 10% Zinngehalt statt, und bei etwa 525°C. erscheint die Dilatationsänderung, welche dem eutektoidischen Horizontale entspricht, stark von ca. 16% Zinngehalt ab.

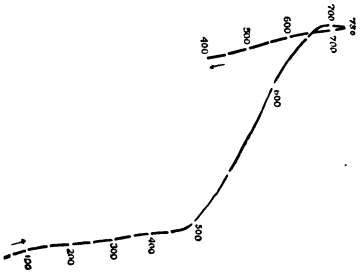
Es wurde nun bei den in die verschiedenen Gussform gegossenen Proben dilatometriert, welche 14% Zinn enthalten und die stärksten Aus-

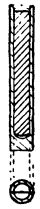


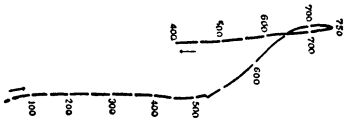


(a) Fe-Kokill bei 250°C.

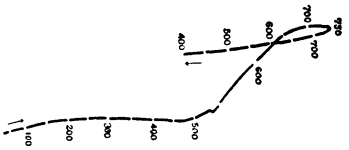






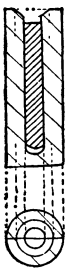


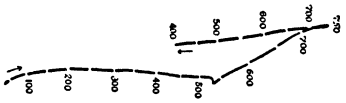
(c) Fe-Kokill bei 20°C.



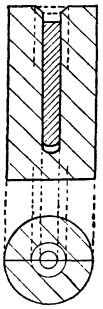
(d) Fe-Kokill bei 20°C.

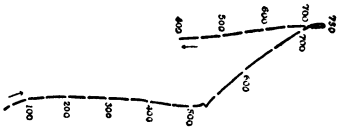
(b) Fe-Kokill bei −7°C.



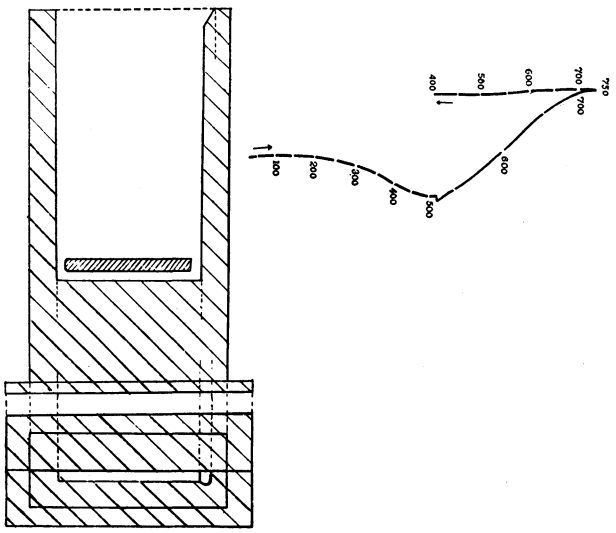


(e) Fe-Kokill bei 20°C.

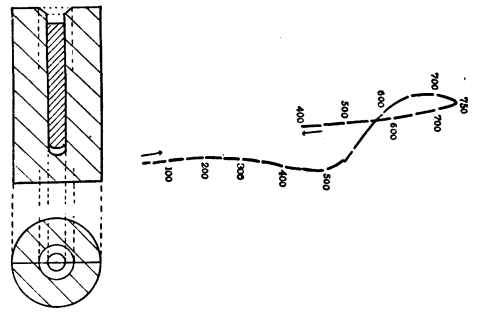




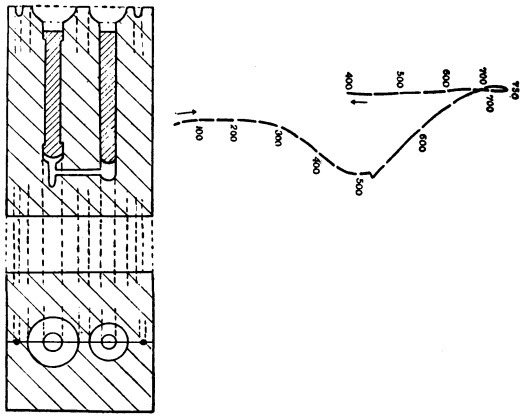
(f) Fe-Kokill bei 20°C.



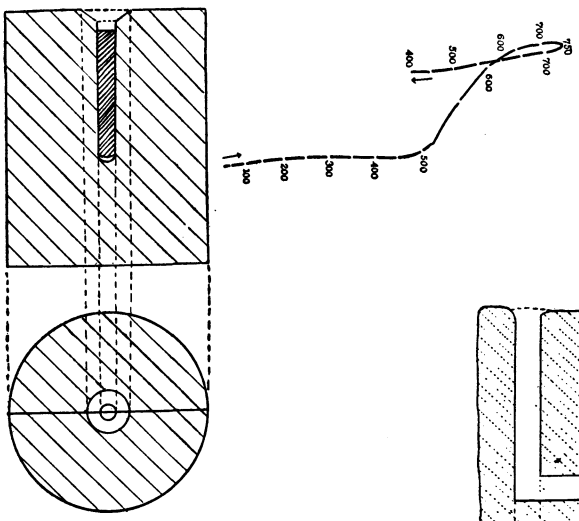
(g) Fe-Kokill bei 20°C.



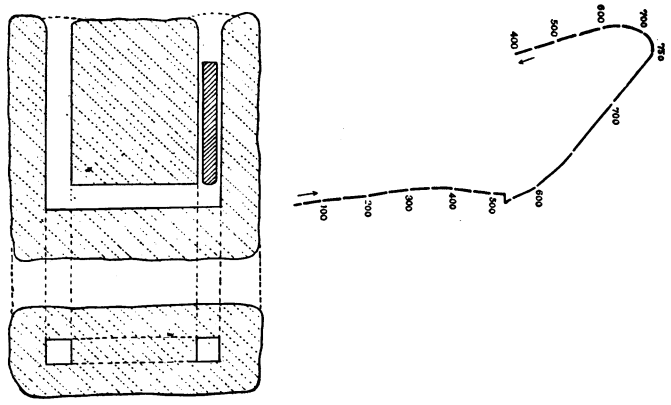
(j) Cu-Kokill bei 20°C.



(h) Fe-Kokill bei −7°C.



(k) Cu-Kokill bei 20°C.



(i) Sandform bei 20°C.

Abb. 3. Verschiedene Gussform und entsprechenden Dilatationskurve bei 14%-zinnhaltigen Bronzen.

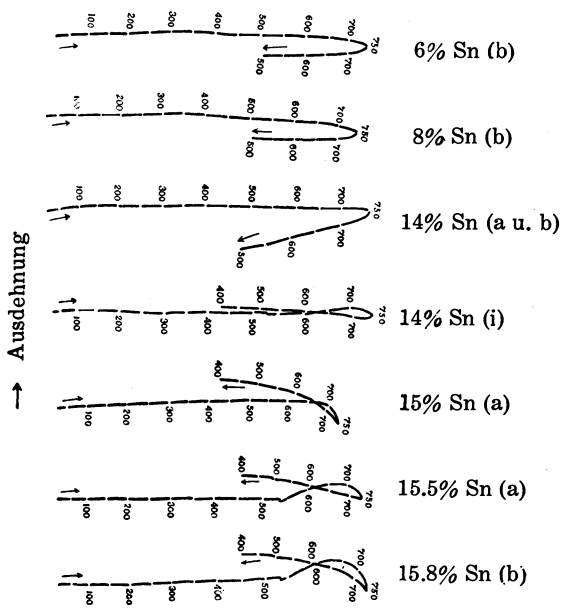


Abb. 4. Differentiale Dilatationskurve der ausgeglühten Bronzen.

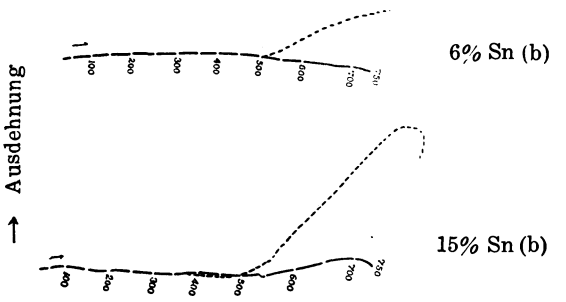


Abb. 5. Differentiale Dilatationskurve der abgeschreckten Bronzen.

dehnung besitzen. In Abb. 3 wurde der Vergleich zwischen den verschiedenen Gussformen und den entsprechenden Dilatationskurven versucht. Wie man sieht in Abb., findet die Ausdehnung bei tieferen Temperaturen statt, wenn die Kühlwirkung der Gussform zunimmt. Beispielsweise tritt in der Kurve der Proben k, j und b die Ausdehnung ein, schon bei etwa 500°C., welche unter grösseren Kühlwirkung gegossen wurden; aber bei etwa 650°C. hört sie auf. Die Ausdehnung setzt im Gegenteil bei höheren Temperaturen d. h. über 550°C. ein, bei der sandgegossenen Probe i, welche weniger Kühleffekt besitzt, und über 750°C. liegt ihr Endpunkt. Es liegt bei anderen Proben der Dilatationseffekte in der Mitte zwischen den obenbeschriebenen beiden Fällen.

Wie in Abb. 4 setzt bis 15% Zinngehalt die abnorme Ausdehnung nicht ein, bei Wiedererhitzung der einmal dilatometrierten Proben. Man kann nun vermuten, dass diese merkwürdige Ausdehnung beim Dilatometrieren der gegossenen Proben auf der Normalisierung der Gussgefüge, nämlich der Diffundierung der Gefügebestandteile beruht. Es wurden wie in Abb. 5 die abgeschreckten Proben dilatometriert, um diese Vermutung weiter zu bestätigen. Wie in Abb. ersichtlich ist, kann man keine besondere Ausdehnung in den Kurven bemerken. Vergleichsweise

wurde die Kurve der Gussproben mit der punktierten Linie gezeigt. Also ist die abnorme Ausdehnung beim Kokillguss nicht hervorgerufen durch den Abschreckeffekt.

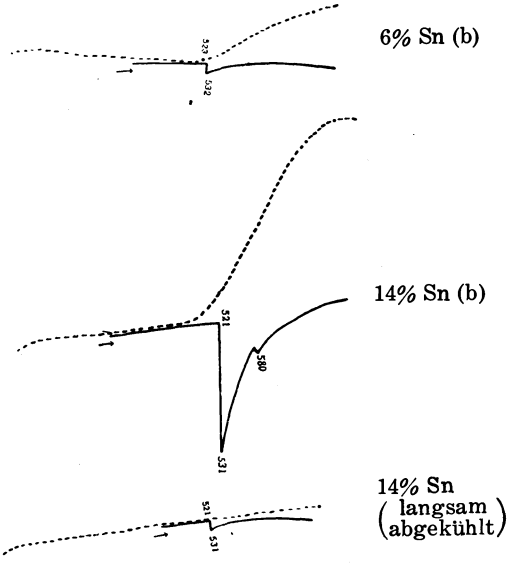


Abb. 6. Differentiale thermische Effekte der Bronzen.

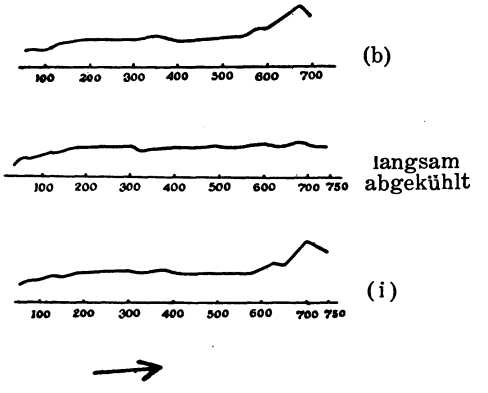


Abb. 7. Direkte Dilatationskurve der Bronzen (14% Sn).

Es wurden die thermischen Effekte während des Normalisierens des Gussgefüges auch untersucht. Abb. 6 zeigt die Wiedergabe der differentialthermischen Kurven, bei welchen reines Kupfer als Vergleichsprobe benutzt wurde; die punktierte Linie zeigt die Dilatationskurve.

Im Falle der Gussproben, welches 14% Zinn enthält, ist die spontane Wärmeabsorption bei etwa 520°C. aufgetreten; bei der ausgeglühten Probe ist sie aber sehr klein geworden. Es wurde deshalb sehr klar, dass die abnorme Ausdehnung der spontanen Wärmeänderung nicht unmittelbar zugrunde liegt.

Gemessen wurde auch die direkte Dilatationskurve bei 14% Zinn wie in Abb. 7; von 550°C. setzt die Ausdehnung bei gegossenen Proben plötzlich aus. Bei ausgeglühten Proben ist die Kurve ungefähr gleichlaufend mit der Temperaturachse.

Die elektrischen Widerstandsänderungen wurden bei den gegossenen sowie den normalisierten Proben auch untersucht. Wie in Abb. 8 ersichtlich ist, im Fall der Gussproben wird die Widerstandsteigerung allmählich schwächer bei etwa 490°C., und bei 520°C. dann bei etwa

650°C. fällt sie plötzlich ab. Bei normalisierter Proben tritt aber keine Änderung auf der kurve ein.

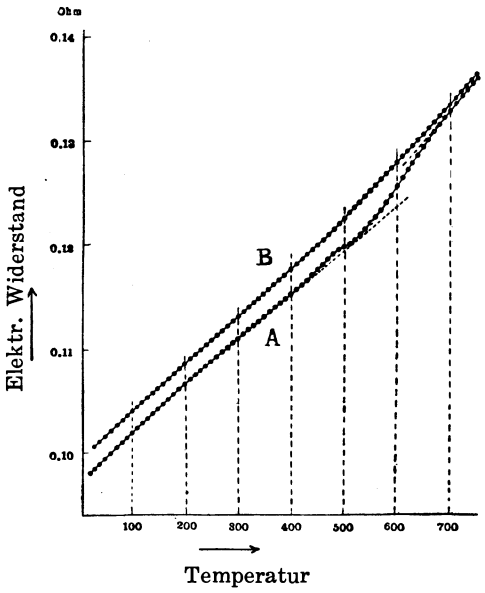


Abb. 8. Elektrischer Widerstand der gegossenen (A) und normalisierten (B) Bronzen (14% Sn).

Es wurden nun über die Beziehungen zwischen der spontanen Ausdehnung und der Diffusion der Gefügebestandteile weiter Versuche angestellt. Während der Dilatometrierung wurde die Gussprobe mit 10% Zinn im einzelnen für eine Stunde je bei 400°, 450° und 500°C. ausgeglüht. Unter Glühen bei 500°C. dehnt sich die Probe stark aus, wie in Abb. 9; bei 400°C. zieht sie sich vielmehr zusammen, aber bei 450°C. dehnt sie sich gleicherweise im Grad wie oben aus.

Man kann aus diesen Ergebnissen den Beginn der Ausdehnung bei etwa 425°C. bestimmen; beim Ausglühen bei 550°C. ist die Dilatationsänderung nach einer Stunde schon vollendet. Bei sandgegossenen ist aber 3 stundiges Ausglühen selbst bei 660°C. nötig, um die Ausdehnung vollenden zu lassen; bei 700°C. aber ist nur halbstündiges Ausglühen schon genug.

Abb. 10 zeigt die Wiedergabe der Dilatationskurve von 14%-zinnhaltiger Proben; bei 600°C. ist nach 2 Stunden die Ausdehnung fertig geworden, und bei 550°C. ist die Doppeldauer nötig. Bei Sandgussproben benötigt man 2½ Stunden selbst bei 700°C.

Abb. 11 zeigt das Mikrogefüge der in Gussform i gegossenen Proben mit 10% Zinn, welches durch die Ätzung in der alkoholischen Lösung von Ammoniumpersulfat hervorgerufen wurde; im Gefüge kann man die starke Seigerung deutlich erkennen. Ätzt man dieselbe Proben durch die Ferrichlorid-Lösung, erscheint die zweite Phase sehr klar wie in Abb. 12. Abb. 13. ist das Gefüge, welches bis 600°C. unter derselben Erhitzungsgeschwindigkeit geglüht wurde; die Seigerung ist etwas weniger geworden. Glüht man die Probe bis 750°C., verschwindet das Seigern beinahe (Abb. 14).

Die Mikrogefüge der Proben mit 14%igem Zinn wurden bei Abb. 15 bis 21 gezeigt; Abb. 15 ist das Gefüge der in Gussform i gegossenen

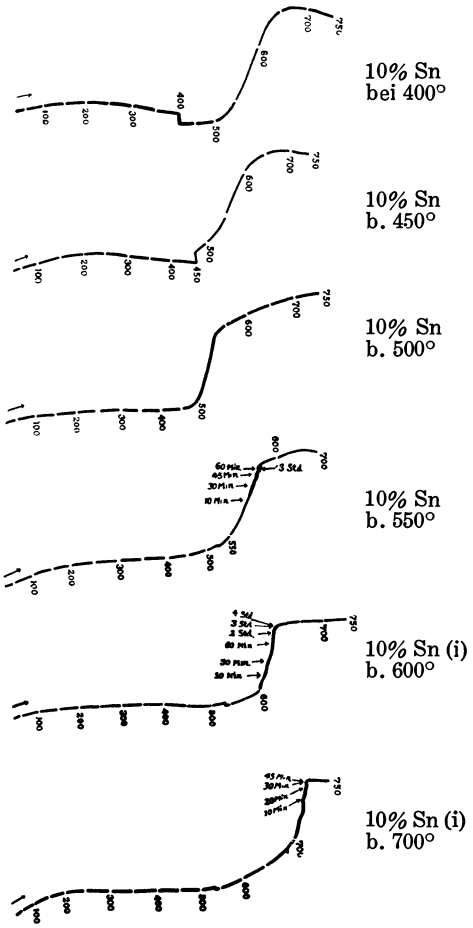


Abb. 9. Dilatationseffekte der 10% Sn bei konstanten Temperaturen.

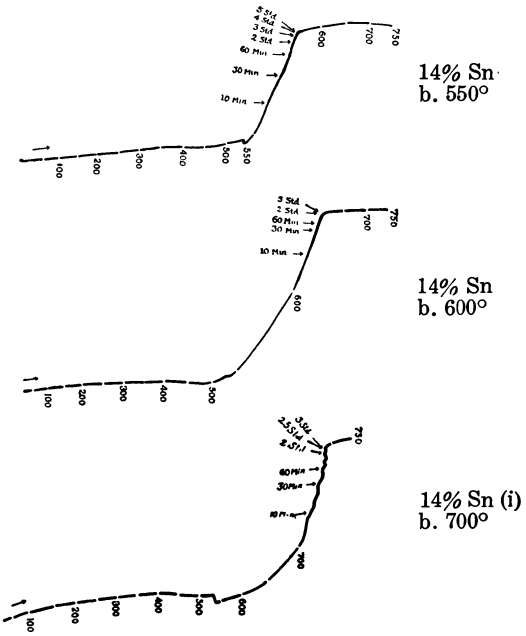


Abb. 10. Dilatationseffekte der 14% Sn bei konstanten Temperaturen.

Proben, und es wurde durch Ammoniumpersulfat-Lösung geätzt. Beim Ätzen der Ferrichlorid-Lösung wird die zweite Phase im Gefüge deutlich erkennbar wie Abb. 16. Bei der Erhitzung unterhalb 500°C. ist das Lösungsgehen von β-Phase schwer zu bemerken (Abb. 17). Erhitzt man auf ca. 700°C., löst sich derjenige beträchtlich im Grundphase auf (Abb. 18); selbst nach einstündigem Glühen, ist das Lösungsgehen noch immer nicht vollendet (Abb. 19). Abb. 20 zeigt das Gefüge der Proben, welches 3 Stunden bei derselben Temperatur geglüht wurde; es ist ganz homogen geworden.

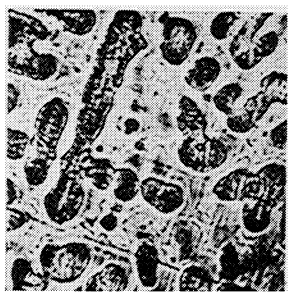


Abb. 11. 10% Sn

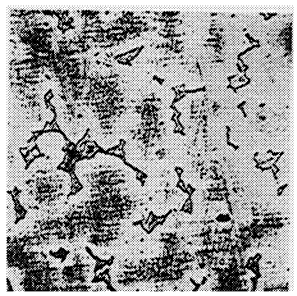


Abb. 12. 10% Sn

Abb. 13. 10% Sn (bei 600°)

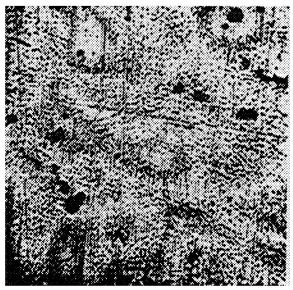


Abb. 14. 10% Sn (bei 750°)

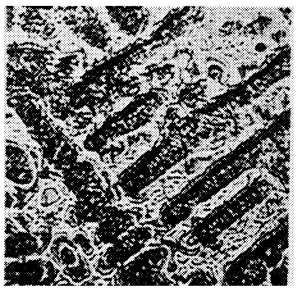


Abb. 15. 14% Sn

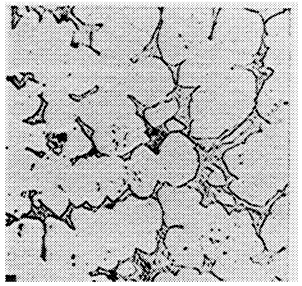


Abb. 16. 14% Sn

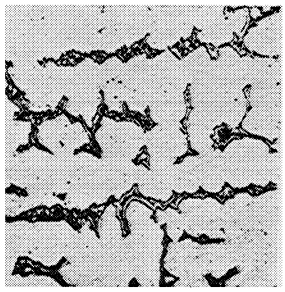


Abb. 17. 14% Sn (bei 500°)

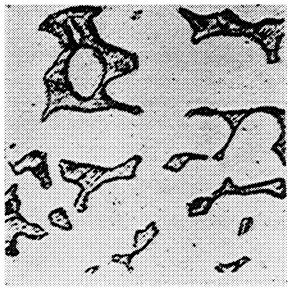


Abb. 18. 14% Sn (bei 700°)

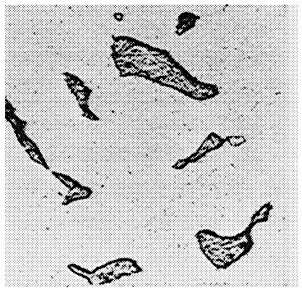


Abb. 19. 14% Sn (1 Std. bei 700°)

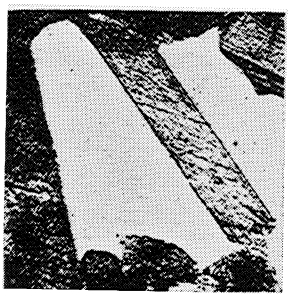


Abb. 20. 14% Sn
(3 Std. bei 700°)

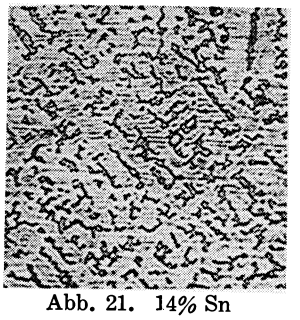


Abb. 21. 14% Sn

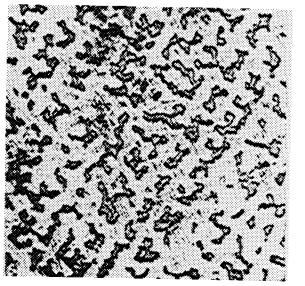


Abb. 22. 14% Sn
(bei 500°)

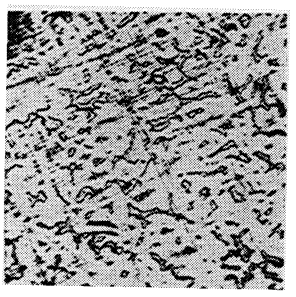


Abb. 23. 14% Sn
(bei 600°)

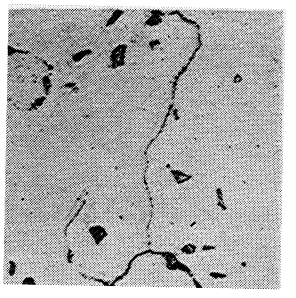


Abb. 24. 14% Sn
(1 Std. bei 600°)

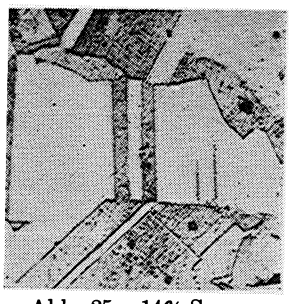


Abb. 25. 14% Sn
(2 Std. bei 600°)

Abb. 11–25. Vergrösserung: 200; Ätzmittel: Am. Persulfat oder Ferrichlorid.

Abb. 21 entspricht dem Gefüge der Proben, welche ins Gussform a gegossen wurde. Erhitzt man bis 500°C., werden die Körner von β-Phase ziemlich grösser (Abb. 22); beim Erhitzen bis 600°C. ist diese Phase durch Lösung beträchtlich weniger geworden (Abb. 23), und nach einstundigen Glühen ist das Gefüge fast homogen geworden (Abb. 24). Die weitere Erhitzung noch ein-stundenlang lässt das Gefüge vollkommen homogen werden (Abb. 25).

Man kann nun aus diesen Ergebnissen die engen Beziehungen zwischen der Dilatations- und der Gefügeänderung gut erkennen.

Man wird weiter hin den Diffusionsgrad der Gefügebestandteilen unmittelbare aus dem Ausdehnungsgrad vermuten können.

DIE KOLLOIDCHEMISCHEN UNTERSUCHUNGEN DER SYSTEME VON DREI FLÜSSIGEN KOMPONENTEN.

I. ÜBER DAS KOLLOIDVERHALTEN KRITISCHER GEMISCHE VON DREI FLÜSSIGKEITEN.

Von **Naoyasu SATA** und **Osamu KIMURA.**

Eingegangen am 28. Mai, 1935. Ausgegeben am 28. September, 1935.

Einleitung.

Wenn eine Substanz von der molekularen Dimension zur makroskopischen Dimension übergeht, ist es ganz klar, dass sie inzwischen von der Kontinuitätsvorstellung aus die "Kolloid-Dimension" durchlaufen wird. Das dürfte auch das Grundprinzip der bekannten von Weimarn'schen Theorie "Allgemeinheit des Kolloidzustandes"[1] sein.

Der einfachste Fall trat schon ein beim kritischen Punkt der Phasengrenze einer reinen Substanz, wie schon von vielen Autoren[2] bemerkt wurde. Neulich hat Wo. Ostwald[3] ein recht schönes, zusammenfassendes Übersichtsbild über dieses Thema vom Standpunkt der Kolloidchemie ausgegeben. Aber solches kolloides System ist jedenfalls ein metastabiles System, das man nicht lange stabil halten kann. Ganz ähnlich kann man auch die kritischen Gemische zweier Flüssigkeiten betrachten. Wo. Ostwald[4] hat auch solche Fälle untersucht um seine Theorie von der Strukturviscosität zu beweisen. Weiter wissen wir von solchen Fällen wie die kritischen Flüssigkeitsgemische, wo das System drei flüssige Komposente enthält, von denen zwei Flüssigkeiten gegeneinander nicht oder begrenzt mischbar sind und wo die dritte mit jeder anderen unbegrenzt mischbar ist. Wenn man hier annimmt, dass einer von den Komponenten keine Flüssigkeit sondern eine feste Substanz wäre, dann entspricht dieser Fall der Herstellungsmethode kolloider Lösungen durch Wechseln des Lösungsmittels, die von P. P. von Weimarn und N. von Weimarn[5] entwickelt worden ist. Bei der Phasenregel-Unter-

(1) P. P. von Weimarn, „Die Allgemeinheit des Kolloidzustandes", Dresden und Leipzig, 1925; *Kolloid-Z.*, **53** (1930), 246.

(2) W. H. Keesom, *Ann. Phys.*, (4), **35** (1911), 591. Wo. Ostwald, *Ann. Phys.*, (4), **36** (1911), 848. I. Traube, *Ann. Phys.*, (4), **8** (1902), 267; *Kolloid-Z.*, **70** (1935), 302. P. Hein, *Z. physik. Chem.*, **86** (1914), 385.

(3) Wo. Ostwald, *Kolloid-Z.*, **64** (1933), 50.

(4) Wo. Ostwald und Malss, *Kolloid-Z.*, **63** (1933), 61.

(5) N. von Weimarn, *Kolloid-Z.*, **54** (1931), 296.

suchung vom System Benzol-Wasser-Alkohol hat Bancroft[6] schon darauf hingewiesen, dass das System beim kritischen Punkt ein typisch kolloides Aussehen, d. h. opaleszierende bläulichweisse Trübung zeigt. V. Rothmund[7] und J. Friedländer[8] haben auch einige solche Fälle studiert und die Viscositätsmessungen u.s.w. ausgeführt. Neulich hat M. Pestemer[9] die Viscosität vom System Benzol-Wasser-Alkohol gemessen. Diese Messung ist aber unter Rührung von 800 Umdrehungen per Minute ausgeführt, und auf das kolloide Verhalten des Systems ist nicht besonders geachtet worden.

Folgende Untersuchung wurde ausgeführt um solche Systeme von drei flüssigen Komponenten zu systematisieren vom Standpunkt der Kolloidchemie aus und um weitere kolloidchemische Eigenschaften solcher emulsoiden Suspension zu studieren.

Experimenteller Teil.

Das Verhalten der oben erwähnten Systeme von drei Komponenten, nämlich, dass die eine Flüssigkeit mit der zweiten begrenzt oder fast unmischbar ist und das die dritte mit anderen in allen Verhältnissen mischbar ist, können wir allgemein nach der Phasenregel schematisch wie Abb. 1 zeigt, ausdrücken. A und B bedeuten zwei nicht oder begrenzt mischbare Flüssigkeiten und C ist eine mit A und B in allen Verhältnissen mischbare Flüssigkeit. Die kritische kolloiddisperse Phase trat nahe der Grenzkurve ein, wenn man zu einem beliebigen Gemisch vorsichtig den dritten Komponenten einführte. Für den idealen Fall, wo das System ziemlich stabil im Kolloid-Gebiet bleiben würde, verläuft die Änderung folgendermassen.

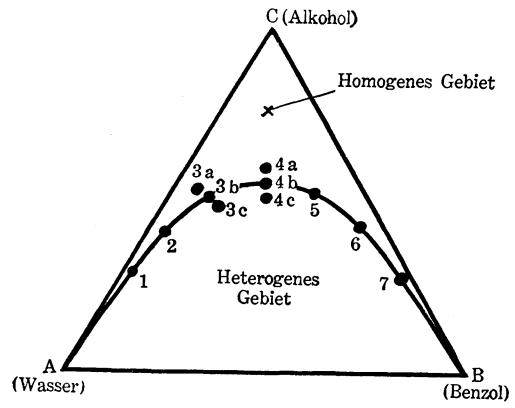


Abb. 1.

Das anfangs ganz klare homogene System wird erst schwach bläulich, danach opaleszierend bläulich und dann bläulichweiss trübe.

(6) Bancroft, *Phys. Rev.*, **3** (1895), 21.
(7) V. Rothmund, *Z. physik. Chem.*, **63** (1908), 54.
(8) J. Friedländer, *Z. physik. Chem.*, **38** (1901), 435.
(9) M. Pestemer, *Kolloid-Z.*, **65** (1933), 25.

Die Trübung wird mehr und mehr beim Zusatz dritter Komponente und endlich scheiden Flüssigkeitstropfen aus, und das System trennt sich in zwei ganz klare Flüssigkeitsschichten.

Wenn man umgekehrt beginnt mit einem zweiflüssigen heterogenen System, das sich anfangs leicht wieder in zwei klare Flüssigkeiten trennt, dann wird es zuerst eine schwer wieder trennbare Milch, dann verschwindet nach und nach diese weisse Trübung und dabei erhält dieses System einen bläulich opaleszierenden Ton, der endlich auch verschwindet, sodass eine ganz klare homogene Flüssigkeit bleibt.

Vorversuche. Wir haben zuerst das Vorhandensein solches kolloiddispersen Gebietes bei verschiedenen Systemen (gekennzeichnet durch bläuliche Opaleszenz bzw. Tyndall-Kegel) in Thermostaten von 30°C. untersucht. Als eine von den unmischbaren Flüssigkeiten haben wir Wasser benutzt, dann wird der zweite Komponent zu Benzol, seine Derivate und andere unpolare Flüssigkeiten fixiert. Als dritter Komponent soll demgemäss Alkohol bzw. Aceton ausgewählt werden.

Die zusammenfassenden Resultate unserer Versuche sind in Tabelle 1 ersichtlich.

Tabelle 1.

Komponent C / Komponent B	Methylalkohol	Äthylalkohol	*n*-Propylalkohol	*i*-Propylalkohol	Aceton
Benzol	+++	+++	+	+	–
Toluol	++	++	++	+	–
Äthylbenzol	++	++	+	+	–
Chlorbenzol	+	+	?	+	–
Nitrobenzol	+	+	?	+	–
Anilin	+	+	?	+	–
o-Xylol	+	+	+	+	–
m-Xylol	+	+	+	+	–
p-Xylol	+	+	+	+	–
Cyclohexan	+	+	?	+	–
n-Pentan	–	–	–	–	–
n-Hexan	–	–	–	–	–
Tetrachlorkohlenstoff	++	++	+	+	–
Chloroform	++	++	+	+	–
Schwefelkohlenstoff	++	++	+	+	–
Chloräthylen	+	+	?	+	–
Äthyläther	–	–	–	–	–

Durchschnittlich haben wir solche Systeme in drei Gruppen klassifiziert, nämlich

(a) bläulich opaleszierendes kolloides Gebiet, das ziemlich lang stabil ist in bezug auf Änderung (Zusatz) eines dritten Komponenten, in der Tabelle mit ++ bzw. +++ bezeichnet;

(b) bläulich opaleszierendes Gebiet, das aber sehr unstabil ist und bei dem die Opaleszenz gleich wieder verschwindet gegen winzigste Änderung dritter Komponente (0.02 c.c.) In der Tabelle mit + ausgedrückt;

(c) bläulich opaleszierendes Gebiet konnten wir in der Genauigkeitsgrenze unserer Versuche (0.02 c.c.) nicht erhalten. In der Tabelle mit − bezeichnet.

Aus der Tabelle merkt man gleich, dass als Komponent B das Benzol und seine Alkyl-Derivate, wie z. B. Toluol und Äthylbenzol und auch unpolare Flüssigkeiten, wie z. B. Tetrachlorkohlenstoff, Schwefelkohlenstoff und Chloroform gegen Methyl- bzw. Äthylalkohol als Komponent C, das beste Resultat zeigt. Chlor-, Nitro- oder Amino-Derivate des Benzols geben nicht mehr so ausgezeichnete Resultate. Merkwürdigerweise geben Pentan und Hexan negative Resultate, obwohl sie unpolar sind, wohingegen die anderen unpolaren Flüssigkeiten, wie Benzol, Tetrachlorkohlenstoff, Chloroform u.s.w. positive Resultate geben. Hier könnte man vermuten, dass diese Erscheinung mit der chemischen Struktur zusammenhängt, wenn man beachtet, dass Pentan und Hexan Ketten-Struktur besitzen und die anderen oben genannten unpolaren Flüssigkeiten ringförmige oder symmetrische Struktur aufweisen. Hier zeigt das Aceton wieder eine Anomalie, wie von einem von uns an anderer Stelle[10] oft bemerkt worden ist. Bei Äther bleiben uns auch als Ausnahme die negativen Resultate, deren Ursache wir auch einmal studieren möchten.

System: Benzol-Wasser-Äthylalkohol. Durch oben ausgeführte qualitative Versuche ist es uns jetzt bekannt, dass die Systeme Benzol-Wasser und Äthyl- bzw. Methylalkohol grössten Bereich stabiler kolloider Systeme besitzt. Die quantitative Untersuchung des Systems wurde zunächst ausgeführt.

Der gebrauchte Alkohol wurde folgendermassen gereinigt: Verkäuflicher reinster 95%iger Alkohol wird erst mit Kaliumpermanganat behandelt und mit CaO für einen Tag mit Rückflusskühler gekocht und dann destilliert. Der erhaltene Alkohol hat das spezifische Gewicht

(10) N. Sata und K. Kurano, *Kolloid-Z.*, **65** (1933), 283. N. Sata und S. Watanabe, *Kolloid-Z.*, **70** (1935), 159.

0.7865 bei 25°C., also 99.53% Reinheit. Das Benzol, und zwar das Merck'sche Präparat "rein kristallisierbar" wurde über Na-Metall destilliert. Das Wasser ist ein zweimal destilliertes Leitfähigkeitswasser nach Bourdillon.[11]

Das Dreieckdiagramm des Systems Benzol-Wasser-Äthylalkohol ist schon sehr oft vom Standpunkt des Phasenregels[12] aus studiert, wie auf Abb. 1 schematisch wiedergegeben ist.

Um das Verhalten bei kritischen Punkten zu studieren, haben wir folgende Versuche angestellt. Denken wir an die verschiedenen Punkte 1–7 auf der kritischen Grenzkurve. Um jeden dieser Punkte haben wir noch einige Punkte 1a, 1b, 1c u.s.w. durch kleine Veränderung (0.02 c.c.) eines Komponenten hergestellt, die in die Probiergläschen 15 mm. Durchmesser und 200 mm. Länge eingeschmolzen sind. Diese Proben wurden dann in Thermostat von 30°C. getaucht und beobachtet. Nach einiger Zeit teilten sich einige Proben in zweiflüssige Systeme. Aber bei einigen bleibt das bläulich bis schwach weissgetrübte bläulich opa-

Tabelle 2.

	C_2H_5OH (c.c.)	%	C_6H_6 (c.c.)	%	H_2O (c.c.)	%	Zustand
1 a	2.00	—	10.00	—	0.12	—	homogen
1 b	2.00	—	10.00	—	0.16	—	homogen
1 b′	2.00	16.58	10.00	82.11	0.18	1.31	weisslich trübe
1 c	2.00	—	10.00	—	0.20	—	weisslich trübe
1 d	2.00	—	10.00	—	0.24	—	weisslich trübe
1 e	2.00	—	10.00	—	0.30	—	weisslich trübe

Tabelle 3.

2 a	5.00	—	10.00	—	0.66	—	homogen
2 a′	5.00	31.85	10.00	63.69	0.68	4.46	bläul. opaleszierend
2 b	5.00	—	10.00	—	0.70	—	bläul. opaleszierend
2 c	5.00	—	10.00	—	0.74	—	bläul. opaleszierend
2 d	5.00	—	10.00	—	0.78	—	bläul. opaleszierend
2 e	5.00	—	10.00	—	0.82	—	bläul. opaleszierend
2 e′	5.00	31.57	10.00	63.13	0.84	5.30	weisslich trübe
2 f	5.00	—	10.00	—	0.86	—	weisslich trübe
2 g	5.00	—	10.00	—	0.90	—	weisslich trübe

(11) R. Bourdillon, *J. Chem. Soc.*, **103** (1913), 791.
(12) Bancroft, *loc. cit.* Lincoln, *J. Phys. Chem.*, **4** (1900), 161. Barbandy, *Rec. trav. chim.*, **45** (1913), 207. Holmes, *J. Chem. Soc.*, **113** (1918), 263. Bogin, *J. Ind. Eng. Chem.*, **16** (1924), 380.

Tabelle 4.

	C_2H_5OH (c.c.)	%	C_6H_6 (c.c.)	%	H_2O (c.c.)	%	Zustand
3 a	5.00	—	5.00	—	1.06	—	homogen
3 a′	5.00	45.13	5.00	45.13	1.08	9.74	bläul. opaleszierend
3 b	5.00	—	5.00	—	1.10	—	bläul. opaleszierend
3 c	5.00	—	5.00	—	1.14	—	bläul. opaleszierend
3 d	5.00	—	5.00	—	1.18	—	bläul. opaleszierend
3 e	5.00	—	5.00	—	1.20	—	bläul. opaleszierend
3 e′	5.00	44.60	5.00	44.61	1.21	10.79	weisslich trübe
3 f	5.00	—	5.00	—	1.22	—	weisslich trübe
3 g	5.00	—	5.00	—	1.24	—	weisslich trübe

Tabelle 5.

4 a	10.00	—	5.00	—	3.44	—	homogen
4 b	10.00	—	5.00	—	3.48	—	homogen
4 c	10.00	—	5.00	—	3.52	—	homogen
4 c′	10.00	53.94	5.00	6.97	3.54	19.09	weisslich trübe
4 d	10.00	—	5.00	—	3.56	—	weisslich trübe
4 e	10.00	—	5.00	—	3.60	—	weisslich trube

Tabelle 6.

5 a	10.00	—	2.00	—	5.50	—	homogen
5 b	10.00	—	2.00	—	5.60	—	homogen
5 c	10.00	—	2.00	—	5.70	—	homogen
5 c′	10.00	56.34	2.00	11.26	5.75	32.40	weisslich trübe
5 d	10.00	—	2.00	—	5.80	—	weisslich trübe
5 e	10.00	—	2.00	—	5.90	—	weisslich trübe

Tabelle 7.

6 a	5.00	—	0.20	—	5.00	—	homogen
6 b	5.00	—	0.25	—	5.00	—	homogen
6 c	5.00	—	0.30	—	5.00	—	homogen
6 c′	5.00	48.54	0.33	2.91	5.00	48.55	weisslich trübe
6 d	5.00	—	0.35	—	5.00	—	weisslich trübe
6 e	5.00	—	0.40	—	5.00	—	weisslich trübe

Tabelle 8.

	C_2H_5OH (c.c.)	%	C_6H_6 (c.c.)	%	H_2O (c.c.)	—	Zustand
7 a	5.00	—	0.04	—	10.00	—	homogen
7 b	5.00	—	0.08	—	10.00	—	homogen
7 b′	5.00	33.11	0.10	0.66	10.00	66.23	weisslich trübe
7 c	5.00	—	0.12	—	10.00	—	weisslich trübe
7 d	5.00	—	0.16	—	10.00	—	weisslich trübe

leszierende, typische kolloide Aussehen unverändert stabil. Die Versuchsergebnisse sind in den Tabellen 2–8 zusammengestellt.

Wenn man die Punkte, wo bläulich opaleszierende Gemische angegeben sind, auf Dreieckdiagramme überträgt, erhält man eine schmale Insel nahe der Grenzkurve, wie in Abb. 2 ersichtlich ist. Alle beliebigen Punkte der in dieser Insel ausgedrückten Gemische bleiben bläulich opaleszierend kolloidal bei 30°C. Es ist zu beachten, dass sich das kolloidstabile Gebiet an der Alkohol-Benzol-Axe, d. h. an der wasserarmen Gegend des Dreieckdiagramms befindet, und dass in dem benzolarmen Gebiet über der kritischen Kurve keine stabile bläulich opaleszierende Emulsion zu erhalten ist.

Dann haben wir den Temperaturbereich der Stabilität dieser Emulsionen untersucht. Wir tauchen z. B. 3b, 3e, 2b, 2e ins Wasserbad und beobachten während der Änderung der Temperatur die Obergrenze, wo

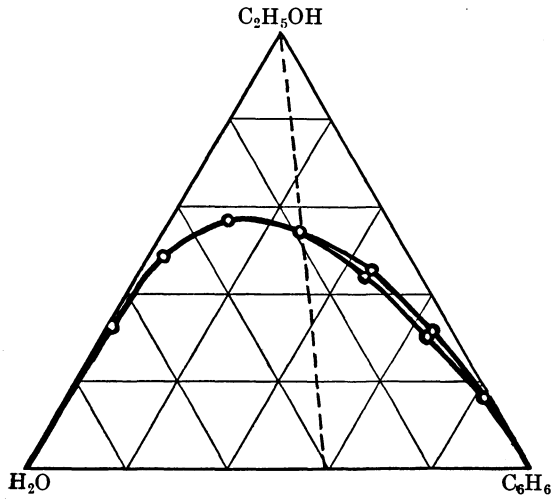


Abb. 2.

Tabelle 9.

	Obergrenze °C.	Untergrenze °C.
2 b	22	14
2 e	44	29
3 b	33	20
3 e	42	29

die bläuliche Opaleszenz gerade verschwindet und das System homogen wird, und die Untergrenze, wo das System weisslich trübe wird und sich in zwei Schichten scheidet. Die Ergebnisse sind gegeben in Tabelle 9. Man sieht aus Tabelle 9, dass ein System während des Temperaturbereichs

Tabelle 10.
Initiale Zusammensetzung
= 1.0 c.c. H_2O+10.0 c.c. C_6H_6

Zugefügte Alkohol (c.c.)	Volum der Unterschicht (c.c.)	Total-Volum (c.c.)
0	1.0	11.0
1.0	1.4	12.0
2.0	1.8	13.0
3.0	2.3	14.0
4.0	3.1	15.0
5.0	4.1	16.0
5.5	4.8	16.5
6.0	17.0	17.0

Tabelle 11.
Initiale Zusammensetzung
= 2.0 c.c. H_2O+10.0 c.c. C_6H_6

0	2.0	12.0
1.0	2.6	13.0
2.0	3.4	14.0
3.0	4.1	15.0
4.0	4.9	16.0
5.0	5.8	17.0
6.0	6.9	18.0
6.5	7.6	18.5
7.0	8.3	19.0
7.5	9.1	19.5
8.0	10.2	20.0
8.5	11.5	20.5
9.0	13.9	21.0
9.5	21.5	21.5

Tabelle 12.
Initiale Zusammensetzung
= 2.0 c.c. H_2O+5.0 c.c. C_6H_6

Zugefügte Alkohol (c.c.)	Volum der Unterschicht (c.c.)	Total-Volum (c.c.)
0	2.0	7.0
1.0	2.7	8.0
2.0	3.5	9.0
3.0	4.5	10.0
4.0	5.7	11.0
5.0	7.3	12.0
5.5	8.4	12.5
6.0	9.5	13.0
6.5	11.0	13.5
7.0	13.0	14.0
7.5	14.5	14.5

Tabelle 13.
Initiale Zusammensetzung
= 5.0 c.c. H_2O+5.0 c.c. C_6H_6

0	5.0	5.0
1.0	5.8	6.0
2.0	6.8	7.0
3.0	7.7	8.0
4.0	8 6	9.0
5.0	9.6	10.0
6.0	10.7	11.0
7.0	11.9	12.0
8.0	13.3	13.0
9.0	14.7	14.0
10.0	16.3	15.0
11.0	18.1	16.0
12.0	20.2	17.0
13.0	22.3	18.0
14.0	19.0	19.0

Tabelle 14.
Initiale Zusammensetzung
= 4.0 c.c. H_2O+2.0 c.c. C_6H_6

Zugefügte Alkohol (c.c.)	Volum der Unterschicht (c.c.)	Total-Volum (c.c.)
0	4.0	6.0
1.0	4.9	7.0
2.0	5.9	8.0
3.0	7.0	9.0
4.0	8.1	10.0
5.0	9.2	11.0
6.0	10.4	12.0
7.0	11.8	13.0
8.0	13.3	14.0
8.5	14.3	14.5

von etwa 10 Grad stabil opaleszierend bleibt, wenn es eine geeignete Zusammensetzung besitzt. Vergleicht man Abb. 2 und Tabelle 9, so kann man auch bemerken, dass der Temperatureinfluss sehr empfindlich ist, besonders hinsichtlich der Anderung von Wassergehalt, und zwar sind wasserarme Gemische bei niedrigerem Temperaturbereich stabiler als wasserreiche Gemische, trotzdem es nur ein sehr kleiner Unterschied an Wasser von 1.5 bis 2.0% ist.

Um das Verhalten zwischen Änderung der Komponente und Phasenzustand klarzumachen, haben wir weiter folgende Versuche angestellt: In die langen Probiergläser mit geschliffenen Stöpseln (30 cm. Länge und 1 cm. Durchmesser) nehmen wir verschiedene Kombinationen von Benzol und Wasser, die sich natürlich in zwei Schichten befinden, Benzol oben und Wasser unten. Fügt man den Alkohol tropfenweise dazu, erfolgt die Änderung des Volumens beider Schichten, bis sich endlich das System homogen mischt. Der Versuch wurde ausgeführt in einem Thermostat von 20°C. Die Ergebnisse sind in Tabellen 10–14 und Abb.

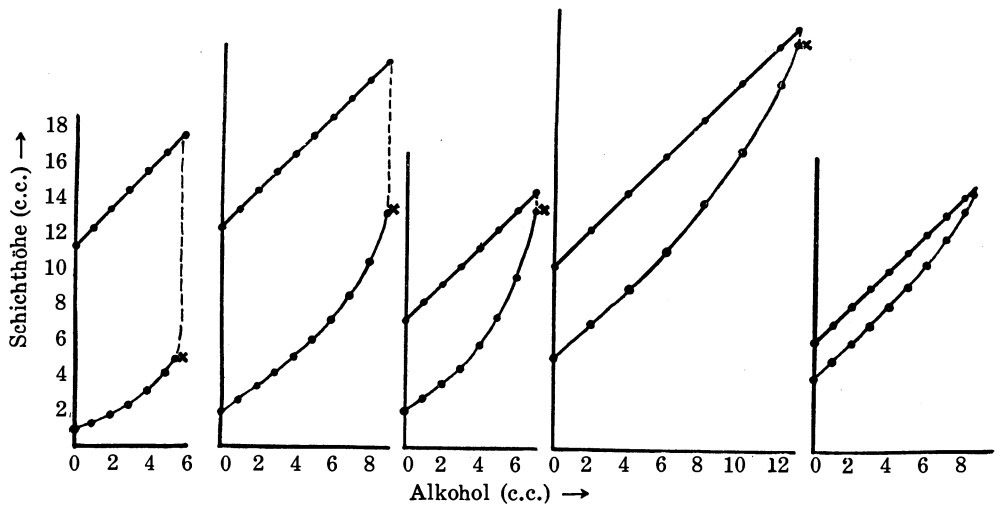


Abb. 3. Abb. 4. Abb. 5. Abb. 6. Abb. 7.

3–7 zusammengestellt. Bei der mit × bezeichneten Zusammensetzung findet ein Platzwechsel beider Schichten statt. (In der Abbildungen wurde es der Einfachheit halber so dargestellt, als ob kein Platzwechsel geschehen wäre). Nach dem Platzwechsel steigt das Volumen einer Schicht durch einen kleinen Alkoholzusatz sehr schnell an, und endlich wird das ganze System homogen und entwickelt sich in dieser Nähe zum bläulich opaleszierenden System. Bei dem wasserreichen System steigt die Kurve anfangs steiler an und an der Stelle des Platzwechsels ist die eine Schicht schon sehr klein im Vergleich zu der anderen Schicht (Abb. 5 und 6). Bei dem System, das mehr als 50% Wasser enthält, findet überhaupt kein Platzwechsel statt. Wenn man die auf Abb. 7 bezeichneten Punkte auf das Dreieckdiagramm von Abb. 2 überträgt, so sieht man sofort, dass sie ausserhalb der Emulsions-Insel fallen: Wenn man auf der Abb. 2 die Alkohol-Spitze mit der Insel-Spitze verbindet, dann trifft die Linie ungefähr auf 40% Wasser, und es ist klar, dass bei mehr als 40% Wasser es unmöglich ist, eine stabile Emulsion zu erhalten. Die entsprechenden Punkte von Abb. 7, die bei 60% Wasser angefangen war, fallen natürlich nicht in die Emulsions-Insel hinein.

Erörterung.

Von den oben ausgeführten Experimenten über das Verhalten dieses dreiflüssigen Systems in der Nähe kritischer Punkte möchten wir Folgendes schliessen:

(1) Die Verteilung von Alkohol zwischen Benzol und Wasser scheint nicht gleich zu sein, und zwar nimmt das Wasser viel stärker Alkohol auf als das Benzol.

(2) Denn, wenn man Abb. 3–7 vergleicht, so nimmt bei der Wasserschicht das Volumen viel mehr zu als bei der Benzolschicht beim Alkoholzusatz. Und der Platzwechsel beider Schichten bei den kritischen Punkten findet auch deshalb statt, weil das Wasser ($d = 1.000$) den Alkohol ($d = 0.781$) aufnimmt und dadurch die Wasserschicht immer leichter wird, sodass endlich ihr spezifisches Gewicht kleiner als das von Benzol ($d = 0.881$) wird, wodurch ein Platzwechsel beider Schichten stattfindet.

(3) Inzwischen wird natürlich die Dichte der Benzolschicht durch Alkoholaufnahme abnehmen, aber dieses scheint viel langsamer vor sich zu gehen als die Dichteabnahme der Wasserschicht.

(4) Nachdem der Platzwechsel geschehen ist, nimmt die Wasserschicht an Volumen plötzlich stark zu durch sehr wenig Alkoholzusatz,

wobei das System bläulich opaleszierendes, kolloides Verhalten zeigt, welches besonders bei Abb. 3 und 4 mit verhältnismässig wasserarmen System deutlich bemerkbar ist. In dieser Gegend scheint das Wasser sein Vermögen an Alkoholaufnahme schon erschöpft zu haben. So kann die Zusammensetzung der Schichten vielleicht bei der Oberschicht alkohol- und benzolreich und bei der Unterschicht alkohol- und wasserreich sein, und das System teilt sich durch die kritische Grenzflächenspannung zwischen Benzol und Wasser in zwei Schichten. Nach einer winzigsten Zunahme von Alkohol scheint das Wasser diese Spannung zu verlieren, und das System wird homogen, d. h. molekular. Inzwischen muss das System die kolloiden Dimensionen durchlaufen, wie Wo. Ostwald[13] u. a. schon erklärt hat.

(5) Daraus könnte man vermuten, dass das disperse System benzolreich und das Dispersionsmittel ein Gemisch von Alkohol, Benzol und Wasser sein müsste. Die Bedingungen, unter welchen ein kritisches dreiflüssiges Gemisch eine stabile kolloide Emulsion angibt, sind noch zu untersuchen, aber dass sie einigermassen mit der chemischen Struktur der Komponente in wichtiger Beziehung stehen, haben wir schon bei den vorläufigen qualitativen Untersuchungen bemerkt. (Siehe Tabelle 1).

Die weiteren Untersuchungen in dieser Richtung sind bereits im Gang, ebenso wie die kolloidchemischen Untersuchungen, wie z. B. Strukturviscosität, kolloid-optische Eigenschaften u.s.w. genannter Systeme.

Zusammenfassung.

(1) Die kritischen Gemische dreier Flüssigkeiten sind auf ihr kolloides Verhalten hin studiert.

(2) Es wurde gezeigt, dass einige Systeme stabile bläulich opaleszierende, emulsoide Suspension in bestimmtem Bereich der Zusammensetzungen bei ziemlich grossem Temperaturintervall von mehr als 10 Grad angeben.

(3) System Wasser-Benzol und Äthyl- bzw. Methylalkohol hat das beste Resultat ergeben.

(4) Normal Hexan oder Pentan, die Kettenstruktur besitzen, an Stelle von Benzol ergeben negative Resultate. Daraus wurde vermutet, dass diese Erscheinung mit der chemischen Struktur der Komponente in Zusammenhang steht.

---

(13) Wo. Ostwald, *loc. cit.*

(5) Das negative Resultat mit Aceton statt Alkohol scheint auch diese Vermutung zu bestätigen.

(6) Die Verteilung von Alkohol zwischen Benzol- und Wasserschicht wurde gemessen und bestätigt, dass der grösste Teil des Alkoholzusatzes zur Wasserschicht aufgenommen wurde.

(7) Von den oben ausgeführten Untersuchungen wurde konstatiert, dass dieses bläulich opaleszierende System eine emulsoide Suspension ist, deren Dispersionsmittel alkohol- und wasserreiche Zusammensetzung aufweist und deren disperse Phase benzolreiche Zusammensetzung besitzt.

Schiomi Institut für Physikalische
und Chemische Forschungen.

ON THE FADING OF DYESTUFFS. I. PHOTOCHEMICAL DECOMPOSITION OF MALACHITE GREEN AND CRYSTAL VIOLET.

By Kenji IWAMOTO.

Received May 29th, 1935. Published September 28th, 1935.

Although it has long been known that dyed fabrics are decolourised by the action of light, it is only quite recently that this phenomenon has been studied chemically. The phenomenon has been accounted for by several authors as oxidation, reduction, or photochemical reaction, according to the varieties of colouring matter used.

The research on this subject is very difficult, owing to the influence dependent on the following factors: (1) light source, namely intensity and wave-length of acting rays, (2) surrounding atmosphere, (3) temperature, (4) added reagents, and (5) varieties of fibres. The mechanism of fading would be qualitatively inferred from the standpoint of organic chemistry, if the decomposition products could be isolated and their constitutions determined exactly. However, our knowledge on this line is still too meagre to permit of generalisation.

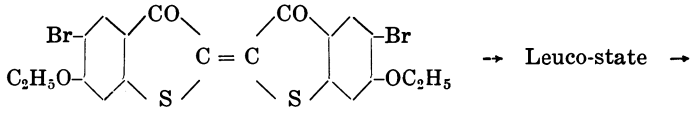
Seyewetz and Mounier[1] found that textiles of animal or vegitable fibres impregnated with nitrophenols or nitroamines turn brown by day-

(1) *Bull. soc. chim.*, (4), **43** (1928), 648.

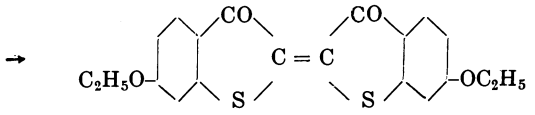
light or ultraviolet rays instead of being decolourised as other dyestuffs, owing to the probable formation of hydroxyazo-compounds.

Hibbert[2] exposed pieces of calico dyed with Indigo to sunlight or ultraviolet rays and isolated a yellow powder, m.p. 200°. This substance gave an indophenine reaction and was identified as isatin. Since isatin is also produced by the action of potassium permanganate and sulphuric acid on the same fabric, it appears that the fading of Indigo is due to the formation of isatin by its oxidation. A similar result was again observed by Haller and Ziersch[3] separately. Hibbert also obtained phthalic acid from Purpurine (1,2,4-trihydroxy-anthraquinone) and proved that the reaction was due to oxidation.

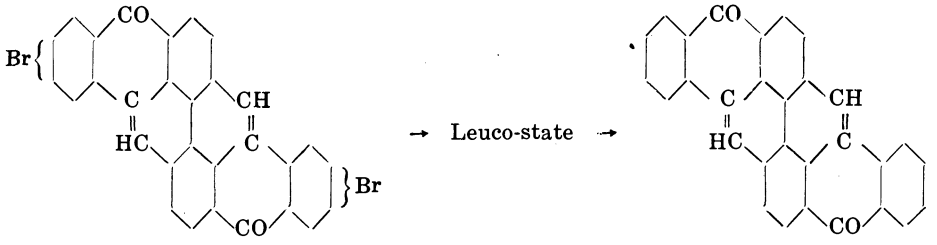
Weber[4] stated that when viscose rayon was exposed to sunlight in a dye-house, while being dyed with Helindone Fast Scarlet R, orange stripes, due to the formation of Helindone Orange R, appeared. Similarly, Indanthrene Gold Orange 4R, belonging to anthraquinone vat dyes, was changed into Indanthrene Gold Orange G:



Helindone Fast Scarlet R



Helindone Orange R.

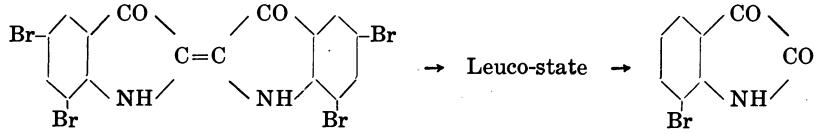


Indanthrene Gold Orange 4R

Indanthrene Gold Orange G.

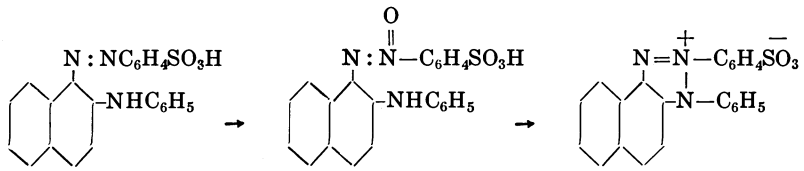
(2) *J. Soc. Dyers Colour.*, **43** (1927), 292; *ibid.*, **44** (1928), 377.
(3) *Melliand Textilberichte*, **10** (1929), 951.
(4) *Rayon Record*, **7** (1933), 227; *Am. Dyestuff Rep.*, **22** (1933), 157.

In other words, if halogen atoms are introduced into the benzene nuclei of vat dyes, the dyes are made very labile in the leuco-state to the light. In some special cases, Brilliant Indigo 4B undergoes not only dehalogenation, but also oxidation, and bromoisatin is formed:



Brilliant Indigo 4B Bromoisatin.

Krollpfeiffer, Mühlhausen and Wolf[5] studied the action of light on azo-dyestuffs and found that aryl-β-naphthylaminoazobenzene sulphonic acid gives rise to triazonium compound on exposure to light. This change may also be accounted for by the formation of azoxy-compound and subsequent conversion of the latter into triazonium compound. In this case, the oxidation was considered to be the most important:



Phenyl-β-naphthylaminoazobenzene sulphonic acid Azoxy-compound Triazonium compound.

So far as we are aware, no definite compound appears to have been isolated in the decolourisation of triphenylmethane dyestuffs. Therefore, the present author has synthesised some pure dyestuffs and studied their decomposition products. In order to simplify the conditions of experiment, the powdered dyestuffs were spread in a thin layer in a large glass dish, covered with Vita-glass or cellophane paper, and exposed to direct sunlight with occasional stirring. In this manner, Malachite Green (oxalate) was rapidly changed into brown powder. The product was extracted with ether and the ethereal solution was evaporated to dryness. The faint, yellow crystals, melting at 90.5–91°, were identified as *p*-dimethylaminobenzophenone by the mixed melting point method.

Crystal Violet (oxalate) was then exposed to sunlight in the same manner, and the pale yellow crystals thus obtained, m. p. 173–174°, were identified as Michler's ketone by comparison with the pure synthetical substance. On the other hand, Georgievices[6] isolated the same ketone

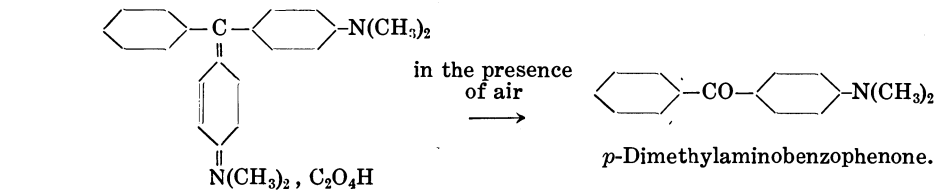
(5) *Ann.*, **508** (1933), 39.
(6) *Ber.*, **38** (1905), 886.

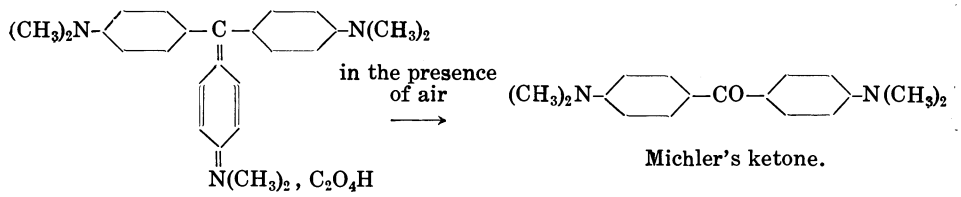
by treating a cold aqueous solution of Crystal Violet with hydrogen peroxide and ammonia. The formation of benzophenone derivatives is interpreted as being caused by either oxidation or hydrolysis.

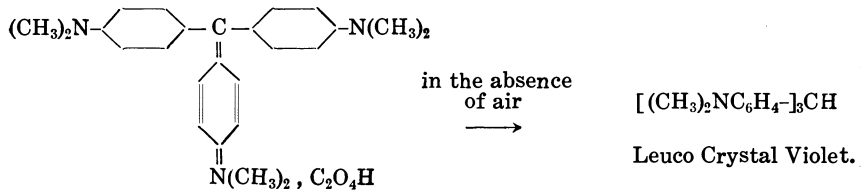
In order to ascertain whether these reactions are due to oxidation or hydrolysis, the present author exposed the same dyestuffs in a sealed tube to sunlight.

The product obtained from Malachite Green was extracted with ether. Nothing definite could be isolated from the ethereal solution, perhaps owing to the presence of impurity and to the small quantity of the material used. Nevertheless, the properties of the residue from the ethereal solution resembled leuco Malachite Green.

A grey substance from Crystal Violet was extracted with benzene and the colourless crystals, melting at 173–174°, which, on standing in the air, coloured blue gradually, were obtained and proved to be identical with leuco Crystal Violet by means of the mixed melting point method. It thus follows that the reduction occurs in this case, as shown in the following scheme:







It will be seen from the above facts that oxidation took place actually in the case where photochemical reaction might be expected. Therefore, it may be said that oxidation plays an important part in the fading of dyestuffs of this class.

Further experiment on the same line is now in progress.

Experimental.

Purification of Malachite Green. Commercial Malachite Green (50 g.) was powdered and treated with concentrated ammonia (100 c.c.) in a mortar, when the whole became colourless and the amino-base was deposited. This was collected, washed well with water, and dried. After three crystallisations from ligroin, it separated in colourless crystals which melted at 138°. The amino-base thus purified (10 g.) was dissolved by boiling with a solution of 8 g. of oxalic acid in 100 c.c. of water, when a blue solution was obtained, which was filtered. On cooling the filtrate, the small crystals of Malachite Green oxalate separated out. This was collected and recrystallised from water, when it separated in small scales and was used for next experiment without further purification.

Action of Sunlight on Malachite Green in the Air. The dye thus purified (2 g.) was ground in a mortar, spread in a Petri glass dish in a thin layer, covered with Vita-glass made by Tokyo Electric Company, and exposed to direct sunlight for about two months in autumn, when it was decomposed and changed into a dark brown powder. The product, amounting to 1.7 g., was extracted with ether and the ethereal solution was evaporated. The greenish crystals (0.54 g.) were recrystallised once from ether and then twice from dilute alcohol, from which they separated in faint, yellow crystals and melted at 90.5–91°. The melting point was unaltered by admixture with an authentic specimen of *p*-dimethylaminobenzophenone. Therefore, there can be no doubt that the substance, melting at 90.5–91°, is identical with *p*-dimethylaminobenzophenone.

For the identification of the above-mentioned substance, *p*-dimethylaminobenzophenone $(CH_3)_2NC_6H_4COC_6H_5$ was synthesised by a method described in the description of the German patent No. 41751. To a mixture of benzanilide (10 g.) and dimethylaniline (20 g.), phosphorus oxychloride (10 g.) was added and the whole was heated gradually on a water-bath with vigorous stirring. After the reaction had ceased, the oily product, $C_6H_5C(:NC_6H_5)C_6H_4N(CH_3)_2$, was hydrolysed by heating with hydrochloric acid. After being recrystallised from dilute alcohol, it melted at 90–91°.

Action of Sunlight on Malachite Green in a Sealed Tube. Malachite Green (0.5 g.) was powdered, sealed in a tube of Vita-glass, and exposed to sunlight. After a month's exposure, the contents became pale and the pressure inside the tube increased greatly. The product was extracted with ether and the ethereal solution was evaporated. The residue amounted to 0.11 g. and nothing definite could be isolated from it, but its properties resembled leuco Malachite Green.

Purification of Crystal Violet. Crystal Violet (50 g.) was treated with a 10 per cent. solution of caustic soda (200 c.c.) and the precipitate was collected, washed

well with water, and dried. This was recrystallised three times from benzene, when it separated in colourless crystals, m.p. 194°. The pure hydroxy-base was changed into a coloured oxalate by boiling with an oxalic acid solution and it was purified further by recrystallisation from hot water.

Action of Sunlight on Crystal Violet in the Air. The oxalate (2 g.) was spread in a Petri dish, covered with a plate of Vita-glass, and exposed to sunlight for two months. The grey powder thus obtained was extracted with benzene and the benzene solution was evaporated, when blue crystals (1.18 g.) were obtained. They were dissolved in dilute hydrochloric acid and filtered. The filtrate was treated with ammonia. The precipitate thus obtained was collected, washed, and dried. The yield was 0.93 g. It was recrystallised from alcohol, when it separated in yellow crystals melting at 173–174°. No lowering of the melting point was caused by admixture with the synthetic specimen of Michler's ketone, m.p. 173–174°.

Action of Sunlight on Crystal Violet in a Sealed Tube. The coloured oxalate (1 g.) was sealed in a tube of thin Vita-glass and exposed to sunlight for a month. The product was extracted with benzene and, after evaporating off the benzene from the solution, the residue (0.26 g.) was recrystallised three times from alcohol, from which it separated in almost colourless scales melting at 172–173°. For the sake of comparison, leuco Crystal Violet was prepared by the reduction of Crystal Violet and it melted at the same temperature as the decomposition product. The melting point was not depressed when mixed with pure leuco Crystal Violet.

Laboratory of Dye-Chemistry,
Kiriu Higher Technical School.

THE CONSTITUTION OF THE DIHYDROXY-DERIVATIVE OF DIPHENYLENE OXIDE OBTAINED FROM RESORCINOL.

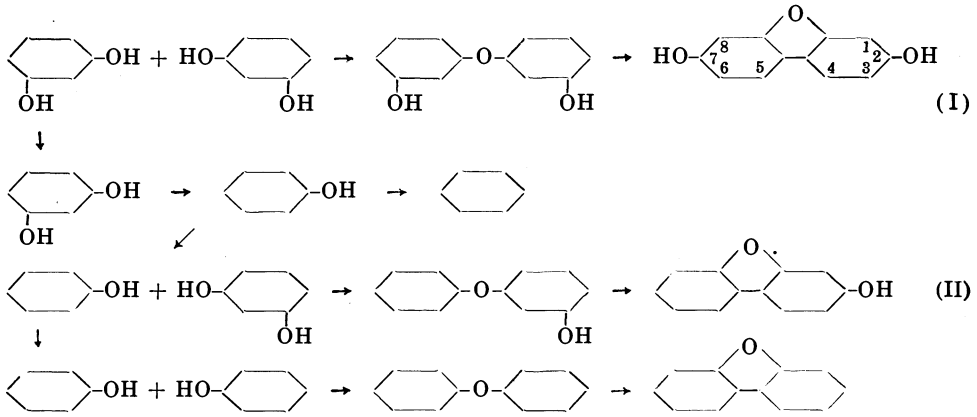
By **Kazuo HATA, Kiyoharu TATEMATSU,** and **Bennosuke KUBOTA.**

Received May 31st, 1935. Published September 28th, 1935.

It was previously reported[1] that resorcinol vapour, being passed over the blue oxide of tungsten at 500–550°, undergoes a certain reduction and condensation, and gives two substances besides benzene, phenol

(1) B. Kubota, Y. Fujimura, and K. Akashi, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **2** (1925), 185; Y. Tsuzuki, *ibid.*, **6** (1927), 301.

and diphenylene oxide. These two substances, one melting at 138–138.5° and the other at 241–242°, were supposed to be monohydroxy- and dihydroxy-derivatives of diphenylene oxide respectively. In the preceding report,[2] we decided that the substance melting at 138–138.5° is 2-hydroxy-diphenylene oxide(II) by synthesizing it from 2-amino-diphenylene oxide, and considered that the substance melting at 241–242° is most probably 2,7-dihydroxy-diphenylene oxide(I). The mechanism of the reactions giving these compounds by the catalytic action of the blue oxide of tungsten, was assumed to be represented by the scheme shown below:



With the view of ascertaining the constitution of the substance melting at 241–242° we have synthesized 2,7-dihydroxy-diphenylene oxide from *p*-anisidine, and compared it with dihydroxy-diphenylene oxide obtained from resorcinol by the catalytic reaction.

The 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine melts at 241–241.5°, and when it is mixed with the substance melting at 241–242° obtained from resorcinol, no depression of melting point can be recognized. The melting points of dimethyl derivatives of these compounds, one obtained by synthesis and the other by catalytic reaction, also coincide with each other. The melting points of these compounds are compared in Table 1.

It can be consequently decided that the substance melting at 241–242°, obtained from resorcinol, is nothing but 2,7-dihydroxy-diphenylene oxide, and that, as we have expected, the reaction follows the process represented by the scheme shown above to produce (I).

(2) K. Tatematsu and B. Kubota, This Bulletin, **9** (1934), 448.

Table 1. Comparison of the Melting Points.

Substance	From resorcinol	From *p*-anisidine	Mixed m.p.
Dihydroxy-diphenylene oxide	241–242°	241–241.5°	241–242°
Dimethoxy-diphenylene oxide	150°(3)	150°	—

Moreover, the ferric chloride reaction and the absorption curve of the synthesized 2,7-dihydroxy-diphenylene oxide quite coincide with those of the dihydroxy-diphenylene oxide obtained from resorcinol, indicating that these two substances are undoubtedly identical.

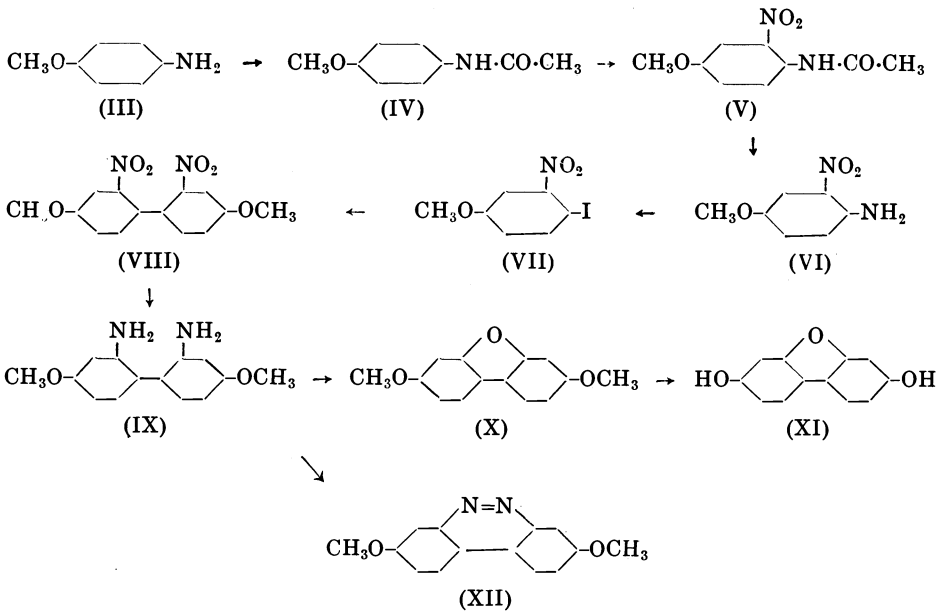
The absorption curve of 2,7-dihydroxy-diphenylene oxide, as shown by the figure in the experimental part, has a remarkable resemblance in form to those of diphenylene oxide and previously synthesized 2-hydroxy-diphenylene oxide. Further, the hydroxyl-groups having bathochromic influence on the absorption spectra, the absorption band is transferred to long wave in proportion to the number of substituted hydroxyl groups.

From these facts we can assert that the dihydroxy-diphenylene oxide melting at 241–242° obtained by the catalytic dehydration and condensation from resorcinol, has the constitution of (I) in the scheme shown above.

2,7-Dihydroxy-diphenylene oxide was synthesized as follows: *p*-anisidine (III) was changed into *p*-acetanisidide (IV) by acetylation, and after a nitro-group was introduced with nitric acid, nitro-*p*-anisidine was obtained by deacetylation,(4) which was already confirmed by H. Hähle(5) to be *o*-nitro-*p*-anisidine (VI). It was converted into *m*-nitro-*p*-iodo-anisol (VII) by the diazo-reaction, which was condensed to 2,2′-dinitro-4,4′-dimethoxy-diphenyl (VIII) with copper bronze by means of F. Ullmann's method.(6) Then it was reduced with stannous chloride and hydrochloric acid to 2,2′-diamino-4,4′-dimethoxy-diphenyl (IX). Applying E. Täuber's method of diphenylene oxide synthesis,(7) this amine was diazotized and the resulted diazonium solution was dropped into boiling copper sulphate solution, when a condensation took place giving

(3) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **6** (1927), 305.
(4) F. Reverdin, *Ber.*, **29** (1896), 2595.
(5) H. Hähle, *J. prakt. Chem.* [2], **43** (1891), 66, 67.
(6) F. Ullmann and J. Bielecki, *Ber.*, **34** (1901), 2174.
(7) E. Täuber and E. Halberstadt, *Ber.*, **25** (1892), 2745.

2,7-dimethoxy-diphenylene oxide(X). Now, by the action of hydroiodic acid, the methyl groups were removed and 2,7-dihydroxy-diphenylene oxide(XI) was obtained.

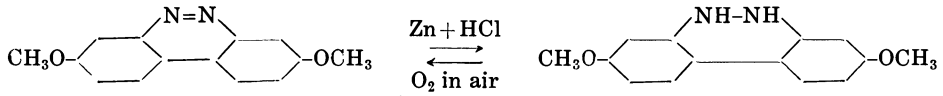


On cooling the mother liquor, from which 2,7-dimethoxy-diphenylene oxide was distilled off with steam, a new substance melting at 197° was obtained. By the investigation of its properties it was found to be 2,7-dimethoxy-phenazone(XII).

This substance separated out in dark yellow needles from water. It turned reddish brown with dilute acid, and again dark yellow when the solution was made alkaline. These colour changes were probably due to the formation and hydrolysis of phenazone salt, phenazone being a weak base. 2,7-Dimethoxy-phenazone was heated with 8% hydrochloric acid to an orange-red solution. On adding zinc dust, the solution immediately turned pale yellow, and subsequently almost colourless; it was supposed that 2,7-dimethoxy-phenazone was reduced to 2,7-dimethoxy-9,10-dihydrophenazone, similarly as phenazone was to dihydrophenazone,[8] and that the elimination of the azo group led to the decoloration. The dihydro-compound, however, was so unstable that, by removing the reducing agent, the decolourized solution soon became yellow; that is, 2,7-

(8) E. Täuber, *Ber.*, **24** (1891), 3086.

dimethoxy-phenazone was supposed to be reproduced by oxidation with air.



Now, J. J. Dobbie and his co-workers[9] reported that, main products of the reaction between the diazonium bromide of 2,2′-diamino-diphenyl and cuprous bromide, were phenazone and carbazole, while only trace of 2,2′-dibromo-diphenyl was obtained. Thereupon, it can be affirmed by this that the above-mentioned substance, melting at 197°, is 2,7-dimethoxy-phenazone. Further, it can be assumed that the black resinous matter which remained in the flask after the steam distillation, presumably contains some 2,7-dimethoxy-carbazole, but an attempt to extract this carbazole derivative was not especially made.

Experimental.

(1) **o-Nitro-*p*-anisidine.** (i) *p-Acetanisidide* (IV). *p*-Anisidine (25 g.) was warmed with water (30 c.c.) to form an emulsion, and acetic anhydride (20 c.c.) was added with stirring. The reaction took place at once with considerable heat evolution. After cooling, the yielded crystals were collected, and recrystallized from hot water, when colourless plates melting at 127.0–127.5° were obtained. (Yield 28 g.).

(ii) *o-Ntiro-p-acetanisidide* (V). According to F. Reverdin,[10] *p*-acetanisidide (38 g.) was mixed with 150 c.c. of 11% nitric acid, and the mixture was gradually heated to boiling. Heating was interrupted when the mixture about began to boil, and boiling continued for a while by the reaction heat. When the reaction mixture was left to cool, brown oil separated out which solidified to crystalline mass after cooling, and at the same time, some yellow needles separated out in the liquid. These were collected together, and recrystallized from water over again, yellow needles melting at 117°. (Yield 19 g.).

(iii) *o-Nitro-p-anisidine* (VI). *o*-Nitro-*p*-acetanisidide (19 g.) was heated with alcoholic potash (110 c.c.) on the water-bath under a reflux condenser. The saponification was completed after one hour. Then the solution was concentrated to about 30 c.c. and a sufficient quantity of water (50 c.c.) was added. Brilliant red crystals separated out at once, these were collected after cooling, and recrystallized from dilute alcohol to obtain red plates melting at 122.5–123.0° (Yield 14.5 g.).

(2) ***m*-Nitro-*p*-iodo-anisol** (VII). *o*-Nitro-*p*-anisidine (13.5 g.) was converted into its sulphate by heating with dilute sulphuric acid (200 c.c. of water and 9.2 c.c. of conc. sulphuric acid). Some insoluble matter was filtered off while still hot, and much quantity of sulphate separated out from the filtrate after cooling. The sulphate

(9) J. J. Dobbie, J. J. Fox, and A. J. Hoffmeister Gauge, *J. Chem. Soc.*, **99** (1911), 1615.

(10) F. Reverdin, *loc. cit.*

was collected, and the mother liquor was boiled with the previous insoluble matter to obtain more sulphate. This procedure was repeated again and again, and all the amine was converted into its sulphate. Then the sulphate was cooled below 10° together with the last mother liquor, and the solution of sodium nitrite (6.5 g. in 20 c.c. of water) was added drop by drop. Being kept for two hours, all the sulphate was diazotized to form yellow solution. It was cooled below 10°, and the potassium iodide solution (20 g. potassium iodide dissolved in 20 c.c. of water) was added drop by drop, when at once nitrogen gas was evolved vigorously, the reaction liquid turning deep black and giving iodine odour. After a while black oil separated out which solidified to a crystalline mass as it was cooled. It was allowed to stand overnight at ordinary temperature, then the black crystals were collected and washed with sodium thiosulphate solution again and again, when the black colour of iodine was easily removed and yellow crystals were obtained. After washed with 5% caustic soda solution and water, they were recrystallized from alcohol, yellow prisms[11] melting at 62°. (Yield 17.5 g.).

(3) **2,2′-Dinitro-4,4′-dimethoxy-diphenyl** (VIII). *m*-Nitro-*p*-iodo-anisol (9 g.) was thoroughly mixed with copper bronze (6 g.) in a large test tube, and heated in an oil-bath with incessant stirring. When the bath-temperature reached 130°, the viscosity of the reaction liquid suddenly increased, and copper lost its lustre to turn green-tinged white, owing to the formation of copper iodide. After being kept at 130–140° for half an hour, the temperature was raised to 160–170°, and the condensation was completed by keeping at this temperature for another half an hour. After cooling the reaction product was extracted with benzene over and over again, till benzene was no more tinged yellow. All the extracts were combined and the solvent was distilled off, when yellow crystals were obtained. They were recrystallized from benzene, yellow plates[12] melting at 136–137°. (Yield 4.0 g. Found: C, 55.70, 55.14; H, 4.32, 4.24; N, 9.28%; Mol. wt. (K. Rast), 305. Calc. for $C_{14}H_{12}N_2O_6$: C, 55.24; H, 3.98; N, 9.21%; Mol. wt., 304.)

(4) **2,2′-Diamino-4,4′-dimethoxy-diphenyl** (IX). 2,2′-Dinitro-4,4′-dimethoxy-diphenyl (5.7 g.) was dissolved in a solution of stannous chloride (60 g.) in glacial acetic acid (200 c.c.) saturated with hydrogen chloride, and after being allowed to stand overnight at room temperature, this solution was heated on the water-bath for an hour. By adding an excess (2000 c.c.) of 10% caustic soda solution, the amino compound separated out in fine crystals. It was collected and dissolved in dilute hydrochlorid acid, and purified by reprecipitation with 5% caustic soda solution after insoluble impurities were filtered off. Further, it was recrystallized from dilute alcohol when it separated out in colourless plates melting at 110.5–111.0°. (Yield 3.0 g. Found: C, 68.87; H, 6.90; N, 11.32%; Mol. wt. (K. Rast), 246. Calc. for $C_{14}H_{10}N_2O_2$: C, 68.81; H, 6.60; N, 11.48%; Mol. wt., 244.)

(5) **2,7-Dimethoxy-diphenylene oxide** (X). 2,2′-Diamino-4,4′-dimethoxy-diphenyl (1.2 g.) was dissolved in dilute hydrochloric acid (100 c.c. of water and 5 c.c. of conc. hydrochloric acid) to obtain its hydrochloride. The solution was cooled with ice,

(11) F. Reverdin described *m*-nitro-*p*-iodo-anisol as red needles melting at 62°, recrystallized from benzine or alcohol (*Ber.*, **29** (1896), 2595).

(12) This substance turns orange-yellow, when it is exposed to light for a long time.

and was diazotized by dropping sodium nitrite solution (0.7 g. sodium nitrite in 5 c.c. of water) with stirring. After being kept for two hours below 5°, the diazonium solution was gradually added drop by drop to a boiling 50% copper sulphate solution (60 g. copper sulphate in 60 c.c. of water), the latter being distilled during the addition so as to keep the volume of the solution in the flask constant.[13] Together with the distilled water, colourless crystals separated out in the condenser and receiver. After all the diazonium solution was added, the distillation was continued with the addition of water, still keeping the concentration of copper sulphate constant, until no more crystals distilled. The crystalline substance in the receiver was collected, and the condenser was washed with alcohol. After the alcoholic solution was evaporated to a small volume, a white crystalline precipitate was obtained by adding water. The products were together recrystallized from dilute alcohol, when the substance separated out in small white plates melting at 150°. (Yield 0.05 g. Found: C, 73.89; H, 5. 58%; Mol. wt. (K. Rast), 230. Calc. for $C_{14}H_{12}O_3$: C, 73.65; H, 5.30%; Mol. wt., 228.).

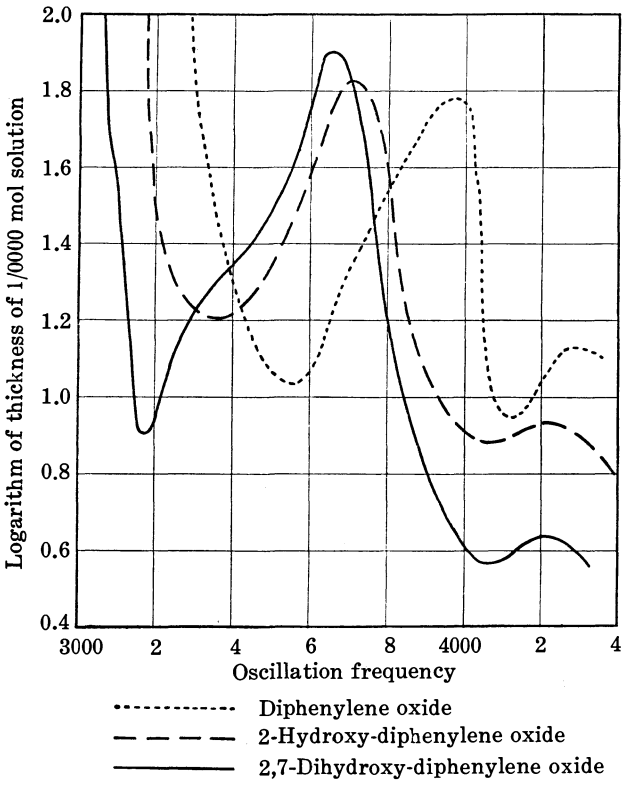
(6) **2,7-Dimethoxy-phenazone** (XII). After 2,7-dimethoxy-diphenylene oxide was thoroughly distilled off with steam, much quantity of black resinous matter in the flask was filtered off from the mother liquor while still hot. From the filtrate reddish brown needles separated out when it was cooled. It was dissolved in hot water, treated with animal charcoal, twice recrystallized from water, and dark yellow needles melting at 197° were obtained. (Yield 0.3 g. Found: N, 11.46%; Mol. wt. (K. Rast), 245. Calc. for $C_{14}H_{12}N_2O_2$: N, 11.67%; Mol. wt., 240.).

(7) **2,7-Dihydroxy-diphenylene oxide** (XI). 2,7-Dimethoxy-diphenylene oxide (50 mg.) was heated with 5 c.c. of hydroiodic acid ($d = 1.7$) in a sulphuric acid bath under a reflux condenser. After boiling for an hour and a half, it was left to cool after adding 10 c.c. of water, when white crystals separated out. They were collected and dissolved in dilute caustic potash solution, and reprecipitated with hydrochloric acid. Then the substance was recrystallized from hot water, some animal charcoal being used, colourless prisms melting at 241–241.5°. (Yield 12 mg.). On being dehydrated in Abderhalden's desiccating apparatus over P_2O_5 at 100° under a diminished pressure, 5.770 mg. of the substance lost 0.246 mg. of water. (Found: H_2O, 4.26. Calc. for $C_{12}H_9O_3 \cdot \frac{1}{2}H_2O$: H_2O, 4.31%.) Analysis and molecular weight determination were made with the anhydrous substance. (Found: C, 72.04; H, 4.35%; Mol. wt. (K. Rast), 204. Calc. for $C_{12}H_8O_3$: C, 71.98; H, 4.03%; Mol. wt., 200.)

2,7-Dihydroxy-diphenylene oxide thus obtained is soluble in alcohol, ether, and hot water, but scarcely soluble in cold water. When it is recrystallized from hot water, it separates out in white prisms, but being exposed to light for a long time it is gradually tinged with faint brown colour. On being heated it becomes almost colourless at 100° and melts at 241–241.5°. On adding a drop of ferric chloride solution to a solution of the substance, made by dissolving it in a very small quantity of alcohol and then adding water till the solution just begins to become turbid, it gives a green colour turning to a light brown on the addition of sodium carbonate solution.

These properties of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine, are perfectly coincident with those of dihydroxy-diphenylene oxide obtained from

(13) D. R. P., 167211.



resorcinol.[14] Moreover, no depression was observed in the mixed melting point of these two substances, indicating the identity of them.

Absorption curves. The absorption curve of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine was observed, and at the same time those of dihydroxy-diphenylene oxide obtained from resorcinol and 2-hydroxy-diphenylene oxide obtained from 2-amino-diphenylene oxide were also observed afresh. The results of their comparative study are shown in the figure, where the absorption curve of dihydroxy-diphenylene oxide obtained from resorcinol is not especially drawn as it is superposed on that of 2,7-dihydroxy-diphenylene oxide obtained from *p*-anisidine. All the observations of absorption spectra were made in a 1/10000 mol alcoholic solution.

As already pointed out, these curves strikingly resemble in form to that of diphenylene oxide,[15] suggesting that the substances melting at 138–138.5° and 241–242° obtained from resorcinol are derivatives of diphenylene oxide. It is remarkable that the absorption band removes to long wave with the increase of substituted hydroxyl groups, which have a bathochromic effect upon the absorption spectra.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(14) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Research, Japan*, **6** (1927), 304. 304.

(15) Y. Tsuzuki, *loc. cit.* K. Tatematsu and B. Kubota, *loc. cit.*

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. VII. THE SEPARATION OF HIGHLY UNSATURATED C_{22}-ACIDS.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received June 3rd, 1935. Published September 28th, 1935.

As stated in the first report[1] of this series, the highly unsaturated acids of sardine oil contain clupanodonic acid $C_{22}H_{34}O_2$ as a most important constituent. It was first separated by Tsujimoto. Regarding its constitution there have been appeared the studies of the same author and also of Inoue and Sahashi, which will be mentioned in a succeeding paper. This acid appears to be of common occurrence in marine animal oils as an important constituent of highly unsaturated acids, since it has hitherto been found in various kinds of marine animal oils besides sardine oil. Tsujimoto and his co-workers[2] found the same acid in giebel oil, in the liver oil from *Stereolepis ischinagi,* in eel oil, cod liver oil and herring roe oil. According to Ueno and Iwai,[3] the menuke oil and the liver oil from *Scoliodon laticaudes* contain clupanodonic acid. We[4] found clupanodonic acid in several kinds of whale oils (oils from the whales belonging to Mysticete), cod liver oil, sperm oil, pilot-whale oil, and in several kinds of the liver oils from Elasmobranch fish. The majority of the oils examined by us seemed to contain, in addition to clupanodonic acid, an acid $C_{22}H_{36}O_2$, whilst there were indications of the presence of a more highly unsaturated acid $C_{22}H_{32}O_2$ in the liver oils from Elasmobranch fish. Suzuki and his co-workers[5] stated, in their studies on glycerides constituents, the separation of some glycerides containing clupanodonic acid as a fatty acid component from a number of marine animal oils, and also a glyceride containing an acid $C_{22}H_{36}O_2$ from

(1) This Bulletin, **4** (1929), 83.

(2) Tsujimoto, *Report of the Tokyo Imperial Industrial Research Laboratory,* **18** (1923), No. 2; *ibid.,* **24**(1929), No. 4; *ibid.,* **26** (1931), No. 10; Tsujimoto and Koyanagi, *ibid.,* **25** (1930), No. 4; Tsujimoto and Kimura, *J. Soc. Chem. Ind., Japan,* **26** (1923), 1162.

(3) *J. Soc. Chem. Ind., Japan,* **37** (1934), 121, 562.

(4) Toyama, *J. Soc. Chem. Ind., Japan,* **28** (1925), 95, 104; *ibid.,* **29** (1926), 531, 538, 624; *ibid.,* **30** (1927), 519; Toyama and Tsuchiya, *ibid.,* **28** (1925), 966; *ibid.,* **30** (1927), 63, 116, 207; Toyama, *Report of the Tokyo Imperial Industrial Research Laboratory,* **27** (1932), No. 2.

(5) *Proc. Imp. Acad. Japan,* **5** (1929), 265, 269.

sardine and herring oils. Brown and Beal[6] found clupanodonic acid and an acid $C_{22}H_{32}O_2$ among the highly unsaturated C_{22}-acids in menhaden, cod liver, herring, salmon and sardine oils. Recent investigations by Ono,[7] Okada,[8] and Tomiyama[9] showed clupanodonic acid to be a constituent of the oil obtained from the egg of *Squalus sucklii* and the tunny body and liver oils. Although the conclusions set forth by some of the above-mentioned authors appear not to have been supported by a sufficient experimental evidence, and although the constituents of the highly unsaturated acids are not alike, depending on the kinds of marine animal oils, it seems as a whole that sardine oil and other marine animal oils contain clupanodonic acid and some other acids, such as $C_{22}H_{32}O_2$ and $C_{22}H_{36}O_2$, as highly unsaturated C_{22}-acids. The acid $C_{22}H_{36}O_2$ has been reported to occur also in alligator oil,[10] badger fat,[11] ox liver fat,[12] and algae oil,[13] besides the marine animal oils.

The following two methods have hitherto been employed for the separation of clupanodonic acid from the marine animal oils:

(1) Bromination of the mixed fatty acids of marine animal oils and the separation of the ether-insoluble bromides give the highly unsaturated acids on subsequent debromination. Methyl esters of these acids are then fractionally distilled and a fraction corresponding to methyl clupanodonate is collected separately.

(2) A concentrated fraction of highly unsaturated acids is first prepared by means of the lithium-soap-acetone method or the sodium-soap-acetone method. This is then converted into methyl esters and the latter subjected to a fractional distillation, by which a fraction corresponding to methyl clupanodonate is collected separately.

These methods will give a good result, indeed, provided that the highly unsaturated C_{22}-acids consist almost entirely of clupanodonic acid, but when clupanodonic acid is present in association with some other highly unsaturated C_{22}-acids, such as $C_{22}H_{32}O_2$ and $C_{22}H_{36}O_2$, it seems quite difficult to separate them into individual constituents by a single application of the above methods; consequently the highly unsaturated

(6) *J. Am. Chem. Soc.*, **45** (1923), 1289.
(7) *J. Agr. Chem. Soc. Japan*, **8** (1932), 788.
(8) *Journal of the Imperial Fisheries Institute*, **28** (1932), 105.
(9) *Bulletin of the Japanese Society of Scientific Fisheries*, **2** (1933), No. 1.
(10) Kobayashi, *J. Soc. Chem. Ind., Japan*, **25** (1922), 691.
(11) Ueno and Kuzei, *J. Soc. Chem. Ind., Japan*, **29** (1926), 525.
(12) Kimura, *J. Soc. Chem. Ind., Japan*, **28** (1925), 1366.
(13) Tsujimoto, *J. Soc. Chem. Ind., Japan*, **28** (1925), 386.

C_{22}-acid which was prepared by the above methods as a clupanodonic acid can not be taken as proved to be a chemical individual. The analytical constants of additive character, such as elementary composition, neutralisation value, iodine value, alone do not furnish a criterion for the purity of the clupanodonic acid prepared by the above methods, since there may be a possibility that a mixture containing the acids $C_{22}H_{32}O_2$ and $C_{22}H_{36}O_2$ together with clupanodonic acid may show the analytical constants which agree with or, at any rate, do not deviate widely from the calculated values for clupanodonic acid. Under these considerations, we have first separated in these experiments the highly unsaturated C_{22}-acids by means of the sodium-soap-acetone method and the fractional distillation of the methyl esters, then we have subjected the highly unsaturated C_{22}-acids to a further separative method in order to effect a separation into the portions having different degrees of unsaturation. For this purpose the sodium-soap-acetone method was modified; i.e., the highly unsaturated acids were separated into more highly and less highly unsaturated portions by dissolving in acetone, partially neutralising with sodium hydroxide solution, and fractionally precipitating the sodium soaps, the amount of water and alcohol in the solvent (acetone) being made extremely small. Each portion was treated again in a similar way to effect a further separation, and after repeating this separative operation many times, we have succeeded in separating clupanodonic acid in a much purer state than was hitherto prepared. There was obtained also a fraction consisting mainly of an acid $C_{22}H_{32}O_2$ on the one hand, and a fraction having a lesser degree of unsaturation than clupanodonic acid on the other. The latter was, however, found to be contaminated with a small portion of cetoleic acid $C_{22}H_{42}O_2$ belonging to mono-ethylenic acid series. The presence of an acid $C_{22}H_{36}O_2$ could not be ascertained.

Experimental.

1. **Separation of Highly Unsaturated C_{22}-acids from Sardine Oil.** In the 4th report,[14] the methyl esters (8 kg.) of crude highly unsaturated acids were subjected to fractional distillation in order to separate the fraction consisting of the methyl esters of highly unsaturated C_{20}-acids. The higher fractions obtained thereby contained the methyl esters of highly unsaturated C_{22}-acids. At first, these fractions were worked up for the separation of highly unsaturated C_{22}-acids, but since they were found to contain some esters formed by intramolecular rearrangement, or intramolecular polymerisation, of highly unsaturated esters, further experiments on these fractions were discontinued, and another specimen of sardine oil was used as

(14) This Bulletin, **10** (1935), 241.

a starting material for the separation of highly unsaturated C_{22}-acids. Such intramolecular rearrangement, together with intermolecular polymerisation, is considered to take place during the fractional distillation when the temperature of the bath is too high.

The sardine oil used for this experiment was procured from Hokkaido and had d_4^{15} 0.9293, n_D^{15} 1.4818, acid value 2.2, saponification value 189.7, iodine value[15] 176.3, unsaponifiable matter 0.59%. The mixed fatty acids yielded 61.49% of ether-insoluble bromides.

This oil was first treated by the sodium-soap-acetone method in the following manner: 50 g. of oil was saponified with 75 c.c. of sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 100 c.c. of water and 200 c.c. of 95% alcohol. After saponification, the excess of sodium hydroxide was neutralised with an acetic acid solution prepared by mixing equal volumes of glacial acetic acid and water. Denoting the number of c.c. of acetic acid solution required for neutralisation by A, 880 c.c. of acetone and $(45-A)$ c.c. of water were added to the soap solution, and the precipitate of insoluble sodium soaps was filtered. The sodium soaps remaining in the filtrate were decomposed with hydrochloric acid to obtain the free fatty acids, which consisted mainly of highly unsaturated acids and had neutralisation value 181.9 and iodine value 311.5. The yield of these fatty acids was about 4 kg. from 10 kg. of sardine oil. These were converted into methyl esters (4 kg.) which on fractionation yielded the results given in Table 1.

Table 1.

Fraction	B.p./2 mm.	Saponif. value	Iodine value	Yield (g.)
(1)	Below 170°	191.6	190.2	610
(2)	170–180°	186.4	236.8	660
(3)	180–190°	177.6	283.3	653
(4)	190–200°	170.4	325.1	744
(5)	200–214°	163.4	365.4	1180
Residue and loss	—	—	—	153

The fraction (4) yielded, on refractionation, appreciable amounts of a fraction boiling over 200°/2 mm. The latter was united with the fraction (5) and subjected to a repeated fractionation, by which a fraction (394 g.) boiling at 207–212°/2 mm. was collected separately. It had d_4^{15} 0.9247, n_D^{15} 1.4959, saponif. value 162.4, iodine value 370.8. The free acids liberated from this methyl ester fraction had d_4^{15} 0.9397, n_D^{15} 1.5039, neutr. value 170.1, iodine value 386.2, and gave 129% of ether-insoluble bromides having Br-content 71.40%. Hydrogenation of the free acids yielded behenic acid which, after recrystallisation from 95% alcohol, had neutr. value 164.5 and melted at 80.5–81° alone or admixed with a pure specimen of behenic acid. Accordingly the free acids obtained above were proved to consist of C_{22}-acids. Their

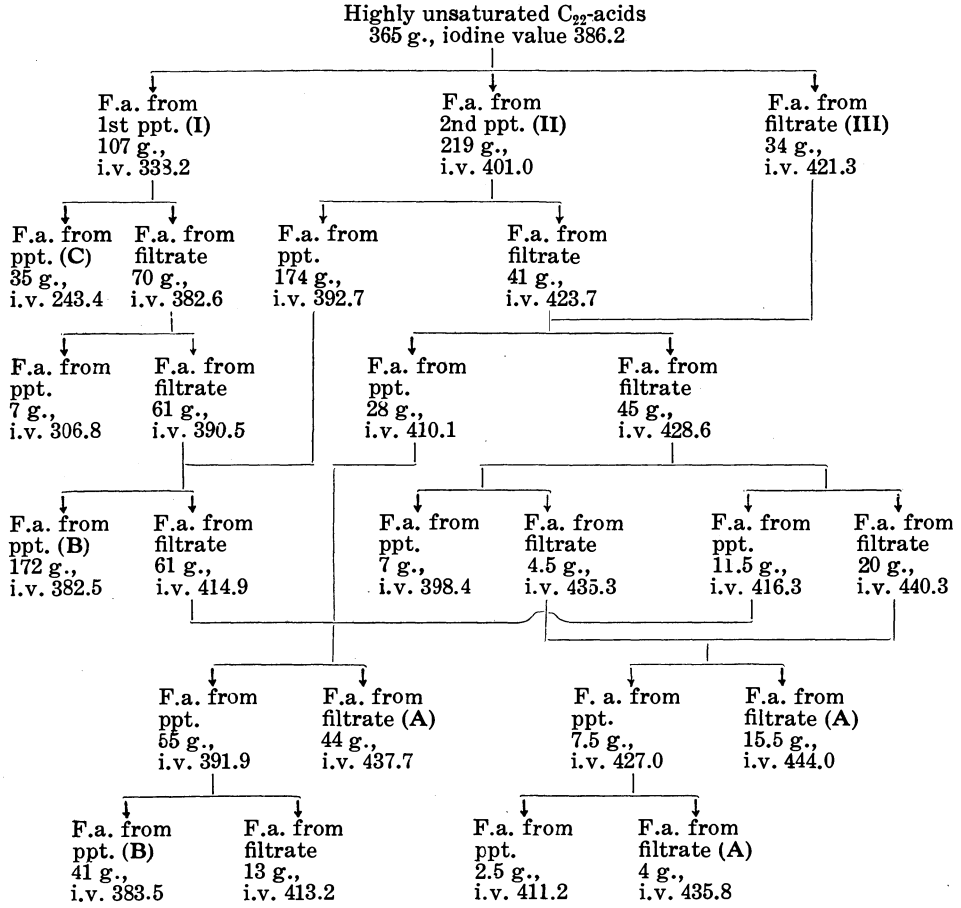
(15) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

iodine value is close to the calculated value (384.2) for clupanodonic acid $C_{22}H_{34}O_2$, but a further examination described below revealed that they contained, in addition to clupanodonic acid, an acid $C_{22}H_{32}O_2$ and some less unsaturated acids.

2. **Further Separation of Highly Unsaturated C_{22}-Acids by Means of Fractional Precipitation of their Sodium Soaps.** The highly unsaturated C_{22}-acids obtained above were separated into the fractions having different degrees of unsaturation in the following manner: 50 g. of the acids were dissolved in 1 l. of acetone and partially neutralised by using a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 100 c.c. of water and 200 c.c. of 95% alcohol. After the precipitate of sodium soaps was once brought into the solution by warming on the water-bath, the solution was allowed to cool to reprecipitate the insoluble sodium soaps which were collected, and on acidification there were obtained the fatty acids (I). The fatty acids remaining in the filtrate were once recovered and dissolved again in acetone, partially neutralised as before and the precipitated sodium soaps on acidification gave the fatty acids (II). The filtrate contained the fatty acids (III) of highest unsaturation which were recovered in the usual way. The fatty acids thus obtained (I, II, and III) were subjected to a further separation by dissolving in a little acetone, partially neutralising by using a portion of the sodium hydroxide solution prepared by dissolving 50 g. of sodium hydroxide in 50 c.c. of water and 100 c.c. of 95% alcohol, and adding more acetone so as to precipitate the insoluble sodium soaps. On decomposing the latter with hydrochloric acid, the fatty acids of comparatively low unsaturation were obtained, whereas the filtrate yielded the remaining fatty acids of highest unsaturation. For every 100 g. of the fatty acids, about 2 l. of acetone was used in most cases; but the quantity of acetone was somewhat changed depending upon the quantity of sodium hydroxide solution used for the partial neutralisation. In short, this method of separation is based upon the fact that the solubility of the sodium soaps of highly unsaturated acids in acetone containing water or alcohol increases with the degree of unsaturation of the highly unsaturated acids. Since the solubility of the sodium soap of a highly unsaturated acid decreases with the decrease in water or alcohol content in acetone and this effect is remarkably high, caution must be taken to determine the purity of acetone when the recovered acetone is used for this purpose. After repeating this separative operation, there were obtained the results given in Table 2.

3. **Separation of a Concentrated Fraction of Docosahexenoic Acid $C_{22}H_{32}O_2$.** It appears from the iodine values that the fractions (A) recorded in Table 2 contain a large amount of docosahexenoic acid $C_{22}H_{32}O_2$. These were combined, and subjected to a fractional precipitation of sodium soaps in acetone. The less unsaturated portion was removed as the precipitate of insoluble sodium soaps. The more unsaturated portion recovered from the filtrate was treated again as before in order to obtain the still more unsaturated portion by removing a further quantity of less unsaturated portion, and after this separative operation had been repeated several times, there was obtained finally a fatty acid fraction of the highest unsaturation which was deemed to consist largely of docosahexenoic acid together with a little clupanodonic acid. It had the following constants: d_4^{15} 0.9521, d_4^{20} 0.9486, n_D^{15} 1.5129, n_D^{20} 1.5109, neutralisation value 170.1, iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 456.0 and 440.8 respectively (calc. for $C_{22}H_{32}O_2$: neutr. value 170.9, iodine value 464.0), thiocyanogen value 225.7 (calc. for the formation of hexathiocyanate:

Table 2.

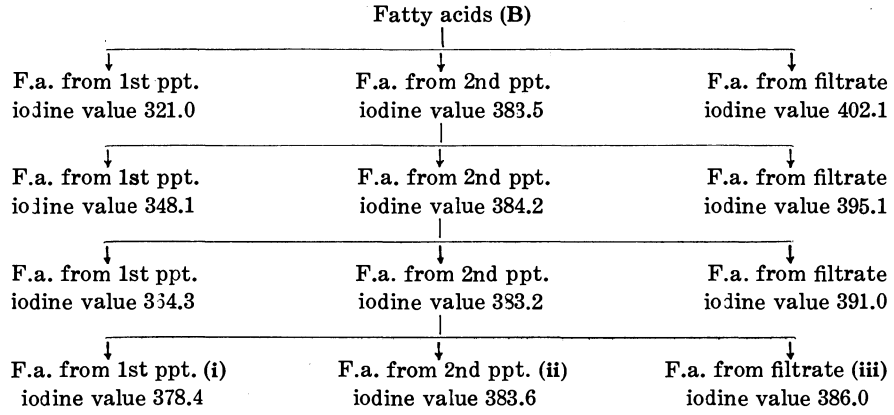


232.0). It yielded 177% of ether-insoluble bromide which turned black at about 240° without melting (Found: Br, 74.00. Calc. for $C_{22}H_{32}O_2Br_{12}$: Br. 74.50%).

4. **Separation of Clupanodonic Acid** $C_{22}H_{34}O_2$. The fatty acid fractions (B) in Table 2 were united and dissolved in acetone, and a small amount of the sodium hydroxide solution was added so as to precipitate a small portion of the fatty acids as insoluble sodium soaps which were filtered. The filtrate was then completely neutralised with the sodium hydroxide solution and the bulk of the fatty acids was precipitated as insoluble sodium soaps. The free fatty acids were isolated from the 1st and 2nd precipitates and also from the final filtrate in the usual way. The fatty acids obtained from the 1st precipitate showed comparatively low iodine value, whilst those obtained from the final filtrate showed the highest iodine value. The fatty acids obtained from the 2nd precipitate were treated again as before in order

to separate into three portions, and after repeating this separative operation, there were obtained the results shown in Table 3.

Table 3.



The iodine values of the fatty acid fractions (i, ii, and iii) obtained by the final separation do not differ much from one another, and the fatty acid fraction (ii) seems to consist largely of clupanodonic acid, the iodine value of which is 384.2.

The fatty acid fraction (ii) was converted into methyl ester and the latter was subjected to the fractional distillation by which a fraction boiling at 207–212°/2 mm. was collected as methyl clupanodonate. It had the following constants: d_4^{15} 0.9240, d_4^{20} 0.9205, n_D^{15} 1.4955, n_D^{20} 1,4934, molecular refraction 108.8 (calc. for $C_{23}H_{36}O_2$ ⌐5: 107.7), saponif. value 163.0 (calc. 163.0), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 368.0 and 353.9 respectively (calc. 368.6), thiocyanogen value 148.9 (calc. for the formation of tetrathiocyanate: 147.5).

Clupanodonic acid set free from the methyl ester showed d_4^{15} 0.9390, d_4^{20} 0.9356, n_D^{15} 1.5035, n_D^{20} 1.4934, molecular refraction 104.1 (calc. for $C_{22}H_{34}O_2$ ⌐5: 103.0), neutr. value 170.4 (calc. 169.8), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 383.2 and 366.3 respectively (calc. 384.2), thiocyanogen value 155.2 (calc. for the formation of tetrathiocyanate 153.7). It yielded 156% of ether-insoluble bromide which turned black at about 240° without melting (Found: Br, 70.88. Calc. for $C_{22}H_{34}O_2Br_{10}$: Br, 70.76%).

5. **Examination of the Comparatively Less Unsaturated Fraction.** The iodine value (243.4) of the fatty acid fraction (C) in Table 2 indicates that this fraction contains some less unsaturated fatty acids than clupanodonic acid. The fraction was separated into two portions by means of fractional precipitation of sodium soaps in acetone, the less unsaturated portion obtained from the precipitate of insoluble sodium soaps was subjected to a further separation, and after repeating this separative operation, there was obtained finally a fatty acid fraction (about 5 g., iodine value 109.9) from the precipitate of insoluble sodium soaps. On cooling the solution of this fraction in 80% alcohol, a crystalline solid separated; it had neutr. value 165.0, iodine value 74.9 and m.p. 32–32.5°, and it was identified as cetoleic acid (neutr. value

165.8, iodine value 75.0, and m.p. 32.5–33°) by the mixed melting point test. It was thus ascertained that the fraction (C) contained cetoleic acid, though in a minor amount. This indicated that when the sardine oil was first treated by the sodium-soap-acetone method, a small amount of cetoleic acid remained in the acetone solution, so that it entered into the concentrated fraction of highly unsaturated acids, and became concentrated in this fraction (C) by subsequent separative operations. The filtrates which came from the separative operations on the fraction (C) yielded the fatty acid fractions having iodine values 350.8, 304.4, and 205.7 respectively, but no individual acid could be isolated from these fractions. Should the sardine oil contain an acid $C_{22}H_{36}O_2$, it would enter into the fatty acid fraction (C), but its presence in the fraction (C) could not be ascertained by this experiment, though the absence of this acid should not be prematurely concluded.[16]

Summary.

A concentrated fraction of highly unsaturated acids has been separated from sardine oil by means of sodium-soap-acetone method. It was converted into methyl esters and the latter subjected to a fractional distillation which yielded a fraction consisting of the methyl esters of C_{22}-acids. This fraction and the free fatty acids liberated from it showed iodine values which were close to those of methyl clupanodonate and clupanodonic acid respectively, but on separating the fatty acids of this fraction by a fractional precipitation of sodium soap in acetone solution, they were found to contain, in addition to clupanodonic acid, some acids of different degrees of unsaturation. After a repeated separation, clupanodonic acid has been separated in much purer state than prepared hitherto, and also a more highly unsaturated portion consisting chiefly of docosahexenoic acid $C_{22}H_{32}O_2$ has been separated. There was obtained also a less unsaturated portion than clupanodonic acid; this was, however, found to be a mixture contaminated with cetoleic acid $C_{22}H_{42}O_2$, though in a minor amount. Docosatetraenoic acid $C_{22}H_{36}O_2$ was not separated, although this acid could not be altogether deemed to be absent.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

(16) In previous studies (*loc. cit.*) on the fatty acids constituents of various kinds of marine animal oils, we have inferred the presence of an acid $C_{22}H_{36}O_2$ from the fact that in the case of the majority of the oils examined, the highly unsaturated C_{22}-acids showed an iodine value somewhat lower than the calculated value for clupanodonic acid. However, taking the results of the present investigation into consideration, the low iodine values of the highly unsaturated C_{22}-acids obtained in the previous studies might have been due to the contamination of some less unsaturated acids, such as cetoleic acid $C_{22}H_{42}O_2$, and not to the presence of the acid $C_{22}H_{36}O_2$.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. VIII. THE CONSTITUTION OF CLUPANODONIC ACID $C_{22}H_{34}O_2$.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received June 8th, 1935. Published September 28th, 1935.

As described in the preceding paper, we have separated from sardine oil a mixture of highly unsaturated C_{22}-acids which was resolved further into the portions of different degrees of unsaturation in order to obtain clupanodonic acid $C_{22}H_{34}O_2$ in a much purer state than prepared heretofore and also a more highly unsaturated fraction consisting chiefly of docosahexenoic acid $C_{22}H_{32}O_2$. The present paper deals with the constitution of clupanodonic acid. The same subject has hitherto been studied by Tsujimoto[1] and also by Inoue and Sahashi.[2] On subjecting clupanodonic acid and its amyl ester to ozonolysis, Tsujimoto found propyl aldehyde, acetaldehyde, carbon dioxide together with comparatively large quantities of succinic acid, and also amyl hydrogen succinate in the case of amyl clupanodonate. Since acetaldehyde and carbon dioxide were considered to be formed by a further degradation of malonic aldehyde, the above results indicated that clupanodonic acid had the following groups: $CH_3{\cdot}CH_2{\cdot}CH=$, $=CH{\cdot}CH_2{\cdot}CH=$, $=CH{\cdot}(CH_2)_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}COOH$, of which it had three of the group $=CH{\cdot}(CH_2)_2{\cdot}CH=$. In regard to the respective positions of the groups $=CH{\cdot}CH_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}CH=$, he showed no experimental evidence, but he assumed clupanodonic acid to have one of the ethylenic linkings in the same position as cetoleic acid ($\Delta^{11:12}$-docosenoic acid) which is found to occur widely in marine animal oils, and ascribed to clupanodonic acid the following alternative formulae:

$CH_3{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}COOH$
or
$CH_3{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}COOH$.

By oxidation of clupanodonic acid with potassium permanganate in acetone, Inoue and Sahashi obtained butyric, pimelic, succinic, adipic,

(1) This Bulletin, **3** (1928), 299.
(2) *Proc. Imp. Acad. Japan*, **8** (1932), 371.

malonic and oxalic acids, of which adipic and oxalic acids were assumed to have been formed by the secondary decomposition of pimelic and malonic acids respectively, and taking the yields of these oxidation products into consideration, they concluded that clupanodonic acid yielded butyric, pimelic, succinic (2 mols) and malonic acids as scission products derived from the respective groups jointed by the unsaturated linkings. In order to determine in what order the respective groups are jointed, these authors subjected clupanodonic acid to a partial hydrogenation, separated the hydrogenation products into the fractions of different degrees of saturation and examined each fraction by the permanganate oxidation with the results given in Table 1.

Table 1.

Clupanodonic acid and its partially hydrogenated products	Oxidation products (acids)				
Clupanodonic acid	Butyric, (C_4)	Pimelic, (C_7)	Succinic, (C_4)	Malonic, (C_3)	Succinic (C_4)
Partially hydrogenated products					
Fraction which yields a hexabromide	Undecanoic, (C_{11})		Succinic, (C_4)	Malonic, (C_3)	Succinic (C_4)
Fraction which yields a tetrabromide	Pentadecanoic, (C_{15})			Malonic, (C_3)	Succinic (C_4)
Fraction which yields a dibromide	Stearic, (C_{18})				Succinic (C_4)

Based on these results Inoue and Sahashi ascribed to clupanodonic acid the following formula having one triple and three double linkings:

$$CH_3\cdot(CH_2)_2\cdot C\equiv C\cdot(CH_2)_5\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH.$$

It is to be noted that the samples of clupanodonic acid used in the experiments of Tsujimoto and the subsequent authors were prepared by means of the lithium-soap-acetone method and the fractional distillation of methyl esters without applying a further separative operation, consequently they must have been contaminated with some other acids of different degrees of unsaturation as pointed out in our previous report.

In this paper, the same sample of clupanodonic acid as described in the preceding paper was converted into the amyl ester, and the latter was subjected to ozonolysis. Among the products of ozonolysis, propyl aldehyde, acetaldehyde, carbon dioxide, succinic acid and amyl hydrogen

succinate were identified; the presence of some lower acids consisting possibly of propionic and acetic acids was also indicated. Of these compounds, propyl aldehyde is evidently derived from the group $CH_3 \cdot CH_2 \cdot CH=$, whilst acetaldehyde and carbon dioxide are attributable to the secondary decomposition of the product of ozonolysis derived from the group $=CH \cdot CH_2 \cdot CH=$. Succinic acid and amyl hydrogen succinate are derived from the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot COOC_5H_{11}$ respectively. Accordingly clupanodonic acid has the following groups: $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot COOH$, $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot CH_2 \cdot CH=$, of which it has three of the group $CH \cdot (CH_2)_2 \cdot CH=$, since it contains 22 carbon atoms in its molecule. These results, however, give no information regarding the respective positions of the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot CH_2 \cdot CH=$, and it requires a further examination to establish the constitution of clupanodonic acid. In the case of moroctic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$-octadecatetraenoic acid), we have determined the respective positions of the groups by preparing tetrathiocyanate (4,5,8,9-tetrathiocyanate) by the selective addition of thiocyanogen to methyl moroctate, and by examining this tetrathiocyanate by ozonolysis. We have, however, found by subsequent studies[3] on the partial bromination of the poly-ethylenic acids of known constitution, such as linoleic and linolenic acids, that the addition of bromine took place selectively at the specified ethylenic linkings of these poly-ethylenic acids; though such a selective addition did not proceed to a quantitative extent, the products of stepwise bromination contained in every case a definite bromide formed by the selective addition as the main constituent which could be separated by means of a suitable separative operation. After having found the above fact, we have applied this to clupanodonic acid, and determined the positions of the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot CH_2 \cdot CH=$ by examining the products of partial bromination of clupanodonic acid by ozonolysis. The results are summarized below. It deserves a special attention that whilst thiocyanogen added selectively to the two ethylenic linkings which existed near the carboxyl group of moroctic acid, bromine attacked preferentially the ethylenic linkings which were further removed from the carboxyl group of clupanodonic acid.[4]

---

(3) *J. Soc. Chem. Ind., Japan*, **38** (1935), 89.

(4) The same relation was observed in the case of linoleic and linolenic acids, viz., whilst thiocyanogen attacked selectively the 9:10-ethylenic linking of linoleic acid and also the 9:10- and the 12:13-ethylenic linkings of linolenic acid, bromine attacked preferentially the ethylenic linking which was the further removed from the carboxyl group. Cf. Toyama and Tsuchiya, *J. Soc. Chem. Ind., Japan*, **38** (1935), 86, 89.

(1) Dibromo-derivative $C_{22}H_{34}O_2Br_2$ obtained by the addition of 1 mol bromine to 1 mol clupanodonic acid yielded, as the products of ozonolysis, acetaldehyde, carbon dioxide, succinic acid and an oily bromo-compound which on debromination and subsequent hydrogenation gave heptoic acid, indicating that the oily bromo-compound obtained above consisted of dibromoheptoic acid. Since clupanodonic acid was shown to contain the group $CH_3 \cdot CH_2 \cdot CH=$ by the ozonolysis of amyl clupanodonate, it follows from the above results that it contains the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=$.

(2) Tetrabromo-derivative $C_{22}H_{34}O_2Br_4$ obtained by the addition of 2 mols bromine to 1 mol clupanodonic acid yielded, as the products of ozonolysis, succinic acid and an oily bromo-compound which on debromination and subsequent hydrogenation gave capric acid. This fact, coupled with the result obtained by the ozonolysis of dibromo-derivative, indicated the presence of the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2\ CH=$.

(3) Hexabromo-derivative $C_{22}H_{34}O_2Br_6$ was prepared by the addition of 3 mols bromine to 1 mol clupanodonic acid. Ozonolysis of this bromide yielded succinic acid and an oily bromo-compound, from which myristic acid was obtained by debromination followed by hydrogenation. Hence clupanodonic acid was found to contain the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=$.

From these results the constitution of clupanodonic acid was established as follows:

$$CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot COOH.$$

Comparing the results of our experiments with those obtained by Tsujimoto, they show a full agreement in that clupanodonic acid consists of the groups: $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot CH=$ (three), $=CH \cdot CH_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$. While Tsujimoto derived two of his formulæ by assuming that clupanodonic acid had one of its ethylenic linkings in the same position as that of cetoleic acid ($\Delta^{11:12}$-docosenoic acid), the result of our further research in order to determine the positions of the respective groups, however, indicated that the above assumption of Tsujimoto was not substantiated, since clupanodonic acid, unlike cetoleic acid, had no ethylenic linking in the 11:12-position. Consequently Tsujimoto's formula should be corrected. Comparing the formula given by Inoue and Sahashi with that established by us, they show much difference with the exception that both formulæ contain the group $=CH \cdot (CH_2)_2 \cdot COOH$ at the side of the carboxyl group. Particularly,

the former is incompatible with the latter in that it contains a C_4-group at the side of the methyl group and a C_7-group in the adjascent place, having a triple linking between these two groups. The reason why these discrepancies occur is unknown to us. According to the results given by these authors, not only clupanodonic acid itself but also its hydrogenated products having one to three ethylenic linkings yielded on oxidation only the compounds corresponding just to the formula given by these authors, but it is quite difficult to understand the formation of the oxidation products found by these authors, such as undecanoic, pentadecanoic and stearic acids with the use of our formula, unless displacements of the unsaturated linkings occur in the course of hydrogenation. Although the possibility is not excluded that the permanganate oxidation method, when applied to a highly unsaturated acid like clupanodonic acid, gives rise to abnormal oxidation products which differ in the number of carbon atoms from those obtained by the ozonide method, it is rather inconceivable that such abnormal decomposition takes place also in the hydrogenated products of clupanodonic acid having one to three unsaturated linkings when the permanganate oxidation method is applied. For it has been generally accepted that the permanganate method, when applied to mono-ethylenic acids, gives a result which is consistent with that obtainable by the ozonide method, and furthermore we have examined the constitution of hiragonic acid having three ethylenic linkings by the permanganate and the ozonide methods, and have found that the both methods gave consistent results. Hence the difference of the oxidation methods alone can not account for the marked discrepancies between the results obtained by these authors and those obtained by us.(5)

It is a very remarkable fact that, as it is seen from our studies hitherto reported, the highly unsaturated acids, not only clupanodonic acid but also eicosatetraenoic, moroctic and hiragonic acids, have no ethylenic linking in the same positions as the corresponding mono-ethylenic acids as shown in Table 2.

(5) After the experiments given in this paper had been completed, there appeared another paper by Inoue and Kato (*Proc. Imp. Acad. Japan*, **10** (1934), 463) in which they maintained their formula having a triple linking. Also Kino (*Bull. Inst. Phys. Chem. Research, Japan*, **13** (1934), 1065) touched upon the constitution of clupanodonic acid in his studies on the polymerisation of highly unsaturated acids.

Table 2.

Number of carbon atoms	Highly unsaturated acids		Mono-ethylenic acids	
22	Clupanodonic	4:5, 8:9, 12:13, 15:16, 19:20	Cetoleic	11:12
20	Eicosatetraenoic	4:5, 8:9, 12:13, 16:17	Gadoleic	9:10
18	Moroctic	4:5, 8:9, 12:13, 15:16	Oleic	9:10
16	Hiragonic	6:7, 10:11, 14:15	Zoomaric	9:10

Judging from the relations between the constitutions of linolenic, linoleic and oleic acids found in vegetable oils, it would seem that one of the ethylenic linkings in the highly unsaturated acids in marine animal oils should be located in the same position as those in the corresponding mono-ethylenic acids. No such relation was, however, found to exist in any of the four above-mentioned highly unsaturated acids in marine animal oils. This is of much interest in connection with the mechanism of the formation of unsaturated fatty acids in living organism.

Experimental.

1. **Ozonolysis of Amyl Clupanodonate.** The same sample of clupanodonic acid as described in the previous paper was used in these experiments. It had d_4^{15} 0.9390, n_D^{15} 1.5035, neutralisation value 170.4 (calc. 169.8), iodine value[6] 383.2 (calc. 384.2), and gave 156% of ether insoluble bromide having Br-content 70.88% (calc. for $C_{22}H_{34}O_2Br_{10}$: 70.76%). It was heated with an equal amount of amyl alcohol containing 2.5% of hydrogen chloride on the water-bath for 1 hour, and after removing the excess of amyl alcohol and some unchanged clupanodonic acid, the amyl clupanodonate was separated. This was dissolved in chloroform, 50 c.c. being used for 5 g. of amyl clupanodonate, cooled with ice-salt, and treated with ozonised oxygen until the solution became saturated with ozone. The solvent was distilled off, and the ozonide was obtained as a light yellow syrup. Since the ozonide was highly unstable and there was a danger of explosive decomposition on undue heating, the chloroform was not thoroughly distilled off, and consequently the ozonide obtained above retained some chloroform. The yield of ozonide thus obtained was 17 g. (170%) from 10 g. of amyl clupanodonate. The theoretical yields for normal ozonide $C_{27}H_{44}O_{17}$ and ozonide peroxide $C_{27}H_{44}O_{18}$ are 159.9 and 163.9% respectively. Water (100 c.c.) was added to the ozonide, and the liquid was heated in a flask on the water-bath for 30 minutes. The flask containing the ozonide was attached by a delivery tube to other three flasks (**a**, **b** and **c**) which were connected in succession, the first (**a**)

(6) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

being filled with ice-cold water, and the second (b) and the third (c) being filled with approximately 1/3 N solution of barium hydroxide. During the heating, a current of hydrogen was passed into the flask containing the ozonide, and the volatile substances (A) formed by the decomposition of ozonide were carried over with hydrogen into the three flasks (a, b and c) where they were absorbed by water and barium hydroxide solution in succession. The decomposition products remained in the initial flask partly separated as an insoluble oil (C) from the aqueous solution. The aqueous solution was saturated with sodium chloride, and extracted with 1 l. of ether which dissolved the decomposition products (B) contained in the aqueous solution. After distilling off ether from the ethereal solution, there remained the decomposition products (B) as a reddish orange liquid. The products of ozonolysis were thus separated into three portions (A, B and C).

(i) *Volatile products* (A). The aqueous solution in the flask (a) produced a pink colouration with Schiff's reagent, and a deep blue colouration with diethylamine and sodium nitroprusside, indicating the presence of acetaldehyde. The presence of propyl aldehyde was also indicated by the smell of scatol which was recognised by heating the phenylhydrazone, prepared from the aqueous solution in the flask (a), with zinc chloride to 180°. A partial separation of these two aldehydes was effected by heating the solution in the flask (a) at about 45° in a current of carbon dioxide. The flask was connected with another flask containing ice-cold water by a delivery tube, and the volatilised substances which were carried over with carbon dioxide were collected in the latter. By these treatments, the substances, dissolved in the aqueous solution in the flask (a) were separated into the portion (a_1) which did not volatilise at 45° and the portion (a_2) which volatilised at 45°. The *p*-nitrophenylhydrazone prepared from the portion (a_1) melted at 122.5–123° after recrystallisation from 50% alcohol; it was found to consist mainly of *p*-nitrophenylhydrazone of propyl aldehyde (Found: N, 21.82. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The same derivative prepared from the portion (a_2) melted at 116–117° after recrystallisation from 50% alcohol; it was considered to be a mixture of *p*-nitrophenylhydrazones of acetaldehyde and propyl aldehyde (Found: N, 22.97. Calc. for $C_8H_9O_2N_3$: N, 23.46. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The solution in the flask (a) showed also an acid reaction and produced a deep red colouration on adding ferric chloride after neutralisation, from which the presence of acetic acid was inferred.

The barium hydroxide solution in the flask (b) was found to contain a large amount of a white precipitate which was also found in the flask (c) in a small amount. This precipitate was found to be barium carbonate, indicating that carbon dioxide was formed by the ozonolysis of amyl clupanodonate. Calculating from the quantity of barium carbonate, the yield of carbon dioxide was found to be 0.81 g. or 8.1% of amyl clupanodonate used for ozonolysis. If amyl clupanodonate has the group $=CH\cdot CH_2\cdot CH=$ and the products of ozonolysis derived from this group undergo a secondary decomposition with the formation of carbon dioxide to a quantitative extent, the yield of carbon dioxide should be 10.99% of amyl clupanodonate.

(ii) *Products obtained from the aqueous solution* (B). Yield 7.7 g. These were boiled out three times with petroleum ether, using 50 c.c. each time. The portion which remained insoluble was a reddish orange liquid with little crystalline deposit at room temperature. Oxidation of this portion with an alkaline solution of potassium permanganate and subsequent acidification yielded a product consisting

largely of a crystalline solid. This was spread on a sheet of filter paper in order to remove the liquid portion by means of absorption, and the remaining solid gave, after being washed with a little cold ether and then recrystallised from ethyl acetate, succinic acid which had neutralisation value 947.6 (calc. for $C_4H_6O_4$: 950.6) and melted at 182–183°, both alone and after admixture with a pure specimen of succinic acid. On removing the solvent from the petroleum ether extract, there remained a reddish orange liquid which on distillation gave 0.5 g. of a colourless distillate at 120–180° of the bath-temperature. The distillate thus obtained showed an acid reaction, and the silver salts prepared from it were found to be a mixture of silver acetate and silver propionate by analyses (Found for 1st crop of silver salt: Ag, 61.31. Found for 2nd crop of silver salt: Ag, 63.25. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

(iii) *Oily substances* (C). Yield 3.7 g. Oxidation of these substances with alkaline permanganate followed by acidification yielded an acid ester which had neutr. value 308.1 and saponif. value 595.5 and was deemed to consist mainly of amyl hydrogen succinate (calc. for $C_9H_{16}O_4$: neutr. value 298.2, saponif. value 596.5). The free acid liberated from this acid ester in the usual way yielded, after recrystallisation from ethyl acetate, a pure succinic acid having neutr. value 948.0, m.p. and mixed m.p. 182–183°.

2. **Ozonolysis of Dibromo-derivative of Clupanodonic Acid.** For the preparation of the dibromo-derivative of clupanodonic acid, 15 g. of the acid was dissolved in 150 c.c. of ether, cooled with ice-salt, and the bromine solution prepared by dissolving 7.5 g. (calc. for the formation of dibromo-derivative: 7.26 g.) of bromine in 15 c.c. of glacial acetic acid was gradually added with constant stirring. After all the bromine solution has been added, the ethereal solution was allowed to stand for 2 hours. No insoluble bromide separated. The ethereal solution was washed with water, then dehydrated, and on distilling off the ether, there remained 22 g. of oily bromides. These were dissolved in 10 volumes of alcohol, and fractionally precipitated by adding a little water in each time. The yield and the iodine value of each precipitate are given in Table 3.

Table 3.

Precipitate	Yield (g.)	Iodine value
1st ppt.	1.5	120.7
2nd ppt.	12	209.2
3rd ppt.	3	209.8
Bromide remaining in the final filtrate	4	230.5

The 2nd and 3rd precipitates were united and dissolved in alcohol, and after fractional precipitation as before, the dibromo-derivative was finally obtained as an oily substance which showed iodine value 208.7 (calc. for $C_{22}H_{34}O_2Br_2$: 207.2). The dibromide (10.5 g.) thus obtained was ozonised in a chloroform solution. The resulting ozonide was decomposed by heating with water in the usual way. The volatile decomposition products (A) formed were passed through the water in the flask (a) and then through the barium hydroxide solution in the two flasks (b and c) in succession. The decomposition products, which did not volatilise, partly dissolved

in water and oily substances (C) separated under the aqueous layer. The latter was thoroughly extracted with ether, and the ethereal extract yielded, on distilling off the ether, the decomposition products (B) initially dissolved in water.

(i) *Volatile decomposition products* (A). The aqueous solution in the flask (a) gives a deep blue colouration with diethylamine and sodium nitroprusside, indicating the presence of acetaldehyde. The *p*-nitrophenylhydrazone prepared from this solution yielded, after recrystallisation from 50% alcohol, yellow needles melting at 123–124°, which appeared to consist mainly of the *p*-nitrophenylhydrazone of acetaldehyde, since the melting point was not lowered on admixture with a pure specimen (m.p. 128°) of the latter in various proportions (Found: N, 23.17. Calc. for $C_8H_9O_2N_3$: N, 23.46%). A somewhat lower melting point compared with the pure specimen is to be attributed to the contamination with a minor amount of other ingredient, possibly *p*-nitrophenylhydrazone of propyl aldehyde. Hence the dibromo-derivative used for ozonolysis was likely not to be an individual compound in a state of purity; it contained, besides the main constituent which yielded acetaldehyde on ozonolysis, a minor amount of the bromo-derivative which yielded other aldehyde, such as propyl aldehyde, on ozonolysis.

The barium hydroxide solution in the flasks (b) and (c) was found to contain a precipitate of barium carbonate indicating the formation of carbon dioxide by ozonolysis. Calculating from the quantity of barium carbonate, the yield of carbon dioxide was found to be 6.6% of the dibromo-derivative used for ozonolysis. Assuming that the dibromo-derivative has one of the group $=CH\cdot CH_2\cdot CH=$, and carbon dioxide is formed to a quantitative extent by the secondary decomposition of the products of ozonolysis derived from that group, the yield of carbon dioxide is calculated to be 8.98% of the dibromo-derivative.

(ii) *Decomposition products obtained from aqueous solution* (B). These were a reddish orange liquid. Oxidation with alkaline permanganate followed by acidification yielded succinic acid which showed, on recrystallisation from ethyl acetate, neutr. value 949.1 and m.p. 182–183°.

(iii) *Oily substances* (C). Yield about 6 g. In order to eliminate the bromine from oily substances, these were dissolved in 10 c.c. of methanol and 6 g. of zinc powder was added in several portions. The mixture was refluxed on the water-bath, 10 c.c. of 5 N solution of hydrogen chloride in methanol was gradually added, and the debrominated product was taken up with ether. On removal of the solvent from the ethereal solution, the residue was heated in an oil-bath and there was obtained 1.4 g. of colourless liquid boiling below 180°. This was saponified, the unsaponifiable matter removed by extraction with ether and the free acid liberated. It had neutr. value 435.7 and iodine value 182.7 (calc. for $C_7H_{12}O_2$: neutr. value 438.0, iodine value 198.2), and was considered to consist mainly of heptenoic acid. The hydrogenation product was shown to be heptoic acid by preparing its barium salt (Found: Ba, 34.69. Calc. for $(C_7H_{13}O_2)_2Ba$: Ba, 34.73%).

3. **Ozonolysis of Tetrabromo-derivative of Clupanodonic Acid.** Fifteen g. of clupanodonic acid was dissolved in 150 c.c. of ether, and on cooling, the bromine solution prepared by dissolving 15 g. (calc. for the formation of tetrabromide:

Table 4.

Precipitate	Yield (g.)	Iodine value
1st ppt.	4	68.1
2nd ppt.	11	117.2
3rd ppt.	9.5	119.5
4th ppt.	0.5	119.1
Bromide remaining in the final filtrate	2.5	142.5

14.52 g.) of bromine in 30 c.c. of glacial acetic acid was added with constant stirring. No precipitate was formed after standing for 2 hours. The ethereal solution was washed with water, dehydrated, and on removal of ether there remained 29.5 g. of bromides. These were dissolved in 10 volumes of alcohol, a minute amount of insoluble bromides was removed by filtration, and the filtrate was admixed with water so as to effect a fractional precipitation of the bromides. The yield and the iodine value of each precipitate are shown in Table 4.

The 2nd and 3rd precipitates were combined, and subjected again to the fractional precipitation from alcoholic solution by adding water, by which a tetrabromo-derivative having iodine value 118.0 (calc. for $C_{22}H_{34}O_2Br_4$: 117.2) was separated. Sixteen g. of this bromide was subjected to ozonolysis in the same manner as described above in the case of amyl clupanodonate and dibromo-derivative. The volatile decomposition products (**A**) were made to be absorbed by water in the flask (**a**) and then by barium hydroxide solution in two flasks (**b** and **c**). The decomposition products, which did not volatilise, were separated into two portions: the decomposition products obtained from aqueous solution (**B**) and the oily substances (**C**).

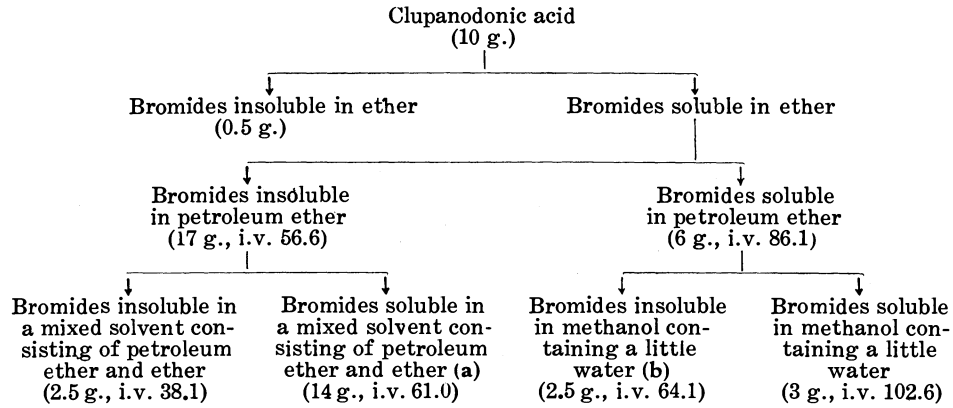
(i) *Volatile decomposition products* (**A**). The aqueous solution in the flask (**a**) showed an aldehyde reaction, and gave a small amount of precipitate on adding *p*-nitrophenylhydrazine. The barium hydroxide solution in the flask (**b**) was found to contain a small amount of the precipitates of barium carbonate, from which the yield of carbon dioxide formed by the ozonolysis was calculated to be 0.69% of the bromo-derivative used for ozonolysis. It is thus seen that volatile aldehyde and carbon dioxide were formed by the ozonolysis, but the yields of these compounds were so small that they were considered to be derived from a minor ingredient contaminating the tetrabromo-derivative, and not from the main constituent.

(ii) *Decomposition products obtained from aqueous solution* (**B**). These were a reddish orange liquid. Oxidation with alkaline permanganate followed by acidification yielded a crystalline product which, after being washed with a little ether, showed m.p. 177–178°, and recrystallisation of this product from ethyl acetate gave succinic acid having neutr. value 945.1 and m.p. 182–183°.

(iii) *Oily substances* (**C**). Yield 11.5 g. These were debrominated with zinc powder and hydrogen chloride in methanol. The debrominated product was distilled, and a fraction boiling in the neighbourhood of 130°/20 mm. was collected separately. This fraction was hydrogenated, saponified, freed from the neutral matter, and the acidic matter was separated which, recrystallised from dilute alcohol, showed neutr. value 324.1 (calc. for $C_{10}H_{20}O_2$: 325.9) and m.p. 29.5–30°. The melting point was not lowered when the substance was admixed with a pure specimen of capric acid, m.p. 30.5–31°, in various proportions.

4. **Ozonolysis of Hexabromo-derivative of Clupanodonic Acid.** Ten g. of clupanodonic acid was dissolved in 100 c.c. of ether, and on cooling, the bromine solution prepared by dissolving 15 g. (calc. for the formation of hexabromide: 14.52 g.) of bromine in 30 c.c. of glacial acetic acid was added gradually with constant stirring. After standing for 2 hours the precipitate of insoluble bromides formed in a minute amount was removed by filtration, and the soluble bromides in an ethereal solution was obtained on distilling off ether. These were subjected to a further separation by means of the solvents as shown in Table 5.

Table 5.



The bromides (a) and (b) were united and treated again with a mixed solvent consisting of petroleum ether and ether, the insoluble portion was removed, the soluble portion was further treated with methanol containing a little water, the soluble portion was discarded; the insoluble portion thus obtained had iodine value 62.0 (calc. for $C_{22}H_{34}O_2Br_6$: 62.7) and it was considered to consist of a hexabromo-derivative.

The hexabromo-derivative (11.5 g.) thus obtained was ozonised in chloroform solution and the ozonide was decomposed with water. Volatile decomposition products were not formed, and the decomposition products were separated into two portions as before, i.e., the products obtained from the aqueous solution and the oily substances. The former consisted of a reddish orange liquid which deposited a crystalline solid at room temperature. Oxidation with alkaline permanganate followed by acidification gave a product which, after being washed with a little cold ether, melted at 178–179° and yielded succinic acid on recrystallisation from ethyl acetate; neutr. value 948.2, m.p. 182–183°. The oily substances (9.5 g.) were debrominated with zinc powder and hydrogen chloride in methanol. Distillation of the debrominated product (2.7 g.) gave 1.3 g. of a distillate boiling below 170°/15 mm. This was hydrogenated and saponified, and the product was separated into acidic and neutral portions in the usual way. The acidic portion, after being recrystallised from 85% alcohol, was shown to be myristic acid $C_{14}H_{28}O_2$; neutr. value 243.7 (calc. 245.8), m.p. and mixed m.p. 53.5–54°. The neutral portion, after being treated with sodium bisulphite solution, showed acetyl value 216.9 (calc. for tetradecanol $C_{14}H_{30}O$: 219.0)

which indicated that it consisted chiefly of higher alcohol. The free alcohol liberated from the acetylated product melted at 30.5–31° after recrystallisation from 85% alcohol. This is considered to consist chiefly of tetradecanol formed by the hydrogenation of the corresponding aldehyde which is likely to be present in the debrominated product, but its melting point is considerably lower than that of pure tetradecanol. Krafft[7] gives m.p. 38° for the same compound.

Summary.

1. Amyl clupanodonate was subjected to ozonolysis. Among the products of ozonolysis were found propyl aldehyde, acetaldehyde, carbon dioxide, succinic acid, amyl hydrogen succinate and also lower acids which were deemed to consist of propionic and acetic acids. Of these compounds, acetaldehyde, acetic acid and carbon dioxide are attributable to the secondary decomposition of the products of ozonolysis primarily derived from the group $=CH\cdot CH_2\cdot CH=$. Accordingly clupanodonic acid was shown to contain the following groups: $CH_3\cdot CH_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot COOH$, $=CH\cdot CH_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot CH=$, of which clupanodonic acid contains three of the last named group.

2. The dibromo-derivative of clupanodonic acid was separated as the chief constituent of the product which was obtained by adding 1 mol bromine to 1 mol clupanodonic acid. Similarly tetrabromo- and hexabromo-derivatives of clupanodonic acid were separated, respectively, as the chief constituents of the product obtained by adding 2 mols and 3 mols bromine, respectively, to 1 mol clupanodonic acid. It is seen from the following results obtained by the ozonolysis of these bromo-derivatives that, in these partial brominations, bromine adds selectively first to the ethylenic linking which is more distant from the carboxyl group. Though this selectivity is not a complete one, any of the above-mentioned bromo-derivatives contains as its chief constituent the product formed in accordance to this selectivity.

3. Ozonolysis of dibromo-derivative of clupanodonic acid thus obtained gave a bromo-compound which on debromination and subsequent hydrogenation yielded, as an acidic product, heptoic acid. This fact, coupled with the results obtained by the ozonolysis of amyl clupanodonate, indicated that clupanodonic acid had the group $CH_3\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=$.

4. Ozonolysis of tetrabromo-derivative of clupanodonic acid gave a bromo-compound which on debromination and subsequent hydrogena-

(7) *Ber.*, (1883), 1714.

tion yielded capric acid, and consequently clupanodonic acid was shown to contain the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=$.

5. Ozonolysis of hexabromo-derivative of clupanodonic acid gave a bromo-compound which on debromination and subsequent hydrogenation yielded myristic acid, and consequently clupanodonic acid was shown to contain the group $CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=$.

6. From the foregoing results, the constitution of clupanodonic acid has been established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$-docosapentenoic acid which is expressed by the following formula:

$$CH_3 \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot COOH.$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

SURFACE POTENTIAL DIFFERENCES OF UNIMOLECULAR FILMS OF FATTY ACIDS.

By Yohei YAMAGUCHI and Saburo MIZUNO.

Received June 3rd, 1935. Published September 28th, 1935.

Introduction.

The measurement of the surface potential difference between air and aqueous solutions of many electrolytes was first studied by Bichat and Blondlot[1] in 1883. Later Kenrick[2] measured the electromotive force of the following type of cells coupled with various inorganic salt solutions:

n. KCl | solution A | air gap | solution B | n. KCl

where the solution A of a certain electrolyte was dropped from a jet placed at the upper part of the axis of the vertically suspended cylinder and insulated from the solution B by an air gap. The solution B of another electrolyte, or of the same electrolyte as A but of different con-

(1) Bichat and Blondlot, *J. physiq.*, [2], **11** (1883), 548.
(2) Kenrick, *Z. physik. Chem.*, **19** (1896), 625.

centration, was flowed very slowly to cover the inner wall of the vertical cylinder. There was found a parallelism between the variation of the surface potential difference with the concentration of the solution of electrolyte and its surface activity.

Since Guyot[3] and Frumkin[4] succeeded independently in measuring the surface potential more accurately and quantitatively, devising an ingenious apparatus, many researches were carried out in this field by several investigators, such as Rideal,[5] Adam,[6] Fosbinde,[7] Zisman,[8] Harkins,[9] and their collaborators. In all these experiments of the above authors a platinum electrode coated with polonium or ionium was used as an ionizer of the air gap instead of Kenrick's dropping electrode, and from the measured surface potentials of the liquids the state of films of polar substances was discussed.

In the present experiment X-ray was used to ionize the air gap instead of radioactive elements. This method was already adopted in 1931 by Yoshikazu Tsunoda and one of the present authors for the study of the similar subject at the same laboratory. X-ray was emitted from an ordinary Coolidge tube and allowed to pass through the air space between the surface of the solution on which a film of fatty acid was spreaded and the platinum disk placed in the air parallel to this surface. Thus the potential differences between air and the films of stearic, oleic, and trichloroacetic acids on 0.02 N KCl aqueous solution were measured respectively. The results, however, were not published.

In the next year 1932 Hayato Shigeno[10] studied the unimolecular films of several fatty acids by the same method, simplifying the apparatus by using a glass dish instead of the funnel used by Tsunoda and others. The present study is to complete this X-ray ionization method by using the former apparatus with a few improved points.

---

(3) Guyot, *Ann. physiq.*, [10], **2** (1924), 506.

(4) Frumkin, *Z. physik. Chem.*, **109** (1924), 34; *ibid.*, **116** (1925), 485; *ibid.*, **123** (1926), 321. Frumkin and Williams, *Proc. Nat. Acad. Sci.*, **5** (1929), 400.

(5) Schulmann and Rideal, *Proc. Roy. Soc.*, A, **130** (1930), 259, 270, 284. Lyons and Rideal, *ibid.*, **124** (1929), 323. Schulmann and Hughes, *ibid.*, **138** (1932), 430. Whally and Rideal, *ibid.*, **140** (1933), 484, 489, 497.

(6) Adam and Harkins, *ibid.*, **138** (1932), 411; *Trans. Faraday Soc.*, **29** (1933), 90, 837. Adam and Miller, *Proc. Roy. Soc.*, A, **142** (1933), 401.

(7) Fosbinder and Lessing, *J. Franklin Inst.*, **215** (1933), 425.

(8) Zisman and Yamins, *J. Chem. Phys.*, **1** (1933), 656.

(9) Harkins and Fischer, *J. Chem. Phys.*, **1** (1933), 852.

(10) H. Shigeno, the results were not published.

Experimental.

The measurement of the surface potential is based upon the principle of ionizing the air space between the platinum electrode and the fatty acid film on the KCl solution by X-ray, and the potential difference between the elctrode and the film is obtained by the compensation method by using Lindemann electrometer which is suitable for this experiment owing to its small capacity. The apparatus and the operation are as follows.

At first a certain quantity of the substrate solution is poured into the glass dish (A) and mounted on the ebonite platform (E); it is raised to a certain height by the screw (S), so that the junction tip (T) of the

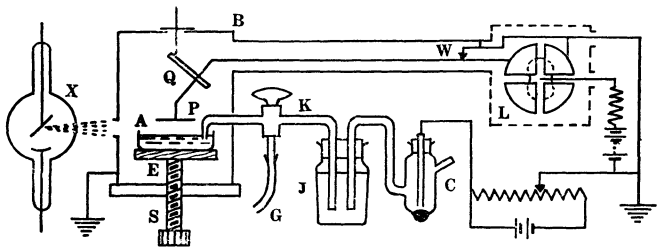


Fig. 1.

connecting tube reaches the surface of the substrate solution and the width of the air gap between the platinum electrode and the solution is reduced to a few millimeters. The substrate solution in the dish (A) is connected to the calomel half cell (C) through the three way cock (K) and the reservoir (J) which contains 0.1 N KCl solution. The liquid junction is made in the three way cock by drawing the solution with the rubber tube (G). After the lid of the brass cover was shut, X-ray of a certain intensity is emitted through the slit into the air gap between the electrode and the solution, and the contact point (W) previously grounded is disconnected. Adjusting the potentiometer so that the needle of the Lindemann electrometer indicates its original position (zero point) which was found at the grounded needle, the potentiometer is read. The current of the Coolidge tube and the primary voltage of the high tension transformer are also observed. Thus the measurement of the surface potential (v) of the pure substrate solution is carried out.

The vessel (A) is now carefully taken outside the brass cover and a few drops of the very dilute solution of the fatty acid in petroleum ether is dropped from the small capillary pipette previously calibrated. The petroleum ether is allowed to evaporate and the thin film of the fatty acid is made on the solution. The dish is again screwed up to the

former position and the surface potential is measured as before. The difference of this value and the former gives the surface potential of the fatty acid film at the concentration known from the number of drops added.

Preliminary Experiment. (1) *The cleanness of the vessel* (A). The cleanness of the vessel is one of the most important factors to obtain reproducible results. Before every measurement all vessels are washed several times with sulphuric acid chromate mixture and then with ordinary water and finally rinsed with distilled water. In washing, good care must be taken not to touch the vessels with fingers by using two glass rods, otherwise fat on the skin spreads rapidly on the wet surface of the vessel and causes a great error in the measurement. The vessels thus washed are placed on sheets of filter paper and dried at room temperature overnight.

(2) *The effect of the width of the air gap.* The variation of the surface potential with the change of the distance between the platinum electrode and the surface of the solution was investigated. The most favourable distance for the measurement is 6–7 mm., and an increase of 10 mm. in distance gives 30–40 mv. increase in potential, i.e. the reading of the potentiometer increases as if a large resistance were put in the air gap.

(3) *The upper limit of the range of the X-ray radiation in the air gap.* The influence of the height of the X-ray radiation on the surface potential of the fatty acid film was investigated. It was found that when the upper range of the radiation is kept at a level the same as, or slightly higher than, that of the platinum electrode, the measured potenial difference is not altered, but when the holder of the electrode is illuminated the measured potential decreases about 10 mv. or more owing to the leakage between the electrode and the grounded brass box. Hence all experiments are carried out at the best condition of the X-ray radiation, i.e. the upper range being kept at the same height as the platinum electrode.

(4) *The decrease of the surface potential with time.* Although the vessel is sufficiently washed, the surface potential decreases gradually with time. But when the junction tip (T) is drawn out from the solution and again dipped into another position of the surface, the potential difference which was once decreased regains the value near the original one. This phenomenon is reproducible during at least half an hour.

(5) *The influence of the hardness and the intensity of X-ray.* The intensity of X-ray is represented by the current of the Coolidge tube and its hardness is proportional to the voltage of the high tension side of the transformer. The effects of these factors on the surface potentials were examined by altering the current and the tension of the X-ray producing apparatus. It was found that there are no perceptible changes or deviations of the surface potential of fatty acid film, when the current of the Coolidge tube is 0.6–1.6 milliamp. and the primary voltage of the X-ray transformer is 70–85 v. Therefore all experiments were carried out at the following conditions: the current of the Coolidge tube about 1.0 milliamp. and the primary voltage of the X-ray transformer about 70 volts.

(6) *The sensibility of the Lindemann quadrant electometer.* The sensibility of the Lindemann electrometer used was already studied by Tsunoda and examined again before the experiment. It depends principally on the applied needle potential and the humidity of the atmosphere. The following results were obtained at the sufficiently good dryness.

Needle potential (v.)	43.5	42.0	40.5	38.6	36.7	34.8	33	31	30
Division/100 mv.	7.7	5.1	3.8	2.7	2.1	1.9	1.3	1.1	0.9

(7) *The concentration of fatty acids.* Fatty acids used for the experiment are myristic, palmitic, stearic, and oleic acids, having melting points 53.8, 60.8, 69, and 14°C. respectively. These acids are weighed and dissolved into purified petroleum ether and diluted further with 20 or 30 times of the same solvent in such dilution that the acid in one drop of the solution from the capillary pipette gives the surface concentration of about 1×10^{-10} g. mol/cm.^{2} after the evaporation of the solvent on the surface of the substrate solution. The volume of one drop from the pipette is about 0.01 c.c. The petroleum ether employed was a product from N. P. C. It was distilled three times and the fraction between 35 and 50°C. was collected.

Measurements and Experimental Results. All experiments were carried out under the following conditions: temperature 17–20°C., substrate solution 0.01 N KCl or 0.11 N HCl, current of Coolidge tube 1.0 milliamp., primary voltage of transformer 70 volts, and needle potential 42 or 43 volts.

The surface potential of the substrate solution is measured at first under the above conditions and by the experimental manipulations already described. A certain number of drops of petroleum ether solution of the fatty acid is then added on the substrate solution and the film of the fatty acid with a certain surface concentration is formed on the solution

Table 1.

Myristic acid			Palmitic acid		
Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution		Surface conc ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution	
	0.111 N HCl 17°C.	0.01 N KCl 18°C.		0.111 N HCl 18°C.	0.01 N KCl 17°C.
	Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)		Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)
0.93	66.6 35.5	—	1.76	191 176 164	119 111
1.87	103 75.5	—	2.64	210 221 234	166 124 123
2.80	98 136	42.5 50.5	3.52	230 242 248	188 190 172
3.74	138 138	49 64.7	4.40	276 270	222 200
4.67	205 194	106 105	5.28	304 304 283	245 218
5.60	243 228	160 164	6.16	305 338 335	245 255 256
6.54	313 270	177 204	7.04	337 337 338	251 261 257
7.47	325 302	236 268	7.92	348 350	262 256
8.41	323 345	268 275	8.80	358	263
9.43	360 360	268	10.56	335	265
12.14	353	271	11.44	—	262
14.01	360	270	13.2	—	257

Table 1 (*Concluded*).

Stearic acid			Oleic acid		
Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution		Surface conc. ($n\times10^{-10}$ g. mol/cm^2.)	Substrate solution	
	0.111 N HCl 18°C.	0.01 N KCl 18°C.		0.111 N HCl 17°C.	0.01 N KCl 17°C.
	Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)		Pot. dif. ΔV (mv.)	Pot. dif. ΔV (mv.)
0.95	45 74	74 81	1.03	107 111	38 53
1.90	120 126	153 145 145	2.06	129 124 128	82 81
2.85	167	200 208 204	3.09	151 147 168	95 106 101
3.80	258 249	243 245 242	4.12	190 198 177	137 146 144
4.75	300 318	248 262	5.15	223 239 204	160 177 186
5.70	320 316	280 289 300	6.18	228 230 230	162 194 153
6.65	348 350	304 300	7.21	253 240	173 189 169
7.60	354 348	314 302	8.24	250 248	188 193
8.55	—	300	9.27	—	190
9.50	355	312 306	10.3	257 256 253	176 185
11.40	358	—	15.45	262 265 262	203 184

by allowing the petroleum ether to evaporate. Finally the surface potential of the film is measured under the same experimental conditions as in the former measurement.

The variation of more than 10 mv. is hardly found in the measured values of the substrate solution without the film. Variations of about

40 mv. are, however, often found in the case of the solution with fatty acid film on it. This large variation is generally found in the case of the small surface concentration giving non-uniform film on the whole surface. In the case of larger concentration probably giving an uniform film on the surface, there is scarcely found a variation over 10 mv. The difference between the mean value of the measured values of the solution with the film and that of the solution without the film is taken as the surface potential difference of the fatty acid film of the surface concentration evaluated from the number of drops added.

Such surface potential differences as the above-mentioned have been obtained from the experimental data for the four fatty acids and these values are shown in Table 1. The first column of the table indicates the surface concentrations of the fatty acid, and the second the surface potential differences in mv. The relations between the potential differences and the surface concentrations are shown graphically in Fig. 2–5. The abscissa of the graphs indicates the surface concentrations (n) in 10^{-10} g. mol/sq. cm., and the ordinate the potential differences (ΔV) in mv. The curve A is the relation obtained by using 0.11 N HCl as the substrate solution and the curve B is that by 0.01 N KCl.

(1) *Myristic acid.* Fig. 2 shows the relation between the surface potential difference of myristic acid film on the solution and its surface concentration. The curve drawn with the dotted line in the figure was plotted with the data obtained by Harkins[11] for the same acid film. Although these data were obtained by Harkins by using 0.01 N HCl as the substrate solution and by an entirely different method, the resulting curve C shows good agreement with curve A. It is found that the two curves A and B are parallel with each other and have almost uniform inclinations.

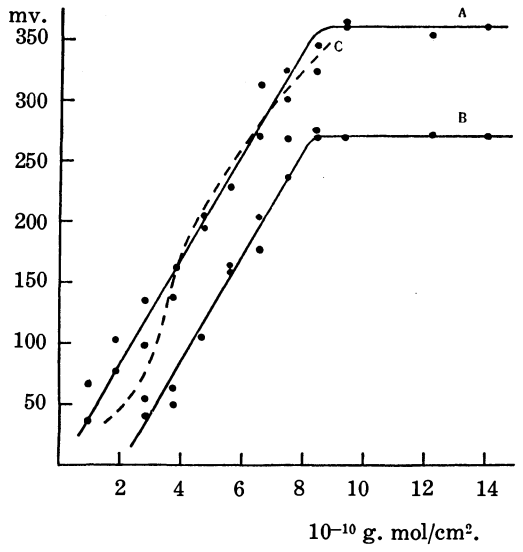
The following well-known formula of Helmholtz is now applied to this case:

$$\Delta V_1 - \Delta V_2 = 4\pi(n_1 - n_2)\bar{\mu} ,$$

where ΔV represents the surface potential difference, n the number of molecules on 1 sq. cm., and $\bar{\mu}$ the mean vertical component of dipole moment. From this formula it may be seen that $\bar{\mu}$ indicates the slope of the ΔV–n-curve, namely the inclination of the (surface potential)—(surface concentration)-curve.

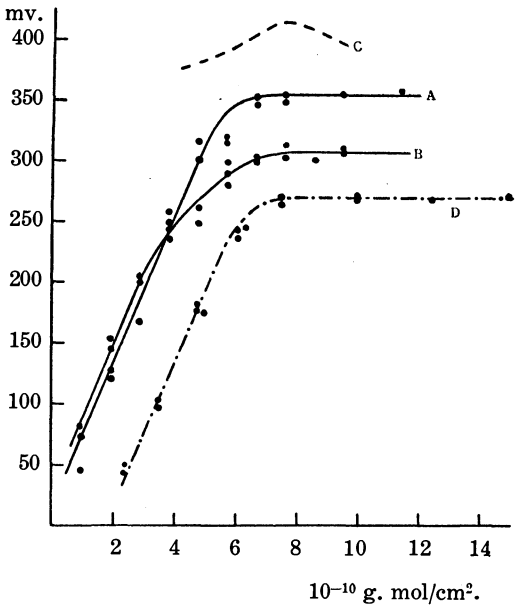
From the fact that two curves A and B are parallel and have the same inclination, it may be considered that the mean vertical component

(11) Harkins, *J. Chem. Phys.*, **1** (1933), 858.



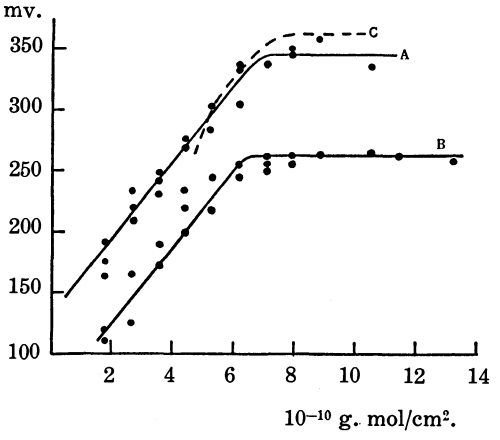
Myristic Acid

Fig. 2.



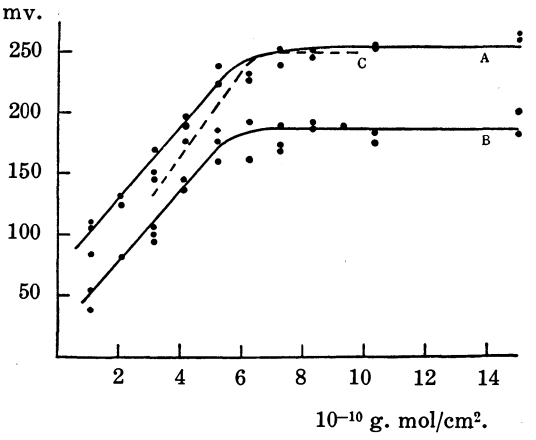
Stearic Acid

Fig. 4.



Palmitic Acid

Fig. 3.



Oleic Acid

Fig. 5.

of dipole moment $\bar{\mu}$ of myristic acid has the same value and alter neither with the surface concentration nor with the substrate solution.

(2) *Palmitic acid.* The results obtained with palmitic acid are plotted in Fig. 3. There is also parallelism between curves A and B and the coincidence of A and C.

(3) *Stearic acid.* Fig. 4 shows the curves for stearic acid. Curve D drawn with a chain line was plotted with the data obtained by Y. Tsunoda[10] with 0.02 N KCl as the substrate solution. Comparing these four curves, if the values of curves A and D are correct, those of B and C are a little higher and if B and C are correct, A and D are a little lower. The slopes of curves A, B, and D, however, are almost similar to one another.

(4) *Oleic acid.* Fig. 5 shows the curves for oleic acid. If a curve be drawn with the data obtained by Y. Tsunoda with 0.02 N KCl as the substrate solution, it falls nearly on curve B, although the former is not drawn in the figure. It is found that curves A and B are parallel as before and curve C falls nearly on A. It is very remarkable in this case that the maximum surface potential attainable is about 100 mv. less than those of the former three fatty acids.

Assuming the surface potentials of the fatty acid films of the same surface concentration are nearly proportional to their length of the molecules or their dipole moments, and basing on the fact that the saturated surface potential of oleic acid film is about 100 mv. less than that of stearic acid with the same number of carbon atoms (18) in the molecule, it may be considered that the vertical length of the former on water is smaller than that of the latter by the amount corresponding

Table 2.

Fatty acid	M.p.	Mean vert. comp. dipole moment ($\bar{\mu}\times10^{-19}$ e.s.u.)	Saturation point		
			Subs. sol.	Area (sq. Å per mol.)	Pot. dif. (mv.)
Myristic acid $CH_3(CH_2)_{12}COOH$	53.8	1.89	HCl KCl	19.6 20.0	360 270
Palmitic acid $CH_3(CH_2)_{14}COOH$	60.8	1.37	HCl KCl	26.4 28.3	340 260
Stearic acid $CH_3(CH_2)_{16}COOH$	69	2.68	HCl KCl	27.0 27.0	350 310
Oleic acid $CH_3(CH_2)_7CH{=}CH{\cdot}(CH_2)_7COOH$	14	1.27	HCl KCl	27.0 30.0	250 190

to this value. This can be explained from the fact that oleic acid has a double linkage in the central part of the molecule and is folded at this point. The mean vertical component of dipole moment ($\bar{\mu}$) is calculated from Helmholtz's formula for the four fatty acids and shown in Table 2. The value for stearic acid is about 2.7×10^{-19} e.s.u., while that of oleic acid is ca. 1.3×10^{-19} e.s.u. and about half that of stearic acid.

Discussion.

The characteristic values calculated from the measured results of the four fatty acids are summarized in Table 2. The third column of the table is the mean vertical component of dipole moment ($\bar{\mu}$) calculated from Helmholtz's formula. The fifth and sixth columns are the area per molecule in sq. Å and the surface potential at the saturation point respectively. It is found that there is always a saturation curve in the (surface potential)—(surface concentration)-curve of the fatty acids. The break point on the curve, i.e. the starting point of the saturation is nearly similar for all the acids and is about 27 sq. Å per molecule and this is the value of the order of a molecular dimension. From this fact it may be considered that at this break point the unimolecular film of fatty acids is established, and in the range of larger area per molecule than that of the break point, i.e. in the inclined part of the curve, the film is in the expanded state and the potential difference changes nearly proportional to the surface concentration. And in the range of smaller area per molecule than the break point, i.e. in the horizontal part of the curve, the film is in the condensed or liquid state as former investigators already described. At extreme concentration, the film is transformed into solid state and sometimes it is considered that small crystals of fatty acid are locally floating on the film.

The maximum or saturation potentials of the saturated fatty acids are almost nearly equal, about 350 mv., but in fact there should be a certain difference in potentials, i.e. about 20–30 mv. for one carbon atom in fatty acid as stated by Harkins and others. Comparing the mean vertical component of dipole moment of fatty acids, that of stearic acid with the largest number of carbon atoms is greatest in value and that of oleic acid is nearly half that of stearic acid, since the length of the molecule of the former is shortened owing to the fold at the point of the double linkage at the central part of the molecule in spite of the same number of carbon atoms.

The value of palmitic acid is less than that of stearic acid. However the value for myristic acid and that for palmitic acid are reversed if the numbers of carbon atoms in them are compared.

One of the authors studied on the similar subject by using a different method of ionizing the air gap at the Physico-chemical Laboratory of University College, London, with the encouragement of Prof. F. G. Donnan to whom he wishes to express his cordial thanks.

Summary.

(1) Gas—liquid interfacial potential difference of fatty acid film was measured by using the method of ionizing air gap between the electrode and the surface of the liquid with X-ray.

(2) Various factors which affect the measurements were studied at first.

(3) Under the most favourable conditions the measurements of the surface potentials were carried out with four fatty acids, i.e. myristic, palmitic, stearic, and oleic acids.

(4) The surface potential difference attains a maximum or a saturation value at a certain definite surface concentration. This value is nearly equal for three saturated fatty acids and is about 350 mv. The value for oleic acid, however, is about 240 mv.

(5) The (surface potential)—(surface concentration)-curves were plotted and the mean vertical component of dipole moment was calculated for these fatty acids by applying Helmholtz's formula.

(6) The break point of the curve or the saturation point of fatty acid is nearly similar for four acids, and the area occupied by a molecule at this point is about 27 sq. Å.

Chemical Institute, Faculty of Science,
Tokyo Imperial University, Tokyo.

DIE KONZENTRATION DER SCHWEREN ISOTOPE IN ZELLULOSEN.

Von Kenzo OKABE und Toshizo TITANI.

Eingegangen am 26. August, 1935. Ausgegeben am 28. September, 1935.

Aus dem Versuch mit einigen Kohlenhydrat-haltigen Substanzen kamen Titani und Harada[1] zur Vermutung, dass schwere Isotope, höchstwahrscheinlich Deuterium, allgemein in allen Kohlenhydraten konzentriert vorhanden sind. Um diese Ansicht weiter zu prüfen, untersuchten wir jetzt einige Zellulose-haltige Substanzen auf ihren Gehalt an schweren Isotopen. Die untersuchten Substanzen waren Filtrierpapier, Baumwolle, Zedernholz und Bambus. Jede Substanz wurde zunächst bei 100°C. in Luft gut getrocknet. Sie wurde dann im Luftstrom verbrannt, und das erhaltene, abdestillierte Wasser wurde sorgfältig nach der früher beschriebenen Weise[2] gereinigt. Das spezifische Gewicht des so gereinigten Wassers verglichen wir mit nach gleicher Weise gereinigtem Osaka-Leitungswasser bei 8.5°C. durch die Schwebemethode mittels eines Quarzschwimmers. Die nebenstehende Tabelle 1 zeigt die gefundenen Differenzen in γ Einheiten ($\gamma = 10^{-6}$) im Vergleich mit dem Standardwasser.

Die Messung für Filtrierpapier wurde von Dr. Harada durchgeführt. Jedes Resultat ist der Durchschnitt aus zwei bis drei Messungen. Aus der Tabelle ersieht man schon, dass schwere Isotope, vermutlich Deuterium, auch in diesen Substanzen in gleicher Menge wie bei den früher untersuchten Kohlenhydrat-haltigen Substanzen konzentriert vorhanden sind. Die Zunahme des spezifischen Gewichts über das des Standardwassers ist umso grösser je reicher die Substanz an Zellulose ist.

Tabelle 1.

Substanz	Differenz
Filtrierpapier	+6.3 γ
Baumwolle	+5.7 γ
Zedernholz	+4.5 γ
Bambus	+4.4 γ

Es wurde von einigen Autoren[3] darauf hingedeutet, dass das Deuterium in den wachsenden Teilen der Pflanzen, z. B. in jungem

(1) T. Titani und M. Harada, dies Bulletin, **10** (1935), 205, 261.

(2) *Ebenda.*

(3) E. W. Washburn und E. R. Smith, *Bur. Standards J. Research*, **12** (1934), 305; *Science*, **79** (1934), 188, 454; H. J. Emeléus, F. W. James, A. King, T. G. Pearson, R. H. Purcell und H. V. A. Briscoe, *J. Chem. Soc.*, **1934**, 1207.

Weidenholz angereichert ist. Als ein solches Beispiel prüften wir Bambussprösslinge. Weil sie sehr schnell wachsen, kann man eine merkliche Anreicherung des Deuteriums in denselben erwarten. Einige Sprösslinge wurden direkt aus dem Feld gezogen, und Schale, Inhalt sowie Presssaft aus dem letzteren wurden gesondert untersucht. Die beiden erst genannten Teile wurden im Luftstrom verbrannt und das abdestillierte Wasser wurde zur Prüfung benutzt. Die Messresultate gibt Tabelle 2 wieder. Dabei muss man die folgenden Tatsachen in Rechnung ziehen. Erstens war der Presssaft stark von den Inhaltssubstanzen verunreinigt. Zweitens war der Inhalt sehr saftreich und es blieb sogar nach dem Pressen noch eine reichliche Menge von Saft darin zurück. Zieht man diese Verhältnisse in Rechnung, dann würde sich der Presssaft etwas leichter, dagegen das Wasser aus dem Inhalt noch schwerer erwiesen. Natürlich darf man nicht aus diesem einzigen Beispiel zu weitgehende Schlüsse ziehen. Aber mindestens darf man in diesem Fall wohl vermuten, dass die Anreicherung der schweren Isotope im Bambussprössling nicht mit dem Wachstum sondern vielmehr mit der allgemein vorhandenen Anreicherung der schweren Isotope in Kohlenhydraten in Zusammenhang steht.

Tabelle 2.

Teil der Sprösslinge	Differenz
Schale	+4.4 γ
Inhalt	+0.6 γ
Presssaft	+1.0 γ

Für die finanzielle Unterstützung sind wir der Gakujutsu-Shinkokai (der Notgemeinschaft der Japanischen Wissenschaft), sowie der Hattori-Hohkohkai (der Hattori-Stiftung) zum besten Dank verpflichtet.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

ON THE ACTION OF PHOSPHATE UPON HEXOSES. II.

By Ryuzaburo NODZU and Kiyotada MATSUI.

Received June 7th, 1935. Published October 28th, 1935.

Is Potassium Phosphate the Unique Catalyst by whose Action Acetol is formed from Glucose under the Experimental Conditions? In the previous work,[1] we observed that when a mixture of glucose and a slightly acidic (*p*H 7–5) concentrated solution of potassium phosphate was distilled, its volume being kept constant by adding water drop by drop, acetol was found in an appreciable quantity (ca. 5% of glucose used) in the distillate, accompanied by traces of methylglyoxal and diacetyl. We can, however, anticipate that such special catalytic action will not be limited solely to potassium phosphate.

To solve this question, similar distillation experiments at *p*H 6.2–7.0 were tried with certain other alkali salts. And it was found that a concentrated solution of sodium phosphate, potassium arsenate, or sodium sulphite, behaves like that of potassium phosphate, actually giving acetol in the distillate from glucose. On the contrary, concentrated solutions of alkali chlorides or sulphates gave no distillate showing the iodoform reaction, and the distilling mixtures turned only faintly yellow in colour even after a prolonged distillation (10 hours).

We may so far infer that there are two classes of alkali salts, one giving acetol when its neutral or slightly acidic concentrated solution is distilled with glucose, and the other not. Since the boiling temperatures all lay between 104° and 109°, this striking difference seems to be attributable simply not to the difference in the reaction temperatures but rather to that in their catalytic activities.

By the same iodometric method as described in the previous article, some determinations were made on yields of the iodine-consuming substances (estimated as acetol) from glucose in the distillation experiments with about 40% solutions of some of these catalytically active salts. It was found that the yield in the experiment with potassium arsenate was about one-fourth, and that with sodium sulphite was less than three-fifth, of that with potassium phosphate. In the previous work, it was also established that the iodine-consuming substances in the experiment with potassium phosphate are mainly (more than 60%) composed of

(1) This Bulletin, **10** (1935), 122.

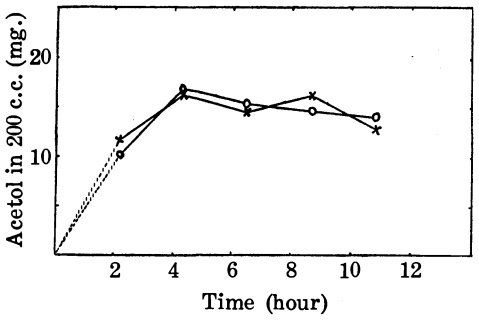
acetol. Taking these facts into consideration, it is probable that among these salts potassium phosphate is the most favourable catalyst for the production of acetol.

Influence of Iron and Copper Ions, etc. In the literature, there is abundant evidence that certain metals have some characteristic actions in the process of oxidative decomposition of carbohydrates under various experimental conditions. According to Meyerhof and Matsuoka,[2] for example, fructose is oxidized to carbon dioxide by aerial oxygen even in an acidic solution of sodium phosphate when copper or iron salt is present. Further, Bernhauer, and Tschinkel[3] have found that various sugars split into methylglyoxal when they are distilled with dilute sulphuric acid and hydrogen peroxide in the presence of ferrous sulphate. The nature of the catalytic action of these metals is not yet well known. It is, nevertheless, not impossible that these catalysts activate the sugar molecules as well as those of the oxidizing agents. There is, therefore, a possibility that iron or some other metals might play some important rôles in the characteristic non-oxidative decomposition of glucose by potassium phosphate, since our experimental materials always contained some metals as impurity, e.g., calcium, magnesium, etc., and especially iron.

To examine this possibility, the rates of appearance of the iodine-consuming substances (estimated as acetol) in the distillates from a mixture of glucose and potassium phosphate solution, either alone or along with iron or other metallic salts, were compared. The potassium phosphate used for this purpose was purified and proved to be free from any heavy metal and alkali earth. The purified glucose was, however, not quite free from a trace of ash—calcium—but it was free from iron. All of the distillations, of course, were carried out under conditions as similar as possible, and in each distillation experiment a rate-curve[4] was prepared. Fig. 1 shows the rate-curves from the experiments with potassium phosphate alone. As seen in the figure, the two curves practically coincide.

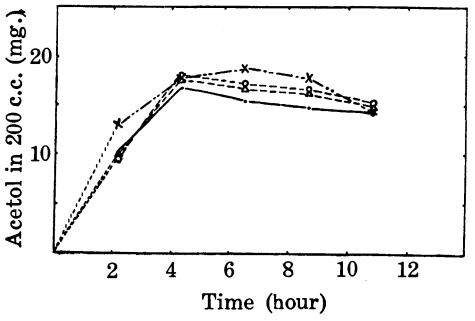
Fig. 2 contains the rate-curves for the experiments with phosphates of calcium, magnesium, zinc, and copper, respectively (in such a quantity as to make 1/100–1/300 molar solution) in addition to potassium phosphate. Fig. 2 indicates that the addition of calcium or magnesium

(2) O. Meyerhof and K. Matsuoka, *Biochem. Z.*, **150** (1924), 1.
(3) K. Bernhauer and H. Tschinkel, *Biochem. Z.*, **230** (1931), 484.
(4) See the experimental part.



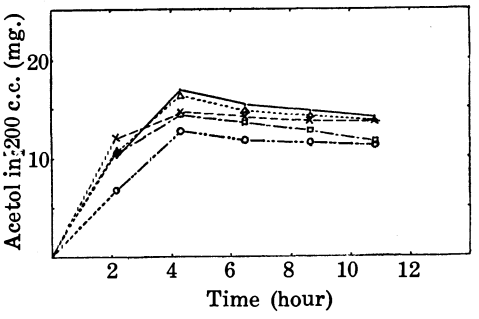
(I): 3 g. Glucose+30 c.c. 40% K-phosphate solution, *p*H 6.2-6.4.

Fig. 1.



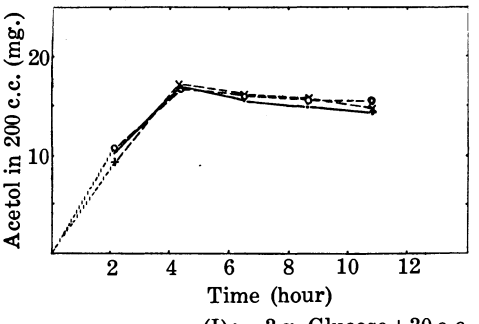
——————— (I): 3 g. Glucose+30 c.c. 40% K-phosphate Solution, *p*H 6.2-6.4.
—··×—··—×—· (VI): (I) +1/100 molar Ferrous sulphate.
---o------o--- (VII): (I) +1/200 molar Ferrous phosphate.
---△------△--- (VIII): (I) +1/300 molar Ferrous phosphate.

Fig. 3.



——————— (I): 3 g. Glucose+30 c.c. 40% K-phosphate solution, *p*H 6.2-6.4.
---△------△--- (II): (I) +1/200 molar Ca-phosphate.
---×------×--- (III): (I) +1/100 molar Mg-phosphate.
-·-□-·-·-□-·- (IV): (I) +1/300 molar Zn-phosphate.
-···o-·-···o···- (V): (I) +1/100 molar Cu-phosphate.

Fig. 2.



——————— (I): 3 g. Glucose+30 c.c. 40% K-phosphate solution, *p*H 6.2-6.4.
---------- (IX): (I) +1/100 molar Ferric phosphate.

Fig. 4.

salt does not notably influence the reaction, whereas zinc and copper salts have a retarding action.

Fig. 3 shows the influence of addition of ferrous salts to the distilling mixture (in such a quantity as to make 1/100–1/300 molar solution). Thus ferrous sulphate or phosphate undeniably accelerates the rate of formation of the iodine-consuming substances. On the contrary, ferric phosphate showed almost no influence upon this rate (Fig. 4).

Thus, among the metal-ions studied, ferrous and cupric ions seem to have some particular effects upon the formation of iodine-consuming

substances. In all of these experiments, the presence of acetol in the distillates was proved by preparing its semicarbazone. Since, however, it is not known to what extent the iodine consumption of these distillates is actually due to acetol, it is impossible to reach any absolute conclusion from these results, as to the catalytic effect of these metal-ions on the acetol formation. But it has become obvious that acetol is produced from pure glucose by the action of pure potassium phosphate under the experimental conditions.

Experimental Part.

The distillations, and the estimations (as acetol) of the iodine-consuming substances in the distillate were carried out in the same ways as described in the previous article, excepting that a distilling flask in Pyrex glass was used this time instead of an ordinary one.

Acetol Formation by Other Salts. The reagents used in these experiments were the commercial "chemically pure" products.

Sodium phosphate. Distilling mixture: 5 g. glucose, 50 c.c. ca. 40% sol. Na-phosphate (from $Na_2HPO_4 \cdot 12H_2O$ and $NaH_2PO_4 \cdot H_2O$). *p*H 6.2–6.5; boiling temperature 106–109°. From 1000 c.c. (0.14 g. as acetol) of the distillate, about 0.1 g. acetolsemicarbazone and a trace of diacetylbissemicarbazone were actually obtained.

Potassium arsenate. Distilling mixture: 3 g. glucose, 30 c.c. ca. 40% sol. K-arsenate (prepared by boiling 40 g. KH_2AsO_4 + 5.2 g. $KHCO_3$ + 62 g. H_2O). *p*H 6.2–6.4; boiling temperature 104–105°. The presence of acetol in the distillate from this mixture was proved by means of preparation of its semicarbazone. In another experiment, the distillation was continued until the distillate gave almost no more iodoform reaction and the acetol content of the total distillate was determined, which amounted to about 1.2% of glucose used.

Sodium sulphite. About 40% solution (*p*H 6.3–6.4; boil. temp. 104–106°) of sodium sulphite gave also acetol and its yield was about 3% of glucose used. In this case, however, the acetol yield should be less than the above value, since it was determined by iodometry and the distillate evidently implied some sulphur dioxide. It is noteworthy in this experiment that the distilling mixture underwent almost no caramelisation even after a prolonged distilling process.

Twenty three per cent. solution of potassium chloride (boil. temp. 105–106°), 28% solution of sodium sulphate (boil. temp. 104°), and 23% solution of potassium sulphate (boil. temp. 103–104°) gave no distillate showing iodoform reaction. A concentrated solution of sodium chloride behaved similarly. It is, however, notable in these experiments that when a distilling flask in ordinary glass instead of Pyrex was used, some iodoform giving substance occurred in a minute quantity in the distillates.

Influence of Metal Ions. A sample of commercial potassium biphosphate (implying Cu, As, Fe, Ca, Mg, etc. as impurities) and glucose (Merck, containing Fe, Ca, etc. as impurities) were purified as follows. To a solution of the potassium biphosphate made alkaline with potassium carbonate, hydrogen sulphide was passed and

the precipitated sulphides were filtered off. The filtrate was made about *p*H 6.5 with phosphoric acid (containing a trace of iron) and then evaporated under a reduced pressure. The turbid concentrated solution was filtered through a pulp mat and further evaporated to crystallization. The crystals (KH_2PO_4) thus obtained were recrystallized twice from the solution of *p*H 6.5 (adjusted with purified potassium carbonate) and twice from their own solution. The product was free from all of the impurities mentioned above.

Glucose was twice recrystallized from glacial acetic acid, washed with alcohol containing a few drops of nitric acid, and dried at 60° under a reduced pressure. The sample thus obtained had still a trace of ash, mainly calcium, but no iron.

Using these materials, the following distillation experiments were performed in the same Pyrex flask and at the same tempo—200 c.c. distillate in ca. 130 minutes. The acetol contents (mg.) in each successive 200 c.c. distillate were plotted against time (hour) and the curves thus obtained are designated as "rate-curves". About 40% stock solution[5] of potassium phosphate (*p*H 6.2–6.4) was prepared by boiling a mixture of 340 g. KH_2PO_4, 68 g. $KHCO_3$ (purified), and 536 g. H_2O.

Distilling mixture (I): 3 g. glucose, 30 c.c. the stock solution.
The rate-curves are plotted in Fig. 1.

Distilling mixture (II): (I) + 0.046 g. $Ca_3(PO_4)_2$ (1/200 molar);
,, ,, (III): ,, + 0.074 g. $MgHPO_4 \cdot 7H_2O$ (1/100 molar);
,, ,, (IV): ,, + 0.046 g. $Zn_3(PO_3)_2 \cdot 4H_2O$ (1/300 molar);
,, ,, (V): ,, + 0.13 g. $Cu_3(PO_4)_2 \cdot 3H_2O$ (1/100 molar).

Each of these experiments was repeated twice and the mean rate-curves are plotted in Fig. 2.

Distilling mixture (VI): (I) + 0.083 g. $FeSO_4 \cdot 7H_2O$ (1/100 molar);
,, ,, (VII): ,, + 0.075 g. $Fe_3(PO_4)_2 \cdot 8H_2O$ (1/200 molar);
,, ,, (VIII): ,, + 0.05 g. ,, (1/300 molar).

The rate-curves for these experiments are plotted in Fig. 3.

Distilling mixture (IX): (I) + 0.067 g. $FePO_4 \cdot 4H_2O$ (1/100 molar).

The results are summarized in Fig. 4. In all of these experiments (I–IX) acetol-semicarbazone was obtained from the distillate and identified with an authentic specimen.

In conclusion the writers wish to thank Prof. S. Komatsu for his valuable advice and at the same time the Department of Education for a research grant.

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

(5) No iron nor any other heavy metals were identified in the solution which had been boiled for 10 hours in the Pyrex flask.

DETERMINATION OF FIXED POINTS IN THE LOW TEMPERATURE WITH A HYDROGEN THERMOMETER.

By Shin'ichi AOYAMA and Eizô KANDA.

Received June 13th, 1935. Published October 28th, 1935.

I. Gas Thermometer. The sensitivity of the constant pressure gas thermometer is expressed by

$$S = dV/dT = 273\ V_0/T^2\ ,$$

and that of the constant volume gas thermometer by

$$S = dP/dT = P_0/273\ ,$$

where V_0 is the volume of the bulb of constant pressure gas thermometer at 0°C., and P_0 the pressure of gas in constant volume gas thermometer also at 0°C. From these expressions we see that the sensitivity of the former becomes larger with the lowering of temperatures, and the volume V_0 must, in consequence, be sufficiently large. On the other hand, if we neglect for a time the error due to the dead space, the sensitivity of the latter would be almost independent of the temperature and the volume of the bulb. The management of the former is very complicated, while the independency of sensitivity from V_0 for the latter may be very convenient, as the dimensions of vessels are limited in the studies at lower temperatures. From these standpoints the authors preferred a thermometer of constant volume to that of constant pressure and constructed one of the former by taking the references of many investigators[1] into consideration.

The thermometer is shown in Fig. 1. Bulb A and the capillary where hydrogen gas is to be filled is made of Jena 16^{III}, and the other parts are of hard glass. B is a bulb for reserving capacity, and C the portion where the level of mercury may be adjusted by means of a platinum wire sealed at its upper part. A, B, and C are connected to the capillary tubes. E_1, E_2, and E_3 are the reservoirs of mercury, the levels of which can be adjusted by changing the pressure. The temperature of the part B is kept at 0°C., and the columns C and D are surrounded by water jackets, the inner pressure of the apparatus being observed with a cathetometer.

(1) Henning, *Ann. Phys.*, **40** (1913), 635; **43** (1914), 282. Heuse and Henning, *Z. Phys.*, **23** (1924), 105; **5** (1921), 285. Heuse and Otto, *Ann. Phys.*, **9** (1931), 486. Onnes, *Comm. Phys. Lab. Leiden*, No. 97 (1906), No. 99 (1907), No. 100 (1907).

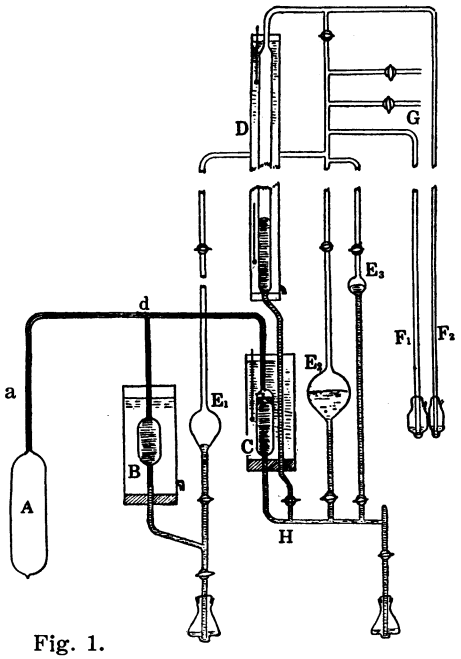


Fig. 1.

Filling of hydrogen. Hydrogen prepared through electrolysis of water is purified by palladium catalyser and also by active charcoal cooled in the liquid nitrogen. The gas is then led into bulbs A, B, and C through the tubes G, D, and H, and the process of filling and evacuating is repeated. After the fifth filling the mercury column cuts off the passage between C and D, and the pressure of hydrogen is adjusted so that it will indicate 90 mm. of mercury when A and B is kept at 0°C.

II. Determination of Temperature. For the convenience of referring in the description, the parts of the thermometer containing gas are indicated by A, B, C, a, and d, the temperatures of which being all different from one another. In Fig. 1 the part A is at a temperature of $t°$ which is to be determined, B is at 0°C., C at the temperature of water which is nearly at room temperature t_r, and a at the mean temperature between $t°$ and t_r. The effect due to the variation of the temperature of the room has been found to be very small, as the apparatus has been set in a special room tripply walled all around admitting no direct rays of the sun.

The volume of each part of the thermometer at 0°C. and under zero atmosphere has been calculated as follows: $V_A = 353.073_4$, $V_B = 19.479_2$, $V_C = 0.258_0$, $V_a = 0.041_3$, and $V_d = 0.344_1$ c.c.

In the determination of temperature the corrections due to the thermal expansion of the glass bulb and the variation of the inner pressure of hydrogen must be applied. The following are the thermal expansion coefficients[2] and the compressibility of the glass Jena 16^{III} applied for the correction.

Cubical expansion coefficient	Range of temperatures
1.992×10^{-5}	13°～−103°C.
$1.53\ \times10^{-5}$	−103°～−183°C.
0.495×10^{-5}	−183°～−253°C.

Compressibility: $\mu = 2.94\times10^{-6}$

(2) Van Agt and K. Onnes, *Comm. Phys. Lab. Leiden*, No. 176 a (1925).

To give an example for calculating the correction, let us suppose that the pressure of the gas is p meter of mercury, and then the volume of the part A at $t°$ (where $t > -103°C.$) may be expressed by

$$V'_A = V_A (1+1.992\times10^{-5}\times t+2.94\times10^{-6}\times p).$$

By expressing the pressure of the thermometer when the bulb is at 0°C. or $t°$ by p_0 or p_t, and the pressure coefficient of hydrogen between 0°C. and 100°C. by β, we have the following relation between p_0 and p_t:

$$p_0\left\{V_A+V_B+\frac{V_a}{1+\beta t_a}+\frac{V_d+V'_c}{1+\beta t_r}\right\} = p_t\left\{\frac{V'_A}{1+\beta t}+V_B+\frac{V_a}{1+\beta t'_a}+\frac{V_d+V'_c}{1+\beta t_r}\right\} \quad (1).$$

The second term on the both sides of the above equation will vanish in case B is filled with mercury. The third and fourth terms on the both sides are corrections due to the dead spaces and may be expressed by $\frac{V_s}{1+\beta t_s}$ and $\frac{V'_s}{1+\beta t'_s}$.

Then we have

$$p_0\left\{V_A+\frac{V_s}{1+\beta t_s}\right\} = p_t\left\{\frac{V'_A}{1+\beta t}+\frac{V'_s}{1+\beta t'_s}\right\} \quad (2).$$

The temperature will thus be determined from the equation

$$t = \frac{1}{\beta}\left[\frac{p_t V'_A}{p_0\left\{V_A+\frac{V_s}{1+\beta t_s}\right\}-p_t\frac{V'_s}{1+\beta t'_s}}-1\right] \quad (3).$$

In the case of the present experiment the following values of p_0 and β have been adopted: $p_0 = 922.15$ mm. of mercury, $\beta = 0.0036621$[3].

III. Accuracy of Temperature. The accuracy of the standard thermometer for low temperatures is very important, because many problems have to be discussed in the temperature of absolute scale. In the following the authors attempt to discuss on the errors generally encountered in the temperature determination with the constant volume gas thermometer, taking the effect of dead spaces into consideration.

Now, if we neglect the effect of dead spaces, we have

(3) Heuse and Otto, *loc. cit.*

$$t = \frac{p-p_0}{\beta p_0} \tag{4},$$

then
$$dt = \frac{1}{\beta}\left\{\frac{dp}{p_0} - \frac{1+\beta t}{p_0}dp_0 - t d\beta\right\}$$

and so
$$\frac{\partial t}{\partial p_0} = -\frac{1+\beta t}{\beta p_0} = -\frac{273+t}{p_0} \tag{5},$$

$$\frac{\partial t}{\partial \beta} = -\frac{t}{\beta} = -273t \tag{6},$$

$$\frac{\partial t}{\partial p} = \frac{1}{\beta p_0} = \frac{273}{p_0} \tag{7}.$$

If we consider the dead space, however, we get from equation (2) the following relation:

$$p_t\left\{\frac{V'_A}{V_A} + \frac{V'_s}{V_A}\frac{1+\beta t}{1+\beta t'_s}\right\} = p_0\left\{1+\frac{V_s}{V_A}\frac{1}{1+\beta t_s}\right\}(1+\beta t)\ .$$

The coefficient $(1+\beta t)$ on the right side of the above equation is the characteristic quantity assigned to each thermometer, the value of which can be determined when A (Fig. 1) is at 0°C. If we equate this term with p'_0 and express the left side by p', we get the relation which is very analogous to equation (4).

Thus
$$p' = p_0(1+\beta t) \qquad \text{or} \qquad t = \frac{p'-p'_0}{\beta p'_0} \tag{8}$$

where
$$p'_0 = p_0\left\{1+\frac{V_s}{V_A}\frac{1}{1+\beta t_s}\right\} \tag{9}$$

and
$$p' = p_t\left\{1+\alpha t+\mu p+\frac{V'_s}{V_A}\frac{1+\beta t}{1+\beta t'_s}\right\} \tag{10}.$$

Then the maximum error of temperature will be

$$\Delta t = \frac{273+t}{p'_0}\times\Delta p'_0 + 273t\times\Delta\beta + \frac{273}{p'_0}\times\Delta p' \tag{11}.$$

The amounts of $\Delta p_0'$ and $\Delta p'$ are determined by the maximum errors of p_0, p_t, V_s/V_A, and t_s in the actual measurements, calculated by the equations (9) and (10). In order to calculate the maximum errors at 0°C. and −200°C. the above method is applied to the thermometer constructed by the authors. In the present case $V_s/V_A = 0.00182$, $\Delta p_0 = 0.05$ mm. Hg, and $\Delta t_s = 0.02°$.

(a) Errors due to p_0': $\Delta t_{p_0'} = \dfrac{273+t}{p_0'}\Delta p_0'$, $p_0 = 922.15$, $p_0' = 923.9$, and $\Delta p_0' = 0.0584$.

Accordingly, $\Delta t_{p_0'} = 0.0173$ at 0°C., and $\Delta t_{p_0'} = 0.0046$ at −200°C.

(b) Errors due to β: $\Delta t_\beta = 273 \times \Delta\beta$.

If we estimate as $\beta = 0.0000001$ ($\beta = 0.0036621$), then $t_\beta = 0$ at 0°C., and $t_\beta = 0.0055°$ at −200°C.

(c) Errors due to p': $\Delta t_{p'} = \dfrac{273}{p_0'}\Delta p'$.

The largest term of corrections for gas pressure is due to the variation of temperature of the mercury column. If we let h be the difference of the height of mercury columns observed with the cathetometer, α' the expansion coefficient of mercury and t_r the temperature of mercury, we then have from the equation (10)

$$p' = h(1-\alpha' t_r)\left\{1+\alpha t+\mu p+\frac{V_s}{V_A}\frac{1+\beta t}{1+\beta t_s}\right\} .$$

As $\Delta h = 0.05$ mm. Hg, and $\Delta t_r = 0.02°$,

$$\Delta p' = \Delta p_h' + \Delta p_{t_r} + \Delta p_{t_s V_s} ,$$

$$\Delta p' = 0.0500+0.00336+0.00914 = 0.0625 \quad \text{at } 0°\text{C.},$$

and $$\Delta p' = 0.0500+0.0001 +0.00007 = 0.05017 \text{ at } -200°\text{C.}$$

Accordingly, $\Delta t_{p'} = 0.0185°$ at 0°C., and $\Delta t_{p'} = 0.0148°$ at −200°C.

Summarizing the above results, we get the following total maximum errors of the temperature: $\Delta t = 0.0358°$ at 0°C., $\Delta t = 0.0249°$ at −200°C.

From the above calculation it is clear that in the range 0° and −200°C. the amount of error decreases from 0.0358° to 0.0249° with the lowering of temperature.

IV. Comparison with the Thermodynamical Scale. The difference between the scale of the constant volume gas thermometer t_v and the thermodynamical scale of temperature t can be expressed by

$$t_v - t = p_0\{2.73(t_v - 100)k_0 - 3.73t_v k_{100} + (273 + t_v)k_t\}$$

where k_0, k_{100}, and k_t mean the inclination of the isothermal curve of the gas in question at 0°C., 100°C., and t°C. respectively. The difference is found to be proportional to the initial pressure p_0. In the present case it is as follows:

t	$t-t_v$	t	$t-t_v$
−225°	0.055	−100°	0.014
−200°	0.043	− 75°	0.009
−175°	0.034	− 50°	0.005
−150°	0.026	− 25°	0.003
−120°	0.019	0°	0.000

V. Determination of Fixed Points. In order to check the accuracy of the thermometer constructed, determinations of the boiling points of nitrogen and oxygen, and that of the sublimation point of carbon dioxide have been made.

(a) *Boiling point of nitrogen.* The apparatus used for the determination of the boiling point of nitrogen is shown in Fig. 2. A Dewar vessel C contains fresh liquid nitrogen, A is the bulb of the gas thermometer, B and D together act as a vapour pressure thermometer, and E and F are the portions of the apparatus where liquid nitrogen is purified through evaporation followed by condensation.

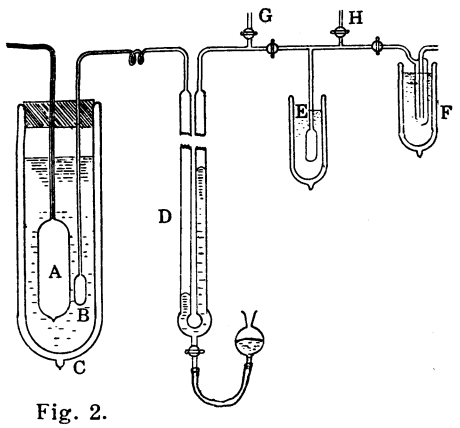


Fig. 2.

Nitrogen to be filled in B is generated by the addition of an aqueous solution of sodium nitrite dropwise to a mixture of warm saturated aqueous solution of ammonium sulphate and potassium chromate. The gas thus generated is passed through a red heated copper gauze and then purified through the process of repeated evaporation and condensation in E and F, respectively. The gas is finally condensed in B, the temperature of the bath being determined with the gas thermometer, and the vapour pressure of nitrogen in B is observed with the vavour pressure thermometer.

Using the temperature coefficient of the vapour of nitrogen ($\Delta p/\Delta t$), the values of which have been obtained from the vapour pressure thermometer scale, the normal boiling point is determined as follows :

Vapour pressure	Temperature	$\Delta p/\Delta t$	Boiling point
870.90	−194.68°C.	94.9	−195.85°C.
857.45	−194.76	94.4	−195.81
815.10	−195.24	93.1	−195.83
			mean $-195.83_3 \pm 0.03$

The mean value corresponds to −195.79°C. on the thermodynamical scale of temperature. According to Henning[4] or Onnes,[5] the fixed point is $-195.81° \pm 0.02°$ or −195.78°, being very close to that obtained in the present experiment.

(b) *Boiling point of oxygen.* Oxygen generated through the electrolysis of the aqueous solution of potassium hydroxide is freed from hydrogen with heated platinum asbestos. The gas is then condensed in a trap cooled in liquid air, and the vapour of oxygen together with any trace of hydrogen present is pumped out. The oxygen of extra purity thus prepared is introduced into B, and the normal boiling point is determined as in case (a). The following are the results obtained :

Vapour pressure	Temperature	$\Delta p/\Delta t$	Boiling point
727.60	−183.44°C.	79.1	−183.03°C.
739.45	−183.28	,,	−183.02
764.00	−182.95	,,	−183.00
			mean $-183.01_7 \pm 0.03$

By calculating the mean value to the thermodynamical scale, it corresponds to −182.98°C. Henning and Heuse[4] give the boiling point $-183.00°\text{C.} \pm 0.02°$, Onnes[5] −182.95°C., and Heuse and Otto[6] −182.962°C.

(c) *Sublimation point of carbon dioxide.* Carbon dioxide is prepared by the addition of dilute sulphuric acid to the milky aqueous mixture of sodium bicarbonate, and it is condensed in a trap cooled by a mixture of solid carbon dioxide and ether. In the bath C a mixture of solid carbon dioxide and ether is placed and well stirred. In the determination of the sublimation

(4) Henning and Stock, *Z. Phys.*, **4** (1921), 226; Henning and Heuse, *loc. cit.*
(5) "Onnes-Festschrift," II (1923).
(6) Heuse and Otto, *loc. cit.*

point, the temperature coefficient of vapour tension $\Delta p/\Delta t = 62.7$ mm. Hg is applied. The observed values are as follows:

Vapour pressure	Temperature	$\Delta p/\Delta t$	Sublimation point
762.35	−78.48°C.	62.7	−78.52°C.
758.85	−78.52	,,	−78.50
768.10	−78.41	,,	−78.53
			mean $-78.51_7 \pm 0.009$

The mean value will correspond to −78.51°C. on the thermodynamical scale. Keys and Young[7] give −78.53°C., and Heuse and Otto[8] −78.48°C.

VI. Calibration of Thermocouples. The calibration of copper-constantan thermocouple is made with the hydrogen thermometer in a cryostat as shown in Fig. 3. Dewar vessel A contains another Dewar vessel B containing pentane and a copper cylinder wound with heating coil H and the space between the two vessels is filled with liquid nitrogen. Gas thermometer G and the thermocouples J and J′ are immersed in the liquid in vessel B. This vessel has a side tube through which hydrogen gas can be either introduced or evacuated to high vacuum. The cooling of vessel B is effected by the cold source of liquid nitrogen through the thermal conduction of hydrogen kept in the space between the double walls of vessel B. The control of the temperature is made possible by evacuating hydrogen and warming the liquid in the vessel gently with coil H. Small particles of aluminium also fill the space between the vessels A and B, and hence a good constancy of temperature has been able to be obtained by the aid of the thermal conductivity of aluminium even in the range of lower temperatures where liquid pentane is frozen. The constancy during the calibration has been ±0.02°.

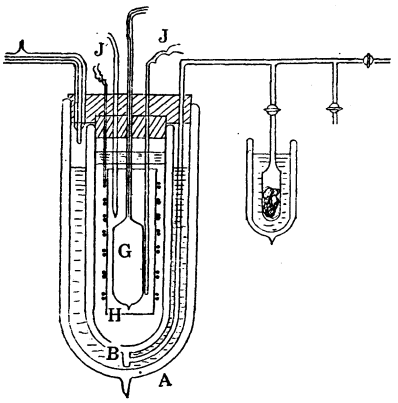


Fig. 3.

The following is the results of calibration:

Couples of Cu-Ni-Cu alloy (Ni 51.86, Cu 47.66, Mn 0.09, Fe 0.38%).

(7) *J. Math. Phys.*, **1** (1922), 241.
(8) *Loc. cit.*

Temperature	e. m. f. (m.v.)	Temperature	e. m. f. (m.v.)
−40.13°C.	1.507	−114.50°C.	3.882
−55.48	2.060	−123.75	4.118
−67.15	2.441	−135.55	4.402
−78.32	2.828	−155.41	4.877
−85.51	3.036	−172.36	5.221
−94.65	3.318	−183.50	5.456
−107.83	3.699	−194.70	5.650

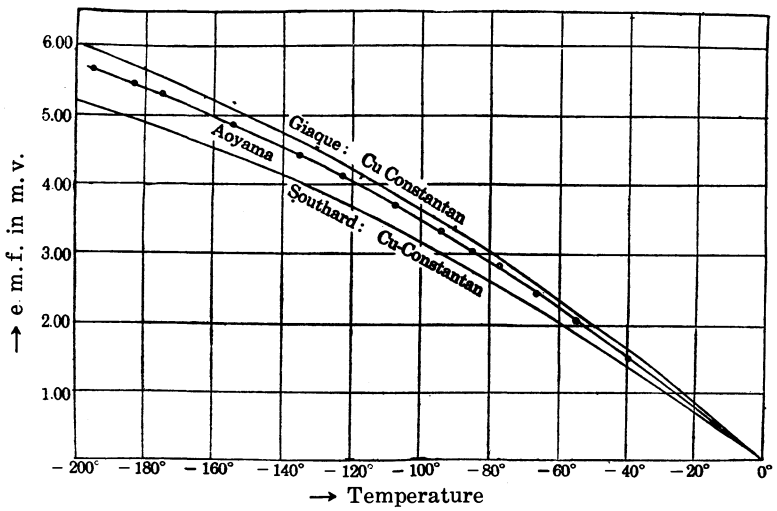


Fig. 4.

The curve in Fig. 4 shows the results given in the above table together with those of other investigators for a comparison. It may be seen that the electromotive force of the couples Cu and Ni-Cu alloy of the present authors is very close to that of copper-constantan thermocouples calibrated independently by Giaque[9] and Southard.[10]

Summary.

A hydrogen gas thermometer for the standard of the low temperature measurement was constructed wholly of glass. The accuracy of temperature obtained, ±0.036° at 0°C. and ±0.025° at −200°C., was discussed, the

(9) Giaque, Buffington, and Schulze, *J. Am. Chem. Soc.*, **49** (1927), 2343.
(10) Southard and Andrews, *J. Franklin Inst.*, **207** (1929), 323.

volume of thermometer bulb, the dead spaces, and the temperature of the room being taken into consideration. The determination of the boiling points of liquid nitrogen and liquid oxygen and that of the sublimation point of solid carbon dioxide were made with this thermometer. The calibration of copper-constantan thermocouples was also made against the thermometer at various low temperatures.

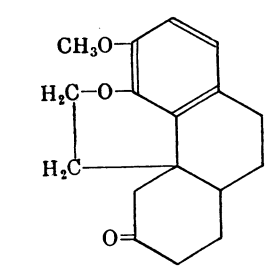
The authors express their cordial appreciation to the Saito Gratitude Foundation whose generous contributions has made it possible to equip fully their laboratory with the provisions necessary for the cryogenic researches.

The Cryogenic Laboratory,
Research Institute for Iron, Steel, and Other Metals,
Imperial University, Sendai.

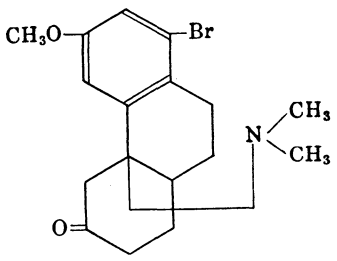
ÜBER (+)- UND (−)-BROM-THEBENON.[1]

Von **Kakuji GOTO, Hiroshi OGAWA** und **Jun SAITO.**

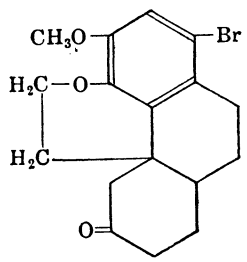
Eingegangen am 19. Juni, 1935. Ausgegeben am 28. October, 1935.



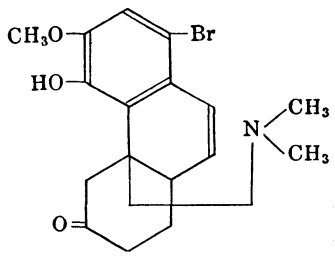
I



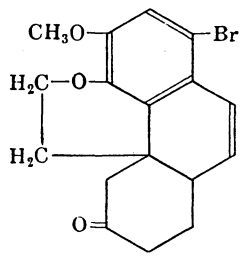
II



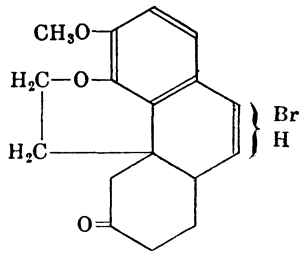
III



IV



V



VI

(1) XLII. Mitteilung über Sinomenin. XLI. Mitteilung, dieses Bulletin, **10** (1935), 252.

Bei der Bromierung von Thebenon (I) erhalten wir kein einheitliches Produkt; dies erklärt sich aus der Tatsache dass C_5 und C_6 ebenso leicht bromiert werden können wie C_1, besonders in Angesicht dass der freie Hydroxyl an C_4 mit Ätherringschluss geschlossen ist.[2] So haben wir mit dem Dihydro-des-N-methyl-demethoxy-dihydro-sinomenin ausgegangen und durch Bromierung zuerst 1-Brom-dihydro-des-N-methyl-demethoxy-dihydro-sinomenin (II) dargestellt. Das Jodmethylat des letzteren wird beim Kochen mit Alkali leicht ins 1-Brom-thebenon (III) übergegangen.

Um (−)-1-Brom-dehydro-thebenon (V) zu gewinnen, haben wir zuerst 1-Brom-demethoxy-dihydro-sinomenin in seine Des-N-methyl-base (IV) umgewandelt und dann das Jodmethylat der letzteren mit Alkali gekocht. Diese Umwandlung war so leicht ausführbar wie bei den nicht bromierten Derivaten.[2]

Beim vorsichtigen Bromierung von (+)-Dehydro-thebenon haben wir ein isomeres Brom-dehydro-thebenon (VI) gewonnen. In diesem Produkt, sitzt das Brom-atom vielleicht an C_9 oder C_{10}, da wir beim Bromierung[3] von Dehydro-thebenon-7-ketofurazan, in denen beide Ketongruppen durch Furazan-ringschluss abgestöpft worden ist, ebenso leicht ein nicht an C_1 bromiertes Produkt erhalten hatten. Dieses Produkt wird daher Iso-brom-dehydro-thebenon genannt.

Alle obige Umwandlungen wurden mit Dihydro-thebainon und seinen Des-N-methylbasen ausgeführt. Dabei wurde es bewiesen dass alle entsprechende Derivate denselben Schmelzpunkt und Drehungsvermögen (im entgegengesetzten Sinne) besitzen und miteinander wohl racemisieren, wie in der folgenden Tabelle zusammengefasst sind.

	Aus Sinomenin		Aus Thebain		Rac. Subst. Schmp.
	Schmp.	Sp. Dreh.	Schmp.	Sp. Dreh.	
II	192°	+ 61.60°	192°	− 62.67°	175—177°
III	70°	− 22.67°	70°	+ 23.33°	191—193°
IV	200—201°	− 8.67°	199°	+ 8°	189—192°
V	145°	−186.80°	148—150°	+187.33°	159—162°
VI	125—133°	−113.33°	127—130°	+112.67°	156—158°

(2) K. Goto, *Ann.*, **485** (1931), 247.
(3) K. Goto und M. Mitsui, dieses Bulletin, **7** (1932), 223.

Aus dieser Tabelle ersieht man dass die schrittenweise Umkehrung des Drehungs-sinnes von Dihydro-thebainon zu Thebenon, was wir schon an nicht bromierten Substanzen bemerkt haben,[2] auch hier begegnet ist. Der grosse Unterschied in Molekular-Drehung in isomeren 1-Brom-dehydro-thebenon und Iso-brom-dehydro-thebenon ist auch bemerkenswertig.

Versuche.

1. **Dihydro-des-N-methyl-1-brom-demethoxy-dihydro-sinomenin** (II). 1.1 g. Dihydro-des-N-methyl-demethoxy-dihydro-sinomenin werden in 5 c.c. Eisessig gelöst und mit 0.55 g. Brom in 10 c.c. Eisessig bei 16°C. bromiert. Das Bromhydrat der bromierten Base krystallisiert sofort aus. Schmp. 257° (heftig zersetzt). Die befreite Des-N-methyl-base wird aus Methanol umkrystallisiert. Prismen, Schmp. 192°. Diazo-reaktion nur bis 5,000 fache Verdünnung. Gefunden bei Makroanalyse: Br, 20.18. Ber. für $C_{19}H_{20}NO_3Br$ (396): Br, 20.20%. Spez. Drehung: 0.1731 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = +1.07°$; $[\alpha]_D^{17} = +61.60°$.

Jodmethylat. Bildet beim Mischen und Stehenlassen beider Komponente in Methanol. Schmp. 273° Gef. bei Makroanalyse: J, 23.62 Ber. für $C_{20}H_{29}NO_3BrJ$: J, 23.61%

Dihydro-des-N-methyl-1-brom-dihydro-thebainon (II). Darstellung wie bei (+)-Substanz aus Sinomenin. Das Bromhydrat zersetzt auch bei 257°. Schmp. von freier Base 192°. Gefunden bei Mikroanalyse: N, 3.50. Ber. für $C_{19}H_{26}NO_3$ Br (396): N, 3.54%. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = -0.94°$; $[\alpha]_D^{17} = -62.67°$.

Das Jodmethylat schmilzt bei 273°.

***d, l*-Dihydro-des-N-methyl-1-brom-dihydro-thebainon.** Je 0.15 g. (+)- und (—)-Substanz wurden in methanolischer Lösung vereinigt. Daraus wurde 0.2 g. racemischer Substanz gesammelt. Schlanke Prismen; Schmp. 175–177°, $\alpha = \pm 0$.

2. **(—)-1-Brom-thebenon** (III) **aus Sinomenin.** Das Jodmethylat, welches aus 1.5 g. obiger Des-N-methyl-base gebildet wurden, werde mit 10 c.c. 25 proz. Kalilauge 20 Min. lang gekocht. Mit der Entwickelung des Amingeruchs, werden Öltröpfen über das Wasser gebildet. Nach Verdünnen mit 3 facher Menge Wasser, wird die Lösung mit CO_2 übergesättigt und der Niederschlag aus Methanol umkrystallisiert Schmp. 70°. Gefunden bei Makroanalyse: C, 57.87; H, 5.41; Br, 22.43. Ber. für $C_{17}H_{19}O_3Br$ (351): C, 58.12; H, 5.41; Br, 22.79%. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = -0.34°$, $[\alpha]_D^{17} = -22.67°$.

(+)-1-Brom-thebenon (III) **aus Thebain.** Darstellung wie oben. Schmp. 70°. Ausbeute ca. 70%. Gefunden bei Mikroanalyse: Br, 22.76. Ber. für $C_{17}H_{19}O_3Br$ (351): Br, 22.79%. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = +0.35$, $[\alpha]_D^{17} = +23\,33°$.

***d, l*-1-Brom-thebenon.** Zur Racemisierung, wurden je 0.15 g. (—)- und (+)-1-Brom-thebenon in Methanol vereinigt. Daraus krystallisierte die racemische Substanz in viereckigen Blättern. 0.25 g. wurde gesammelt. Schmp. 191°–193°, $\alpha = \pm 0$.

3. **Des-N-methyl-1-brom-demethoxy-dihydro-sinomenin** (IV). 3 g. 1-Brom-demethoxy-dihydro-sinomeninjodmethylat werden mit 15 c.c. 15 proz. Natronlauge 12 Min. gekocht. Nach Zusatz von 8 c.c. Wasser wird die Lösung mit CO_2 gesättigt. Der ausfallende Niederschlag wird gesammelt, in Methanol gelöst und mit 1–1.5 fachen Menge Wasser gefällt. Prismen, Schmp. 200–201°. Ausbeute 1.5 g. Gefunden bei Makroanalyse: C, 57.79; H, 6.16 Ber. für $C_{19}H_{24}NO_3Br$ (394): C, 57.87; H, 6.09%. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = -0.13°$, $[\alpha]_D^{17} = -8.67°$.

Jodmethylat. Entsteht beim Mischen beider Komponente. Zersp. 243°. Gefunden bei Makroanalyse: J, 23.76. Ber. für $C_{20}H_{27}NO_3BrJ$ (538): J, 23.61%.

Des-N-methyl-1-brom-dihydro-thebainon (IV). Darstellung wie bei (—)-Substanz aus Sinomenin. Schmp. 199°. Gef. bei Mikroanalyse: N, 3.55. Ber. für $C_{19}H_{24}NO_3Br$ (394): N, 3.55%. Spez. Drehung: 0.1 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = +0.08°$, $[\alpha]_D^{17} = +8.00°$.

Jodmethylat. Schmp. 243° (aus Wasser).

***d, l*-Des-N-methyl-1-brom-dihydro-thebainon.** Je 0.1 g. (—)- und (+)-Substanz wurde in Athanol gelöst und vereinigt. Beim Kühlen mit Eis krystallisiert die racemische Substanz. Schmp. 189–192°, $\alpha = \pm 0$.

4. **(—)-1-Brom-dehydro-thebenon** (V) **aus Sinomenin.** 2.5 g. des Jodmethylates der obigen Des-N-methyl-base wurden in 30 c.c. 11 proz. Natronlauge 40 Min. gekocht. Nach Ansäuern mit Salzsäure wurde 1-Brom-dehydro-thebenon in Chloroform aufgenommen. Beim Verdünsten des Chloroforms krystallisierte das Produkt in Prismen aus. Schmp. 145°. Gef. bei Makroanalyse: C, 58.57; H, 4.94; Br, 22.69. Ber. für $C_{17}H_{17}O_3Br$ (349): C, 58.45; H, 4.87; Br, 22.92%. Spez. Drehung: 0.1424 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = -2.66°$, $[\alpha]_D^{17} = -186.80°$.

(+)-1-Brom-dehydro-thebenon (V) **aus Thebain.** Darstellung wie bei (—)-Substanz aus Sinomenin. Schmp. 148–150°. Gef. bei Mikroanalyse: Br, 23.07. Ber. für $C_{17}H_{17}O_3Br$ (349): Br, 22.92%. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = +2.81°$, $[\alpha]_D^{17} = +187.33°$.

***d, l*-1-Brom-dehydro-thebenon.** Je 0.15 g. (—)- und (+)-Substanz werden in Methanol vereinigt. Daraus wurde 0.2 g. racemischer Substanz gesammelt. Schmp. 159–162°, $\alpha = \pm 0$.

5. **(—)-Iso-brom-dehydro-thebenon** (VI) **aus Sinomenin.** 1.8 g. (—)-Dehydro-thebenon, in 10 c.c. Eisessig gelöst, werden mit 1.1 g. Br in 5 c.c. Eisessig unter Eiskühlung bromiert. Das Produkt wird mit Wasser gefällt und aus Aceton umkrystallisiert. Schmp. 125–133°. Ausbeute ca. 1 g. Gef. bei Makroanalyse: C, 58.25; H, 5.06; Br, 22.11. Ber. für $C_{17}H_{17}O_3Br$ (349): C, 58.45; H, 4.87; Br, 22.92%. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = -1.70°$, $[\alpha]_D^{17} = -113.33°$

(+)-Iso-brom-dehydro-thebenon (VI) **aus Thebain.** Diese Substanz wurde wie bei (−)-Substanz aus Sinomenin dargestellt. Schmp. 127–130°C. Spez. Drehung: 0.15 g. Subst. in 10 c.c. Chloroform, 1 dm. Rohr, $\alpha = +1.69$, $[\alpha]_D^{17} = +112.67°$.

***d, l*-Iso-brom-dehydro-thebenon.** Aus dem Gemisch von je 0.15 g. (−)- und (+)-Iso-brom-dehydro-thebenon, gelöst in Methanol, wurde 0.25 g. racemische Substanz gesammelt. Prismen von Schmp. 156–158°, $\alpha = \pm 0$.

Chemisches Laboratorium des Kitasato Institut,
Shiba, Tokyo.

SORPTION OF GAS BY MINERAL. V.

By Jitsusaburo SAMESHIMA and Noriyoshi MORITA.

Received June 25th, 1935. Published October 28th, 1935.

In this paper the experimental results obtained with the following minerals are described: mordenite, thomsonite, scolecite, epistilbite and phillipsite. The sorptions of ammonia and carbon dioxide by these minerals have been measured. The procedure of measurements have already been described in the preceding reports.(1) In the present report the results of the measurements with zeolite minerals from foreign countries are given, while in the former reports the Japanese minerals have only been tested.

Mordenite. The locality of mordenite described in this report is Custer County, Idaho, U.S.A. It is a white soft matter of fibrous structure. The results of measurements are given in Tables 1, 2 and 3. The mineral was dehydrated by heating at 350°C. (Table 1) or 200°C. (Table 2 and Table 3) under evacuation. The pressures of the gases were kept at 760 mm. throughout the experiments.

The amounts of ammonia and carbon dioxide sorbed by this sample of mordenite is thus inferior to that which has been described in the former report.(2) The present sample sorbs ammonia with extreme rapidity, about 90 per cent. of the total amount being sorbed during the

(1) Sameshima, this Bulletin, **2** (1927), 2; **4** (1929), 96. Sameshima and Hemmi, *ibid.*, **9** (1934), 27.

(2) Sameshima and Hemmi, this Bulletin, **9** (1934), 32.

Table 1.

Sorption of Ammonia by Mordenite.

Mode of dehydration: Heating at 350°C. for 30 minutes under evacuation.
Loss of weight by dehydration: 4.89%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of mordenite
0.5	39.47
1	41.94
5	44.13
60	45.27
1440	45.94
1800	46.32

Table 2.

Sorption of Ammonia by Mordenite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 4.75%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of mordenite
0.5	33.62
1	35.81
5	38.20
60	40.20
1620	41.15

Table 3.

Sorption of Carbon Dioxide by Mordenite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 4.41%.

Time (min.)	Vol. (c.c.) of CO_2 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of mordenite
1	1.68
5	3.97
30	9.27
60	11.82
120	14.09
480	17.22
1440	18.18
3000	18.37

first few minutes. The behaviour is quite the same with that of chabazite,[3] silica gel,[4] and charcoal,[5] and differs from other zeolite minerals.[6] This fact shows that the dewatered mordenite does not form a compound with ammonia but only sorbs it into the cavities among the molecular gratings of the crystal. The dewatered mordenite forms a molecular sieve, and the sorption by such a matter may be classified as "the sorption of chabazite type."

Thomsonite. The composition of thomsonite is said to be $2[(Na_2Ca)Al_2Si_2O_8]\cdot 5H_2O$. The mineral from Table Mountains, Golden, Colorado, U.S.A., has been used. It is an aggregate of radial groups of white fibrous crystals. The experimental results are given in Tables 4 and 5.

(3) Sameshima, *ibid.*, **4** (1929), 100.
(4) Sameshima, *ibid.*, **7** (1932), 133.
(5) Sameshima, *ibid.*, **5** (1930), 173.
(6) Sameshima, *ibid.*, **4** (1929), 97; **5** (1930), 304. Sameshima and Hemmi, *ibid.*, **9** (1934), 27.

Table 4.

Sorption of Ammonia by Thomsonite.

Mode of dehydration: Heating at 350°C. for 1 hour under evacuation.
Loss of weight by dehydration: 11.68%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of thomsonite
0.5	0.60
1	0.80
120	0.92
1440	1.32
1800	1.46

Table 5.

Sorption of Ammonia by Thomsonite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 4.27%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of thomsonite
0.5	1.07
10	2.06
60	3.54
180	5.10
480	7.27
1440	10.66
2880	13.44
15 days	23.84

These tables show that the thomsonite dehydrated at 200°C. sorbs ammonia in a considerable amount, while that dehydrated at 350°C. sorbs but a small amount.

One gram of thomsonite, after dehydrated by heating to 200°C. for 2.5 hours under evacuation, sorbs 0.27 c.c. of carbon dioxide (N.T.P.) at 25°C. and 1 atmospheric pressure of gas during 4260 minutes. Thus the carbon dioxide is not practically sorbed by the dehydrated thomsonite.

It is probable that ammonia combines chemically with the partially dehydrated thomsonite. The chemical analysis of the thomsonite from Table Mountains, Golden, Colorado, U.S.A., being the same locality with our sample, shows that the water content is 12.7% in average.[7] The weight loss of our sample on heating at 350°C. amounts to 11.68%, so the dehydrated sample at this temperature is almost anhydrous and this sample has no combining power to ammonia. The mineral dehydrated at 200°C. lost water of only 4.2%, and this partially dehydrated sample has the ability of combining with ammonia. The dehydration of thomsonite at various temperatures was studied by Zambonini, whose observation agrees well with our present results.[8]

(7) Doelter, "Handbuch der Mineralchemie", Vol. II, 3rd Part (1921), 19.
(8) Doelter, *ibid.*, p. 24.

Scolecite. The mineral from Taigerhorn, Iceland, has been used. It is a big transparent colourless prismatic crystal. The composition of this mineral is said to be $CaAl_2Si_3O_{10}\cdot 3H_2O$. The result of measurement is given in Table 6.

Table 6.

Sorption of Ammonia by Scolecite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.

Loss of weight by dehydration: 4.99%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of scolecite
1	2.00
5	3.90
30	8.31
60	11.50
120	16.87
180	21.91
300	30.23
1440	55.26
2880	58.51
3060	58.64

The sample dehydrated by heating at 200°C. for 2.5 hours under evacuation has been tested for the sorption of carbon dioxide. One gram of the mineral sorbed only 0.13 c.c. of carbon dioxide at 25°C. and 1 atmospheric pressure during 1680 minutes. Thus the mineral sorbs ammonia but no carbon dioxide.

It is probable that ammonia combines with the partially dehydrated sample of scolecite. The loss of water in the process of dehydration of the present sample amounts to 4.99%. On the other hand, the loss should be 4.59% or 57.1 c.c. of water vapour at normal conditions from one gram of the mineral by the calculation under the assumption that one mol of water evaporates from one mol of mineral. The present sample of the ammoniacal scolecite, therefore, corresponds to the composition $CaAl_2Si_3O_{10}\cdot 2H_2O\cdot NH_3$.

Epistilbite. The locality of the mineral used is Giebelbach near Fiesch, Valais, Switzerland. It is colourless transparent crystals of a few millimeter size. The composition is said to be $H_4CaAl_2(SiO_3)_6\cdot 3H_2O$.[9] The result of the sorption experiment of ammonia is given in Table 7.

The sorption of ammonia does not yet arrive at saturation point and proceeds slowly. Sorption of 37 c.c. (N.T.P.) of ammonia by one gram of epistilbite corresponds to one mol of ammonia for one mol of

(9) Doelter, *ibid.*, p. 201.

the mineral, assuming the formula described above. Thus the ammoniacal epistilbite has the composition $H_4CaAl_2(SiO_3)_6 \cdot NH_3$.

The mineral sorbs carbon dioxide only in a small amount. One gram of the mineral, after being dehydrated by heating at 200°C. for 2.5 hours, sorbs 0.55 c.c. of CO_2 gas (N.T.P.) at 25°C. during 2820 minutes. So the sorption of ammonia by epistilbite may be considered as the chemical combination between these two substances.

Table 7.

Sorption of Ammonia by Epistilbite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 9.26%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of epistilbite
1	0.59
5	1.36
60	3.72
300	7.56
1440	16.49
2880	20.83
5760	29.08
9 60	36.12

Table 8.

Sorption of Ammonia by Phillipsite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 13.14%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of phillipsite
5	2.81
30	10.67
60	19.96
120	27.61
240	32.89
1440	44.67
7200	54.47
14460	58.82

Phillipsite. The locality of the mineral is Capo di Bove, Rome, Italy. It is a cluster of spherites of small translucent crystals. The composition may be $(K_2Ca)Al_2Si_6O_{16} \cdot 6H_2O$. The sorption of ammonia by this mineral has been measured and the result is given in Table 8.

From the result given in this table, the composition of the ammoniacal phillipsite may be $(K_2Ca)Al_2Si_6O_{16} \cdot 2NH_3$.

The sorption of carbon dioxide was measured. One gram of phillipsite, after being dehydrated by heating at 200°C. for 2.5 hours under evacuation, sorbed 0.59 c.c. of CO_2 (N.T.P.) at 25°C. and 1 atmospheric pressure of the gas during 1440 minutes. Thus the mineral sorbs a considerable amount of ammonia but not carbon dioxide, so the sorption of ammonia may be considered as a chemical combination.

Summary.

(1) The sorptions of ammonia and carbon dioxide under one atmospheric pressure at 25°C. by the dehydrated samples of mordenite, thomsonite, scolecite, epistilbite, and phillipsite have been measured.

(2) Mordenite sorbs either ammonia or carbon dioxide in a considerable amount. This is a sorbent of the chabazite type.

(3) Thomsonite, scolecite, epistilbite, and phillipsite sorb ammonia in a large amount but not carbon dioxide. These minerals combine chemically with ammonia and form definite compounds.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

SORPTION OF GAS BY MINERAL. VI.

By Jitsusaburo SAMESHIMA and Noriyoshi MORITA.

Received June 25th, 1935. Published October 28th, 1935.

The present report is a continuation of the preceding one. The sorptions of ammonia and carbon dioxide by sepiolite, talc, serpentine, asbestos, acid clay, bentonite, and vivianite are described in this paper.

Sepiolite. The sepiolite from Eskihi-Sher, Asia Minor, has been used. This is a light, porous, opaque mass of white colour. The composition of sepiolite is $H_4Mg_2Si_3O_{10}$. The results of the measurements are given in Tables 1, 2, 3, and 4.

The sepiolite sorbs either ammonia or carbon dioxide in a considerable amount. The sorption of gas by this substance resembles that by the silica gel or charcoal, and may be classified as "the sorption of silica gel type".

Talc. The mineral from Kaijoken, Mukden, Manchukuo, has been used. It is a translucent white mass of greasy lustre and the density is 2.86. The composition of talc is $H_2Mg_3Si_4O_{12}$. The weight loss on heating at 200°C. for 2.5 hours under evacuation was only 0.03%. The dried substance thus obtained sorbed 0.22 c.c. (N.T.P.) of ammonia and 0.02 c.c.

Table 1.

Sorption of Ammonia by Sepiolite.

Mode of dehydration: Heating at 350°C. for 30 minutes under evacuation.
Loss of weight by dehydration: 20.68%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of sepiolite
1	60.1
5	81.8
30	92.5
60	96.1
300	103.0
1500	110.8

Table 2.

Sorption of Ammonia by Sepiolite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 17.45%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of sepiolite
1	102.9
5	123.1
30	124.9
360	125.7
5760	127.0

Table 3.

Sorption of Carbon Dioxide by Sepiolite.

Mode of dehydration: Heating at 350°C. for 30 minutes under evacuation.
Loss of weight by dehydration: 21.34%.

Time (min.)	Vol. (c c.) of CO_2 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of sepiolite
1	14.4
30	15.6
300	16.6

Table 4.

Sorption of Carbon Dioxide by Sepiolite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 17.24%.

Time (min.)	Vol. (c.c.) of CO_2 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of sepiolite
1	22.8
5	24.7
30	24.9
1380	25.2

(N.T.P.) of carbon dioxide at 25°C. and 1 atmospheric pressure of gases. The present sample of talc sorbs, therefore, neither ammonia nor carbon dioxide.

Serpentine. The locality of the mineral used is Chichibu, Saitama Prefecture, Japan. It is a greenish mass and the density is 2.84. The composition of serpentine is $H_4Mg_3Si_2O_9$. The amount of sorption of ammonia is given in Table 5.

The sample dehydrated in the manner given above has been tested for carbon dioxide. It sorbed only 0.32 c.c. (N.T.P.) of carbon dioxide during 300 minutes. Thus, the serpentine sorbs a small amount of ammonia but not carbon dioxide.

Asbestos. The asbestos of long fibres has been used in this experiment, the locality, however, is not known. The experimental results are given in Table 6.

Table 5.

Sorption of Ammonia by Serpentine.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.

Loss of weight by dehydration: 0.41%.

Time (min.)	Vol. (c.c.) of NH_3 (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of serpentine
1	1.32
5	1.84
30	2.34
1500	2.85

Table 6.

Sorptions of Gases by Asbestos.

Mode of dehydration: Heating at 200°C. for 30 minutes under evacuation.

Loss of weight by dehydration: 3.1%.

Gas	Time (min.)	Pressure of gas (mm.)	Vol. (c.c.) of gas (N.T.P.) sorbed at 25°C. by 1 g. of asbestos
NH_3	1	754.4	9.51
	5	754.4	10.55
	30	754.5	11.03
	1230	760.5	11.64
	2890	760.3	11.80
CO_2	1	760.1	1.30
	60	759.4	1.46
	2900	766.1	1.70

Table 7.

Sorptions of Gases by Acid Clay.

Mode of dehydration: Heating at 200°C. for 1 hour under evacuation.

Loss of weight by dehydration: 20.59%.

Gas	Time (min.)	Pressure of gas (mm.)	Vol. (c.c.) of gas (N.T.P.) sorbed at 25°C. by 1 g. of acid clay
NH_3	1	769.3	34.37
	10	769.3	68.05
	30	769.3	72.70
	60	769.2	73.49
	1450	760.8	76.28
CO_2	1	765.4	2.81
	10	765.4	2.97
	160	765.1	3.02
	1620	762.0	3.04

Acid Clay. The sample from Itoigawa, Niigata Prefecture, Japan, has been used. It is a mass of yellowish white colour. The results of measurements are shown in Table 7.

Thus acid clay sorbs a great amount of ammonia but only a small amount of carbon dioxide. It is, therefore, probable that the ammonia combines with the dewatered sample of acid clay, and compounds are formed between them.

Bentonite. The bentonite from Rock River, Wyoming, U.S.A., has been used in the present experiment. It is a greenish yellow mass. The Japanese bentonite was already tested and described in one of the former reports.[1] The results of the sorption measurements of the American bentonite are shown in Table 8.

It seems that the present sample of bentonite shows the same behaviour toward ammonia and carbon dioxide with the Japanese acid clay. It may combine chemically with ammonia. The Japanese bentonite, when elutriated or dialysed, sorbs many kinds of gases as shown in the former paper.

Vivianite. The mineral from Ashio Mine, Tochigi Prefecture, Japan, has

Table 8.

Sorptions of Gases by Bentonite.

Mode of dehydration: Heating at 200°C. for 2.5 hours under evacuation.
Loss of weight by dehydration: 7.35%.

Gas	Time (min.)	Vol. (c.c.) of gas (N.T.P.) sorbed at 25°C. and 1 atm. press. by 1 g. of bentonite
NH_3	1	32.5
	5	41.8
	30	43.6
	360	45.4
	1440	46.1
CO_2	5	0.6
	480	1.0

Table 9.

Sorptions of Gases by Vivianite.

Mode of dehydration: Heating at 200°C. for 30 minutes under evacuation.
Loss of weight by dehydration: 23.66%.

Gas	Time (min.)	Pressure of gas (mm.)	Vol. (c.c.) of gas (N.T.P.) sorbed at 25°C. by 1 g. of vivianite
NH_3	2	766.4	2.46
	60	766.2	2.94
	3210	757.3	3.52
CO_2	5	761.9	0.33
	330	761.9	1.29
	2880	765.5	1.29

(1) Sameshima and Hemmi, this Bulletin, **9** (1934), 38.

been used. It is a transparent crystal of dark blue colour and vitreous lustre. The composition of vivianite is $Fe_3P_2O_8 \cdot 8H_2O$, from which the water content is calculated to be 28.7%. On heating at 200°C. the crystal takes an opaque black colour. The results are given in Table 9.

Summary.

(1) The sorptions of ammonia and carbon dioxide under one atmospheric pressure at 25°C. by the dehydrated samples of sepiolite, talc, serpentine, asbestos, acid clay, bentonite, and vivianite have been measured.

(2) Sepiolite sorbs either ammonia or carbon dioxide in a considerable amount. It is already known that this mineral sorbs various kinds of gases and that this is a sorbent of silica gel type.

(3) Acid clay and bentonite sorb ammonia but no carbon dioxide. Asbestos sorbs some amount of ammonia.

(4) Talc, serpentine, and vivianite sorb neither ammonia nor carbon dioxide.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.

INFLUENCE OF CALCIUM ON CARBOHYDRATE METABOLISM.

By Taichi HARADA.

Received July 11th, 1935. Published October 28th, 1935.

Extensive studies on the calcium metabolism of body, particularly from the point of view of explaining the cause of ricket, tetany, and other diseases have been made. But so far as the author knows very little study has been made on the influence of calcium on carbohydrate metabolism regarding diabetes. The present investigation is undertaken on this point with a connection with diabetes.

It is known that a normal adult needs more than 0.5 g. of calcium per day. Pregnant women and nursing mothers require a greater amount. It is believed that an average daily intake of calcium per capita exceeds

0.5 g. However only a small amount of calcium thus taken in is absorbed through the upper intestine while the rest is excreted mostly in the feces and partly in the urine as its salts.[1] The absorption depends upon its form in the food, or the degree of its solubility of the state.

Acid-base Balance. The balance of calcium content in the blood serum is ordinarily disturbed little in mild diabetes, but in the severe case with ketosis as well as in severe malnutrition, the amount of calcium in the serum is slightly lowered.[2] In these conditions the calcium deficiencies in the blood serum may be associated with low serum proteins. The most interesting symptom in diabetes is the acidosis which is commonly developed as a result of retention of ketonic acid, and is formed by the incomplete combustion of fats. Accordingly the CO_2 content in the plasma is lowered from 45–55 to somewhere 35–45 volume per cent.[3] with the fall of the *p*H before the symptoms appear (Table 1). In severe cases the whole electrolyte in the blood is strongly affected,[3][4] for example in the terminal condition of the diabetes the *p*H in the plasma falls below 7.1 and, the CO_2 content likewise becomes somewhere below 15 volume per cent. In addition to the fall of the *p*H and CO_2 content in the plasma there may also be a decrease in the content of Cl while the glycemia and glycosuria increase with an increase of the blood diastatic activity (Table 1).

Effect of Insulin Injection. After the injection of insulin, the ketosis and glycemia may be reduced with a transitory increase of the serum calcium[5] and the blood lactic acid,[6] while inorganic phosphorus in the serum decreases[7] either directly or indirectly. Accordingly the blood bicarbonate may likewise rise in this instance. This opposite effect is observed after adrenalin injection.[8]

---

(1) T. F. Zucker, *Proc. Soc. Exp. Biol. Med.*, **18** (1921), 272.

(2) W. H. Jansen, *D. Arch klin. Med.*, **144** (1924), 14.

(3) E. Stillman, D. D. Van Slyke, G. E. Cullen, and R. Fitz, *J. Biol. Chem.*, **30** (1917), 405.

(4) A. V. Bock, H. Field Jr., and G. S. Adair, *J. Metab. Res.*, **4** (1932), 27; G. E. Cullen and L. Janas, *J. Biol. Chem.*, **57** (1923), 541; A. F. Hartmann and D. C. Darrow, *J. Clin. Invest.*, **6** (1928), 257; J. P. Peters, H. A. Bulger, A. J. Eisenmann, and C. J. Lee, *ibid.*, **2** (1925), 167.

(5) J. C. Brougher, *Am. J. Physiol.*, **80** (1927), 411.

(6) C. H. Best and J. H. Ridout, *J. Biol. Chem.*, **63** (1925), 197; C. F. Cori, *ibid.*, **63** (1925), 253.

(7) J. P. Peters and L. Eiserson, *ibid.*, **84** (1929), 155; V. B. Wigglsoworth, *J. Physiol.*, **57** (1923), 447.

(8) J. P. Peters and H. R. Geyelin, *J. Biol. Chem.*, **31** (1917), 471.

Insulin Substitutes and their Actions. If insulin is taken by mouth there is little influence on the fall of glucose in the blood and urine. For this reason, recently various substitutes for insulin, which can be taken by mouth, have been proposed and tried. Among these an extract of huckleberry leaves[9] and guanidine derivatives[10][11] may be mentioned. Allen claims that the extract of huckleberry leaves reduces both hyperglycemia and glycosuria without any toxic action. Guanidine derivatives also have a distinct reducing effect on the hyperglycemia and glycosuria with an increase of the calcium in the serum,[12] but they have deleterious effect upon the livers and kidneys.[10] Both hydrazine derivatives[13] and sodium selenite[14] have actions similar to guanidine compounds, but the former is known to be injurious to the livers.

It is presumed that all these substitutes which are claimed by some to have therapeutic actions on diabetes mellitus, have no specific actions upon the disease, but they elevate the calcium content of the blood serum, and thereby both hyperglycemia and glycosuria may be reduced, either by the stimulation of calcium metabolism or by the decalcification of calcium stored in the body. If so, the parathyroid gland might play an important rôle on diabetes, since it controls the calcium metabolism of the body. The extract of parathyroid gland is effective on the metabolism, either when given by mouth or by intravenous injection, but an over-dose of the extract causes a negative calcium balance[15]. Therefore, the calcium for the metabolism must be supplied by intake of sufficient calcium in the form of food or of calcium compound. The commonest food to supply calcium is milk which contains about 1.2 g. per liter.

Food as a Cause of Diabetes. It is doubtful that all diabetes is due to disease of pancreas (the Islands of Langerhan) since there are no definite evidences given by either chemical or pathologic studies of the

(9) F. M. Allen, *Am. J. Physiol.* (*Soc. Proc.*), **81** (1927), 462.

(10) F. Bischoff, M. Sahyun, and M. L. Long, *J. Biol. Chem.*, **81** (1929), 325; N. R. Blatherwick, M. Sahyun, and E. Hill, *ibid.*, **75** (1927), 671; R. Bodo and H. P. Marks, *J. Physiol.*, **65** (1928), 83.

(11) E. Frank, M. Nothmaun, and A. Wagner, *Klin. Woch.*, **5** (1926), 2100.

(12) L. Nelken, *ibid.*, **2** (1923), 261.

(13) S. Izume and H. B. Lewis, *J. Biol. Chem.*, **71** (1926), 51; H. B. Lewis and S. Izume, *ibid.*, **71** (1926), 33.

(14) V. E. Levine and R. A. Flaherty, *Proc. Soc. Exp. Biol. Med.*, **24** (1926), 251.

(15) I. Greenwald and J. Gross, *J. Biol. Chem.*, **68** (1926), 325; S. H. Liu, *J. Clin. Invest.*, **5** (1928), 259.

gland. It seems that dietary in-balance is one of the most important factors causing diabetic acidosis. Whether the food has an acidifying or alkalinizing effect depends upon the amount of protein and unoxidizable acid or upon the amount of alkaline elements in the food.[16] Meat and other foods consisting largely of protein have acidifying effects. It is shown by Hasselbalch[17] that a change from a high carbohydrate to a high protein diet causes the fall of CO_2 capacity of blood about three per cent. by volume. Therefore, it seems that the high protein diet rather than high carbohydrate is responsible for a cause of diabetes.[18] If so, there might exist an important relation between the calcium, protein, and the carbohydrate in food, which prevents the causing of diabetes.

The author is interested only in the calcium compounds, which could increase the serum calcium by oral administration without accompanying acidosis or other toxic action, in order to carry out the present experiment.

Effect of Calcium Salts on the Serum. Inorganic calcium compounds such as $CaCl_2$[19] and $CaSO_4$ cause acidosis by selective excretion but not selective absorption. However, oral administration of calcium lactate does not cause acidosis because of its organic radical, and when absorbed, it is burned in the organism. After an oral administration of 5 g. of calcium lactate there is a rise of 5–14 per cent. of calcium in the serum[20] and keeps the elevation above normal level long as for 12 hours. However the increase of the amount of calcium appears to lengthen the duration rather than to elevate the calcium content.[21] Calcium lactate is a neutral drug and has no toxic action. The influence of orally administered calcium salts on the serum calcium content have been studied by Hjört.[22] The following order is given according to the degree of its absorption power or of its solubility:

$$CaCl_2 > CaFeC_9H_9O_{10}{}^{(23)}\,(C_6H_5O_7Fe + Ca(C_3H_5O_3)_2 = C_6H_5O_7Fe\cdot Ca\,C_3H_4O_3 + C_3H_6O_3) > Ca(C_3H_5O_3)_2 > Ca\,PO_4C_3H_5(OH)_2 > CaCO_3\,.$$

(16) N. R. Blatherwick, *Arch. Int. Med.*, **14** (1914), 409.
(17) K. A. Hasselbalch, *Skand. Arch. Physiol.*, **27** (1912), 1.
(18) R. M. Wilder, W. M. Boothby, and C. Beeler, *J. Biol. Chem.*, **51** (1922), 311.
(19) J. Dadlez, *Biochem. Z.*, **171** (1926), 146.
(20) W. Bauer and M. W. Ropes, *J. Am. Med. Assoc.*, **87** (1926), 1902.
(21) B. S. Kahn and J. H. Roe, *ibid.*, **86** (1926), 1761.
(22) A. M. Hjört, *J. Biol. Chem.*, **65** (1925), 783.
(23) T. Harada, this Bulletin, **10** (1935), 82.

Animal Experiment. Experiment 1. The influence of calcium lactate on the glucose tolerance in rabbits: 200 c.c. of 37.5% glucose aqueous solution was made by aid of heat, boiled for a few minutes, and the solution was divided into two equal parts. To one part 2.5 g. of calcium lactate was dissolved while it was hot. Both solutions were boiled again for a couple of minutes under same condition and cooled down to room temperature; then the solutions were made up to 100 c.c. with sterilized distilled water.

The urine in the bladder of rabbits were first evacuated by means of a catheter, and the rabbits were allowed to fast for 24 hours and at the end of that period the urine was collected by the same means as before for the control.

Then 20 c.c. of the glucose solution was injected to one rabbit in the peritonial cavity and the glucose-calcium-lactate solution to the other. While they were kept in this condition, the blood was taken out first one half hour then one hour intervals for four hours and also at the end of twenty four hours from the veins of each rabbit.

On the urine collected at the end of twenty four hours the sugar content was determined by the method of Benedict on one hand, and the sugar content in the blood was determined by Jeghers-Myer's modification of Folin's micro-method[24] on the other. The results are tabulated in Table 2 and 3.

Experiment 2. The influence of calcium lactate on blood sugar which should be elevated by the injection of adrenalin in rabbits was also studied in same manner as Experiment 1. The injection was made as follows: One with 0.2 c.c. of adrenalin (1:1000 dilution) only as a control, and the other with the same amount of adrenalin which was followed immediately after the injection of 20 c.c. of 2.5 per cent. calcium lactate solution. The results are given in Table 4 and 5.

Experiment 3. The influence of adrenalin-glucose (Table 6-A and 7-C) of adrenalin-glucose-calcium-lactate (Table 6-B and 7-B), and of adrenalin-calcium-lactate (Table 7-A) on the glycemia and the glycosuria were studied and compared as described in Experiment 1 and 2. However in this experiment the concentration of glucose-calcium-lactate, and calcium-lactate were reduced to one half with sterilized distilled water.

(24) H. J. Jeghers and V. C. Myers, *J. Lab. Clin. Med. St. Louis*, **15** (1930), 982.

Table 1.

Condition	Volume % plasma with CO_2 reduced to 0°., 760 mm.[25]	Diastatic units[25]	24 hr. excretion of 0.1 N acid NH_3 for 60 kg.[26] (c.c.)	*p*H of plasma corresponding to CO_2 combing power[27]	Blood sugar[25] (%)	$NaHCO_3$ required to turn urine alkaline for 60 kg.[26] (g.)
Normal resting adult	75—55	15—20	0—1600	7.51—7.40	0.09—0.12	0—30
Mild diabetic acidosis	55—45	20—40	1600—4000	7.40—7.34	0.15—0.30	30—50
Moderate diabetic acidosis	45—35		4000—6000	7.34—7.28		50—65
Severe diabetic acidosis	below 35	35—75	over 6000	below 7.28	0.30—1.20	over 65

Table 2. A.

♂ Wt.: 2015 g. Glucose (15 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1063	0.1617	0.1894	0.2188	0.1457	0.1169	0.1111
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	37 c.c., 0.250%, 0.093 g.			33 c.c., 1.736%, 0.573 g.			

B.

♂ Wt.: 2125 g. Glucose (15 g.) and calcium lactate (0.5 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.0968	0.1530	0.1546	0.1578	0.1457	0.1071	0.1111
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	50 c.c., 0.250%, 0.125 g.			37 c.c., 0.592%, 0.219 g.			

(25) V. C. Myers, "Pract. Chem. Anal. of Blood," St. Louis Mosby Co., (1921), 16.
(26) D. D. Van Slyke, *J. Biol. Chem.*, **33** (1918), 271.
(27) V. C. Myers and L. E. Booher, *ibid.*, **59** (1924), 699.

Table 3. A.

♂ Wt.: 2125 g. Glucose (15 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1095	0.1578	0.2205	0.2.05	0.1704	0.1119	0.0920
Urine sugar	for 24 h. before treament			24 h. after treatment			
	40 c.c., 0.250%, 0.100 g.			60 c.c., 2.000%, 1.200 g.			

B.

♂ Wt.: 1800 g. Glucose (15 g.) and calcium lactate (0.5 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1034	0.1471	0.1578	0.1578	0.1500	0.1234	0.1127
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	23 c.c., 0.266%, 0.061 g.			42 c.c., 1.407%, 0.591 g.			

Table 4. A.

♂ Wt.: 2040 g. Adrenalin (0.2 c.c.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1127	0.1428	0.1851	0.1327	0.1250	0.1136	0.1127
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	115 c.c., 0.182%, 0.209 g.			60 c.c., 0.388%, 0.233 g.			

B.

♂ Wt.: 1990 g. Adrenalin (0.2 c.c.) and calcium lactate (0.5 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.0938	0.1250	0.1281	0.1851	0.1472	0.1270	0.1000
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	95 c.c., 0.216%, 0.206 g.			45 c.c., 0.529%, 0.238 g.			

Table 5. A.

♂ Wt.: 2050 g. Adrenalin (0.2 c.c.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.0904	0.1327	0.1744	0.1530	0.1875	0.1630	0.1127
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	115 c.c., 0.182%, 0.209 g.			30 c.c., 1.071%, 0.321 g.			

B.

♂ Wt.: 2000 g. Adrenalin (0.2 c.c.) and calcium lactate (0.5 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1027	0.1250	0.1500	0.1744	0.1401	0.1292	0.0938
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	95 c c., 0.216%, 0.206 g.			66 c.c., 0.341%, 0.225 g.			

Table 6. A.

♂ Wt.: 2280 g. Adrenalin (0.2 c.c.) and glucose (15 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1095	0.3333	0.3750	0.4545	0.5000	0.4687	0.0980
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	35 c c., 0.074%, 0.026 g.			13 c.c., 3.934%, 0.511 g.			

B.

♂ Wt.: 2300 g. Adrenalin (0.2 c.c.), glucose (15 g.) and calcium lactate (0.5 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.0987	0.2586	0.2727	0.2500	0.2830	0.2885	0.0820
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	24 c.c., 0.121%, 0.029 g.			15 c.c., 2.522%, 0.378 g.			

Table 7. A.

♂ Wt.: 2240 g.: Adrenalin (0.2 c.c.) and calcium lactate (0.25 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1154	0.1667	0.1724	0.2239	0.2235	0.1875	0.1292
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	30 c.c., 0.04%, 0.012 g.			17 c.c., 4.638%, 0.789 g.			

B.

♂ Wt.: 2100 g. Adrenalin (0.2 c.c.), glucose (7.5 g.) and calcium lactate (0.25 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1154	0.3125	0.2778	0.2778	0.2459	0.2143	0.1119
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	95 c.c., 0.190%, 0.181 g.			28 c.c., 1.875%, 0.525 g.			

C.

♂ Wt.: 2135 g. Adrenalin (0.2 c.c.) and glucose (7.5 g.)

	Control	1/2 h.	1	2	3	4	24
Blood sugar in %	0.1200	0.3846	0.4167	0.4167	0.3750	0.3571	0.1281
Urine sugar	for 24 h. before treatment			24 h. after treatment			
	95 c.c., 0.130%, 0.124 g.			28 c.c., 7.200%, 2.016 g.			

Conclusion from the Results. When calcium in the form of organic salts as described above was injected with glucose (Table 2 and 3) especially with glucose-adrenalin (Table 6 and 7) into rabbits it prevented considerably the elevation of the sugar contents in both the blood and urine, which would occur when glucose alone or glucose-adrenalin without calcium was administered. However the calcium had little influence on the activity of adrenalin on the blood sugar (Table 4 and 5). Why calcium assists the combustion of the carbohydrate in the body is not clear. It is presumed that the disease of diabetes is probably attended by an imperfect calcium metabolism, thereby the combustion of carbohydrate being disturbed either directly or indirectly.

In other words the production or the activity of insulin will probably depend upon the calcium content in the blood.

Summary.

(1) The glucose tolerance on albino-rabbits was studied.

(2) The influence of calcium upon the activity of adrenalin on the blood sugar in the rabbit was experimented. It gave little change.

(3) An interesting relation between calcium and the carbohydrate metabolism of the body was observed: that is, calcium prevents considerably the elevation in both hyperglycemia and glycosuria which would occur when glucose alone or glucose-adrenalin without calcium was administered.

The author is indebted to Dr. Katayama in the use of the laboratory of St. Luke's International Medical Center, Tokyo, and his helpful suggestions in carrying out this experiment.

ISOTOPIC SHIFT OF WATER BY DISTILLATION

J. HORIUTI and G. OKAMOTO.

Received September 7th, 1935. Published October 28th, 1935.

The isotopic shift of water by distillation has been observed by several authors[1] mainly at the normal boiling temperature and pressure. We have determined the shift in a heavy water sample of 2.60% deuterium content on slow vacuum distillation at several lower temperatures.

Ten milligrams water was distilled each time from 20 g. of the same sample, which was kept at a constant temperature within a few hundredths of a degree. The distillation took place within 40 to 60 minutes at a temperature difference of about half a degree. The distillate was analysed by means of a micropycnometer[2] and was compared with the original water sample as shown in the table.

(1) Lewis and Cornish, *J. Am. Chem. Soc.*, **55** (1933), 2661. Hall and Jones, *ibid.*, **56** (1934), 749. Harada and Titani, *this Bulletin*, **10** (1935), 39.

(2) Gilfillan and Polanyi, *Z. physik. Chem.*, [A], **166** (1933), 254. The original method was improved by the authors and accuracy appreciably increased.

Deuterium Content of Distillates from 2.60% Heavy Water.

Temp. of distillation (°C.)	0.05	20.42	−5.94	−6.42	0.08	21.48	21.00
Deuterium content (%)	2.42	2.49	2.39	2.38	2.38	2.46	2.47

The deuterium content of the original water sample was measured from time to time during the experiment and was proved to be constant within limits of error.

The heterogeneous equilibrium studied here might be expressed by the following formula:

$$H_2O_{vap} + HDO_{liq}\text{-}xH_2O_{liq} = HDO_{vap} + H_2O_{liq}\text{-}xH_2O_{liq},$$

where xH_2O_{liq} denotes environments of the molecule in the liquid state. H_2O_{liq}-xH_2O_{liq} may be a polymer. D_2O concentration was neglected here and environments both of H_2O and of HDO molecules were assumed to be the same, because of the low deuterium content. The measured shift of the distillate gives directly the equilibrium constant of the reaction, $RT \ln\frac{p_{HDO}}{p_{H_2O}} + \text{const.}$ The heat toning of the reaction or the difference between partial molar heat of vaporisation for HDO and H_2O was calculated from the temperature variation of the equilibrium constant as -215 ± 24 calories.

The heat toning of the reaction might also be correlated with spectroscopic data. We assumed that the rotational energies are fully excited at the temperatures, that the rotational degree of freedom in liquid phase is exactly the same for HDO_{liq} and for H_2O_{liq} and that vibrational energies are at their lowest quantum states both for single molecule and for polymers in the liquid. The heat toning Q is then given by the difference of zero point energies of aggregates,

$$Q = \frac{1}{2}\sum h\nu_{H_2O_{vap}} + \frac{1}{2}\sum h\nu_{HDO_{liq}\text{-}xH_2O_{liq}} - \frac{1}{2}\sum h\nu_{HDO_{vap}} - \frac{1}{2}\sum h\nu_{H_2O_{liq}\text{-}xH_2O_{liq}},$$

where νs means fundamental vibrational frequencies. Fundamental frequencies were given for H_2O_{vap} and HDO_{vap} by Bartholomé and

Clusius,[3] and by Wood,[4] and for liquid by Ellis and Sorge.[5] Ellis and Sorge assume the fourth fundamental frequency ω^* for polymerisation and give 2130 cm.$^{-1}$ for H_2O and 1640 cm.$^{-1}$ for D_2O. Should Q by the above expression give the measured heat toning taking ω^* into account, lacking data of ω^* for HDO would be 1740 cm.$^{-1}$, which lies between those for H_2O and for D_2O. The expression for Q would give positive value +300 cals. without taking ω^* into consideration, in contrary to the measured endothermicity of the reaction.

We wish to thank Prof. Yoshimichi Hori for the heavy water sample used in this experiment.

Chemical Department, Faculty of Science,
Hokkaido Imperial University,
Sapporo, Japan.

---

(3) Bartholomé and Clusius, *Z. Elektrochem.*, **40** (1934), **529.**
(4) Wood, *Phys. Rev.*, **45** (1934), 732.
(5) Ellis and Sorge, *J. Chem. Phys.*, **2** (1934), **558.**

A NEW MICROSCOPIC METHOD FOR MEASURING THE VISCOSITY OF A LIQUID.

By **Fumio HIRATA**

Received July 17th, 1935. Published November 28th, 1935.

Although the methods and apparatus for measuring the viscosity of a liquid found in literature are numerous in number and differ in principle, we can classify them into following categories:

(1) Those based on the measurement of the velocity of the liquid efflux from a horizontal or a vertical capillary tube.

(2) Those based on the measurement of the motion of a spherical or a cylindrical body in the liquid.

(3) Those based on the measurement of the angle of rotation of one cylinder dipped co-aixally in another hollow cylinder filled with the liquid.

(4) Those based on the measurement of the rotatory oscillation of a sphere, a cylinder, or a circular disk in the liquid.

(5) Other special methods.[1]

The new method of measurement proposed here differs in principle from those cited above and, having several characteristic features, is very useful, especially for the measurement of viscosity of viscous liquids, e.g. colloidal solutions of high concentration.

Theoretical.

The principle of this new method of measurement is quite simple. The liquid to be measured is made to flow under a definite pressure in a capillary tube of definite radius and length. The velocity of flow on the axis of the capillary tube is measured directly under a microscope and thus the absolute viscosity is determined. The theoretical formula is derived in the same way as in the case of Poisuille's law. When a

(1) A. Lampel, *Sitzb. Akad. Wiss. Wien*, (2a), **93** (1886), 291. H. Helmholtz and G. Piotrwski, *Sitzb. Akad. Wiss. Wien*, (2a), **40** (1868), 607. R. Ladenburg, *Ann. Physik*, (4), **27** (1908), 157. K. Mützel, *Wied. Ann.*, **43** (1891), 15. Subrahmaniam. *Indian J. Physics*, **1** (1926), 267. G. Stokes, *Phil. Mag.*, (4), **1** (1882), 337. F. Watson, *Phys. Rev.*, **15** (1902), 20. C. E. Guye and S. Mintz, *Arch. sci. phys. nat.*, (4), **26** (1908), 136. Gümbel, *Z. tech. Physik*, **1** (1920), 72. R. O. Boswall, *Phil. Mag.*, (7), **3** (1927), 994. G. Richardson, *J. Scient. Instrument*, **6** (1927), 337. H. A. Wilson, *Proc. Cambridge Phil. Soc.*, **10** (1900), 25. R. Z. Fürth, *Z. Physik*, **60** (1903), 313.

liquid flows without slip or turbulence in a capillary tube, the following relation is given:

$$v = \frac{P}{4l\eta}(R^2-r^2) \qquad (1),$$

in which, v is the velocity of the flow at the distance r from the axis, l the length, and R the radius, of the capillary tube, P the difference of pressure at the two ends of the capillary tube, and η the viscosity of the liquid. Putting $r = 0$, we have v_0, the velocity on the axis of the tube:

$$v_0 = \frac{PR^2}{4l\eta} \qquad (2), \qquad \text{hence} \qquad \eta = \frac{PR^2}{4lv_0} \qquad (3).$$

As P, R, and l are known, we can determine the value η, if we can measure v_0. In practice, the measurement of P, R, and l is so simple that no explanation will be needed. It would be necessary to discuss how we can measure v_0, or whether v_0 is a measurable quantity.

I. v_0, a Measurable Value. Let us assume the viscosity of the liquid to be 10 (in absolute unit), the order of the viscosity of glycerine at ordinary temperature, and also, the radius of the capillary tube to be 0.05 cm. and its length 10 cm. Putting these values in the equation (2), we have $v_0 = 0.000625P$. Suppose a pressure is given by a water column, and let the height of the column be h, and we have $v_0 = 0.0613h$. The relations between v_0 and h are shown in Table 1. From this Table, we see that, under the pressure of the water column ranging from 1/100 mm. to 100 cm. in height, the velocity may be measured with the aid of a microscope and an ocular micrometer. For, as the displacement in the microscopic field is v_0t (t being the time required for the displacement), if we assume t=1000 sec., the measurement of the minimum value of v_0 in the table is possible. For a larger value of v_0, it is possible to measure with the same accuracy up to the value ca. h=0.1, if we take t smaller than above. In short, it may be said that, as v_0 is a measurable value even when radius R is 0.05 cm., we can always bring the value v_0 within the possible range of measurement by regulating the radius, the length,

Table 1.

h (cm.)	v (cm./sec.)
0.001	0.0000613
0.01	0.000613
0.1	0.00613
1	0.0613
10	0.613
100	6.13

and the pressure. So, it may be concluded that v_0 is a value measurable in the microscopic method.

II. The Range η can be Measured. Putting reasonable values for P,R,l in equation (3) let us try to determine the range where the measurement of η is possible.

R	(minimum value) 0.01 cm.	(maximum value) 0.5 cm.
l	5 cm.	20 cm.
P	1 cm. (water column)	150 cm. (mercury column)
v_0	0.00005 cm./sec.	0.005 cm./sec.

Measuring under these conditions with the aid of a stop watch, we have, within the accuracy of 0.001, the following numbers for η:

minimum value 2.4×10^{-1} (absolute unit), maximum value 5.0×10^{8} (absolute unit).

Therefore, the range is 10^9. For trial, if we calculate the range measurable with an Ostwald type viscosimeter, under the similar conditions, assuming the volume of liquid to be 5 c.c., and the time of flow 50 sec. (minimum), and 1000 sec. (maximum), we have:

minimum value 3.9×10^{-6} (absolute unit), maximum value 1.9×10^{6} (absolute unit).

In the method of falling ball, let the conditions be:

radius of the ball	(minimum value) 0.1 cm.	(maximum value) 0.5 cm.
time of fall	100 sec.	1000 sec.
density of ball	1.06	16.6

Furthermore, let the density of the liquid be 1 and the distance of the fall 10 cm., and we have, with the aid of Ladenburg's equation of correction:

minimum value 1.4×10^{0} (absolute unit), maximum value 6.5×10^{6} (absolute unit).

In practice, it is difficult to get perfectly spherical balls with different densities. Therefore, if we use the steel balls for ball-bearing on the market, we have the following numbers:

minimum value 16×10^{2} (absolute unit), maximum value 2.8×10^{6} (absolute unit).

Comparing these results, we see that the ordinary capillary viscosimeter is suitable for liquids of smaller viscosity, while the microscopic method is more useful for liquids of higher viscosity, and that the possible range of measurement is the largest in the latter.

III. Practical Method of Measuring v_0. A practical method of measurement in this microscopic method is as follows: first, fine solid particles are mixed with, and uniformly dispersed in, the liquid, and the liquid is put in a capillary tube. Then, with the aid of a microscope, we select any one particle among the particles which lie on the axis of the capillary tube. With this particle for an indicator, the velocity of the translation of the liquid is determined with the aid of an ocular micrometer and a stop watch. Therefore, it is necessary that the properties, the quantity to be added, and the radii of these particles should be examined.

(a) *Selection of Particles.* It is necessary that we should use the particles of a solid substance which is perfectly free from chemical reaction with, or from being dissolved by, the liquid to be investigated. For example, powder of carbon, platinum, silica, glass, Al_2O_3, SiC, etc. are suitable for this purpose. Though adsorption by the particles may be supposed to occur, this is negligible as the quantity to be added is very small. Of course, there is no need of taking this into consideration when the sample liquid is pure. It may be added that the particles must be free from swelling in the liquid.

(b) *Quantity of Particles to be Added.* The effect of the particles added on the viscosity of the liquid is as follows. Suppose that η, the viscosity of the sample, changes to η', on account of the addition of the particles, and that the measurements are done with the same capillary tube and under the same pressure, we have, by the equation (3),

$$\eta = \frac{R^2}{4lv_0} \quad (4), \qquad \eta' = \frac{R^2}{4lv_0'} \quad (5).$$

As the relation given by Einstein is applicable between the viscosity of the dispersed system and that of the medium, we have:

$$\eta' = \eta(1+2.5\varphi),$$

where φ is the value of the total volume the particles occupy, divided by the whole volume of the dispersed system. From (4), (5), and (6),

$$v_0 = (1+2.5\varphi)v_0', \qquad \text{hence} \qquad v_0' = v_0\left(\frac{1}{1+2.5\varphi}\right);$$

therefore, $v_0' = v_0(1-2.5\varphi)$, $\quad \frac{v_0'-v}{v_0} = -2.5\varphi$, $\quad \frac{\Delta v_0}{v_0} = -2.5\varphi$.

Let m be the quantity of the fine particles in 100 c.c. of the dispersed system, and ρ the density of the particle, then

$$\frac{\Delta v_0}{v_0} = -0.025\frac{m}{\rho}.$$

Assuming $m = 0.01$ g., we have Table 2.

Table 2.

ρ	$\Delta v_0/v_0$
0.5	0.0005
1	0.00025
2	0.00013
3	0.00008
4	0.00006
5	0.00005

As has already been noted, if the measurements of v_0 are done, in the case of $m = 0.01$ g., in the accuracy of 1/1000, all values of Table 2 becomes already less than the accuracy. Therefore, the velocity of the particle may be taken as the velocity of the liquid when the latter contains no particle. If we assume $\rho = 3$, the value $m = 0.1$ g. become within the range of the experimental errors. So, the use of the particle up to this value may well be admitted.

(c) *Radius and Number of the Particles.* The particle must be large enough to be an objective in the microscopic field, and the number of the particles must be sufficient so that the selection of the particle on the axis of the capillary tube may be done with ease. If we assume that one cubic millimetre of liquid contains 100 particles, the particle must be present in the probability of 10 particles on one millimetre of the axis. In order to obtain distribution of this density the radius of the particle ought to be

$$r = \sqrt[3]{\frac{3}{4}\frac{m}{\pi\rho n}}$$

where n is the number of particles in 1 cm.^{3}; r radius of the particle, m total mass of the particles, and ρ the density. Let $m = 0.001$ g., $\rho = 1$, $n = 10$, then we have $r = 0.0029$ cm. Therefore, it is sufficient, if we add the particles of radius of 0.03 mm. at the rate of 0.01 g. per 100 c.c. Moreover, this will also satisfy the conditions of the paragraph (b). In practice, as the selection of the objective particle can be done in the state of flow, the number of the particles may be far less than the rate just given.

(d) *Distance of Sedimentation Occurring during the Time of Measurement.* It may happen that, the particle, as the result of sedimentation due to gravity, escapes away from the focus of the microscope while being observed. This point may here be discussed. The distance

of sedimentation of a sphere, whose radius is r and density ρ_2, in a liquid with viscosity η and density ρ_1, will be given by the Stokes' law:

$$x = \frac{2}{9}\frac{r^2}{\eta}(\rho_2-\rho_1)gt\ .$$

If we assume the particle to be that of carborundum in water, then the distance x will be equal to 0.014 cm. for the time interval of $t = 1000$ sec.; and if $r = 0.0001$ cm., we have $x = 0.0003$ cm. Therefore, in this case, it is necessary to use the particle of $r = 0.0001$ cm., that is, 1 μ in radius. If the liquid has the density of the degree of glycerine, the particle may be of the radius of about 0.01 cm. With the liquid of higher viscosity, it is almost unnecessary to take this matter into consideration. From these investigations, it may be concluded that the microscopic method of measuring the viscosity of a liquid is a proposition not only practical, but also very convenient. Before describing the results of measurement, some distinctive characteristics of this method may be enumerated here:

(1) The measurement can be secured with a small quantity of the sample, only a few c.c. being sufficient.

(2) The possible range of measurement is wide.

(3) The measurement of the density of the sample is not necessary. In general, it is very difficult to measure the density of a viscous fluid. From this point of view, the present method may be said to be very useful.

(4) No special apparatus of measurement is required.

(5) As the presence of anomalous viscosity or a turbulent flow is recognized directly, the normal value of viscosity may be obtained.

Experimental.

I. Apparatus for Measurement. The measuring cell is made of glass with a horizontal capillary of ca. 10 cm. length and a vertical side tube of ca. 5 cm. height (Fig. 1). The schematic figure of the whole arrangement of the apparatus is given in Fig. 2. In the figure, AB is the measuring cell, M a microscope furnished with an ocular micrometer, F a green light filter which is used to get a sharp image of the objective particle in the field, S an incandescent electric lamp of Leitz make, the light source used in microphotography. At middle C of the capillary tube, two small pieces of glass plates are attached with balsam one above

and one below. They serve the purpose of keeping the rays from the light source parallel and of securing a sharp outline of the objective particle. D is a three-way stop cock, N a liquid manometer, P and Q

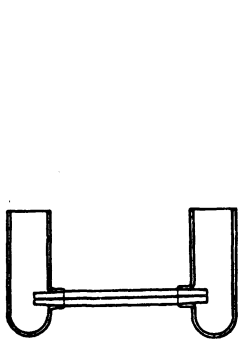


Fig. 1.

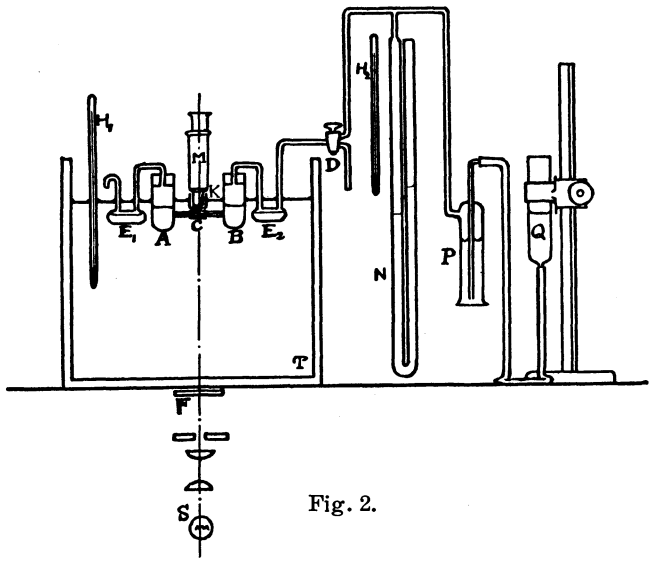


Fig. 2.

water holders which serve to produce pressure, P being fixed, Q movable up and down by a microscrew. E_1 and E_2 are small glass bulbs containing the same liquid as the sample, and serve to prevent the latter from evaporation or concentration, or taking moisture. In the experiments (1) and (2), where glycerine was used as the material for test, the measuring cell was kept at room temperature, but in the experiment (3), the cell was dipped in a thermostat, and the objective of the microscope was covered with a small glass cap K with a plane bottom, and was dipped in the liquid of the thermostat. The liquid used in N, P, and Q, was pure water, but, if necessary, mercury might be used.

II. Procedure. First, the tube for measurement AB is filled with the sample uniformly dispersed with objective particles and then all the connections are completed, as shown in Fig. 2. Then the selection of the objective particle in microscopic field is done. For this purpose, the axis of the capillary tube must be determined in the microscopic field. In order to do this, the ocular micrometer is fixed at right angles to the capillary tube. Then by the image of the walls of tube, the position of the axis of the tube is determined on the scale of the micrometer. Now

the ocular is turned, the microscope being fixed, just 90° and the scale of the micrometer is made to coincide with the axis of the tube. Then by raising and lowering the microscope vertically with the focus on the upper and then on the lower limit of the inner wall of the tube, two readings of the microscrew are obtained. The microscope is then fixed at the point just in the middle of these readings. Thus, the focus of the microscope is fixed on the axis of the capillary tube. In this position, the particle seen sharply in the centre of the field may be regarded to be on the axis of the tube. Now opening D, and making the liquid to flow in the capillary tube, a suitable particle is waited for to appear. When the objective particle is selected, the time is measure, with a stop watch, needed for the passage of the particle between two fixed points on the scale of the micrometer. Then the readings of the manometer as well as the thermometer are recorded. It is necessary to repeat the measurement several times under the same pressure until the maximum value of the velocity of the particle is obtained. Then the pressure is changed and measurement is done in the same manner. The measurement must also be done with the flow in the reverse way. The reason for this is that the pressure which causes the liquid to flow is not merely the pressure which is read on the manometer. Besides this, there is also a pressure, which affects the flow, due to the difference of the levels of the liquid in the two side tubes. In many cases, the levels in the side tubes are not equal in height under the condition with the stop-cock D closed. Especially, when the viscosity of the sample is very high, it is difficult that the levels in the two side tubes should become equal in height; and moreover when the surface of the liquid are in a curved state as it may well be, a considerable time will be required for it to regain the normal meniscus. It is necessary, therefore, to determine the value of the pressure due to this difference of the levels. Let us assume that under the positive or negative values of the pressure indicated on the manometer P_1, P_2, P_3, ... P_n, the velocities of flow, v_{01}, v_{02}, v_{03}, ... v_{0n}, have been obtained respectively. Plotting the diagram with P and v_0 as the coordinate axis, we get straight lines. In general, these straight lines do not pass through the origin. The distance, from the point where the line crosses the P-axis to the origin, indicates exactly the value of the pressure due to the difference of the levels. It may be assumed that this value is practically constant during measurements. A simple calculation shows this. Let the inner radius of the capillary tube be 0.05 cm., that of the side tube be 1.5 cm., and the number of the times of measurement be 10, the time needed for each measurements, the liquid passes only in one direction, and the volume of the liquid translated will be

$V = 1.47 \times 10^{-2}$ cm.^{3}, as $V = \dfrac{\pi R^4 P t}{8 l \eta}$, $R = 0.05$ cm., $P = 10^3$ dyne/cm., $l = 10$ cm., $\eta = 10$, and $t = 600$ sec. Therefore, the change of the levels in the side tubes will be $\Delta h = 2.00 \times 10^{-3}$ cm. which is within the error of the readings of the manometer. In practice, as the liquid travels in both directions, this value becomes smaller; and the pressure due to the difference of levels in the side tubes may be treated as unchanged during measurements. Now, the relation between P and v_0 becomes linear. (Of course, as is indicated in equation (2), it must be so theoretically.) The value P must be the algebraic sum of the two pressures, that is, $P = P_1 + P_2$, where P_1 is the value indicated in manometer, and P_2 is the value due to the difference of the levels. As regards the selection of the signs of P_1 and P_2, the pressures which make the objective particle move in the same direction have been given the same sign.

Now, we try to derive an equation by which the calculation can be worked out with the experimental data. Taking a general equation of a straight line, $P = a + bv_0$, where a corresponds to P_2 and may be put as constant and b is also a constant which must be determined from the experimental data. With the method of least square, the equations of condition may be obtained:

$$\frac{\delta}{\delta a}(P-a-bv_0)^2 = 0\,, \qquad \frac{\delta}{\delta b}(P-a-bv_0)^2 = 0\,,$$

therefore $$P-a-bv_0 = 0\,, \qquad Pv_0-av_0-bv_0^2 = 0\,.$$

From n numbers of observations, we have:

$$\sum_{i=1}^{n} P_i - na - b\sum_{i=1}^{n} v_{0i} = 0\,, \qquad \sum_{i=1}^{n} P_i v_{0i} - a\sum_{i=1}^{n} v_{0i} - b\sum_{i=1}^{n} v_{0i}^2 = 0\,.$$

From these equations, we get b:

$$b = \frac{\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0i} - n\sum_{i=1}^{n} v_{0i}P_i}{\left(\sum_{i=1}^{n} v_{0i}\right)^2 - n\sum_{i=1}^{n} v_{0i}^2}\,.$$

Thus if we have b, the viscosity η will be calculated with the equation (3).

$$\eta = \frac{R^2}{4l}\frac{P}{v_0} = \frac{R^2(P-a)}{4lv_0} = \frac{R^2}{4l}b = \frac{R^2}{4l}\frac{\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0i} - n\sum_{i=1}^{n} P_i v_{0i}}{\left(\sum_{i=1}^{n} v_{0i}\right)^2 - n\sum_{i=1}^{n} v_{0i}^2}\,.$$

III. Experimental Materials and Conditions of Measurement. The liquids used for the experiment were glycerine, acetone solution of cellulose acetate, the former being of the highest grade of Price make. The density of the sample used in the experiments (1) and (2), was $D_4^{30°} = 1.2506$, and that in the experiment (3) was $D_4^{25°} = 1.2532$. For the acetone solution of cellulose acetate, "Cellit L, low viscosity" was used. A certain quantity of this substance was dissolved in pure acetone and then made free from solid matters with a centrifuge. Then, to determine the concentration, a certain quantity was drawn and dried up under reduced pressure and the residue was weighed. The concentration was 15.90%. This solution was used in the experiments (4), (5), (6), and (7).

For the objective particles, carbon and carborundum particles were used. The carbon particles had been made by burning benzene, then washing, defatting with CS_2, and heating at about 300°C. The diameter of the carbon particles was ca. 1/10 mm. to 1/100 mm. The carborundum powder used was that on the market for use in grinding. The powder was made to suspend in water and, after a while, the middle layer of the suspension was collected. The powder thus obtained had

Table 3.

Exp. No.	1	2	3	4	5	6	7
Sample liquid	Glycerine No. 1	do.	Glycerine No. 2	Acetone solution of cellulose acetate	do.	do.	do.
Capillary tube	Tube No. 1 $R=$ 0.040 cm. $l=9.96$ cm.	do.	do.	do.	do.	Tube No. 2 $R=$ 0.0545 cm. $l=9.91$ cm.	Tube No. 3 $R=$ 0.0965 cm. $l=9.94$ cm.
Objective	Carbon particle	do.	do.	Carborundum particle	do.	do.	do.
Quantity of particles added	0.1 g. per 100 c.c.	do.	do.	0.2 g. per 100 c.c.	do.	do.	do.
Measuring temp.	At room temp.	do.	25.00°C. ±0.01	30.0°C. ±0.1	26.4°C. ±0.1	do.	do.
Room temp.	30.0°C.	do.	20.0°C.	25.0°C.	29.5°C.	29.5°C.	28.0°C.
Remark			In thermostat	In simple bath	do.	do.	do.
Table No.	4	5	6	7	8	9	10
p–v Diagram	Fig. 3	Fig. 4	Fig. 5	Fig. 6.	Fig. 7	Fig. 8	Fig. 9

the diameter of the order of 1/50 mm. to 1/500 mm. These particles were treated first with concentrated hydrochloric acid, then with dilute hydrochloric acid, separated from the liquid with a centrifuge, made alkaline with ammonia, and washed with pure water, the centrifuge always being resorted to separate the liquid. Other experimental conditions are tabulated in Table 3.

IV. Results of Measurement and Their Discussion. (1) *Effect of the Quantity of Particles on Viscosity.* The experiment relative to the point discussed in **Theoretical, III, (b),** that is, the effect of quantity of particles added on viscosity was carried out and the following results were obtained.

(i) With an ordinary capillary viscosimeter, and glycerine without the particles, the following numbers were obtained: temp. 25.00°C. ± 0.01 (in thermostat); time of flow, (1) 19 min. 34.1 sec., (2) 19 min. 35.7 sec., (3) 19 min. 35.9 sec., (4) 19 min. 35.5 sec., mean value 19 min. 35.3 sec.

(ii) In the same glycerine, the carbon particles were mixed at the rate of 0.1 g. in 100 c.c. of glycerine, and the time of flow was measured with the same viscosimeter. The following data were obtained: temp. 25.00°C. ± 0.01; time of flow (1) 19 min. 36.2 sec., (2) 19 min 33.9 sec., (3) 19 min. 35.0 sec., (4) 19 min. 37.7 sec., mean value 19 min. 35.7 sec.

The increase of the time of flow due to the addition of the particle was 0.4 sec. This is 0.04% against 1175.3 sec. of the time of flow. This shows that the effect is within the experimental error and is quite negligible.

(2) *The Result of Measurement of Viscosity by the Microscopic Method.* (i) *Measurement at Room Temperature.* This was a preliminary measurement, which was indicated as experiment (1) and (2), and the results are given in Table 4 and 5. As the mean value $\eta = 4.36$ (absolute unit) was obtained. With an Ostwald viscosimeter, using the same sample, we obtained $\eta = 4.54$ (absolute unit). This is the value obtained in the thermostat of 30°C. As accuracy was not maintained in point of temperature, the comparison of the data is, strictly speaking, unreasonable but the result shows that the present method of viscosity measurement is quite a practical one.

(ii) *Measurement in the Thermostat.* From the preliminary test, the practical value of the present method of measurement was ascertained. So, definitive measurements were carried out. To gain the accuracy possible, the measuring tube was put in the thermostat, and the mano-

meter was read with a measuring microscope up to the order of 0.01 mm. The sample was glycerine No. 2. The results are shown in Table 6 as exp. (3). The observed value was $\eta^{25°} = 5.93_3$ (absolute unit).

The viscosity of the liquid relative to water was measured with the same sample, in the same thermostat with an ordinary capillary viscosimeter and with the aid of the value of absolute viscosity of water, $\eta^{25°} = 5.93_2$ (absolute unit) was obtained. In this case, the time of flow of water was 24.8 sec. and that of the sample liquid was 13120 sec., the density was 1.2532, and as density and absolute viscosity of water, the values $D_4^{25°} = 0.99707$ and $\eta_{H_2O}^{25°} = 0.008941$ respectively were used in the calculation.

The comparison of these two values of viscosity shows that coincidence is quite satisfactory. But, the coincidence at the second decimal place seems to be by chance, as the error of time measurement is to appear at this decimal place. As regards other factors, the errors will appear at the fourth decimal place. Therefore, it is not difficult to increase the accuracy of measurement by increasing the time of measurement. From this definitive measurement, it may be accepted that this new method of measurement gives quite satisfactory results in point of accuracy.

(iii) *Measurement of Viscosity of Acetone Solution of Cellulose Acetate.* With this new method, a measurement of absolute viscosity of acetone solution of cellulose acetate was carried out. The results of measurement are given in Table 7. (Exp. No. 4)

(3) *The Relation between the Inner Radius of the Capillary Tube and the Value of Viscosity Measured.* When the inner radius of the capillary part of measuring tube changes, the relation comes in as the power of square of the radius by equation (3). To verify this relation, experiments were carried out, with the same liquid and with the measuring tubes of different radius in capillary parts. These are exp. (5), (6), (7), and the results are shown in Table 8–11.

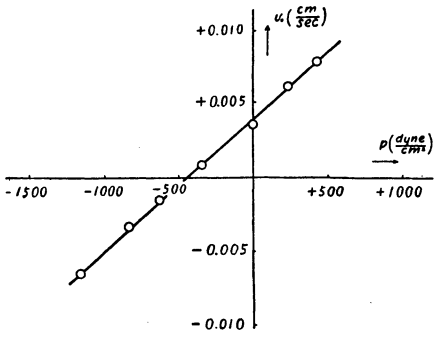


Fig. 3.

The sample was an acetone solution of cellulose acetate, same as stated in the preceding section. As the measurements were carried out in a simple bath, the results obtained are by no means perfect. However,

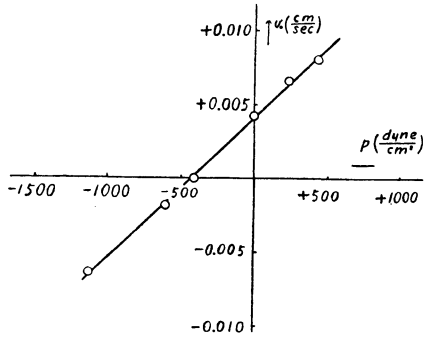


Fig. 4.

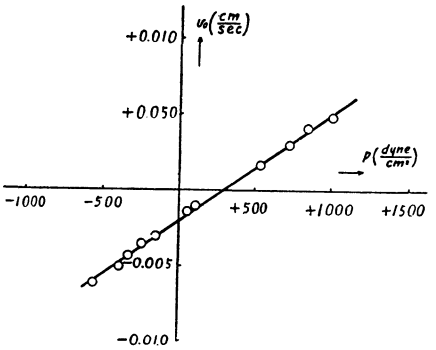


Fig. 5.

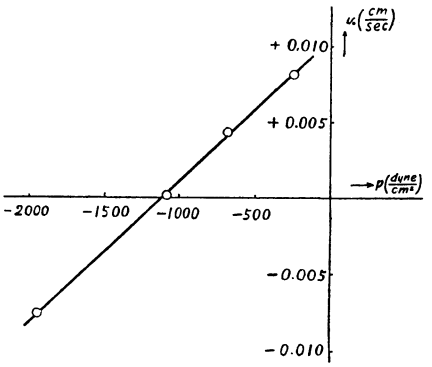


Fig. 6.

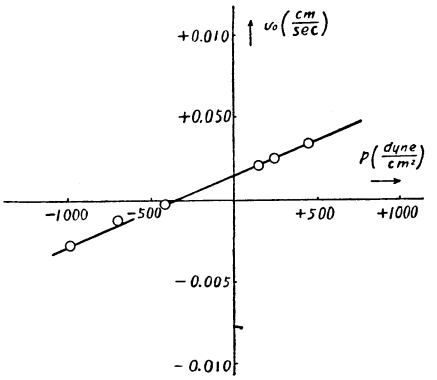


Fig. 7.

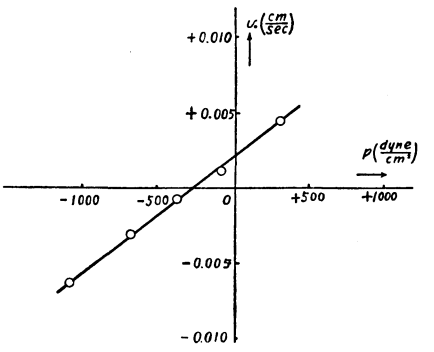


Fig. 8.

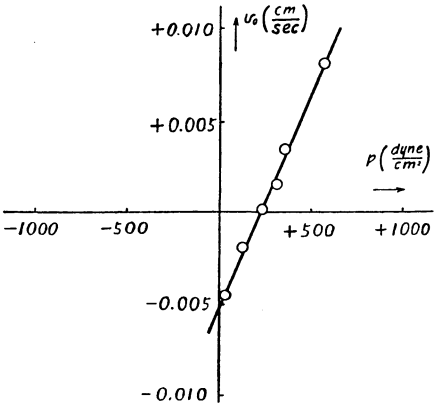


Fig. 9.

Table 4.

No.	$v_0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	−0.006413	−1133.0	0.00004113	+7.266	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = -15.73$
2	−0.001914	− 605.4	0.00000366	+1.159	$n \sum_{i=1}^{n} P_i v_{0_i} = +81.34$
3	−0.000161	− 410.1	0.00000003	+0.066	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.0001126$
4	+0.004275	± 0.000	0.00001828	±0.000	$n \sum_{i=1}^{n} v_{0_i}^2 = +0.001044$
5	+0.006678	+ 234.4	0.00004460	+1.565	$\frac{R^2}{4l} = 0.00004016$
6	+0.008144	+ 429.7	0.00006632	+3.500	$b = 1.043 \times 10^5$
$\sum_{i=1}^{n}$	+0.01061	−1484	+0.0001740	+13.56	$\eta = 4.18_7$
Viscosity (obs.)		1. By microscopic method			$\eta = 4.18_7$ (abs. unit)
		2. By capillary viscosimeter			$\eta = 4.54_4$ (abs. unit)

Table 5.

No.	$v^0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	+0.007895	+429.7	0.00006233	+3.393	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = -17.50$
2	+0.006256	+234.3	0.00003914	+1.466	$n \sum_{i=1}^{n} P_i v_{0_i} = +110.18$
3	+0.003620	±0.000	0.00001310	±0.000	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.00005664$
4	+0.000862	−351.5	0.00007430	−0.3030	$n \sum_{i=1}^{n} v_{0_i}^2 = +0.001187$
5	−0.001496	−624.9	0.00000224	+0.9348	$\frac{R^2}{4l} = 0.00004016$
6	−0.003268	−839.8	0.00001068	+2.732	$b = 1.130 \times 10^5$
7	−0.006413	− 1172	0.00004113	+7.516	$\eta = 4.53_8$
$\sum_{i=1}^{n}$	+0.007526	− 2324	0.0001695	+15.74	
Viscosity (obs.)		1. By microscopic method			$\eta = 4.53_8$ (abs. unit)
		2. By capillary viscosimeter			$\eta = 4.54_4$ (abs. unit)

Table 6.

No.	$v_0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	−0.001394	+59.71	0.00000194	−0.08384	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = -17.47$
2	−0.003000	−152.7	0.00000300	+0.4581	$n \sum_{i=1}^{n} P_i v_{0_i} = +214.35$
3	−0.003538	−243.7	0.00001252	+0.8623	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.0001184$
4	−0.004275	−331.8	0.00001828	+1.4185	$n \sum_{i=1}^{n} v_{0_i}^2 = +0.0016874$
5	−0.005130	−394.5	0.00002633	+2.0236	$\frac{R^2}{4l} = 0.00004016$
6	−0.006181	−560.9	0.00003820	+3.4666	$b = 1.478 \times 10^5$
7	−0.001016	+112.6	0.00000103	−0.1143	$\eta = 5.93_3$
8	+0.001676	+533.5	0.00000281	+0.8944	
9	+0.003054	+723.4	0.00000933	+2.2088	
10	+0.004171	+832.4	0.00001740	+3.4701	
11	+0.004750	+1028.0	0.00002256	+4.8820	
$\sum_{i=1}^{n}$	−0.010884	+1605.6	0.0001534	+19.486	
Visocity (obs.)		1. By microscopic method			$\eta = 5.93_3$ (abs. unit)
		2. By capillary viscosimeter			$\eta = 5.93_2$ (abs. unit)

Table 7.

No.	$v_0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	+0.008143	−254.2	0.00006631	−2.070	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = -7.919$
2	+0.004385	−684.5	0.00001928	−3.001	$n \sum_{i=1}^{n} P_i v_{0_i} = +76.80$
3	+0.0005109	− 1085	0.00000026	−0.5543	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.000002048$
4	−0.007600	− 1946	0.00005776	+14.79	$n \sum_{i=1}^{n} v_{0_i}^2 = +0.0007980$
5	−0.004008	− 1564	0.00001606	+6.196	$\frac{R^2}{4l} = 0.00004016$
$\sum_{i=1}^{n}$	+0.001431	− 5534	0.0001596	+15.36	$b = 1.064 \times 10^5$
Viscosity (obs.)		$\eta = 4.27_4$ (abs. unit)			

Table 8.

No.	$v_0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	+0.003466	+449.3	0.00001201	+1.5573	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = +32.70$
2	+0.002559	+253.9	0.00000256	+0.6497	$n\sum_{i=1}^{n} P_i v_{0_i} = +295.60$
3	+0.002129	+156.3	0.00000453	+0.3328	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.00005663$
4	−0.0002392	−420.0	0.00000006	+0.1005	$n\sum_{i=1}^{n} v_{0_i}^2 = +0.00151$
5	−0.001207	−713.0	0.00000146	+0.8606	$\frac{R^2}{4l} = 0.00004016$
6	−0.002788	−986.5	0.00000777	+2.7504	$b = 2.403\times10^5$
7	−0.01166	−3086	0.00013596	+35.983	
$\sum_{i=1}^{n}$	−0.007525	−4346	0.00016435	+42.23	
Viscosity (obs.)	$\eta = 9.65_4$ (abs. unit)				

Table 9.

No.	$v_0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	−0.006334	−1104.0	0.00004012	+6.993	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = +8.765$
2	−0.003109	−693.5	0.00000967	+2.156	$n\sum_{i=1}^{n} P_i v_{0_i} = +52.10$
3	−0.0006503	−390.7	0.00000042	+0.2541	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.00001934$
4	+0.001196	−97.67	0.00000143	−0.1168	$n\sum_{i=1}^{n} v_{0_i}^2 = +0.0003595$
5	+0.004500	+293.0	0.00002025	+1.1318	$\frac{R^2}{4l} = 0.00007593$
$\sum_{i=1}^{n}$	−0.004398	−1992.9	0.00007189	+10.42	$b = 1.274\times10^5$
Viscosity (obs.)	$\eta = 9.67_6$ (abs. unit)				

Table 10.

No.	$v_0\left(\frac{\text{cm.}}{\text{sec.}}\right)$	$P\left(\frac{\text{dyne}}{\text{cm.}^2}\right)$	v_0^2	Pv_0	Remark
1	−0.004499	+29.31	0.00002024	−0.1319	$\sum_{i=1}^{n} P_i \sum_{i=1}^{n} v_{0_i} = +11.036$
2	−0.001936	+136.8	0.00000375	−0.2649	$n\sum_{i=1}^{n} P_i v_{0_i} = +35.598$
3	+0.0001494	+234.5	0.00000002	+0.03503	$\left(\sum_{i=1}^{n} v_{0_i}\right)^2 = +0.00004629$
4	+0.001560	+302.9	0.00000243	+0.4725	$n\sum_{i=1}^{n} v_{0_i}^2 = +0.0006186$
5	+0.003514	+342.0	0.00001235	+1.202	$\frac{R^2}{4l} = 0.0002342$
6	+0.008016	+576.4	0.00006426	+4.620	$b = 4.222\times10^4$
$\sum_{i=1}^{n}$	+0.006804	+1622	0.0001031	+5.933	
Viscosity (obs.)	$\eta = 9.88_7$ (abs. unit)				

Table 11.

Tube No.	l (Length of tube)	R (Radius of tube)	R^2/l	b	$K\left(=\frac{R^2}{l}\times b\right)$
1	9.96	0.0400	0.0001606	2.403×10^5	38.6
2	9.91	0.0545	0.0003037	1.274×10^5	38.7
3	9.94	0.0965	0.0009368	4.222×10^4	39.6

as is shown in Table 11, the products of R^2/l and b are almost constant for all capillary tubes. This is what the theory requires. These results also indicate that the microscopic method of measurement is practical.

Summary.

(1) In connection with the method for measuring the viscosity of a liquid, a microscopic method, quite different from the methods hitherto known has been proposed and its possibility has been examined.

(2) The advantages of this microscopic method has been enumerated.

(3) The apparatus and the procedure of the measurement has been described.

(4) The theoretical relation of the influence of the fine particles added to the sample liquid on the viscosity of the liquid has been confirmed by experiment.

(5) The viscosity of glycerine and acetone solution of cellulose acetate has been measured by this new method.

(6) The results of measurements by the new method and those by the Ostwald viscosimeter have been compared, and the accuracy of the new method has been shown.

(7) It is shown that the relation between the viscosity and the radius of the measuring capillary tube is in accord with the theory.

The author desires to express here his feeling of obligation to Professor S. Horiba for his kind guidance throughout the investigation. The author also desires to express his gratitude to the Department of Education which supplied him with the necessary expenses for the investigation by granting him a Subsidy for Encouragement of the Study of Natural Science. The author is also indebted to Mr. T. Daimon who assisted him in the experiments.

Laboratory of Colloid Chemistry,
Kiriu Higher Technical School.

BIOCHEMICAL STUDIES ON "SOTETSU" (*Cycas revoluta* Thunb.). IV. ON SOTETSU-EMULSIN.

By Kôtaro NISHIDA.

Received July 23rd, 1935. Published November 28th, 1935.

Dr. K. Yoshimura[1] in our college discovered that "Sotetsu," especially its seed, contains a fair amount of formaldehyde, and stated that the sotetsu-poison is due to the presence of the formaldehyde. He prepared a distillate from the alcoholic extract of mashed sotetsu-seed, in which he detected formaldehyde by using Nessler's reagent and ammoniacal silver nitrate solution, and then identified by preparing hexamethylene-tetramine. His study greatly arouses our interest, especially from the biochemical point of view; he did not, however, investigate the form of formaldehyde in "Sotetsu."

(1) K. Yoshimura, *Bull. Kagoshima Agr. College*, **5** (1922), 25.

The writer[2] at first confirmed Yoshimura's experimental results by a different method, Rimini's and Vitali's colour reactions, and by preparing formaldomedon for identification. And then the writer found that the formaldehyde in "Sotetsu" is in the combined state of a new glucoside, and liberated it from the glucoside by the action of the emulsin in "Sotetsu."

So the writer intended to study the new glucoside containing formaldehyde and the sotetsu-emulsin. In the present paper, mainly some properties of sotetsu-emulsin are described.

I. Identification of Formaldehyde in Sotetsu-seed. Twenty hulled sotetsu-seeds were mashed and extracted with boiling 90% alcohol, and the alcoholic extract was evaporated to a small volume under reduced pressure. The distillate of the steam distillation of the above solution gave intensive Rimini's and Vitali's reactions, and 0.8 g. of its domedon crystallized out on adding 1.0 g. dimedon. The domedon thus obtained formed lustrous colourless prisms and melted at 188°C. (uncorr.), agreeing with formaldomedon.

II. The Form of Formaldehyde in Sotetsu-seed. Experiment A. A hulled sotetsu-seed was mashed and put into the thermostat at 35°C., and after 4 hours it was steam-distilled. The distillate gave intensive colour reactions for formaldehyde. Sulphuric acid was added to the residue of steam distillation and the distillation was continued further; in the second distillate, the formaldehyde reaction was inferior. **Experiment B.** A carefully hulled sotetsu-seed was boiled for 30 minutes under a reflux condenser, and treated in the same way as above. In this case, even in the first distillate the reactions of formaldehyde were very weak.

The results of quantitative estimation of formaldehyde are shown in Table 1.

Table 1.

Experiment	Sample (g.)	HCHO mg. in 1st distillate	HCHO mg. dissolved in boiling water
A	9.3374	13.3	—
B	8.4887	1.3	5.3

Thus, the formaldehyde in sotetsu-seed is an enzymatic decomposition product from its compound.

(2) K. Nishida, *J. Agr. Chem. Soc. Japan*, **11** (1935), 357.

III. Preparation of Sotetsu-emulsin. The hulled sotetsu-seeds were mashed and mixed thoroughly with an equal weight of water containing a small amount of toluene, and put into an ice-box. After one night, the mass was pressed on a cloth, and the filtered liquid was acidified with acetic acid to precipitate proteins. From the filtrate, the crude enzyme was precipitated with alcohol or acetone. The precipitate was washed with absolute alcohol or acetone, then with ether and finally it was dried in vacuo over sulphuric acid. For the further purification the resulting precipitate was redissolved in water and reprecipitated with alcohol or acetone and treated similarly to the above operation. By using acetone as precipitant, the yield of the emulsin-preparation from 4 kg. sample was 6.0 g.

IV. Usual Methods of Estimation of Enzyme Activity. The digestion mixtures usually consisted of 15 c.c. of 1% salicin solution, 5 c.c. of 0.4–0.8% sotetsu-emulsin solution, and 2 c.c. of Sörensen's buffer solution. The mixtures, preserved with toluene, were kept at 37°, usually for digestion hours of 90 minutes. Enzyme solution, inactivated by heat, were employed as controls in usual way. The enzyme activity has been measured by determining the reducing action of the decomposed salicin, e.g. with respect to Fehling's solution according to Bertrand.

V. Optimum *p*H of the Sotetsu-emulsin. In determining the *p*H optimum, citrate-HCl or phosphate buffer was used. The activity of

Table 2.

Salicin Hydrolysis at Various Hydrogen Ion Concentrations.

(15 c.c. of 1% salicin, 5 c.c. of 0.4% enzyme, 37°, 90 mm.)

*p*H	Standard $KMnO_4$ (c.c.)	Salicin hydrolysed (%)	$\frac{10^3}{t}\ln\frac{a}{a-x}$	$\frac{\varphi}{\Phi}$
3.6	3.10	16.8	2.04	0.52
4.3	5.05	27.7	3.60	0.92
4.5	5.15	28.3	3.70	0.95
4.8	5.35	29.5	3.88	0.99
5.1	5.40	29.7	3.91	1.00
5.2	5.20	28.6	3.74	0.96
5.8	4.90	26.9	3.48	0.89
5.9	4.80	26.3	3.39	0.87
6.1	4.55	24.8	3.17	0.81
7.0	2.45	13.2	1.57	0.40

sotetsu-emulsin at various values of *p*H are summarized in Table 2, in which the *p*H value indicates the mean of the initial and final reactions.

Thus the sotetsu-emulsin exhibited optimum activity for salicin hydrolysis, in the solution of *p*H 5.1. E. Vulquin[3] stated that almond-emulsin had an optimum activity at *p*H 4.4; whereas *p*H 4.7 to 5.1 for β-methylglucoside, 6.0 for amygdalin, and 4.2 for lactose were optimum for almond-emulsin according to Willstätter and Csányi.[4]

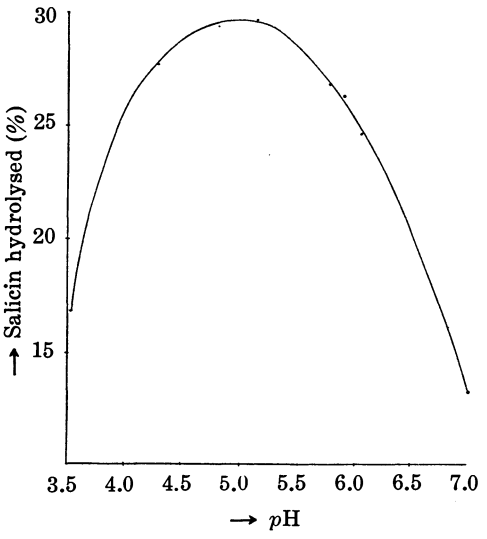


Fig. 1.

VI. Optimum Temperature of the Sotetsu-emulsin. The optimum temperature of sotetsu-emulsin was sought by using the usual mixtures of *p*H 4.8. Each of these mixtures was immersed in a water bath at different temperatures for 90 minutes. The rate of decomposition of salicin by sotetsu-emulsin at various temperatures was estimated as shown in Table 3.

Table 3.

Optimum Temperature for Salicin Hydrolysis by Sotetsu-emulsin.

(15 c.c. of 1% salicin, 5 c.c. of 0.8% enzyme, *p*H 4.8, 90 min.)

Temperature (°C)	Standard $KMnO_4$ (c.c.)	Salicin hydrolysed (%)	$\frac{10^3}{t}\ln\frac{a}{a-x}$	$\frac{\varphi}{\Phi}$
30	8.95	50.8	7.88	0.44
35	9.70	55.4	8.97	0.50
40	10.35	58.9	9.88	0.55
45	11.15	64.5	11.50	0.64
50	12.85	75.3	15.53	0.87
55	13.55	80.0	17.88	1.00
60	13.45	79.3	17.40	0.97
65	10.15	58.2	9.69	0.54

(3) E. Vulquin, *Soc. biol., Paris*, **70** (1911), 270, 763.
(4) R. Willstätter and W. Csányi, *Z. physiol. Chem.*, **117** (1921), 172.

According to the above results, the reaction velocity of the sotetsu-emulsin is accelerated as the temperature is raised to 55°C. On further elevation of the temperature the reaction velocity begins to diminish, and when the *p*H value of the solution is 4.8, we see that the sotetsu-emulsin may act at a maximum activity at 55–60°C.

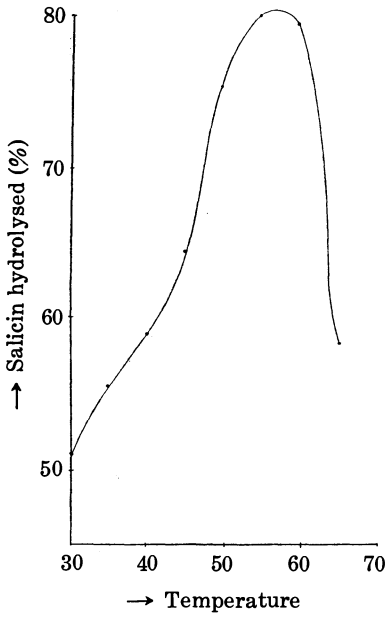


Fig. 2.

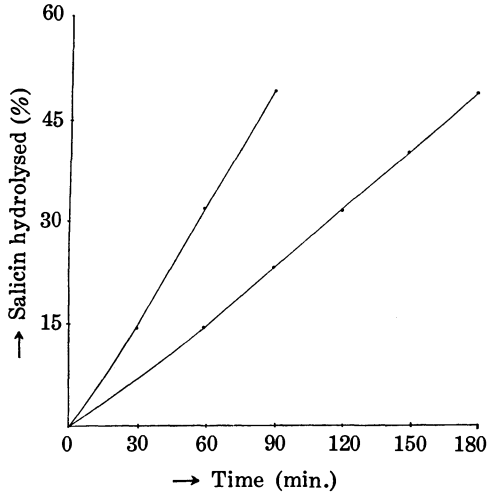


Fig. 3.

VII. Reaction Course of Sotetsu-emulsin. Hudson and Paine[5] studying the hydrolysis of salicin with almond-emulsin found that the reaction course of the enzyme follows the monomolecular reaction. J. Giaga[6] states that the reaction course of emulsin varies with the enzymes used and follows a sort of selective mass action law. Willstätter and Csányi[7] reported that the reaction of almond-emulsin for amygdalin hydrolysis was not found as a monomolecular reaction. And also according to Helferich's experiment,[8] in the reaction of Kahlbaum's emulsin-preparation for salicin hydrolysis, the monomolecular reaction constant increased in course of time. In our experiments with sotetsu-emulsin, as shown in table 4, we found almost the same tendency.

(5) Hudson and Paine, *J. Am. Chem. Soc.*, **31** (1909), 1242.
(6) J. Giaga, *J. chim. phys.*, **19** (1921), 77; *Chem. Abst.*, **16** (1922), 2336.
(7) *Loc. cit.*
(8) B. Helferich, *Z. physiol. Chem.*, **117** (1921), 159.

Table 4.

Kinetics of Salicin Hydrolysis by Sotetsu-emulsin.

(15 c.c. of 1% salicin, 5 c.c. of 0.4% enzyme, pH = 4.4, 37°)

Time (min.)	Standard $KMnO_4$ (c.c.)	Salicin hydrolysed (%)	$\frac{10^3}{t}\ln\frac{a}{a-x}$
60	2.70	14.2	2.55
90	4.30	22.9	2.89
120	5.80	31.4	3.14
150	7.25	39.7	3.37
180	8.80	48.9	3.73

VIII. Reaction Velocity and Enzyme Amount. According to Auld,[9] the reaction velocity of amygdalin hydrolysis by almond-emulsin is proportional to the concentration of the enzyme. Willstätter and Csányi[10] reported that the reaction velociy of hydrolysis of amygdalin, β-methyl-glucoside lactose and raffinose by enzyme is proportional to the amount of the enzyme. In our experiments, also on the decomposition of salicin the same relation was observed. The results are summarized in Table 5.

Table 5.

Reaction Velocity and Enzyme Amount. (pH = 4.4, 37°)

Substrate	Sotetsu-emulsin	Time (min.)	Standard $KMnO_4$ (c.c.)	Salicin hydrolysed (%)
15 c.c. of 1% Salicin	5 c.c. of 0.4% solution	60	2.70	14.2
,,	5 c.c. of 0.8% solution	30	2.70	14.2
,,	5 c.c. of 0.4% solution	120	5.80	31.3
,,	5 c.c. of 0.8% solution	60	5.85	31.7
,,	5 c.c. of 0.4% solution	180	8.80	48.9
,,	5 c.c. of 0.8% solution	90	8.80	48.9

IX. Total Hydrolysis of Salicin by Sotetsu-emulsin. Bertrand and Compton[11] reported that the salicin in concentration very much superior to that found in plants was completely hydrolysed by the action of emulsin. Also we found that glucose was completely splitted off from salicin, as shown in Table 6.

(9) S. J. M. Auld, *J. Chem. Soc.*, **93** (1908), 1251.

(10) *Loc. cit.*

(11) G. Bertrand and A. Compton, *Ann. Inst. Pasteur*, **39** (1925), 355; *Chem. Abst.*, **19** (1925), 2962.

Table 6.

Total Hydrolysis of Salicin by Sotetsu-emulsin.

(15 c.c. of 1% salicin, 5 c.c. of 0.8% emulsin, pH = 4.8, 37°)

Time (hour)	Standard $KMnO_4$ (c.c.)	Salicin hydrolysed (%)	$\frac{10^3}{t}\ln\frac{a}{a-x}$
5	15.70	94.5	9.67
7	16.15	97.5	8.79
8	16.50	100.0	9.59
15	16.50	100.0	—

Summary.

The principal experimental results described above are summarized as follows:

(1) Sotetsu-seed contains a glucoside of formaldehyde and this substance splits off formaldehyde by the action of sotetsu-emulsin.

(2) The emulsin was easily prepared from sotetsu-seed and some of its properties were studied in the case of salicin as substrate.

(3) The sotetsu-emulsin exhibited maximum activity in the solution of pH near 5.0.

(4) It was observed that the optimum temperature of sotetsu-emulsin for salicin hydrolysis is 55–60°C. near the optimum hydrogen ion concentration.

(5) In the reaction course of sotetsu-emulsin for salicin hydrolysis, the monomolecular reaction constant increased in course of time.

(6) The reaction velocity of salicin hydrolysis is proportional to the amount of sotetsu-emulsin.

(7) The salicin in 15 c.c. of 1% solution was completely hydrolysed by the action of sotetsu-emulsin in 5 c.c. of 0.8% solution, at the end of 8 hours in the digestion mixture of pH value 4.8 and temperature 37°C.

In conclusion, the writer wishes to express his thanks to Mr. A. Yamada for the kind assistance. He is also indebted to the Nippon Gakujutsu Shinkokwai, a part of the research expenses being defrayed from its grant.

Laboratory of Agricultural Chemistry,
Kagoshima Agricultural College,
Kagoshima.

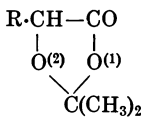
CATALYTIC HYDROGENATION OF ACETONE-COMPOUNDS OF α-HYDROXY-ACIDS.*

By Haruomi ÔEDA.

Received July 27th, 1935. Published November 28th, 1935.

In a previous communication,(1) preparation of acetone-compounds of some α-hydroxy-acids was reported. As already described in that paper, the manipulation for their preparations is simple and their yields are fairly good in almost all cases and there is the prospect that they can be favourably used as a starting material for several reactions.

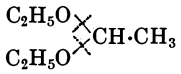
In the present communication studies on catalytic hydrogenation of these compounds under pressure are reported. Copper-chromium oxide was used as catalyzer, which had been proved by H. Adkins(2) to be very effective in the reduction of esters into alcohols.



In the heterocyclic ring of acetone-compounds of α-hydroxy-acids, one of the oxygen atoms (1) may functionate as ester, and on hydrogenation, it is probable that the cleavage of linking might occur in carbonyl side of the oxygen, as in the hydrogenation of esters:

$$R{\cdot}COOC_2H_5 \longrightarrow R{\cdot}CH_2OH + HOC_2H_5$$

Another oxygen (2) in the ring may be compared with those in ethers or acetals. Several papers(3) are published on the hydrogenation of acetals and in every instance cleavage of the molecule occurs in the aldehyde side of the oxygen with regeneration of the alcohol, detaching the aldehyde as a hydrocarbon:



$$\longrightarrow 2\,C_2H_5OH + CH_3{\cdot}CH_3$$

Recently K. Yoshikawa(4) obtained hexahydric alcohols in the hydrogenation of many hexoses. It may also be regarded as the same cleavage

* Studies on Hydroxy-Acids and their Derivatives. III.

(1) H. Ôeda, this Bulletin, **10** (1935), 187.

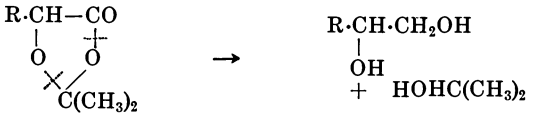
(2) H. Adkins, K. Folkers, *J. Am. Chem. Soc.*, **53** (1931), 1095; **54** (1932), 1145. H. Adkins, B. Wojcik, L. Covert, *ibid.*, **55** (1933), 1669.

(3) T. Kariyone, *J. Pharm. Soc. Japan*, **43** (1923), 51. M. Bergmann, N. Carter, *Z. physiol. Chem.*, **191** (1930), 211. L. Covert, R. Connor, H. Adkins, *J. Am. Chem. Soc.*, **54** (1932), 1651.

(4) K. Yoshikawa, *Bull. Inst. Phys. Chem. Research, Japan*, **13** (1934), 1045.

of acetal linking in the sugar molecules. These facts suggest that, through hydrogenation, cleavage in linking (2) may occur in isopropylidene side of the oxygen.

From the above consideration, the hydrogenation of these acetone-compounds may result in the formation of corresponding glycols as well as isopropyl alcohol.



The experimental results of the present study agree with the above expectation except in one case and they are summarized in Table 1.

H. Adkins has studied on the hydrogenation of ethyl lactate[5] and ethyl mandelate[6] in the presence of copper-chromium oxide and he found that the former yielded propylene glycol, while, it was not the case

Table 1.

Substance	Products
$CH_3 \cdot CH(O-CO)-C(CH_3)_2$ (O) Acetone-lactic acid	$CH_3 \cdot CHOH \cdot CH_2OH$ Propylene glycol + $HOHC(CH_3)_2$ Isopropyl alcohol —
$(CH_3)_2CH \cdot CH_2 \cdot CH(O-CO)-C(CH_3)_2$ (O) Acetone-leucic acid	$(CH_3)_2CH \cdot CH_2 \cdot CHOH \cdot CH_2OH$ Isohexylene glycol + $HOHC(CH_3)_2$ Isopropyl alcohol + $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_2OH$ Isohexyl alcohol
$C_6H_5 \cdot CH(O-CO)-C(CH_3)_2$ (O) Acetone-mandelic acid	— + $HOHC(CH_3)_2$ Isopropyl alcohol + $C_6H_5 \cdot CH_2 \cdot CH_2OH$ β-Phenyl-ethyl alcohol + Aromatic hydrocarbon
$C_6H_5 \cdot CH_2 \cdot CH(O-CO)-C(CH_3)_2$ (O) Acetone-phenyl-lactic acid	$C_6H_5CH_2 \cdot CHOH \cdot CH_2OH$ Benzyl-ethylene glycol + $HOHC(CH_3)_2$ Isopropyl alcohol + $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$ γ-Phenyl-propyl alcohol + $C_6H_5 \cdot CH_2 \cdot CHOH \cdot CH_3$ Benzyl methyl carbinol

(5) K. Folkers, H. Adkins, *J. Am. Chem. Soc.*, **54** (1932), 1145.

(6) H. Adkins, B. Wojcik, L. Covert, *J. Am. Chem. Soc.*, **55** (1933), 1669.

with the latter, which never yielded glycol, but gave a considerable amount of ethyl-benzene together with phenyl-ethyl alcohol. He concluded that hydroxyl attached to a carbon having benzenoid ring was very labile and hydrogenation of further advanced stage occurred in this case.*

The results obtained in the present study are in good agreement with the works of Adkins as shown in Table 1. Hydrocarbon yielded from mandelic ester was mentioned by Adkins as ethyl-benzene. Corresponding fraction in distillation has been also obtained from the acetone-compound.**

Expected course of hydrogenation was observed in the other two acetone-compounds. Both of them were found to give corresponding glycol and monohydric alcohol or alcohols which may be regarded as products of further hydrogenation of the glycol.

A viscous odourless liquid boiling at 111–113.5° under 15 mm. was obtained from acetone-leucic acid and it was found to be isohexylene glycol by the analysis as well as by the formation of bis-phenylurethane (m.p. 115–116°). No information of this glycol is found in literature.

By the action of phenyl magnesium bromide upon α-monochlorohydrine of glycerol, Grignard[7] obtained a mixture of two isomeric glycols, which boils at 163–165° under 12 mm. Benzyl-ethylene glycol[8] yielded from acetone-phenyl-lactic acid corresponds to one of the glycols of Grignard. Its bis-phenylurethane was prepared, which was isolated in two forms with different melting points. Neither of them contains solvent of crystallisation. The form, which was obtained by crystallisation from alcohol, is crystalline and melts at 108–109°, while the other obtained from benzene solution is amorphous and melts at 132–133°. They are interconvertible by changing the solvent in crystallisation. Monotropic change was also observed on heating, that is, the urethane melting at 108–109° was gradually transformed into the other form on prolonged heating at 100–110°.

---

* It was shown by Adkins that compounds of similar type respecting their hydroxyls such as benzyl alcohol, phenyl methyl carbinol, and diphenyl carbinol were readily hydrogenated with the same catalyzer to the corresponding hydrocarbons at 150 to 200°, temperature lower than that necessary for hydrogenation of esters.

** In the present study it could not be identified as ethyl-benzene, it yielded benzoic acid on oxidation and it corresponds to a mixture of toluene and ethyl-benzene with regards to its boiling point.

(7) V. Grignard, *Compt. rend.*, **141** (1905), 45; *Ann. chim. phys.*, (8), **10** (1907), 31.

(8) Recently this glycol was prepared by Hershberg, starting from allyl-benzene through the di-benzoic ester, *Helvetica Chim. Acta*, **17** (1934), 351.

Experimental Part.

Copper-chromium oxide catalyzer (containing a little barium) was prepared according to the description of Adkins[9] by the calcination of the precipitates formed by mixing ammoniacal solutions of copper and barium nitrates and of ammonium bichromate. Its composition is to be $2(0.9CuO + 0.1BaO) + Cr_2O_3$ when estimated from the proportion of reagents used.

Acetone-compound (prepared from hydroxy-acid and acetone by dehydration with conc. sulphuric acid) was mixed with 1/5–1/10 of its weight of the above catalyzer without any diluent. The hydrogenation was carried out at the temperature of 240–260° for 0.5–4.5 hours in an autoclave (capacity 250 c.c.) provided with shaking equipment, initial pressure of hydrogen being 100–120 atmospheres at room temperature.

Hydrogenated products were separated from catalyzer with glass filter and they were fractionated through Widmer column into several fractions under ordinary or reduced pressure.

Hydrogenation of Acetone-*dl*-lactic acid. Acetone-compound (b.p. 49.0–49.5° under 11 mm.) 30 g. (0.23 mol). Catalyzer 5.0 g. Time of hydrogenation 4.0 hours at 240–260°. Reaction product was fractionated into two parts.

I	79–81° under ordinary pressure	4.0 g.
II	82–85° under 11 mm.	10.2 g.

Fraction I was found to be isopropyl alcohol by converting it into naphthylurethane. *Naphthylurethane.* Mixture of the alcohol (1.0 g.) and α-naphthyl isocyanate (2.5 g.) was heated up to 150° (in glycerine bath) for one hour. On cooling, it turned to a hard cake, which was dissolved in hot ligroin and filtered. Naphthylurethane (0.8 g.) was obtained from the filtrate, which melted at 104–105° after repeated recrystallisation from ligroin (Table 2).

Fraction II distilled at 94–96° under 20 mm. after refractionation and it was found to be propylene glycol by converting it into bis-phenylurethane. *Bis-phenylurethane.* The glycol (1.0 g.) and phenyl isocyanate (2.0 g.) were mixed and heated at 120–140° for one hour. Five times of ligroin was added, the mixture well stirred, the ligroin was decanted off, and the remaining liquid was dissolved in benzene. The solution was evaporated to a small bulk, from which the crude urethane crystallized out (1.0 g., m.p. 120–135°). After repeated recrystallisation from ligroin and finally from alcohol it melted at 143–144° and showed no change of m.p. on further purification (Table 2).

Hydrogenation of Acetone-*l*-leucic acid. Acetone-compound (b.p. 84.5–85.5° under 13 mm.) 30 g. (0.175 mol). Catalyzer 4.0 g. Time of hydrogenation 4½ hours at 240–260°. Fractionation (filtered solution, 24.6 g.):

I	80– 81° under ordinary pressure	7.6 g.
II	140–150° ,,	4.4 g.
III	56–105° under 15 mm.	1.1 g.
IV	110–116° ,,	9.3 g.

(9) R. Connor, K. Folkers, H. Adkins, *J. Am. Chem. Soc.*, **54** (1932), 1139. The above catalyzer is specified as No. 37 KAF in this paper.

Fraction II was treated with 10% NaOH to remove acetone-compound and the neutral part was collected by extracting with ether and the extract was refractionated. Main part (3.2 g.) boiled at 140–147°, which was found to be isohexyl alcohol by converting it into 3,5-dinitrobenzoic ester. The boiling point mentioned above is lower and extends in wider range than the value in literature (b.p. 153°) and the sample is suspected to be mixed with isomeric secondary alcohol (inactive form, b.p. 129–134°) but the latter could not be identified. *Dinitrobenzoic ester.* It was prepared by treating the alcohol with 3,5-dinitrobenzoyl chloride according to the description of Mulliken.[10] The ester obtained melted at 68–69° after repeated recrystallisation from 95% alcohol (Table 2).

Fraction IV. After treating with 10% NaOH it was refractionated, b.p. 111–113.5° under 15 mm., 7.7 g. It was found to be isohexylene glycol by analysis (Table 3). *Bis-phenylurethane.* Mixture of the glycol (0.5 g.) and phenyl isocyanate (1.0 g.) was heated at 120–130° for 0.5 hour. On cooling, it changed to a viscous fluid. Ligroin (1:5) was added, well stirred, and colourless amorphous powder gradually deposited. It melted at 115–116° after recrystallisation from mixture of ligroin and alcohol (5:1) (Table 2).

Hydrogenation of Acetone-*dl*-mandelic acid. Experiment A. Acetone-compound (m.p. 46–47°) 38.5 g. (0.20 mol). Catalyzer 6.0 g. Time of hydrogenation 1.5 hours at 240–260°. Fractionation (filtered solution, 28.0 g.):

I	78– 80° under ordinary pressure	13.4 g.
II	30– 35° under 17 mm.	2.7 g.
III	102–107° under 14 mm.	8.4 g.

Fractions I and II had the odour of aromatic hydrocarbon. Twice its volume of water was added to them to dissolve isopropyl alcohol and the part not miscible with water was separated, which (5.8 g.) was distilled over metallic sodium. Even after repeated fractionation with the aid of Widmer column, it was not possible to separate it into fractions of distinct boiling points:

(a)	up to 110°	1.3 g.
(b)	110–114°	0.5 g.
(c)	115–122°	1.1 g.

An attempt was made to prepare crystalline nitro-compounds with the object of identifying the hydrocarbons, nitration being carried out, regarding (b) as toluene, by the method of Mulliken,[11] (c) as ethyl-benzene, according to the description of Schultz.[12] But the products thereby obtained always remained as oil and could not be brought into crystallisation. *Oxidation of* (a). It (0.8 g.) was boiled with potassium permanganate solution (3.0 g of salt in 75 c.c. of water) for one hour. After filtration and evaporation, the solution was acidified with hydrochloric acid. Crystals (0.1 g) which melted at 121° after recrystallisation from water were obtained and identified as benzoic acid by the mixed melting point determination. These fractions which gave benzoic acid on oxidation can be assumed to be a mixture of toluene and ethyl-benzene.

(10) Mulliken, "Identification of Organic Compounds," Vol. I, 168.
(11) Mulliken, *ibid.*, Vol. I, 202.
(12) G. Schultz, *Ber.*, **42** (1909), 2634.

Fraction II. Boiling point of this fraction corresponds to that of phenyl-ethyl alcohol and it was identified as such by converting it into phenylurethane. *Phenylurethane.* The alcohol (1.0 g.) and phenyl isocyanate (1.0 g.) were mixed and heated at 100–120° for one hour. On cooling, the mixture became a semi-fluid, to which an equal volume of petroleum ether was added, well stirred, and filtered. The crude urethane (1.5 g.) thus prepared was repeatedly recrystallized from alcohol. It melted at 78–79° (Table 2) and showed no lowering of melting point when mixed with a specimen of urethane prepared from pure phenyl-ethyl alcohol (Takeda).

Experiment B. Acetone-compound 25.2 g. (0.13 mol). Catalyzer 4.0 g. Time of hydrogenation 0.75 hour at 240–260°. Fractionation:

I	78– 80° under ordinary pressure	5.6 g.
II	105–106° under 16 mm.	5.4 g.
III	over 110° ,,	3.0 g.

In this experiment hydrogenation was interrupted before the absorption of hydrogen has been completed. The yield of fraction I (isopropyl alcohol and hydrocarbon) was inferior to that in Exp. A, while a fraction of higher boiling point (III) was obtained, which was not met with in Exp. A.

Fraction III has a odour reminding of aromatic ester. After removing acid by treating with 10% sodium carbonate, it was hydrolyzed by boiling with sodium hydroxide (10%) for three hours. The reaction mixture was acidified and extracted with ether. From the ether extract crystals (0.7 g.) were obtained, which melted at 75–76° after recrystallisation from water and were identified as phenyl-acetic acid by mixed melting point determination.

Hydrogenation of Acetone-*l*-phenyl-lactic acid. Experiment A. Acetone-compound (m.p. 63–64°) 25.0 g. (0.12 mol). Catalyzer 4.0 g. Time of hydrogenation 1.5 hours at 240–260°. Fractionation (15.1 g.):

I	77– 80° under ordinary pressure	2.5 g.
II	110–120° under 16 mm.	2.8 g.
III	120–123° ,,	2.4 g.
IV	164–166° ,,	6.3 g.

Fractions II and III and corresponding ones in the next experiment were combined and treated as follows. The substance has a pleasant odour reminding of cinnamic ester. It was boiled with 10% sodium hydroxide for one hour to hydrolyze the ester and was extracted with ether. The ether extract was separated into three fractions by fractionation:

(a)	up to 100°	under 9 mm.	2.4 g.
(b)	100–108°	,,	2.6 g.
(c)	108–109°	,,	6.2 g.

These fractions were found to be a mixture of phenyl-propyl alcohol (b.p. 120–121° under 13 mm.) and benzyl methyl carbinol (active form, b.p. 125° under 25 mm.) by converting them into phenylurethanes. *Phenylurethanes.* Though the differentiation of isomeric alcohols by above fractionation never seemed complete, their phenyl-

urethanes could be obtained separately from fractions rich in corresponding alcohols, as solubilities of the phenylurethanes in ethyl alcohol are markedly different from each other. The alcohol from fraction (a) (1.2 g.) and phenyl isocyanate (1.2 g.) were mixed and heated at 130° for two hours. On cooling, an equal volume of petroleum ether was added and the phenylurethane thus separated was filtered (1.2 g.). It melted at 88–89° after recrystallisations from alcohol (Table 2).

The alcohol from fraction (c) (1.0 g.) was treated with phenyl isocyanate just in the same way as above. On cooling, it was dissolved in alcohol, filtered and was concentrated. Phenylurethane gradually deposited after long standing. It melted at 45–46° after recrystallisations from little alcohol (Table 2) and showed no lowering when mixed with a specimen of urethane prepared from pure phenyl-propyl alcohol (Takeda, b.p. 110–113° under 9 mm.).

The alkaline solution used for hydrolysis of ester was acidified and extracted with ether. A small amount of crystals was obtained from the extract after long standing in the desiccator. It melted at 46–47° and was identified as hydrocinnamic acid by the mixed melting point determination.

Fraction IV. After treating with 10% sodium hydroxide it was extracted with ether. The extract was fractionated, and the main part distilled at 168–170° under 17 mm., which was found to be benzyl-ethylene glycol by analysis (Table 3) as well as by the formation of bis-phenylurethane (Table 2). *Bis-phenylurethane.* The glycol (1.0 g.) and phenyl isocyanate (2.0 g.) were mixed and heated at 120–130° for 0.5 hour. After cooling, twice its volume of ligroin was added, well stirred, from which crude urethane (2.6 g.) crystallized out on standing. It can be recrystallized from either alcohol or benzene. *Recrystallisation from alcohol.* Half amount of the crude urethane was dissolved in hot alcohol and filtered. The filtrate was concentrated to a syrup which gradually changed to crystalline mass. It melted at 108.5–109.5° after recrystallisation from the same solvent (A) (Table 2). *Recrystallisation from benzene.* Another half of the crude urethane was treated with benzene instead of alcohol just in the same way. The phenylurethane thus purified was amorphous powder and melted at 132–133° after recrystallisation from benzene (B) (Table 2).

Samples A and B showed the same nitrogen content corresponding to bis-phenylurethane, while their melting points were distinctly apart from each other. Sample A can be converted into B (melting at 129–131°) after one recrystallisation from benzene and the reverse change was observed when sample B was treated with alcohol (melting 109–110°). The monotropic transformation from A to B takes place on mere heating. Sample A was put in Abderhalden drying apparatus and maintained at 100° in vacuum for three hours and then at 110° for seven hours, during which the weight and melting point were determined from time to time. The loss of weight was never observed during whole operation, while melting point gradually changed and finally reached a constant value 131–133°, which shows that the sample was completely changed into B. The sample thus prepared can be reconverted into A (melting at 108–109°) by twice recrystallizing from alcohol.

Experiment B. Acetone-compound 25.0 g. (0.12 mol). Catalyzer 4.0 g. Time of hydrogenation 4.5 hours at 240–260°. Fractionation (19.3 g.):

I	79– 82° under ordinary pressure	7.5 g.
II	100–120° under 11 mm.	10.1 g.

Fraction I smelt of aromatic hydrocarbon as in the case of acetone-mandelic acid and when put into water, it did not dissolve completely, but the part insoluble in water was too minute to test its boiling point.

Fraction II was combined with the corresponding fraction in experiment A as already mentioned. In the present experiment higher boiling fraction corresponding to glycol was lacking. The glycol seemed to have been completely hydrogenated to monohydric alcohols in prolonged hydrogenation in this experiment.

Table 2.

Alcohol and glycol	Derivative prepared	N		
		Found*	Calc.	for
$CH_3 \cdot CH(OH) \cdot CH_3$	α-Naphthylurethane, m.p. 104–105°	6.07	$C_{14}H_{15}O_2N$,	6.11%
$(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	3, 5-Dinitrobenzoic ester,[13] m.p. 68–69°	9.64	$C_{13}H_{16}O_6N_2$,	9.46%
$C_6H_5 \cdot CH_2 \cdot CH_2OH$	Phenylurethane, m.p. 78–79°	5.77	$C_{15}H_{15}O_2N$,	5.81%
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	Phenylurethane, m.p. 44–45°	5.63	$C_{16}H_{17}O_2N$,	5.49%
$C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot CH_3$ (active)**	Phenylurethane,[14] m.p. 88–89°	5.48	$C_{16}H_{17}O_2N$,	5.49%
$CH_3 \cdot CH(OH) \cdot CH_2OH$ (*dl*)	Bis-phenylurethane,[15] m.p. 143–144°	8.87	$C_{17}H_{18}O_4N_2$,	8.90%
$(CH_3)_2CH \cdot CH_2 \cdot CH(OH) \cdot CH_2OH$ (active)**	Bis-phenylurethane, m.p. 115–116°	7.79	$C_{20}H_{24}O_4N_2$,	7.87%
$C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot CH_2OH$ (active)**	Bis-phenylurethane, m.p. 108–109° (A) m.p. 132–133° (B)	7.18 7.13	$C_{23}H_{22}O_4N_2$,	7.18%

* Nitrogen was estimated by micro-Kjeldahl method except in case of nitro-compound.

** The activities were not examined. During hydrogenation they might be subjected to racemisation to some extent. E. Bowden, H. Adkins, *J. Am. Chem. Soc.*, **56** (1934), 689.

(13) G. B. Malone, E. E. Reid, *J. Am. Chem. Soc.*, **51** (1929), 3426.

(14) Phenylurethane of active alcohol is unknown. That of *dl*-alcohol melts at 92°. M. Tiffeneau, *Compt. rend.*, **146** (1908), 698.

(15) G. S. Walpole, *Proc. Roy. Soc. London* (B), **83** (1911), 272. Walpole gives the m.p. 152.5–153.5° for the same bis-phenylurethane of *dl*-glycol, but in the present study it could not be raised above 144°. That of active glycol, m.p. 145–146°, P. A. Levene, A. Walti, *J. Biol. Chem.*, **73** (1927), 263.

Table 3.

Glycol	Analytical results	
	Found	Calc. for
Isohexylene glycol, b.p. 111–113.5° under 15 mm.	C, 60.82; H, 11.84	$C_6H_{14}O_2$: C, 60.95; H, 11.96%
Benzyl-ethylene glycol, b.p. 168–170° under 17 mm.	C, 70.94; H, 8.11	$C_9H_{12}O_2$: C, 71,01; H, 7.96%

The present study was carried out in the Chemical Institute, Faculty of Science, Imperial University of Tokyo. The author wishes to express his sincere thanks to Prof. K. Matsubara for the kind inspection of this paper. His best thanks are also due to Dr. Y. Takayama for the constant encouragements during this study.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. IX. THE CONSTITUTION OF DOCOSAHEXENOIC ACID $C_{22}H_{32}O_2$.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received July 31st, 1935. Published November 28th, 1935.

In previously reported studies[1] on the highly unsaturated C_{22}-acids in sardine oil, clupanodonic acid $C_{22}H_{34}O_2$ was isolated in much purer state than obtained before, and its constitution was established as $\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$-docosapentenoic acid. A concentrated fraction of docosahexenoic acid $C_{22}H_{32}O_2$ was also separated. The present paper records the experimental results obtained by the ozonolysis of the amyl ester prepared from the concentrated fraction of docosahexenoic acid.

Among the products of ozonolysis acetaldehyde $CH_3 \cdot COH$, acetic acid $CH_3 \cdot COOH$, carbon dioxide CO_2, succinic acid $HOOC \cdot (CH_2)_2 \cdot COOH$ and amyl hydrogen succinate $HOOC \cdot (CH_2)_2 \cdot COOC_5H_{11}$ were found; the presence of the aldehydes corresponding to succinic acid and amyl hydrogen succinate was also indicated. Although the amyl ester used for ozonolysis was contaminated with a small proportion of

(1) This Bulletin, **10** (1935), 433, 441.

amyl clupanodonate which yielded on ozonolysis the above compounds as shown in a preceding paper,[2] the yields of the above compounds obtained in these experiments indicated that they owed their origin largely to amyl docosahexenoate which constituted the bulk of the amyl ester used for ozonolysis. The volatile aldehydes formed by the ozonolysis appeared not to consist exclusively of acetaldehyde, but no other volatile aldehydes than acetaldehyde were identified.[3] Of the products of ozonolysis obtained in these experiments, succinic acid and amyl hydrogen succinate are derived from the groups $=CH\cdot(CH_2)_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot COOC_5H_{11}$ respectively, whilst carbon dioxide is formed, together with acetaldehyde and acetic acid, by the secondary decomposition of the products of ozonolysis derived from the group $=CH\cdot CH_2\cdot CH=$, and the yield of carbon dioxide indicated the presence of at least three of the group $=CH\cdot CH_2\cdot CH=$ in amyl docosahexenoate. Accordingly the free docosahexenoic acid was found to contain the following groups: $=CH\cdot(CH_2)_2\cdot CH=$, $=CH\cdot CH_2\cdot CH=$ (at least three), and $=CH\cdot(CH_2)_2\cdot COOH$. Although the group attached to the opposite side of the carboxyl group was left undetermined in these experiments, it must be $CH_2=$ or $CH_3\cdot CH=$ depending on whether docosahexenoic acid has three or four of the group $=CH\cdot CH_2\cdot CH=$, since it has 22 carbon atoms in total. Hence, docosahexenoic acid is composed of either one of the following two sets of the groups:

(1) $CH_2=$, $=CH\cdot CH_2\cdot CH=$(three), $=CH\cdot(CH_2)_2\cdot CH=$(two), $=CH\cdot(CH_2)_2\cdot COOH$.
(2) $CH_3\cdot CH=$, $=CH\cdot CH_2\cdot CH=$(four), $=CH\cdot(CH_2)_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot COOH$.

No evidence was brought out in these experiments regarding the respective positions of the groups $=CH\cdot CH_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot CH=$. If, however, the group $=CH\cdot(CH_2)_2\cdot CH=$ is assumed to lie near the carboxyl group side of docosahexenoic acid, as is the case with previously studied moroctic,[4] eicosatetraenoic[5] and clupanodonic acids,[6] the constitution of docosahexenoic acid is to be expressed by either one of the following formulae:

$$CH_2=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (I)$$

$$CH_3\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot CH_2\cdot CH=CH\cdot(CH_2)_2\cdot CH=CH\cdot(CH_2)_2\cdot COOH \quad (II)$$

(2) This Bulletin, **10** (1935), 441.
(3) Propyl aldehyde must have been formed, though in a small amount, by the ozonolysis of the amyl ester, since the ester was contaminated with amyl clupanodonate.
(4) This Bulletin, **10** (1935), 232.
(5) This Bulletin, **10** (1935), 296.
(6) This Bulletin, **10** (1935), 441.

The yield of C_4-compounds obtained by the ozonolysis could not be determined accurately, but it seemed to indicate the presence of more than one of the group $=CH\cdot(CH_2)_2\cdot CH=$ in amyl docosahexenoate. Accordingly the formula (I) seems most probable. Further experiments will be done when pure docosahexenoic acid is obtained in sufficient quantity.

Experimental.

Docosahexenoic acid used in these experiments is the same sample which was obtained in the previous study.[7] It had d_4^{15} 0.9521, n_D^{15} 1.5129, neutr. value 170.1 (calc. 170.9), iodine value by the Wijs method 456.0 (calc. 464.0) and gave 177% of an ether insoluble bromide having Br-content 74.00% (calc. for $C_{22}H_{32}O_2Br_{12}$: 74.50%). Assuming that this sample is contaminated exclusively with clupanodonic acid, the purity of docosahexenoic acid is calculated to be 89.97% from its iodine value. The free acid was converted into its amyl ester by heating with an equal amount of amyl alcohol containing 2.5% of hydrogen chloride on the water-bath under a reflux condenser for one hour. Five g. of the amyl ester thus obtained was dissolved in 50 c.c. of chloroform, cooled with ice-salt, and a current of ozonised oxygen was passed into the solution until it became saturated with ozone. On distilling chloroform from the solution under diminished pressure, there was obtained 8.9 g. of ozonide as an orange yellow syrup. Chloroform was, however, not thoroughly removed from the ozonide, since there was a danger of explosive decomposition on undue heating. Water (50 c.c.) was added to the ozonide, and the liquid was heated on the water-bath in a current of hydrogen. The flask was attached by a delivery tube to other three flasks (**a**, **b**, and **c**) which were connected in succession; the first (**a**) was filled with ice cold water, the second (**b**) and the third (**c**) with approximately 1/3 N barium hydroxide solution. The volatile decomposition products (**A**) carried over with hydrogen were passed into the above three flasks where they were caught by absorption. The decomposition products remained in the initial flask dissolved partly in water, and the remainder separated as oily substances (**C**) under aqueous solution (**B**).

1. **Volatile Decomposition Products (A).** The aqueous solution in the flask (**a**) produced a pink colouration with Schiff's reagent and a deep blue colouration with diethylamine and sodium nitroprusside, indicating the presence of acetaldehyde. On addition of *p*-nitrophenylhydrazine and hydrochloric acid, there was formed a precipitate of *p*-nitrophenylhydrazone which on recrystallisation from 50% alcohol gave yellow needles with m.p. 125–126° which was not lowered when the substance was admixed with a pure specimen of *p*-nitrophenylhydrazone of acetaldehyde (m.p. 128°) in various proportions.

The barium hydroxide solution in the flasks (**b**) and (**c**) were found to contain a precipitate of barium carbonate, indicating that carbon dioxide was formed by the ozonolysis. The quantity of carbon dioxide calculated from the quantity of barium carbonate was found to be 1.26 g. or 25.2% of the amyl ester used for ozonolysis.

(7) This Bulletin, **10** (1935), 433.

This is higher than the maximum yield (22.1%) of carbon dioxide obtainable on assumption that amyl docosahexenoate has two of the group $=CH\cdot CH_2\cdot CH=$, and that the products of ozonolysis derived from that group undergoes secondary decomposition with the formation of carbon dioxide to a quantitative extent. Consequently amyl docosahexenoate must have at least three of the group $=CH\cdot CH_2\cdot CH=$.

2. **Aqueous Solution (B).** This was extracted with a large quantity of ether. On removal of ether from the ethereal extract, there remained 3.6 g. of a reddish orange liquid, which was then treated with petroleum ether and was separated into petroleum ether solution and petroleum ether insoluble portion. On distilling off petroleum ether from the solution, the distillate (petroleum ether) had a smell of acetic acid. The residue was then heated in an oil-bath, yielding 0.6 g. of a colourless distillate below 150° of the bath-temperature. It had a smell of acetic acid, and the silver salt prepared from it was proved to be silver acetate by analysis (Found: Ag, 64.48. Calc. for $C_2H_3O_2Ag$, 64.64%).

The petroleum ether insoluble portion (1.9 g.) consisted of a mixture of reddish orange liquid and crystalline solid, and showed aldehydic character. Oxidation with an alkaline solution of potassium permanganate followed by acidification yielded a crystalline product which, after being washed with a little cold ether, showed neutr. value 947.6 (calc. for succinic acid $C_4H_6O_4$: 950.6) and m.p. 179–180°. Recrystallisation from ethyl acetate yielded pure succinic acid with m.p. and mixed m.p. 182–183°. The petroleum ether insoluble portion was considered to consist almost exclusively of C_4-compounds (succinic acid and the corresponding aldehyde), and the yield was 1.9 g. or 38% of the amyl ester used for ozonolysis. This is considerably higher than the maximum yield of C_4-compounds (as succinic acid) 27.1% which is obtainable on condition that amyl docosahexenoate has only one of the group $=CH\cdot(CH_2)_2\cdot CH=$.

3. **Oily Substances (C).** Yield 1.9 g. These substances had acid and aldehydic characters. Oxidation with alkaline permanganate followed by acidification yielded an acid ester which showed neutr. value 297.1 and saponification value 594.8, and was considered to be amyl hydrogen succinate $C_9H_{16}O_4$ (neutr. value 298.2 and saponif. value 596.5). The free acid liberated from its acid ester in the usual way yielded succinic acid after recrystallisation from ethyl acetate; neutr. value 946.9 and m.p. 182–183°. From these results it is seen that the oily substances consist chiefly of amyl hydrogen succinate and the corresponding aldehyde.

Summary.

1. A concentrated fraction of docosahexenoic acid was converted into the amyl ester, and the latter was subjected to ozonolysis. Among the products of ozonolysis were found: acetaldehyde, acetic acid, carbon dioxide, succinic acid and amyl hydrogen succinate. The presence of the aldehydes corresponding to succinic acid and amyl hydrogen succinate was also indicated. Of these compounds, carbon dioxide together with acetaldehyde and acetic acid is attributable to the secondary decomposition of the products derived from the group $=CH\cdot CH_2\cdot CH=$. The yield of carbon dioxide indicated the presence of at least three of the group

$=CH\cdot CH_2\cdot CH=$ in amyl docosahexenoate. Consequently docosahexenoic acid has the following groups: $=CH\cdot CH_2\cdot CH=$, $=CH\cdot(CH_2)_2\cdot CH=$, and $=CH\cdot(CH_2)_2\cdot COOH$, of which it has at least three of the group $=CH\cdot CH_2\cdot CH=$. The yield of C_4-compounds (succinic acid and the corresponding aldehyde) obtained by the ozonolysis gave an indication of the presence of more than one of the group $=CH\cdot(CH_2)_2\cdot CH=$ in docosahexenoic acid.

2. Although the group attached to the CH_3-side and the respective positions of the groups $=CH\cdot CH_2\cdot CH=$ and $=CH\cdot(CH_2)_2\cdot CH=$ were left undetermined in these experiments, the most probable structure of docosahexenoic acid was derived from the results obtained above.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

Correction to the 7th paper on the Highly Unsaturated Acids in Sardine Oil:

Read n_D^{20} 1.5014 *for* $n_D^{2)}$ 1.4934 *in line 16 from bottom on page 439 of this volume.*

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL X. THE SEPARATION OF HIGHLY UNSATURATED C_{24}-ACIDS.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received July 31st, 1935. Published November 28th, 1935.

After having examined the highly unsaturated C_{16}-, C_{18}-, C_{20} and C_{22}- acids in sardine oil, we extended our investigations to the highly unsaturated C_{24}-acids. Concerning the highly unsaturated C_{24}-acids in sardine oil, nothing has hitherto been known. However, the highly unsaturated C_{24}-acids in marine animal oils other than sardine oil have been studied by a few authors. Bull[1] stated to have found an acid $C_{24}H_{40}O_2$ in herring oil. Ueno and Iwai[2] have recently shown the presence of a highly unsaturated acid $C_{24}H_{38}O_2$, which they named scoliodonic acid, in

(1) *Chem. Ztg.*, **23** (1899), 996.
(2) *J. Soc. Chem. Ind., Japan*, **37** (1934), 562.

the liver oil of *Scoliodon laticaudus*. We[3] separated a highly unsaturated acid $C_{24}H_{36}O_2$, named nisinic acid, from herring oil, and found the same acid also in cod-liver oil, pilot-whale oil and in the liver oil from *Squalus sucklii*.

For the separation of highly unsaturated C_{24}-acids in the present experiment, the residue from the distillation of the highly unsaturated methyl esters described in the 7th report[4] of this series was used as the starting material. The fatty acids liberated from it consisted mainly of highly unsaturated C_{24}-acids and some polymerised acids. These were separated into the fractions of different degrees of unsaturation by the fractional precipitation of sodium soaps in acetone, and there was obtained nisinic acid $C_{24}H_{36}O_2$[5] from the fraction of the highest degree of unsaturation. Examination of each fraction seemed to indicate the presence of some other highly unsaturated C_{24}-acids, such as scoliodonic acid $C_{24}H_{38}O_2$ and also an acid $C_{24}H_{40}O_2$, besides nisinic acid, but no individual acid other than nisinic acid was separated.

Experimental.

1. **Separation of Highly Unsaturated C_{24}-Acids.** In the previously reported experiment[6] of the separation of highly unsaturated C_{22}-acids, 10 kg. of sardine oil was treated by means of sodium-soap-acetone method, and the concentrated fraction of highly unsaturated acids was obtained from the sodium soaps soluble in acetone. This was converted into the methyl esters and the latter were subjected to the fractional distillation which was continued up to 214°/2 mm. For the present experiment the residue from the distillation was used as the starting material. It was saponified, the unsaponifiable matter was removed by extraction with ether, and the soap solution on acidification yielded free fatty acids. These were reconverted into the methyl esters and the latter were distilled up to 215°/2 mm., yielding about 69 g. of a residue which had saponif. value 150.5 and iodine value 308.3.[7] The residue was saponified, and the fatty acids obtained on acidification were treated with charcoal in petroleum ether. The fatty acids (62. g.) thus obtained showed neutr. value 156.8 and iodine value 324.5. The product of hydrogenation of these fatty acids showed neutr. value 151.5 (calc. for $C_{24}H_{48}O_2$: 152.3) and m.p. 81.5–82° after recrystallisation from alcohol. The melting point was not lowered when the substance was admixed in various proportions with a specimen of *n*-tetracosanic acid, m.p. 84–84.5°, prepared from behenic acid

(3) *J. Soc. Chem. Ind., Japan*, **37** (1934), 1176.

(4) This Bulletin, **10** (1935), 433.

(5) Strictly speaking, nisinic acid or an acid having the same composition as nisinic acid.

(6) This Bulletin, **10** (1935), 433.

(7) Unless otherwise stated, the iodine values recorded in this paper were determined by the Wijs method.

by malonic ester synthesis. It follows from these results that the fatty acids having m.p. 81.5–82° consist mainly of *n*-tetracosanic acid, and consequently the highly unsaturated acids prior to hydrogenation consist chiefly of C_{24}-acids.

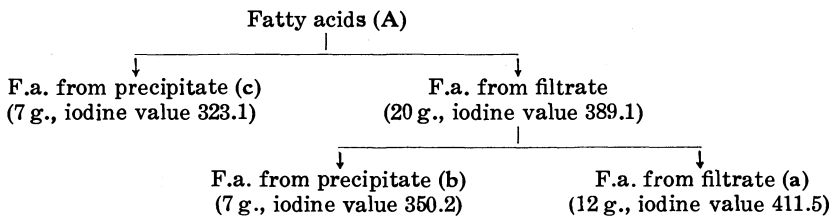
2. **Fractional Precipitation of Sodium Soaps in Acetone.** The highly unsaturated C_{24}-acids (neutr. value 156.8 and iodine value 324.5) obtained above were neutralised with a portion of sodium hydroxide solution prepared by dissolving 10 g. of sodium hydroxide in 20 c.c. of water and 40 c.c. of 95% alcohol, and then 60 c.c. of acetone was added by which a precipitate of insoluble sodium soaps was formed. The precipitate was filtered, and the fatty acids were separated from the precipitate and the filtrate, respectively, in the usual way. Fifty-nine grams of the highly unsaturated C_{24}-acids gave the following results (Table 1).

Table 1.

	Yield (g.)	Iodine value
Fatty acids from filtrate (A)	29	371.7
Fatty acids from precipitate (B)	29	277.6
Loss	1	—

Fatty acids from filtrate (A). These were dissolved in a little acetone, partially neutralised by using a portion of sodium hydroxide solution prepared by dissolving 10 g. of sodium hydroxide in 10 c.c. of water and 20 c.c. of 95% alcohol, and a sufficient quantity of acetone was added, by which a precipitate of insoluble sodium soaps was formed. The precipitate was once brought into solution by warming the solution on the water-bath, reprecipitated on cooling, and then filtered. The fatty acids were separated from the precipitate and the filtrate, respectively, in the usual way, and those obtained from the filtrate were again treated as before to effect a further separation. The results of these treatments are given below (Table 2).

Table 2.



For the sake of comparison, the neutralisation value and the iodine value for the highly unsaturated C_{24}-acids and also the Br-content of the corresponding bromo-derivatives are shown in Table 3.

The iodine value of the fatty acids (a) is close to the calculated value for $C_{24}H_{36}O_2$. The fatty acids (b) showed an iodine value which was close to the calculated value for $C_{24}H_{38}O_2$, but the ether insoluble bromide obtained from them showed

Table 3.

Acid	Neutr. v.	Iodine v.	Bromo-derivative	Br-content (%)
$C_{24}H_{36}O_2$	157.5	427.5	$C_{24}H_{36}O_2Br_{12}$	72.91
$C_{24}H_{38}O_2$	156.6	354.2	$C_{24}H_{38}O_2Br_{10}$	69.05
$C_{24}H_{40}O_2$	155.7	281.8	$C_{24}H_{40}O_2Br_8$	63.96
$C_{24}H_{42}O_2$	154.9	210.2	$C_{24}H_{42}O_2Br_6$	56.96

Br-content 70.84%, which lies between the calculated values for $C_{24}H_{36}O_2Br_{12}$ and $C_{24}H_{38}O_2Br_{10}$. Accordingly the fatty acids (**b**) are believed to be a mixture of acids of different degrees of unsaturation. The fatty acids (**c**) seem to contain some less unsaturated acids than $C_{24}H_{38}O_2$ according to their iodine value.

The fatty acids (**a**) were partially neutralised with sodium hydroxide solution in acetone as before, and the precipitate of insoluble sodium soaps was removed. The fatty acids obtained from the filtrate were again subjected to the same treatment, and these separative operations were repeated several times, until the fatty acids obtained from the precipitate and the filtrate showed iodine values which did not differ much from one another. The fatty acids from the final filtrate had the following constants and were considered to consist chiefly of nisinic acid $C_{24}H_{36}O_2$: d_4^{15} 0.9486, d_4^{20} 0.9451, n_D^{15} 1.5140, n_D^{20} 1.5120, mol. refraction 113.1 (calc. for $C_{24}H_{36}O_2$: 111.8), neutr. value 157.0, iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 422.5 and 407.2 respectively. Bromination in ethereal solution yielded 138% of an ether insoluble bromide which showed Br-content 72.76% and turned black at about 240° without melting.

Fatty acids from precipitate (**B**). Twenty-eight grams of these fatty acids were neutralised by using a portion of sodium hydroxide solution prepared by dissolving 10 g. of sodium hydroxide in 30 c.c. of water and 60 c.c. of 95% alcohol, and then 300 c.c. of acetone was added by which a precipitate of insoluble sodium soaps was formed. The fatty acids (18.5 g.) liberated from the insoluble sodium soaps had iodine value 260.1 and n_D^{15} 1.5208. The iodine value lies between the calculated values for $C_{24}H_{40}O_2$ and $C_{24}H_{42}O_2$. Bromination in ethereal solution yielded, however, an ether insoluble bromide having Br-content 68.09% which was higher than the calculated value for $C_{24}H_{40}O_2Br_8$, indicating that the fatty acids from the insoluble sodium soaps contained some more highly unsaturated acids than $C_{24}H_{40}O_2$. After distilling off the solvent from the filtrate from ether insoluble bromide, the residue was treated with petroleum ether, and there was separated a petroleum ether insoluble bromide which melted at about 70° and had Br-content 57.55% which was close to the calculated value for $C_{24}H_{42}O_2Br_6$. It should, however, be noted that the fatty acids obtained from the insoluble sodium soaps showed an abnormally high refractive index in comparison with their iodine value, giving an indication of contamination of some polymerised fatty acids, and consequently it is not excluded that the petroleum ether insoluble bromide obtained above may have been derived from polymerised fatty acids, but not from $C_{24}H_{42}O_2$.

Summary.

A concentrated fraction of highly unsaturated acids was separated from sardine oil by means of sodium-soap-acetone method, and was distilled as its methyl esters up to 215°/2 mm. The residue from the distillation consisted mainly of the methyl esters of highly unsaturated C_{24}-acids and some polymerised products. The free fatty acids liberated from the residue were separated into the fractions of different degrees of unsaturation by means of fractional precipitation of sodium soaps in acetone. The fraction of the highest degree of unsaturation consisted of nisinic acid $C_{24}H_{36}O_2$. Examination of other fractions seemed to indicate the presence of some less unsaturated acids, such as $C_{24}H_{38}O_2$ and $C_{24}H_{40}O_2$, but no individual acids other than nisinic acid were separated.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

THE HIGHLY UNSATURATED ACIDS IN SARDINE OIL. XI. THE CONSTITUTION OF NISINIC ACID $C_{24}H_{36}O_2$ IN SARDINE OIL.

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received August 22nd, 1935. Published November 28th, 1935.

As stated in the 10th report of this series,[1] nisinic acid $C_{24}H_{36}O_2$ was separated as an individual component of highly unsaturated C_{24}-acids in sardine oil. In continuation to the previous study this paper deals with the experimental results obtained by the ozonolysis of amyl nisinate with a view to gain an insight into the constitution of nisinic acid.

On examining the products obtained by the ozonolysis of amyl nisinate, the following compounds were found: propyl aldehyde $CH_3 \cdot CH_2 \cdot COH$, propionic acid $CH_3 \cdot CH_2 \cdot COOH$, acetaldehyde $CH_3 \cdot COH$, acetic acid $CH_3 \cdot COOH$, carbon dioxide CO_2, succinic acid $HOOC \cdot (CH_2)_2 \cdot COOH$ and amyl hydrogen succinate $HOOC \cdot (CH_2)_2 \cdot COOC_5H_{11}$.

(1) This Bulletin, **10** (1935), 543.

Of these compounds, propyl aldehyde and propionic acid are derived from the group $CH_3 \cdot CH_2 \cdot CH=$. Acetaldehyde and acetic acid together with carbon dioxide are attributable to the secondary decomposition of malonic acid and the corresponding aldehyde which are derived from the group $=CH \cdot CH_2 \cdot CH=$, while succinic acid and amyl hydrogen succinate are derived from the groups $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot COOC_5H_{11}$ respectively. Accordingly, amyl nisinate was found to contain the following groups: $CH_3 \cdot CH_2 \cdot CH=$, $=CH \cdot CH_2 \cdot CH=$, $=CH \cdot (CH_2)_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot COOC_5H_{11}$. It was also found from the yield of carbon dioxide obtained by the ozonolysis that amyl nisinate contained more than two of the group $=CH \cdot CH_2 \cdot CH=$. These results, coupled with the fact that nisinic acid consists of 24 carbon atoms, show that nisinic acid is composed of the following groups: $CH_3 \cdot CH_2 \cdot CH=$, three of $=CH \cdot CH_2 \cdot CH=$, two of $=CH \cdot (CH_2)_2 \cdot CH=$, and $=CH \cdot (CH_2)_2 \cdot COOH$. No evidence was brought out in these experiments regarding the respective positions of the groups $=CH \cdot CH_2 \cdot CH=$ and $=CH \cdot (CH_2)_2 \cdot CH=$. If, however, it is assumed that nisinic acid has ethylenic linkings in 4:5-, 8:9- and 12:13-positions as is the case with the previously studied moroctic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16}$),[2] eicosatetraenoic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 16:17}$),[3] and clupanodonic acid ($\Delta^{4:5,\ 8:9,\ 12:13,\ 15:16,\ 19:20}$),[4] the constitution of nisinic acid should be represented by the following formula:

$$CH_3 \cdot CH_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot CH_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot CH=CH \cdot (CH_2)_2 \cdot COOH.$$

Experimental.

1. **Separation of Nisinic Acid.** In previously reported experiments of the separation of hiragonic, moroctic and eicosatetraenoic acids, 60 kg. of the ethyl ester prepared from sardine oil had been distilled, yielding two fractions boiling below and above 215°/10 mm. respectively. The distillation had been continued up to 225°/3 mm., leaving ca. 4 kg. of residue. For the present experiments, 1.5 kg. of this residue was used as the starting material. It was first treated by means of the sodium-soap-acetone method; the sodium soaps insoluble in acetone were removed, and the highly unsaturated acids were obtained from the sodium soaps soluble in acetone in the usual way. These were converted into the methyl esters, and the latter were subjected to distillation by which all the esters boiling below 215°/2 mm. were removed. The residue was saponified, the unsaponifiable matter was removed by extraction with ether, and the fatty acids liberated from the soap solution on acidification were treated with decolorizing carbon in petroleum ether. After these treatments there were obtained 145 g. of fatty acids having neutralisation value 155.8 and

(2) This Bulletin, **10** (1935), 232.
(3) This Bulletin, **10** (1935), 296.
(4) This Bulletin, **10** (1935), 441.

iodine value 319.1.[5] In order to effect a further separation of these fatty acids into individual components, they were dissolved in acetone and partially neutralised with sodium hydroxide solution in a similar manner as described in the previous experiment.[6] The precipitate of insoluble sodium soaps was filtered, and the fatty acids were recovered from the filtrate. These were again subjected to a fractional precipitation of sodium soaps in acetone, and the less highly unsaturated portion was removed as sodium soaps insoluble in acetone. After repeating these separative operations several times there were obtained finally 25 g. of fatty acids having iodine value 397.8 from the filtrate. These were brominated in ethereal solution, and the ether insoluble bromide was separated. On debrominating the ether insoluble bromide with zinc powder and glacial acetic acid, there were obtained 6.6 g. of fatty acids which had neutr. value 155.4 and iodine value 419.1, and were considered to consist mainly of nisinic acid. They were united with the sample (7 g.) of nisinic acid (iodine value 422.5) obtained in the previous experiment[7] and converted into the methyl esters, and the latter were subjected to distillation by which a fraction boiling at 198–204°/0.4 mm. was taken as methyl nisinate $C_{25}H_{38}O_2$. It had the following constants: d_4^{15} 0.9342, d_4^{20} 0.9307, n_D^{15} 1.5064, n_D^{20} 1.5044, saponif. value 151.1 (cal. 151.5), iodine value 408.5 (calc. 411.3).

Nisinic acid $C_{24}H_{36}O_2$ liberated from its methyl ester had the following constants: d_4^{15} 0.9487, d_4^{20} 0.9452, n_D^{15} 1.5143, n_D^{20} 1.5122, neutr. value 157.0 (calc. 157.5), iodine values by the Wijs and the Rosenmund-Kuhnhenn methods 424.5 and 410.3 (calc. 427.5) respectively.

On brominating nisinic acid in ethereal solution it yielded 140% of an ether insoluble bromide which had Br-content 72.78% (calc. for $C_{24}H_{36}O_2Br_{12}$: 72.91%) and turned black at about 240° without melting. The hydrogenation product of nisinic acid crystallised from alcohol in lustrous laminae which showed neutr. value 152.4 (calc. for $C_{24}H_{48}O_2$: 152.3) and m.p. 82.5–83°. The melting point was not lowered when the substance was admixed with various proportions of a specimen of *n*-tetracosanic acid $C_{24}H_{48}O_2$ which was prepared from behenic acid by malonic ester synthesis and melted at 84–84.5°.

2. **Ozonolysis of Amyl Nisinate.** Nisinic acid obtained above was heated with an equal amount of amyl alcohol containing 2.5% of hydrogen chloride on the water-bath under a reflux condenser for one hour. The resulting solution containing amyl nisinate was taken up with ether, and the ethereal solution was washed with sodium carbonate solution in order to remove hydrogen chloride and the unchanged nisinic acid, and then washed thoroughly with water. On distilling off ether and amyl alcohol from the ethereal solution, there remained amyl nisinate. Nine grams of the amyl nisinate was dissolved in 90 c.c. of chloroform, and a current of ozonised oxygen was passed into the solution under cooling with ice-salt until the solution became saturated with ozone. On removal of chloroform under diminished pressure there was obtained 16.2 g. (or 180%) of ozonide as an orange yellow syrup. The ozonide was, however, not thoroughly freed from chloroform, since there was a danger of frothing towards the end of the distillation of chloroform. The theoretical yields of ozonides obtainable from amyl nisinate are 167.5% for normal ozonide $C_{29}H_{46}O_{20}$ and 171.3% for ozonide

(5) Unless otherwise stated, the iodine values were determined by the Wijs method.

(6), (7) This Bulletin, **10** (1935), 543.

peroxide $C_{29}H_{46}O_{21}$. Water (90 c.c.) was added to the ozonide, and the liquid was heated on the water-bath for 30 minutes. The flask containing the ozonide was attached to other two flasks (a and b) in succession by means of a delivery tube; the first (a) was filled with ice-cold water, and the second (b) with barium hydroxide solution. During heating a current of hydrogen was passed through the flask containing the ozonide, and the volatile products (A) carried over with hydrogen were caught by absorption in the above two flasks. The products of ozonolysis remaining in the initial flask dissolved partly in water, and the remainder separated as oily substances C) under aqueous solution (B). Each portion (A, B and C) was examined in the following manner.

(i) **Volatile products (A).** The aqueous solution in the flask (a) produced a pink colouration with Schiff's reagent, and a deep blue colouration with sodium nitroprusside and diethylamine, indicating the presence of acetaldehyde. When the phenylhydrazone prepared from this solution was heated with zinc chloride at 180°, a smell of scatol was recognised, which indicated the presence of propyl aldehyde. A partial separation of two aldehydes was attempted by warming a portion of the solution in a flask (a_1) at 45°, and passing a current of carbon dioxide into the flask so as to drive off the volatile substances into other flask (a_2) which was connected with the initial flask by means of a delivery tube. The flask (a_2) was filled with ice-cold water, which served to absorb the volatile substances carried over with carbon dioxide. The *p*-nitrophenylhydrazone prepared from the solution in the flask (a_1) melted at 120–121° after recrystallisation from 50% alcohol, and was considered to consist largely of *p*-nitrophenylhydrazone of propyl aldehyde (Found: N, 21.84. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%). The solution in the flask (a_2) yielded *p*-nitrophenylhydrazone, which melted at 115–116° after recrystallisation from 50% alcohol and seemed to be a mixture of *p*-nitrophenylhydrazones of two aldehydes (Found: N, 22.95. Calc. for $C_8H_9O_2N_3$: N, 23.46. Calc. for $C_9H_{11}O_2N_3$: N, 21.76%).

The aqueous solution in the flask (a) showed also an acid reaction, and the presence of acetic acid was inferred from a red colouration developed on addition of ferric chloride to the neutralised solution.

The barium hydroxide solution in the flask (b) was found to contain a precipitate of barium carbonate, indicating the formation of carbon dioxide by the ozonolysis. Calculating from the quantity of the precipitate of barium carbonate, the yield of carbon dioxide formed by the ozonolysis was found to be 23.5% of amyl nisinate used for the ozonolysis. This is higher than the maximum yield 20.64% of carbon dioxide obtainable on assumption that amyl nisinate contains two of the group $=CH\cdot CH_2\cdot CH=$, and consequently amyl nisinate must have more than two of the group $=CH\cdot CH_2\cdot CH=$.

(ii) *Aqueous solution* (B). The products of ozonolysis dissolved in the aqueous solution (B) were extracted by shaking the solution with 900 c.c. of ether, and on removal of ether from the ethereal solution there remained 4.1 g. of an orange yellow liquid. This was washed three times with petroleum ether using 50 c.c. each time, and the petroleum ether solution and the insoluble portion were separated. The petroleum ether solution was heated on the water-bath to drive off petroleum ether, and the residue was then heated in the oil-bath yielding 0.7 g. of colourless distillate before the temperature of the bath reached 180°, when the distillation was discontinued. The distillate showed an acid reaction. The silver salts prepared from it were fractionally precipitated, yielding two crops which were found to be mixtures of silver

acetate and silver propionate by analyses (Found for 1st crop: Ag, 61.64. Found for 2nd crop: Ag, 63.59. Calc. for $C_2H_3O_2Ag$: Ag, 64.64. Calc. for $C_3H_5O_2Ag$: Ag, 59.63%).

The portion insoluble in petroleum ether (2.5 g.) was an orange yellow liquid. Oxidation with an alkaline solution of potassium permanganate followed by acidification gave a product consisting mostly of crystalline solid. It crystallised from ethyl acetate in needles having neutr. value 947.5 (calc. for succinic acid $C_4H_6O_4$: 950.6) and m.p. 181–182°. The melting point was not lowered when the substance was admixed with a pure specimen of succinic acid (m.p. 182–183°).

(iii) *Oily substances* (C). Yield 3.1 g. These were oxidised with alkaline permanganate. The product obtained after acidification had neutr. value 303.1 and saponif. value 590.5, and seemed to consist mainly of amyl hydrogen succinate $C_9H_{16}O_4$ (neutr. value 298.3, saponif. value 596.5). The free acid liberated from the acid ester yielded succinic acid after recrystallisation from ethyl acetate; neutr. value 948.1 and m.p. 181–182°.

Summary.

Nisinic acid $C_{24}H_{36}O_2$ has been separated from sardine oil, and its amyl ester subjected to ozonolysis. Among the products of ozonolysis were found: propyl aldehyde, propionic acid, acetaldehyde, acetic acid, carbon dioxide, succinic acid and amyl hydrogen succinate. Of these compounds propyl aldehyde and propionic acid are derived from the group $CH_3{\cdot}CH_2{\cdot}CH=$, whilst acetaldehyde and acetic acid together with carbon dioxide are attributable to the secondary decomposition of malonic acid and the corresponding aldehyde which are derived from the group $=CH{\cdot}CH_2{\cdot}CH=$. The yield of carbon dioxide indicated the presence of more than two of the group $=CH{\cdot}CH_2{\cdot}CH=$. Succinic acid and amyl hydrogen succinate are derived from the groups $=CH{\cdot}(CH_2)_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}COOC_5H_{11}$ respectively. Accordingly, nisinic acid was found to be composed of the following groups: $CH_3{\cdot}CH_2{\cdot}CH=$, $=CH{\cdot}CH_2{\cdot}CH=$ (three), $=CH{\cdot}(CH_2)_2{\cdot}CH=$ (two), and $=CH{\cdot}(CH_2)_2{\cdot}COOH$. The respective positions of the groups $=CH{\cdot}CH_2{\cdot}CH=$ and $=CH{\cdot}(CH_2)_2{\cdot}CH=$ were not determined in these experiments. If, however, it is assumed that three of the ethylenic linkings in nisinic acid lie at 4:5-, 8:9- and 12:13-positions as is the case with previously studied moroctic, eicosatetraenoic and clupanodonic acids, the constitution of nisinic acid is expressed by the following formula:

$$CH_3{\cdot}CH_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}CH_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}CH=CH{\cdot}(CH_2)_2{\cdot}COOH.$$

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

ISOTOPENAUSTAUSCH IN SOJABOHNEN.

Von Kenzo OKABE und Toshizo TITANI.

Eingegangen am 18. September 1935. Ausgegeben am 28. November 1935.

Auf die Austauschreaktionen zwischen H- und D-Atomen im Organismenkörper wurde zuerst von Hevesy und Hofer[1] hingewiesen. Bringt man z.B. einen kleinen Goldfisch in verdünntes schweres Wasser, dann findet ein lebhafter Austausch von H- und D-Atomen zwischen dem Inhaltswasser des Fisches und dem umgebenden schweren Wasser statt. Die Austauschgeschwindigkeit ist so gross, dass das Gleichgewicht schon innerhalb von wenigen Stunden erreicht wird. In diesem Zustand sind die D-Konzentrationen des Wassers innerhalb und ausserhalb des Fischkörpers ausgeglichen. Deshalb kann man aus der Gesamtmenge des umgebenden Wassers sowie dessen Konzentrationen an Deuterium vor und nach dem Experiment leicht den Wassergehalt des Fisches errechnen. Auf diese Weise fanden Hevesy und Hofer den Wassergehalt des lebenden Goldfisches, der sich mit dem durch Analyse ermittelten Wert als gut übereinstimmend erwies. Genau dieselben Resultate erhielt man auch, wenn man eine gegebene Menge von schwerem Wasser eingab[2] oder in den Tierkörper einspritzte.[3] Um zu sehen, ob man dasselbe Verfahren zur Ermittelung des Wassergehalts im Pflanzenkörper anwenden kann, untersuchten wir die Sojabohnen.

Die zum Versuch benutzten Bohnen waren gewöhnliche, japanische Sojabohnen, deren Durchmesser durchschnittlich 9 mm. betrug. Diese wurden an der Luft getrocknet und enthielten immer noch 10.4% Wasser. Der Wassergehalt der Bohnen wurde auf folgende Weise bestimmt: Eine abgewogene Menge Bohnen wurde zuerst sorgfältig zerkleinert und dann in einem Luftbad konstant bei 100°C. bis zum konstanten Gewicht getrocknet. Dazu waren ungefähr fünf Stunden erforderlich.

In sechs Erlenmeyerkolben brachten wir je 150 g. von nur an der Luft getrockneten Bohnen und versetzten jede Menge mit 300 c.c. von 0.14% schwerem Wasser, dessen spezifisches Gewicht 131 γ grösser als gewöhnliches Wasser war. Die Kolben wurden dann von Zeit zu Zeit mit der Hand sanft geschüttelt. Nach einer bestimmten und zwar für den einzelnen Kolben verschiedenen Zeit, wurde das Wasser von den

(1) G. von Hevesy und E. Hofer, *Z. physiol. Chem.*, **225** (1934), 28; *Nature*, **133** (1934), 495.

(2) G. von Hevesy und E. Hofer, *Nature*, **134** (1934), 879.

(3) E. J. McDougall, F. Verzar, H. Erlenmeyer und H. Gärtner, *Nature*, **134** (1934), 1006.

Bohnen abgetrennt und sorgfältig gereinigt. Die Reinigung des Wassers führten wir nach der schon oft beschriebenen Methode mittels erhitzten Kupferoxyds u.s.w. durch.[4] Das spezifische Gewicht des so gereinigten Wassers wurde dann nach der Schwebemethode mittels eines Quarzschwimmers im Vergleich zu dem des Standardwassers bestimmt. Die Messresultate gibt die folgende Tabelle wieder.

Kolben Nr.	Eintauchsdauer in Stdn.	Dichteabnahme des umgebenden Wassers in γ
1	$\frac{1}{6}$	1
2	$\frac{1}{2}$	2
3	$1\frac{1}{2}$	5
4	$4\frac{1}{2}$	10
5	20	17
6	46	16

Die letzte Reihe zeigt die Abnahme in der Dichte des abgetrennten Wassers in bezug auf dessen Anfangsdichte. Wie aus der Tabelle ersichtlich ist, ging die Austauschreaktion nicht so schnell vor sich, aber zum Schluss stellte sich das Gleichgewicht sicherlich ein. Rechnet man aus diesen Daten den Wassergehalt der Bohnen, dann ergeben sich 25%. Dieser Wert erwies sich sogar über doppelt so gross wie der durch Analyse ermittelte von 10%. Rechnet man dagegen die Dichteabnahme des umgebenden Wassers aus dem analytisch bestimmten Wassergehalt der Bohnen (10%), dann sollte sie beim Gleichgewicht 7 γ sein. Die Frage nach der Ursache dieser grossen Diskrepanz kann man natürlich nicht leicht beantworten. Aber es scheint dafür zwei Möglichkeiten zu geben. Entweder enthielten die benutzten Bohnen noch eine Menge Wasser, das durch blosse Trocknung bei 100°C. nicht entfernt werden konnte. Oder es traten nicht nur die H-Atome des Inhaltswassers der Bohnen, sondern auch die anderen austauschbaren H-Atome in den Bohnensubstanzen mit den D-Atomen des umgebenden Wassers in Austausch. Und zwar scheint die zweite Möglichkeit wahrscheinlicher als die erste. Denn bei den Versuchen von Bonhoeffer[5] und seinen Mitarbeitern wurde gefunden, dass die an O gebundenen H-Atome in der Kohlenhydraten sowie die an N gebundenen H in Eiweiss alle mit D-Atomen austauschbar sind. Und es ist kaum nötig zu bemerken, dass solche Substanzen reichlich in Bohnen vorhanden sind.

(4) Vgl. z.B. T. Titani und M. Harada, dies Bulletin, **10** (1935), 261.
(5) Vgl. z.B. K. F. Bonhoeffer, *Z. Elektrochem.*, **40** (1934), 469.

Wir sind der Hattori-Hohkohkai (Hattori-Stiftung) sowie der Gakujutsu-Shinkokai (Notgemeinschaft der japanischen Wissenschaft) für ihre finanzielle Unterstützung zum herzlichsten Dank verpflichtet.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka,
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

ISOTOPENAUSTAUSCH ZWISCHEN WASSER UND EINIGEN ORGANISCHEN VERBINDUNGEN.

(Vorläufige Mitteilung.)

Von Masao HARADA und Toshizo TITANI.

Eingegangen am 19. Oktober 1935. Ausgegeben am 28. November 1935.

Eine der interessantesten Anwendungen von Deuterium liegt darin, dass die D-Atome beim Versuch über den Austausch von H-Atomen als Indikatoren verwendet werden. Wenn z.B. eine H-haltige Verbindung in schwerem Wasser gelöst, oder falls sie nicht löslich ist, damit vermischt und geschüttelt wird, findet ein Austausch von H- bzw. D-Atomen zwischen beiden Substanzen statt. Dieser Austausch wird dadurch nachgewiesen, dass die Dichte des verwendeten schweren Wassers während des Versuchs abnimmt, bis ein Gleichgewichtszustand, ein Austausch- oder Isotopengleichgewicht, erreicht wird. Infolgedessen kann man aus solch einem Versuch Schlüsse ziehen über die Austauschbarkeit von H-Atomen in der betreffenden Substanz. Bonhoeffer und seine Schüler haben auf diesem Wege zahlreiche Versuche über die Austauschreaktion zwischen Wasser und organischen Verbindungen ausgeführt.[1] Aus diesen Versuche ergab sich, dass nur solche H-Atome, die an O oder N gebunden sind, mit denen des Wassers ausgetauscht werden, aber die an C gebundenen H-Atome allgemein nicht direkt austauschbar sind. Diesen Umstand kann man eventuell dazu benutzen, um die Anzahl von Hydroxyl- oder Aminogruppen in einem gegebenen Molekül zu ermitteln.

(1) Vgl. z.B. K. F. Bonhoeffer, *Z. Elektrochem.*, **40** (1934), 469.

Aber dabei muss man, wenn quantitative Schlüsse gezogen werden sollen, auch die Verteilung von D-Atomen zwischen Wasser und verwendeten Verbindungen in Betracht ziehen, worauf Bonhoeffer schon hingewiesen hat. Denn die D-Atome zeigen oft die Neigung aus dem Wasser in die organischen Verbindungen mehr oder weniger absorbiert zu werden. Aber nicht selten gibt es auch einen entgegengesetzten Fall, wie an einem Beispiel weiter unten gezeigt wird. Diese Neigung zur Akkumulation der D-Atome kann man entweder durch den Verteilungskoeffizienten der D-Atome zwischen beiden Substanzen oder durch die Gleichgewichtskonstante der betreffenden Austauschreaktion quantitativ messen.

Falls die D-Konzentration nicht zu gross ist, kann die Austauschreaktion zwischen einem organischen Molekül RH_n, das n austauschbare H-Atome von gleicher Natur enthält, und schwerem Wasser durch die folgende Gleichung dargestellt werden.

$$RH_n + HDO \quad \rightleftarrows \quad RH_{n-1}D + H_2O,$$

wobei das D_2O-Molekül und solche wie $RH_{n-2}D_2$ u.s.f. wegen der Kleinheit der D-Konzentration vernachlässigt werden. Die Gleichgewichtskonstante K für diese Reaktion ist dann offenbar:

$$K = \frac{[RH_{n-1}D][H_2O]}{[RH_n][HDO]},$$

und der Verteilungskoeffizient k der D-Atome wird durch die folgende Formel definiert.

$$k = \frac{\text{(Atomare Konz. von D in den gesamten austauschbaren H der organischen Substanz)}}{\text{(Atomare Konz. von D in den gesamten H des Wassers.)}}.$$

Die so definierten Konstanten K und k stellen beide für eine gegebene Verbindung eine charakteristische Konstante dar, so lange wie die D-Konzentration genügend klein bleibt. Aber für den praktischen Zweck ist der Verteilungskoeffizient k anschaulicher. Denn falls $k = 1$ ist, verteilen sich die D-Atome gleichmässig zwischen dem Wasser und der organischen Verbindung, dagegen wenn $k > 1$ ist, werden sie in die organische Substanz akkumuliert und vice versa. Wir haben die oben genannten beiden Konstanten k und K für einige organische Verbindungen experimentell bestimmt. Die Ergebnisse dieses Experimentes wollen wir vorläufig mitteilen.

Durchschnittlich 2 c.c. von 1 bis 2 prozentigem schweren Wasser wurde mit einer geeigneten Menge von organischer Verbindung im

zugeschmolzenen Glasröhrchen verschiedene lange erwärmt. Dann wurde das Wasser von der organischen Verbindung auf verschiedene Wege, je nach der verwendeten Substanz, meistens bei Zimmertemperatur abgetrennt und gereinigt.(2) Die Dichte des so gereinigten Wassers wurde durch Schwebe-methode mittels eines kleinen Quarzschwimmers genau bestimmt. Die vom Wasser abgetrennte organische Substanz wurde zunächst gut getrocknet und dann im Luftstrom mittels Kupferoxyds verbrannt. Das abdestillierte Wasser wurde sorgfältig gereinigt und dessen Dichte ebenfalls genau bestimmt. Sicherheitshalber haben wir aus diesen beiden Daten sowie der Anfangsdichte des verwendeten Wassers k und K ausgerechnet, und zwar durch die Kombination von je zwei aus drei Dichtebestimmungen. Die Versuchsergebnisse sind in der folgenden Tabelle zusammengestellt, wo die festgedruckten Buchstaben **H** in der zweiten Vertikelreihe austauschbare H-Atome darstellen. Jedes dieser

Versuchsergebnisse

Substanz	Formel	Verteilungskoef. k	Gleichgewichtskonst. K
Chloroform	CH_3Cl	(kein Austausch)	
Äthyläther	$C_2H_5OC_2H_5$	(kein Austausch)	
Anilin	$C_6H_5NH_2$	1.11	1.11
Phenol	C_6H_5OH	1.07	0.54
Pyrol	C_4H_4NH	0.88	0.44
Benzaldehyd	C_6H_5CHO	(kein Austausch)	
Benzoesäure	C_6H_5COOH	1.04	0.52
Benzylalkohol	$C_6H_5CH_2OH$	1.10	0.55

Resultate ist der Durchschnitt aus zwei bis fünf unabhängig durchgeführten Messungen und die Genauigkeit dürfte durchschnittlich $\pm 5\%$ sein. Wie man leicht aus der Tabelle ersieht, ist der Verteilungskoeffizient k in jedem Fall nicht viel von eins verschieden, mindestens unter den vorliegenden Versuchsbedingungen.

Zum Schluss möchten wir Herrn Dr. Morita in unserem Laboratorium, der uns einen Teil des verwendeten schweren Wassers zur Verfügung gestellt hat, besten Dank aussprechen. Zugleich ist es unsere angenehme Pflicht der Hattori Hohkohkai (Hattori-Stiftung) sowie der

(2) Die ausführliche Publikation über die Arbeitsmethode wird später in diesem Bulletin erfolgen.

Gakujutsu-Shinkokai (Notgemeinschaft der japanischen Wissenschaft) für ihre finanzielle Unterstützung unseren herzlichsten Dank auszusprechen.

Schiomi Institut für Physikalische
und Chemische Forschungen,
und
Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka.

MONODEUTERIOBENZOL.

Von Noriyoshi MORITA und Toshizo TITANI.

Eingegangen am 2. November 1935. Ausgegeben am 28. November 1935.

Hinsichtlich des Benzolproblems hat die Untersuchung über die Deuteriobenzole so grosses Interesse hervorgerufen, dass schon viele Versuche über deren Darstellungsmethoden veröffentlicht wurden. Aber in manchen Fällen handelt es sich um das total substituierte Hexadeuteriobenzol C_6D_6, oder ein Gemisch aus teilweise substituierten verschiedenen Deuteriobenzolen. Nur selten kam in die Reindarstellung von einzelnen Deuteriobenzolen in Frage. Ingold und seine Mitarbeiter wendeten die Grignardreaktion zur Darstellung von reinem Monodeuteriobenzol an.[1] Wir haben zu demselben Zweck die Doppelumsetzung zwischen Calciumbenzoat und Calciumhydroxyd benutzt. Diese Reaktion ist schon früher als Darstellungsmethode von reinem Benzol allgemein verwendet worden. In der vorliegenden Arbeit haben wir natürlich Calciumhydrat durch Calciumdeuterat ersetzt:

$$(C_6H_5COO)_2Ca + Ca(OD)_2 = 2C_6H_5D + 2CaCO_3 .$$

In der Praxis sind wir folgendermassen verfahren: 15 g. Calciumbenzoatdihydrat $Ca(C_7H_6O_2)_2 \cdot 2H_2O$ wurden bei 150°C. im Vacuum gut entwässert. Das Calciumdeuterat $Ca(OD)_2$ wurde aus 7.5 g. Calciumoxyd CaO, das im voraus bei 500°C. im Vakuum getrocknet war, und 1 g. 97% D_2O gewonnen. Das so hergestellte Calciumbenzoat und Calcium-

(1) W. R. Angus, A. H. Leckie, C. R. Bailey, C. G. Raisin, J. L. Gleave, C. L. Wilson und C. K. Ingold, *Nature*, **135** (1935), 1033.

deuterat wurden miteinander gut vermischt und im elektrischen Ofen bis auf ca. 300°C. erhitzt. Das entstehende und abdestillierte Monodeuteriobenzol wurde durch die Abkühlung mit kaltem Wasser kondensiert. Das erhaltene Produkt wurde mit Phosphorpentoxyd getrocknet und durch paarmalige Destillationen gereinigt. Die Ausbeute war 5 g. gegenüber der theoretischen von 8 g.

Nach derselben Methode, aber unter Benutzung von gewöhnlichem Wasser, haben wir auch gewöhnliches Benzol hergestellt und einige von dessen physikalischen Eigenschaften mit denen des Monodeuteriobenzols verglichen. Das spezifische Gewicht von C_6H_6 betrug $d_{25}^{25} = 0.8754$, während das des 97 prozentigen C_6H_5D $d_{25}^{25} = 0.8869$ war. Der erste Wert stimmt sehr gut mit dem Standardwert für reines C_6H_6 überein. Dies kann als ein Beweis für die Reinheit des von uns hergestellten C_6H_6 sowie C_6H_5D betrachtet werden. Angenommen, C_6H_5D besäße dasselbe Molekularvolumen wie C_6H_6, dann sollte das spezifisches Gewicht von 97% C_6H_5D $d_{25}^{25} = 0.8864$ sein. Dieser Wert erwies sich als gut übereinstimmend mit dem gefundenen. Der Schmelzpunkt von C_6H_5D liegt um etwa 0.1°C. höher als der des C_6H_6. Zum Schluss haben wir das Brechungsvermögen von beiden Benzolen mittels eines Interferometers verglichen. Dabei ergab sich, dass die Brechungszahl von C_6H_5D für weisses Licht bei 23°C. um 0.00065 kleiner als die des C_6H_6 ist.

Die oben beschriebene Methode gestattet uns durch die verhältnismässig einfache Manipulation ein reines Produkt zu erhalten. Aber ein anderer Vorteil der Methode liegt darin, dass man alle Deuteriumatome im verwendeten schweren Wasser zur Substitution benutzen kann. Nach demselben Prinzip kann man auch andere verschiedenen Deuteriobenzole rein herstellen. Solche Versuche sind jetzt im Gang.

Zum Schluss ist es unsere angenehme Pflicht der Gakujutsu-Shinkokai (der Notgemeinschaft der japanischen Wissenschaft) sowie der Hattori-Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung unseren herzlichsten Dank auszusprechen.

Physikalisch-Chemisches Laboratorium
der Kaiserlichen Universität zu Osaka,
und
Schiomi Institut für Physikalische
und Chemische Forschungen.

SPECTROSCOPIC STUDIES OF LUMINESCENCE AT THE CATHODE DURING ELECTROLYSIS.

By Iturô UHARA.

Received August 9th, 1935. Published December 28th, 1935.

Luminescence has been observed during electrolysis in many cases, mostly at the anode, and it is attributed to the formation of a thin film of insoluble matters, for examples, oxide, hydroxide, oxygen on aluminium electrode, mercurous chloride on the surface of mercury; and the spectra are continuous. There are a few examples of luminescence at the cathode. M. Fraymann[1] observed that, when a sulphuric acid solution was electrolysed in high current density with various metals as the cathode, arc lines of the metals and H_α- and often H_β-lines were emitted by sparking through the film of hydrogen on the cathode. A. W. Dumanski and his co-workers[2]

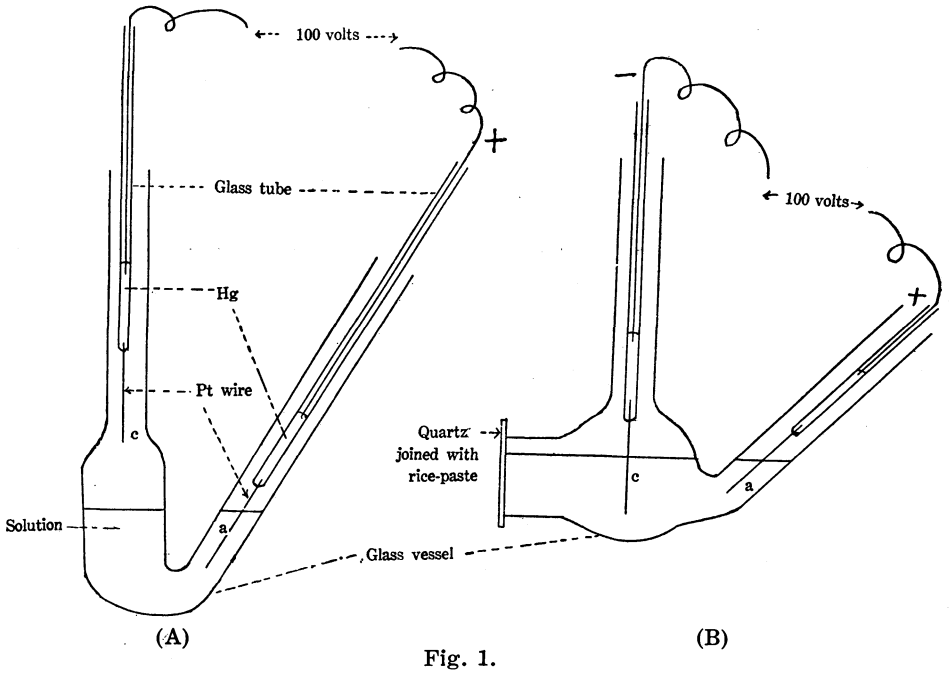


Fig. 1.

(1) M. Fraymann, *Recherches et Inventions*, **1 1**, 36-41; *Chem. Zentr.*, **101** (1930), I 1902.

(2) A. W. Dumanski, A. W. Banow, M. W. Lichoscherstow, *Chem. J. Ser. W. J. physik. Chem.*, **2** (1931), 806-813; *Chem. Zentr.*, **104** (1933), II, 1307.

observed very weak luminescence when the current was reversed during electrolysis of the solutions of zinc chloride, etc., with mercury electrodes, and calcium salts and magnesium nitrate with platinum electrodes; and he remarked that this was not explicable as an oxidation reaction as in the cases of luminescence at the anode.

The writer observed luminescence at the cathode during electrolysis of the solutions of many electrolytes with electrodes of platinum wire, and studied the spectra. The apparatus for electrolysis is shown in Fig. 1(A).

The solutions of Merck's and Kahlbaum's products in the concentration of 1–3 N, or 1.5–1 N for acid solutions, were electrolysed. When the platinum electrode (c) was immersed quietly in the solution, scintillation took place over the surface of the electrode with hydrogen evolution and noise. When the voltage was too low, or when the solution was too dilute, or when the circuit was closed after the cathode (c) was immersed in the solution, only violent electrolysis was observed. This suggests that the formation of a thin film of hydrogen over the cathode under high current density is necessary. The spectra of luminescence were studied under the following conditions with Hilger's glass spectrograph of constant deviation type: current 0.2–0.5 amperes or more; current density 0.6–1.5 amperes per sq. cm. or more; slit about 0.2 mm.; photographic plates Wratten hypersensitive panchromatic plates; exposure one hour (for intense lines like D-line from sodium salt solutions a few minutes is sufficient). The temperature of the solution rose to about 80°.

The spectra obtained consist of sharp lines and are independent of the anions (NaCl, $NaNO_3$, NaOH, and Na_2CO_3 gave the same spectra). Sometimes Na^+ and Ca^{++} go into the solution from the glass vessel during electrolysis and give their lines. The spectra are shown in Fig. 2, and the wave

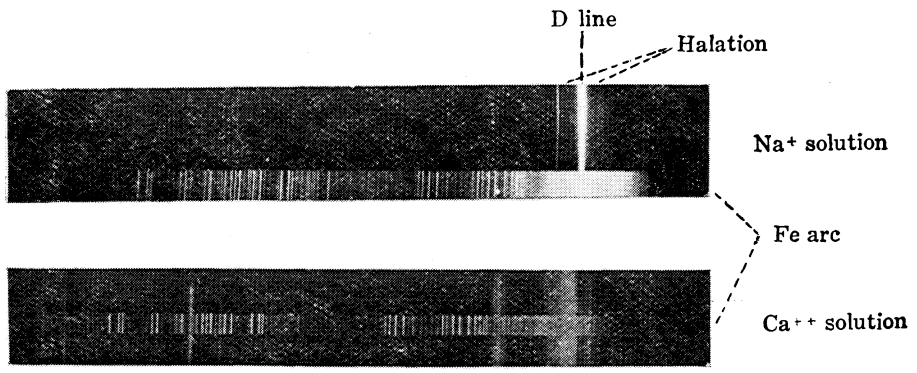


Fig. 2.

lengths (Å) of the observed lines are given in Table 1 (intensity is shown by asterisks).

Table 1.

Na^+ Solution.

Lines	Remarks
5890***, 4985, 4670, 5690**, 6164*	Due to Na I
6563* (H_α), 4860(H_β)	Due to H I
4227, 5140	Due to Ca I
3830	Due to Mg I

K^+ Solution.

4608, 4388, 4309, 4263, 4226, 4135, 4115	Spark lines of K
6563** (H_α), 4861* (H_β)	Due to H I
4849, 4654*	Due to H_2
5890**	Due to Na I
4418	Due to O(?); Kayser's table: O 4416.97; H_2 4412.25
4353	Kayser's table: Mg I 4352.1; O II 4351.38
4370	Kayser's table: O II 4369.28; O I 4368.30; Cs 4373.0
4593	Kayser's table: O II 4596.19, 4590.98; Cs 4593.2
4647	Kayser's table: O II 4649.15; Rb 4648.56
4829	Kayser's table: Cs 4830.2
4838	?

HCl Solution.

6563** (H_α), 4860 (H_β), 4340 (H_γ)	Due to H I
6032, 6327, 4491*, 4205*	Due to H_2
4520, 4548, 4165, 4120	Due to Pt; sometimes black powder of platinum is precipitated.
5896, 5688	Due to Na I
5855, 5270**, 5041, 4435	Due to Ca I
4150	Kayser's table: O II 4153.31; Al III 4150.1
6318	Due to Mg I

Table 1 (*Concluded*).

NH_4^+ Solution.

Lines	Remarks
6530* (H_α), 4860 (H_β), 4340 (H_γ)	Due to H I
5435, 4490, 5055, 4205	Due to H_2
4548	Due to Pt
6550	Due to O(?)
5270, 5350, 5140, 4455	Due to Ca

Ca^{++} Solution.

6494*, 6472**, 6470**, 6439**, 6162*, 6122*, 5858*, 5595**, 5589**, 5350, 5270**, 5189, 5042, 4878, 4586, 4455**, 4435**, 4426**, 4308*, 4303**, 4290*, 4227*	Due to Ca I
3969*, 3934*	Due to Ca II
6563(H_α)	Due to H I
5537**, 5505*, 6135*	Due to H_2
5890, 5688	Due to Na I
4390	Due to Mg II (?)
5455	Kayser's table : Sr I 5450.83 ; Hg I 5460.724

$Hg(NO_3)_2+HNO_3$ Solution.

5791, 5770, 5461**, 4358*	Due to Hg I
5890**	Due to Na I

To study the ultraviolet region an apparatus as shown in Fig. 1 (B) and Hilger's quartz spectrograph were used. Lines of metals and hydrogen were observed, but OH-band was not (this band was not observed when carbon arc was lit in hydrogen which had been passed through boiling water under one atmospheric pressure).

In electrolysis with the alternating current (100 volts) luminescence takes place sometimes on both electrodes, sometimes on one electrode of higher current density. Even with the solutions of those metallic salts (e.g. aluminium and magnesium salts) which give weak luminescence, or such luminescence as disappears in the course of time, owing to the formation of insoluble hydroxide in the electrolysis with the direct current, we can observe lumines-

cence for a long time in electrolysis with the alternating current. The spectra are the same as in the case of the direct current.

Solutions of Ba^{++}, Sr^{++}, Mg^{++}, Al^{+++}, Cd^{++}, Zn^{++}, Hg_2^{++}, Fe^{++}, Co^{++}, Mn^{++}, Bi^{+++}, and Sn^{++} gave those lines which are observed in their arc spectra.

Summary.

If the current density at the cathode is high enough for the formation of a thin film of hydrogen in the electrolysis of the electrolyte solutions with platinum wire electrodes, considerably intense cathode luminescence takes place; and the spectra are in most cases the same as the arc spetra (sometimes spark spectra) of the elements forming cations, and further Balmer lines of H and the molecular spectra of H_2 are often observed.

In conclusion the author wishes to express his best thanks to Mr. H. Wakesima for his kind advice and assistance and to Mr. A. Tamai and Mr. M. Nakamura for their assistance.

Taihoku Higher School.

TETRADECENOIC AND DODECENOIC ACIDS IN SPERM OIL. I. TETRADECENOIC AND DODECENOIC ACIDS IN SPERM BLUBBER OIL.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received September 3rd, 1935. Published December 28th, 1935.

Sperm oil is obtained from the sperm whale, *Physeter macrocephalus* L., and the oil obtained from the body blubber is generally kept separate from that of the head cavities. Sperm blubber (or body) oil and sperm head oil are, therefore, known in the foreign market. In this country, however, four kinds of oils are differentiated, i.e. head oil, blubber oil (skin oil), intestine oil and bone oil; the blubber oil is obtained exclusively from the blubber under the skin and has the largest yield, while the intestine oil is obtained from the intestines and the surrounding flesh. Sperm oil is frequently allowed to crys-

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1050.

tallise at a low temperature and subjected to pressure, by which the solid portion is removed and the oil having a low cold-test is obtained. The solid portion is used for further preparation of spermaceti. However, these separative operations are not generally carried out in this country. The constituents of sperm oil have been studied since a very earlier date. Far back in about 1820, Chevreul in his classic studies found cetyl alcohol in spermaceti, and also pointed out the presence of some peculiar constituents in sperm head oil. Afterwards there have appeared many studies, among which those of Hofstädter,[1] Bull,[2] Fendler,[3] Walker and Warburton,[4] Procter and Bennet,[5] Dunlop,[6] Lewkowitsch,[7] Allen,[8] and Nakajima[9] may be mentioned. Much contributions have been made recently to the knowledge of the constituents of sperm oil by the closer studies of Tsujimoto[10] on the fatty acids and the alcohols of sperm head oil, André and François[11] on the alcohols of sperm head oil and spermaceti, and Hilditch and Lovern[12] on the fatty acids, the alcohols as well as the component esters of sperm blubber and head oils. One of the present authors (Toyama)[13] also examined the fatty acids and the alcohols of sperm blubber oil. For a thorough account of the results set forth by these authors the original papers should be consulted. Only a short review on the literature relating to the theme of the present paper, i.e. tetradecenoic acid $C_{14}H_{26}O_2$ and dodecenoic acid $C_{12}H_{22}O_2$ in sperm oil, is given below. Tsujimoto[14] isolated a tetradecenoic acid from sperm head oil and established its constitution as $\Delta^{5:6}$-tetradecenoic acid. He inferred the presence of a tetradecenoic acid also in sperm blubber oil. The same author[15] found a tetradecenoic acid also in Tsuzu oil (seed oil of *Tetradenia glauca* Matsum.), the constitution of which was, however, proved to be $\Delta^{4:5}$-tetradecenoic acid. He assigned the name physeteric acid to $\Delta^{5:6}$-acid in sperm head oil and the name tsuzuic acid to $\Delta^{4:5}$-acid in Tsuzu oil. According to Hilditch and Lovern,[16] on the other hand, the fatty acids of sperm head oil contain 14% of tetradecenoic acid and 4% of dodecenoic acid, whilst the fatty acids of sperm blubber oil contain 4% of tetradecenoic acid, but no dodecenoic acid.

---

(1), (2), (3), (4), (5), (6), (7) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", Vol. II (6th Edition), 875-876.

(8) "Commercial Organic Analysis", Vol. II (3rd Edition), Part I, 204-205.

(9) Dissertation, College of Engineering, Tokyo Imperial University (1917).

(10) *J. Soc. Chem. Ind., Japan*, **24** (1921), 41; **26** (1923), 608; **29** (1926), 102.

(11) *Compt. rend.*, **183** (1926), 663; **185** (1927), 279.

(12) *J. Soc. Chem. Ind.*, **47** (1928), 105 T; **48** (1929), 359 T; **48** (1929), 365 T.

(13) *J. Soc. Chem. Ind., Japan*, **30** (1927), 519, 527.

(14) *Loc. cit.*, (10).

(15) *J. Soc. Chem. Ind., Japan*, **29** (1926), 105; *Reports of the Tokyo Imperial Industrial Research Laboratory*, **23** (1928), No. 3.

(16) *Loc. cit.*, (12).

As for the constitutions of these acids, they stated that tetradecenoic acid in head oil is identical with physeteric acid ($\Delta^{5:6}$-acid) discovered by Tsujimoto, whereas tetradecenoic acid in blubber oil is $\Delta^{9:10}$-acid which is identical with the acid found in South Georgia whale oil by Armstrong and Hilditch.[17] The constitution of dodecenoic acid in head oil was stated to be $\Delta^{3:4}$-acid. However, Hilditch and Lovern did not separate the individual acids. In their experiments the mixed fatty acids were treated by the lead-soap-alcohol method, the methyl esters of the liquid fatty acids were fractionated, and the fractions corresponding to C_{14}- and C_{12}-acids respectively were separately collected. The constitutions of tetradecenoic and dodecenoic acids were derived from the results of the permanganate oxidation of these fractions which, however, were still contaminated with a large proportion of the methyl esters of saturated acids. In this connection it may be noted here that a dodecenoic acid, named linderic acid, was first isolated by Iwamoto[18] from the seed oil of *Lindera obtusiloba*, and its constitution was established by him as $\Delta^{4:5}$-acid.[19] Toyama[20] in his previous work on the sperm blubber oil, obtained some indications of the presence, though in a small proportion, of tetradecenoic acid, but the separation of this acid could not be attained. In a continuation of the previous work, we have undertaken the present experiments with a view to separate tetradecenoic acid starting with a large quantity of sperm blubber oil, and to ascertain by a closer examination of its constitution whether it differs from physeteric acid, as stated by Hilditch and Lovern, or not. Furthermore we have separated a dodecenoic acid from sperm blubber oil as well as from head oil, and examined its constitution. In this paper the experimental results concerning tetradecenoic and dodecenoic acids in blubber oil are described, while those of dodecenoic acid in head oil will be given in a succeeding paper.

In dealing with the unsaponifiable matter of sperm blubber oil, as described in a separate communication, a fatty acid fraction was obtained, mainly from the barium soaps soluble in acetone, in the course of the operations carried out for the separation of unsaponifiable matter. It contained large proportions of highly unsaturated acids and lower members of monoethylenic acids. The greater part of tetradecenoic and dodecenoic acids originally present in sperm blubber oil was thought to have entered into this fraction. For the present experiments this fraction was used as the starting

(17) *J. Soc. Chem. Ind.*, **44** (1925), 180 T.

(18) *J. Soc. Chem. Ind., Japan*, **24** (1921), 1143; **26** (1923), 708.

(19) It is also reported that Grün and his co-workers found dodecenoic ($\Delta^{11:12}$?) and tetradecenoic ($\Delta^{13:14}$?) acids together with $\Delta^{9:10}$-decenoic acid in butter fat. Cp. *Z. angew. Chem.*, **37** (1924), 228.

(20) *Loc. cit.*, (13).

material. It was first converted into the methyl esters, and the latter fractionated, by which the fraction boiling below 170°/15 mm. was separately collected. This was saponified, the free fatty acids obtained was further fractionally distilled, and two fractions, (a) 192–197°/15 mm. and (b) 172–177°/15 mm., were separated. The fraction (a) was treated with lead acetate in 90% alcoholic solution under strong cooling, the precipitate of the lead soaps of saturated acids were filtered off, and the filtrate yielded tetradecenoic acid. The same treatment of the fraction (b) yielded dodecenoic acid. Tetradecenoic acid thus obtained was then converted into dihydroxymyristic acid by Hazura's method, and its methyl ester was subjected to the permanganate oxidation in acetone. After saponification of the ester contained in the oxidation products, *n*-nonoic acid $CH_3\cdot(CH_2)_7\cdot COOH$ and glutaric acid $HOOC\cdot(CH_2)_3\cdot COOH$ were identified, and consequently the constitution of dihydroxymyristic acid was shown to be $CH_3\cdot(CH_2)_7\cdot CHOH\cdot CHOH\cdot(CH_2)_3\cdot COOH$. Hence, the constitution of tetradecenoic acid is $\Delta^{5:6}$-tetradecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. Tetradecenoic acid in sperm blubber oil was thus proved to be identical with physeteric acid in sperm head oil; no evidence was obtained to indicate the presence of $\Delta^{9:10}$-tetradecenoic acid which was stated by Hilditch and Lovern to occur in sperm blubber oil. Methyl dihydroxylaurate prepared from dodecenoic acid was subjected to oxidation in the same manner as methyl dihydroxymyristate, and *n*-heptoic acid $CH_3\cdot(CH_2)_5\cdot COOH$ and glutaric acid $HOOC\cdot(CH_2)_3\cdot COOH$ were identified after saponification of the ester in the oxidation products. From these results dihydroxylauric acid was found to have the formula $CH_3\cdot(CH_2)_5\cdot CHOH\cdot CHOH\cdot(CH_2)_3\cdot COOH$, and consequently the constitution of dodecenoic acid was shown to be $\Delta^{5:6}$-dodecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_5CH{=}CH\cdot(CH_2)_3\cdot COOH$. $\Delta^{3:4}$-Dodecenoic acid, which was stated by Hilditch and Lovern to occur in sperm head oil, could not be detected. We propose to assign to $\Delta^{5:6}$-decenoic acid the name denticetic acid[21] in order to distinguish it from its isomer linderic acid ($\Delta^{4:5}$-dodecenoic acid).

Experimental.

1. **Separation of Tetradecenoic Acid.** As described in a succeeding paper[22] dealing with the unsaponifiable constituents of sperm blubber oil, a specimen of sperm blubber oil having d_4^{25} 0.8735, n_D^{25} 1.4635, acid value 0.85, saponification value 126.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98% was heated with a little excess of barium hydroxide and water in an autoclave under 5–6 atm. for one hour, and the reaction products

(21) Derived from *Denticete*.

(22) This Bulletin, **10** (1935), 579.

consisting of barium soaps and free unsaponifiable matter were extracted with acetone. The substances obtained on distilling off the solvent from the acetone solution were, however, contaminated with a small proportion of barium soaps and neutral oil which escaped saponification. They were heated with an excess of alcoholic potash to effect a complete saponification of the remaining neutral oil, the soaps were decomposed with hydrochloric acid, and the unsaponifiable matter contaminated with a small amount of free fatty acids was taken up with ether. The ethereal solution was then washed with potassium hydroxide solution which dissolved out free fatty acids as their potassium soaps. For the present experiments the fatty acids regenerated from the potassium soaps thus obtained were used as the starting material. They were obtained in a yield of 2.4% of the oil, and showed neutralisation value 199.1 and iodine value 133.0. Five hundred grams of these fatty acids, corresponding to 21 kg. of the oil, were refluxed with an equal amount of methanol containing 2.5% of hydrogen chloride for 30 minutes, and the resulting methyl esters were separated from excess of methanol and some unchanged fatty acids. These were distilled, and there was obtained 26 g. of a fraction boiling below 170°/15 mm. and having saponif. value 234.8 and iodine value 78.3. This fraction was converted into free fatty acids, and the latter were fractionated. Two fractions were separately collected; (a) b. p. 192–197°/15 mm., 8.4 g. and (b) b. p. 172–177°/15 mm., 1.9 g. The fraction (a) showed neutr. value 249.8 and iodine value 84.9, and was used for further separation of tetradecenoic acid, whilst the fraction (b) was used for the separation of dodecenoic acid.

The fraction (a) was dissolved in 90% alcohol, and a solution of lead acetate (about half the theoretical quantity) in 90% alcohol was added, the total quantity of 90% alcohol being about 10 times the quantity of the fraction (a). The solution was cooled down to −15°, the precipitate of lead soaps were filtered off, and the filtrate yielded tetradecenoic acid $C_{14}H_{26}O_2$ having the following constants (Found: C, 74.39; H, 11.49. Calc. for $C_{14}H_{26}O_2$: C, 74.27; H, 11.58%).

d_4^{15} 0.9081, d_4^{20} 0.9046, n_D^{15} 1.4571, n_D^{20} 1.4552, mol. refraction (based on the data at 15°) 67.86 (calc. for $C_{14}H_{26}O_2$ Γ_1: 67.92), neutr. value 248.8 (calc. 248.0), iodine value 107.8 (calc. 112.2).

The hydrogenation product of tetradecenoic acid gave myristic acid $C_{14}H_{28}O_2$ which showed neutr. value 244.9 (calc. 245.8), m.p. and mixed m.p. 53.5–54° after recrystallisation from 80% alcohol. On oxidising tetradecenoic acid by Hazura's method, it yielded dihydroxymyristic acid $C_{14}H_{28}O_4$ which showed neutr. value 215.0 (calc. 215.6) and m.p. 118.5–119° after recrystallisation from 75% alcohol.

2. **Oxidation of Methyl Dihydroxymyristate.** Dihydroxymyristic acid described above was converted into its methyl ester by using hydrogen chloride in methanol. The methyl ester (3.5 g.) thus obtained was dissolved in 35 c.c. of acetone, and 7 g. of powdered potassium permanganate was added in small portions. The liquid was refluxed on the water-bath for one hour, and then acetone was removed by distillation. The residue was mixed with 70 c.c. of water, and a current of sulphur dioxide was passed into the mixture until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted by using 400 c.c. of ether, and after the ethereal solution was concentrated to less than half its original volume, it was then shaken with potassium carbonate solution by which the acidic substances were dissolved out as their potassium salts, while the neutral substances were left in ethereal solution. The aqueous solution containing the potassium salts was separated, and after addition of 2 g. of potassium hydroxide, the solution was heated on

the water-bath so as to saponify the acid ester contained in the oxidation products. After acidification with hydrochloric acid, the acidic substances liberated were taken up with ether. The ethereal solution was washed with water, and on removal of ether by distillation, there remained 2.3 g. of acidic substances. The low yield is thought to be due either to an incomplete oxidation with potassium permanganate or to the loss caused by washing the ethereal solution with water. The acidic substances were treated with 60 c.c. of petroleum ether (b.p. below 60°) to effect a separation into petroleum ether solution and insoluble portion. On removal of the solvent from the petroleum ether solution by heating on the water-bath, the residue was then distilled by heating in the oil-bath and there was obtained about 1 g. of colourless distillate boiling below 193°/100 mm. and having neutr. value 353.1 (calc. for $C_9H_{18}O_2$: 354.8) and n_D^{20} 1.4318. The amide prepared from the distillate was found to be *n*-nonoic acid amide which showed m.p. and mixed m.p. 98.5–99°[23] when recrystallised from 50% alcohol (Found: N, 9.00. Calc. for $C_9H_{19}ON$: N, 8.91%).

The portion insoluble in petroleum ether (0.8 g.) consisted of a crystalline solid. It crystallised from benzene in lustrous needles which showed neutr. value 845.8 (calc. for $C_5H_8O_4$: 849.7) and m.p. 97–97.5° (Found: C, 45.49; H, 6.21. Calc. for $C_5H_8O_4$: C, 45.43; H, 6.11%). The melting point was not lowered when the substance was admixed with a pure specimen of glutaric acid, m.p. 97.5–98°.

3. **Separation of Dodecenoic Acid.** The fraction (b) described above had neutr. value 282.4 and iodine value 83.5. It was dissolved in 90% alcohol, and a solution of lead acetate (approximately theoretical quantity) in 90% alcohol was added, the total quantity of 90% alcohol used being about 10 times the quantity of the fraction (b). The solution was cooled down to −15°, the precipitated lead soaps were filtered, and there was obtained dodecenoic acid $C_{12}H_{22}O_2$ having the following constants from the filtrate (Found: C, 72.99; H, 11.30. Calc. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19%).

d_4^{15} 0.9130, n_D^{15} 1.4535, mol. refraction 58.72 (calc. for $C_{12}H_{22}O_2$ $\overline{F}_1$: 58.69), neutr. value 232.0 (calc. 283.1), iodine value 118.7 (calc. 128.1).

Oxidation of dodecenoic acid by Hazura's method gave dihydroxylauric acid $C_{12}H_{24}O_4$ which had neutr. value 240.9 (calc. 241.6) and m.p. 106–107° after recrystallisation from ether. Since the precipitate of lead soaps obtained in the final separative operation for dodecenoic acid was thought to contain a considerable amount of lead dodecenoate besides the lead soaps of saturated acids, the fatty acids liberated from the precipitate on acidification were subjected to Hazura's oxidation method so as to separate dihydroxylauric acid which showed neutr. value 241.0 (calc. 241.6) and m.p. 105–106° after recrystallisation from ether.

4. **Oxidation of Methyl Dihydroxylaurate.** The specimens of dihydroxylauric acid were combined, and converted into the methyl ester by using hydrogen chloride in methanol. The methyl ester (1.1 g.) was dissolved in 10 c.c. of acetone, and 2 g. of powdered potassium permanganate was added in small portions. After the liquid had been heated on the water-bath under a reflux condenser for one hour, acetone was removed by distillation, 20 c.c. of water was added to the residue, and a current of sulphur dioxide was passed into the solution, until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The solution was shaken with ether in order to extract the oxidation products. The ethereal solution was treated with potassium carbo-

(23) The specimen of *n*-nonoic acid amide used for the mixed melting point test was prepared from *n*-nonoic acid which was obtained by the ozonolysis of oleic acid.

nate solution, and the acidic substances were dissolved out as their potassium salts. The aqueous solution containing potassium salts were separated from the ethereal solution, a little potassium hydroxide was added, and the solution was heated on the water-bath to effect the saponification of the acid ester contained in the oxidation products. The free acidic substances obtained on acidification with hydrochloric acid were once taken up with ether, the ethereal solution was washed with water, and after removal of ether by distillation the residue was treated with petroleum ether, yielding the petroleum ether solution and the insoluble portion.

The petroleum ether solution was heated on the water-bath to distill off the solvent, and there was obtained a residue (0.5 g.) which, after being washed with a little water, showed neutr. value 439.8 (calc. for $C_7H_{14}O_2$: 431.5) and n_D^{20} 1.4235, and appeared to be *n*-heptoic acid. The amide prepared from it melted at 91–92° after recrystallisation from petroleum ether, and no depression of melting point was observed when the amide was admixed with various proportions of a pure specimen of *n*-heptoic acid, m.p. 94.5–95°.(24)

The portion insoluble in petroleum ether (0.2 g.) was recrystallised from benzene in needles which had neutr. value 845.2 (calc. for $C_5H_8O_4$: 849.7) and melted at 95–96°. The melting point was not lowered when the substance was admixed with various proportions of a pure specimen of glutaric acid $C_5H_8O_4$, m.p. 97.5–98°.

Summary.

Tetradecenoic acid $C_{14}H_{26}O_2$ and dodecenoic acid $C_{12}H_{22}O_2$ have been separated from sperm blubber oil. They are converted into dihydroxymyristic acid $C_{14}H_{28}O_4$ and dihydroxylauric acid $C_{12}H_{24}O_4$ respectively, and the methyl esters of these hydroxy-derivatives are subjected to the permanganate oxidation in acetone. From the results of an examination of the oxidation products, the following constitutions have been established:

Tetradecenoic acid	$CH_3\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_8\cdot COOH$,
Dodecenoic acid	$CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$.

It is thus seen that tetradecenoic acid in sperm blubber oil is identical with physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) in sperm head oil, whilst dodecenoic acid in sperm blubber oil, to which the name denticetic acid is assigned, is $\Delta^{5:6}$-acid and is an isomer of linderic acid ($\Delta^{4:5}$-dodecenoic acid) in the seed oil of *Lindera obtusiloba*.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

(24) For the preparation of *n*-heptoic acid amide used for the mixed melting point test, castor oil was subjected to dry distillation, and a fraction consisting of *n*-heptyl aldehyde (b.p. 153–154°) was separated. This was oxidised with potassium bichromate and sulphuric acid, the product was fractionated, and a fraction of *n*-heptoic acid (b.p. 220–224°) was separated and then converted into its amide.

TETRADECENOIC AND DODECENOIC ACIDS IN SPERM OIL. II. DODECENOIC ACID IN SPERM HEAD OIL.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received September 3rd, 1935. Published December 28th, 1935.

As described in the preceding paper,[1] tetradecenoic and dodecenoic acids were separated from sperm blubber oil, and their constitutions were determined with the results that tetradecenoic acid was proved to be identical with physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) found by Tsujimoto in sperm head oil, whilst dodecenoic acid, named denticetic acid, was found to be $\Delta^{5:6}$-dodecenoic acid and not $\Delta^{3:4}$-dodecenoic acid which was stated by Hilditch and Lovern[2] to occur in sperm head oil. We have now separated dodecenoic acid from sperm head oil, and examined whether its constitution is really $\Delta^{3:4}$-dodecenoic acid as stated by Hilditch and Lovern or not.

In these experiments, the head oil was first subjected to methanolysis, and the product consisting of the methyl esters and the free unsaponifiable matter (chiefly higher alcohols) was fractionated. The fraction boiling below 150°/15 mm. was separately collected, the unsaponifiable matter was removed from it, and the fatty acids were separated. These were treated with lead acetate in 90% alcoholic solution at the room temperature. However, the lead soaps of saturated acids were not precipitated to a sufficient extent; the liquid acids obtained from the filtrate appeared from their iodine value (41.6) to contain still more than 50% of saturated acids. The liquid acids were then fractionated, and a fraction corresponding to C_{12}-acids was separated. It was then subjected to the bromo-ester method of Grün and Janko;[3] i.e. it was converted into the methyl esters and then brominated, the product was distilled so as to remove the saturated methyl esters, leaving the bromides of unsaturated methyl esters as the residue which was debrominated afterward to regenerate unsaturated methyl esters. These were saponified to obtain free fatty acids which had iodine value 98.2 and contained still saturated acids in not insignificant amount. In order to remove the saturated acids as far as possible, the fatty acids obtained above were treated with lead acetate in 90% alcohol, the solution was cooled down to -15°, and the precipitate of

---

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1055.

(1) This Bulletin, **10** (1935), 563.

(2) *J. Soc. Chem. Ind.*, **47** (1928), 105T.

(3) *Z. deuts. Oel- u. Fett-Ind.*, **41** (1921), 553, 572.

lead soaps was filtered off. The liquid acids obtained from the filtrate consisted essentially of dodecenoic acid. For the determination of the position of ethylenic linking in dodecenoic acid, it was first converted into dihydroxylauric acid by Hazura's method, and the methyl ester of this hydroxy-derivative was oxidised with potassium permanganate in acetone. Among the oxidation products, after saponification of the acid ester, *n*-heptoic acid and glutaric acid were identified. Accordingly the constitution of dihydroxylauric acid was found to be expressed by the formula $CH_3\cdot(CH_2)_5\cdot CHOH\cdot CHOH\cdot(CH_2)_3\cdot COOH$, and consequently the constitution of dodecenoic acid is $\Delta^{5:6}$-dodecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. It is seen from these results that dodecenoic acid in sperm head oil is nothing else than denticetic acid ($\Delta^{5:6}$-dodecenoic acid) found in sperm blubber oil. $\Delta^{3:4}$-Dodecenoic acid described by Hilditch and Lovern is not found.

Experimental.

1. **Separation of Dodecenoic Acid.** Sperm head oil used for the present experiments deposited a considerable amount of crystalline solid at the room temperature, and had the following characteristics: d_4^{40} 0.8654, n_D^{40} 1.4523, acid value 3.1, saponification value 147.7, iodine value (Wijs) 53.4, unsaponifiable matter 36.52%. It was first pressed at the room temperature, the solid portion was removed, and the clear oil was obtained with about 80% yield. An equal amount of methanol containing 3% of sodium hydroxide was added to the clear oil, and the mixture was well shaken for 40 minutes at about 40°, when it became homogeneous due to the formation of methyl esters and free unsaponifiable matter. A large quantity of water was then added to the solution, and the oily layer separated was washed with water to remove the contaminated soaps which had been formed to a slight extent in the course of methanolysis. The product of methanolysis thus obtained consisted of the methyl esters and the free unsaponifiable matter (mainly higher alcohols). It was distilled, and the fraction boiling below 150°/15 mm. was separated, the yield of this fraction being 139 g. from 4 kg. of the product of methanolysis. This fraction was saponified, and the unsaponifiable matter was removed by extraction with ether in the usual way. The fatty acids liberated from the soap solution was dissolved in 90% alcohol, lead acetate (approximately the theoretical quantity) dissolved in 90% alcohol was added, and the solution was kept at the room temperature over a night. The precipitated lead soaps were filtered, and the fatty acids were regenerated from the filtrate; yield 91 g., neutr. value 298.9 and iodine value 41.6. These were distilled, and a fraction boiling at 170–180°/15 mm. and having neutr. value 285.8 and iodine value 50.2 was separately collected in a yield of 31 g. It was converted into the methyl esters, and the latter were brominated in ethereal solution. The product of bromination was then distilled until the rate of distillation became very slow at about 110°/5 mm., when the distillation was discontinued. The residue was treated with zinc powder and sulphuric acid in methanol,[4] the debrominated methyl esters were converted into the free fatty acids which were then distilled, yielding 8.5 g. of a fraction

(4) Kimura, *J. Soc. Chem. Ind., Japan*, **34** (1931), 958.

having b.p. 172–177°/15 mm., neutr. value 283.1 and iodine value 98.2. This fraction was then dissolved in 90% alcohol, and lead acetate (approximately the theoretical quantity) dissolved in 90% alcohol was added, the total quantity of 90% alcohol being about 10 times the quantity of the fatty acid fraction. The solution was cooled down to −15°, the precipitate of lead soaps was removed by filtration, and there was obtained from the filtrate 4.5 g. of fatty acids which were found to consist mainly of dodecenoic acid (Found: C, 72.71; H, 11.22. Calc. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19%).

d_4^{15} 0.9132, d_4^{20} 0.9097, n_D^{15} 1.4538, n_D^{20} 1.4519, mol. refraction (based on the data at 15°) 58.74 (calc. for $C_{12}H_{22}O_2$ $\overline{1}$: 58.69), neutr. value 283.0 (calc. 283.1), iodine value 122.5 (calc. 128.1).

Hydrogenation of dodecenoic acid yielded lauric acid $C_{12}H_{24}O_2$, which after recrystallisation from 80% alcohol, showed neutr. value 280.4 (calc. 280.3), m.p. and mixed m.p. 43.5–44°. On oxidising dodecenoic acid by Hazura's method there was obtained dihydroxylauric acid $C_{12}H_{24}O_4$ which showed neutr. value 241.0 (calc. 241.6) and m.p. 106–107° when recrystallised from ether (Found: C, 61.93; H, 10.51. Calc. for $C_{12}H_{24}O_4$: C, 62.02; H, 10.42%). The melting point was unaltered when it was admixed with dihydroxylauric acid prepared from dodecenoic acid which was isolated from sperm blubber oil, but it melted at about 90° when admixed with dihydroxylauric acid[5] prepared from linderic acid.[6]

The precipitate of lead soaps, which was removed by the final separative operation for dodecenoic acid, contained a considerable proportion of lead dodecenoate besides the lead soaps of saturated acids, and the fatty acids regenerated from the precipitate of lead soaps yielded a crystalline product by Hazura's method, from which dihydroxylauric acid having neutr. value 241.1 and m.p. 106–107° was easily obtained by a single recrystallisation from ether.

2. **Oxidation of Methyl Dihydroxylaurate**, Dihydroxylauric acid obtained above was converted into its methyl ester by means of hydrogen chloride in methanol. The methyl ester (3.2 g.) was dissolved in 30 c.c. of acetone, and 6 g. of potassium permanganate was added in small portions. The mixture was gently boiled on the water-bath under a reflux condenser for one hour, and then acetone was removed by distillation. The residue was mixed with 60 c.c. of water, and a current of sulphur dioxide was passed into the mixture, until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted by shaking the solution with 300 c.c. of ether, and the ethereal solution was separated and washed with potassium carbonate solution, by which the acidic substances were dissolved out as their potassium salts. On distilling off ether from the ethereal solution there remained 0.2 g. of neutral substances which escaped oxidation. The aqueous solution containing potassium salts was heated on the water-bath with the addition of potassium hydroxide to

(5) The methyl esters of the mixed fatty acids prepared from the seed oil of *Lindera obtusiloba* were fractionated, a fraction boiling at 136–142°/15 mm. was separately collected, and the fatty acids liberated from this fraction were oxidised by Hazura's method. The product was recrystallised from ether, yielding dihydroxylauric acid melting at 100–101° (Iwamoto gave m.p. 102°). Its methyl ester was subjected to permanganate oxidation in acetone. Caprylic acid and methyl hydrogen succinate were identified among the oxidation products, and consequently the constitution of linderic acid was confirmed to be $\Delta^{4:5}$-dodecenoic acid which had been established by Iwamoto.

(6) Iwamoto, *J. Soc. Chem. Ind., Japan*, **24** (1921), 1143; **26** (1923), 708.

saponify the acid ester. After acidification with hydrochloric acid, sodium chloride was added to the solution, and the liberated acidic substances were extracted with 300 c.c. of ether. The ethereal solution was washed with water containing sodium chloride, and on removal of ether by distillation there was obtained 2.9 g. of acidic substances. These were further treated with 50 c.c. of petroleum ether, and the insoluble portion was separated from the petroleum ether solution. On removal of the solvent from the petroleum ether solution by heating on the water-bath, the residue was then subjected to distillation by which about 1 g. of colourless distillate boiling below 170°/100 mm. was separately collected. It had neutr. value 437.5 (calc. for heptoic acid $C_7H_{14}O_2$: 431.2) and n_D^{20} 1.4222, and the amide prepared from it crystallised from petroleum ether in lustrous laminae; it melted at 94.5-95° both alone or admixed with a pure specimen of *n* heptoic acid amide (Found: N, 10.83. Calc. for $C_7H_{15}ON$: N, 10.85%).

The portion insoluble in petroleum ether (0.4 g.) consisted of a white crystalline solid. Recrystallisation from benzene yielded needle-shaped crystals of glutaric acid $C_5H_8O_4$; neutr. value 851.2 (calc. 849.7), m.p. and mixed m.p. 97.5-98° (Found: C, 45.40; H, 6.05. Calc. for $C_5H_8O_4$: C, 45.43; H, 6.10%).

Summary.

Dodecenoic acid $C_{12}H_{22}O_2$ has been isolated from sperm head oil, and methyl dihydroxylaurate $C_{13}H_{26}O_4$ prepared from it has been subjected to permanganate oxidation in acetone. On examining the oxidation products the constitution of dodecenoic acid has been proved to be $CH_3 \cdot (CH_2)_5 \cdot CH=CH \cdot (CH_2)_3 \cdot COOH$. It is thus seen that dodecenoic acid in sperm head oil is identical with denticetic acid ($\Delta^{5:6}$-dodecenoic acid) in sperm blubber oil described in the preceding paper.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

HEXADECENOL AND TETRADECENOL IN SPERM HEAD OIL.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

Received September 3rd, 1935. Published December 28th, 1935.

The higher alcohols contained in the unsaponifiable matter of sperm oil have hitherto been studied by many authors, among whom Tsujimoto,[1]

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1072.

(1) *J. Soc. Chem. Ind., Japan*, **24** (1921), 41.

André and François,[2] and Hilditch and Lovern[3] deserve a special mention. For a thorough description of the results set forth by these authors the original papers should be consulted; only a short review on the literature relating to the theme of the present paper, i.e. hexadecenol $C_{16}H_{32}O$ and tetradecenol $C_{14}H_{28}O$ in sperm oil, is given below. Tsujimoto stated the possible existence of hexadecenol in sperm head oil, but he found no tetradecenol. André and François, in their studies on the unsaturated alcohols of sperm head oil, found neither hexadecenol nor tetradecenol. Hilditch and Lovern found 4% of hexadecenol in the unsaponifiable matter of sperm head oil, but no hexadecenol in sperm blubber oil. One of us (Toyama)[4] concluded in his previous study that hexadecenol could have been present, if any, only in a very minute amount in sperm blubber oil. The foregoing notes show that though the presence of hexadecenol in sperm oil has been pointed out by a few authors, it has not been isolated with certainty, and nothing is known of its constitution. Tetradecenol has so far never been found in sperm oil and other fatty oils.

In the experiments of the separation of denticetic acid ($\Delta^{5:6}$-dodecenoic acid) from sperm head oil, as described in the preceding paper,[5] the product of methanolysis consisting of the methyl esters and the free unsaponifiable matter was first fractionated. The fatty acids and the unsaponifiable matter were separated from the lowest fraction boiling below 150°/15 mm. Whilst the fatty acids were worked up further for the separation of dodecenoic acid, a comparatively high iodine value of the unsaponifiable matter pointed to the possible presence of some lower members of unsaturated alcohols, besides oleyl alcohol, in sperm head oil. Accordingly the present experiments have been carried out with the object of separating these lower members of unsaturated alcohols starting with a large quantity of sperm head oil. For these purposes, sperm head oil was converted into a mixture of methyl esters and free unsaponifiable matter by methanolysis, and the mixture was fractionally distilled. From the fraction boiling below 180°/15 mm. the unsaponifiable matter was separated and then acetylated. The acetates thus obtained were brominated, and the product was distilled so as to remove the saturated acetates as distillate, leaving the bromides of unsaturated acetates as residue. This was debrominated and reconverted into the unsaturated acetates, from which hexadecenyl acetate and tetradecenyl acetate were separated on fractionation. Saponification of the acetates yielded hexadecenol

(2) *Compt. rend.*, **183** (1926), 663; **185** (1927), 279.
(3) *J. Soc. Chem. Ind.*, **48** (1929), 365.
(4) *J. Soc. Chem. Ind., Japan*, **30** (1927), 527.
(5) This Bulletin, **10** (1935), 570.

and tetradecenol which, however, were contaminated with a small proportion of saturated alcohols. A complete removal of the latter was not attained in these experiments.

For the determination of the position of ethylenic linking in two alcohols, the acetates were oxidised with potassium permanganate in glacial acetic acid. Hexadecenyl acetate yielded *n*-heptoic acid $CH_3\cdot(CH_2)_5\cdot COOH$ and acetyl-hydroxynonoic acid $HOOC\cdot(CH_2)_7\cdot CH_2O\cdot COCH_3$; hydroxynonoic acid liberated from its acetyl ester yielded, on further oxidation, azelaic acid $HOOC\cdot(CH_2)_7\cdot COOH$. Tetradecenyl acetate yielded, on subsequent saponification of the ester in the oxidation products, *n*-nonoic acid $CH_3\cdot(CH_2)_7\cdot COOH$ and hydroxyvaleric acid $HOOC\cdot(CH_2)_3\cdot CH_2OH$; the latter yielded on further oxidation glutaric acid $HOOC\cdot(CH_2)_3\cdot COOH$. From these results the following constitutions were established:

Hexadecenol $CH_3\cdot(CH_2)_5\cdot CH=CH\cdot(CH_2)_7\cdot CH_2OH$,
Tetradecenol $CH_3\cdot(CH_2)_7\cdot CH=CH\cdot(CH_2)_3\cdot CH_2OH$.

According to the above constitutions, hexadecenol in sperm head oil corresponds to zoomaric acid ($\Delta^{9:10}$-hexadecenoic acid) which is of common occurrence in marine animal oils, and tetradecenol in sperm head oil corresponds to physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) found in sperm oil. A similar relation exists between oleyl alcohol ($\Delta^{9:10}$-octadecenol) found in sperm oil and some other marine animal oils and oleic acid ($\Delta^{9:10}$-octadecenoic acid). It is, therefore, advisable to designate hexadecenol and tetradecenol in sperm head oil as zoomaryl alcohol and physeteryl alcohol respectively.

Experimental.

1. **Separation of Hexadecenol.** The same specimen of sperm head oil[6] as used for the separation of denticetic acid was employed for the present experiments. The oil was pressed at the room temperature to remove the solid portion, and the liquid portion was subjected to methanolysis by means of methanol containing sodium hydroxide. The product of methanolysis (10 kg.), consisting of the methyl esters and the free unsaponifiable matter, was distilled, the fraction boiling below 180°/15 mm. was separated and saponified, and the soap solution was treated with ether for the extraction of unsaponifiable matter. The yield of unsaponifiable matter was 357 g. It was acetylated by heating with acetic anhydride. The resulting acetates (410 g.) having saponification value 206.6 and iodine value (Wijs) 24.3 were dissolved in 4 l. of ether, and a little excess of bromine was gradually added with constant stirring under cooling with ice. The excess of bromine was removed from the ethereal solution by washing with sodium thiosulphate solution, and the ethereal solution was then washed with water and dehydrated. On removal of ether, the product of bromination was subjected to distillation. The rate of

(6) This Bulletin, **10** (1935), 570.

the distillation of saturated acetates became very slow at about 180°/2 mm. when the distillation was discontinued, and there was obtained 160 g. of residue consisting of the bromides of unsaturated acetates. It was dissolved in 250 c c. of methanol, 160 g. of zinc powder was added, and the liquid was heated on the water-bath under a reflux condenser, while 250 c.c. of 5 N hydrogen chloride in methanol was gradually added. After heating for one hour, the insoluble residue was filtered off, the filtrate was diluted with a large quantity of water, and the debrominated product was extracted with ether. The insoluble residue was washed thoroughly with ether, and the washing was added to the main ethereal solution. After washing with water and subsequent removal of ether from the united ethereal solution, the residue was heated with acetic anhydride to regenerate acetates since it was found that the hydrolysis of acetates had taken place in the course of debromination with the formation of free alcohols. The acetates (97 g.) thus obtained was fractionally distilled up to 200°/15 mm., and the following fractions were separately collected.

Fraction	B.p. /15 mm.	Saponif. value	Iodine value	n_D^{20}	Yield (g.)
(1)	Below 160°	—	—	—	1.1
(2)	160–175°	215.7	91.1	1.4459	4.5
(3)	175–185°	209.2	87 1	1.4469	5.4
(4)	185–195°	200.3	84.3	1.4477	15.0
(5)	195–200°	195.2	82.2	1.4486	40.1
Residue and loss	—	—	—	—	30.9

The fraction (4) was subjected to a further fractionation, by which the portion boiling above 195°/15 mm. was separated. This was united with the fraction (5), and repeatedly fractionated, by which 12.2 g. of a fraction boiling at 195–198°/15 mm. and having the following constants was separated as hexadecenyl acetate $C_{18}H_{34}O_2$.

d_4^{15} 0.8760, d_4^{20} 0.8725, n_D^{15} 1.4506, n_D^{20} 1.4486, mol. refraction (based on the data at 15°) 86.70 (calc. for $C_{18}H_{34}O_2$ F_1: 86.51), saponif. value 197.5 (calc. 198.8), iodine value 83.2 (calc. 89.9).

Hexadecenol obtained by saponification of the acetate showed the following constants (Found: C, 79.91; H, 13.45. Calc. for $C_{16}H_{32}O$: C, 79.91; H, 13.42%).

d_4^{15} 0.8537, d_4^{20} 0.8503, n_D^{15} 1.4605, n_D^{20} 1.4584, mol. refraction (based on the data at 15°) 77.15 (calc. for $C_{16}H_{32}O$ F_1: 77.14), iodine value 98.6 (calc. 105.7).

The hydrogenation product of hexadecenol crystallised from 90% alcohol in lustrous laminae which showed acetyl value 197.1 (calc. for cetyl alcohol $C_{16}H_{34}O$: 197.4) and melted at 49.5–50° both alone or admixed with cetyl alcohol. On oxidising the hydrogenation product with chromic acid in glacial acetic acid, it yielded palmitic acid $C_{16}H_{32}O_2$; neutr. value 218.1 (calc. 219.0), m.p. and mixed m.p. 62–62.5°.

2. **Oxidation of Hexadecenyl Acetate.** Ten grams of hexadecenyl acetate was dissolved in 100 g. of glacial acetic acid, and 20 g. of powdered potassium permanganate was added in small portions. After heating for one hour on the water-bath under a reflux condenser,

the solution was diluted with water, and the oxidation products were extracted with a large quantity of ether. After a portion of the solvent had been distilled off, the ethereal solution was shaken with potassium carbonate solution which separated the acidic substances as their potassium salts from the neutral substances remaining in the ethereal solution. The aqueous solution containing potassium salts was acidified with hydrochloric acid, the liberated acidic substances were taken up with ether, and the ethereal solution was washed with water until the acidity of the washing became very faint. On removal of ether, there was obtained 6.5 g. of acidic substances. A comparatively low yield may be attributed to an incomplete oxidation with potassium permanganate or to the loss caused by washing the ethereal solution with water. These were distilled; 1.8 g. of a fraction (a) boiling below 185°/100 mm. was first separated, and then the distillation was carried out under a lower pressure, giving 3.1 g. of a fraction (b) boiling below 198°/5 mm.

The fraction (a) was redistilled, and a fraction boiling below 170°/100 mm. was collected. It was washed with a little water for the removal of the contaminated acetic acid, and the remaining liquid showed neutr. value 433.2 (calc. for $C_7H_{14}O_2$: 431.2) and n_D^{20} 1.4217, and was identified as *n*-heptoic acid by preparing its amide which, after being recrystallised from petroleum ether, melted at 94.5–95° both alone or admixed with *n*-heptoic acid amide[7] (Found: N, 10.70. Calc. for $C_7H_{15}ON$: N, 10.85%).

On subjecting the fraction (b) to a further fractionation, a fraction boiling at 200–204°/15 mm. was separated which was found to be acetyl-hydroxynonoic acid $C_{11}H_{20}O_4$.

d_4^{20} 1.0187, n_D^{20} 1.4462, mol. refraction 56.61 (calc. for $C_{11}H_{20}O_4$: 56.19), neutr. value 255.1 (calc. 259.6), saponif. value 509.4 (calc. 519.1).

Hydroxynonoic acid $C_9H_{18}O_3$ obtained by saponification of its acetyl derivative was a viscous oil having neutr. value 315.3 (calc. 322.2). Oxidation of hydroxynonoic acid with chromic acid in glacial acetic acid gave a solid product. It was taken up with ether, the ethereal solution was washed with water containing sodium chloride, and after distilling off ether from the ethereal solution the residue was recrystallised from water, yielding azelaic acid $C_9H_{16}O_4$ which had neutr. value 594.5 (calc. 596.5), m.p. 104–105°, and mixed m.p. 105–106°[8] (Found: C, 57.30; H, 8.50. Calc. for $C_9H_{16}O_4$: C, 57.41; H, 8.57%).

3. **Separation of Tetradecenol.** As described above, 97 g. of unsaturated acetates were fractionated, and five fractions (1)–(5) were separately collected. For the separation of tetradecenol, the fraction (2) and the portion boiling below 175°/15 mm. obtained by a repeated fractionation of the fraction (3) were combined and subjected to a further fractionation, and there was obtained 3.4 g. of a fraction boiling at 165–170°/15 mm. as tetradecenyl acetate $C_{16}H_{30}O_2$. It had the following constants.

d_4^{15} 0.8729, d_4^{20} 0.8694, n_D^{15} 1.4477, n_D^{20} 1.4457, mol. refraction (based on the data at 15°) 77.93 (calc. for $C_{16}H_{30}O_2$ $\overline{1}$: 77.28), saponif. value 218.2 (calc. 220.7), iodine value 92.7 (calc. 99.8).

Tetradecenol $C_{14}H_{28}O$ liberated from its acetate showed the following constants (Found: C, 79.29; H, 13.23. Calc. for $C_{14}H_{28}O$: C, 79.16; H, 13.30%).

---

(7) The specimen used for the mixed melting point test was prepared in the following way: castor oil was first subjected to dry distillation, and a fraction corresponding to *n*-heptyl aldehyde was separated. The latter was oxidised into *n*-heptoic acid, which was then converted into the amide; m.p. 94.5–95°.

(8) Azelaic acid used for the mixed melting point test was obtained by the ozonolysis of oleic acid.

d_4^{15} 0.8507, d_4^{20} 0.8473, n_D^{15} 1.4573, n_D^{20} 1.4553, mol. refraction (based on the data at 15°) 67.98 (calc. for $C_{14}H_{28}O$ F_1: 67.91), iodine value 111.2 (calc. 119.6).

When hydrogenated, tetradecenol yielded a crystalline solid which on recrystallisation from 80% alcohol melted at 37–37.5°. The melting point is nearly the same as recorded for *n*-tetradecanol (38°).[9] On oxidising the hydrogenation product with chromic acid in glacial acetic acid, it yielded myristic acid $C_{14}H_{28}O_2$ which, after being recrystallised from 80% alcohol, showed neutr. value 244.2 (calc. 245.8), m.p. and mixed m.p. 53.5–54°.

4. **Oxidation of Tetradecenyl Acetate.** Tetradecenyl acetate (2.7 g.) was dissolved in 27 g. of glacial acetic acid, 6 g. of powdered potassium permanganate was added, and the solution was heated on the water-bath under a reflux condenser for 2 hours. Water was then added, the oxidation products were extracted with a large quantity of ether, and the ethereal solution was concentrated and shaken with potassium carbonate solution. By these treatments acidic substances were converted into their potassium salts and separated from the ethereal solution, while the neutral substances which escaped oxidation remained in the ethereal solution. The aqueous solution containing potassium salts was heated with the addition of potassium hydroxide on the water-bath in order to saponify the ester. The free acidic substances liberated on acidification with hydrochloric acid was once taken up with ether, the ethereal solution was washed with water containing sodium chloride, and then the ether was driven off. The acidic substances (2.2 g.) thus obtained were treated with a little water, yielding the aqueous solution and the insoluble portion.

The insoluble portion (1.2 g.) was distilled, and a fraction boiling below 195°/100 mm. was separated. It showed neutr. value 358.1 (calc. for $C_9H_{18}O_2$: 354.8) and n_D^{20} 1.4322. Its amide, when recrystallised from 50% alcohol, melted at 97.5–98°. The melting point was not lowered when the substance was admixed with varying proportions of a pure specimen of *n*-nonoic acid amide,[10] m.p. 98.5–99°.

Sodium chloride was added to the aqueous solution separated from the insoluble portion, and the solution was shaken with ether. On removal of ether from the ethereal solution, the residue was treated with petroleum ether, and the insoluble portion was separated which consisted of an oily liquid and had neutr. value 482.1 (calc. for hydroxyvaleric acid $C_5H_{10}O_3$: 475.2). This was subjected to oxidation with chromic acid in glacial acetic acid, and the product was collected by using ether. The residue obtained by distilling off ether was recrystallised from benzene, yielding crystals of m.p. 96–96.5°. The melting point was not lowered when the crystals were admixed with varying proportions of glutaric acid (m.p. 97.5–98°).

Summary.

Hexadecenol and tetradecenol have been isolated from the unsaponifiable matter of sperm head oil, and the acetates of these alcohols have been oxidised with potassium permanganate in glacial acetic acid. From the results of an examination of the oxidation products, the constitutions of these alcohols have been established as follows:

(9) "Beilsteins Handbuch der organischen Chemie", 4th Ed., I, 428.

(10) Prepared from *n*-nonoic acid which was obtained by the ozonolysis of oleic acid.

$\Delta^{9:10}$-Hexadecenol (zoomaryl alcohol) $CH_3\cdot(CH_2)_5CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$

$\Delta^{5:6}$-Tetradecenol (physeteryl alcohol) $CH_3\cdot(CH_2)_7CH{=}CH\cdot(CH_2)_3\cdot CH_2OH$

It is thus seen that hexadecenol and tetradecenol in sperm head oil are the mono-ethylenic alcohols corresponding to zoomaric acid ($\Delta^{9:10}$-hexadecenoic acid) and physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) respectively.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

HEXADECENOL IN SPERM BLUBBER OIL.*

By Yoshiyuki TOYAMA and Goroku AKIYAMA.

Received September 3rd, 1935. Published December 28th, 1935.

In a previous study on the unsaponifiable matter of sperm blubber oil by one of us (Toyama),[1] oleyl alcohol, cetyl alcohol and octadecyl alcohol were separated, and the presence of cholesterol in a small proportion was also indicated. Other minor components were, however, not closely studied; hexadecenol was not separated and it was thought that this alcohol could have been present, if any, only in an extremely small amount. We have now made a closer examination of the minor components of the unsaponifiable matter of sperm blubber oil. The present paper deals with the experimental results concerning hexadecenol.

The higher aliphatic alcohols are now being produced on industrial scale by the high pressure hydrogenation of the corresponding fatty acids or their esters, and find a wide application in the industrial field. On the other hand, sperm oil has recently attracted much interest owing to its high content of higher alcohols, and the methods of the separation of these higher alcohols from sperm oil have been much studied. A method is now being carried out on industrial scale in this country. Furthermore, it should be noted that the unsaturated higher alcohols, such as oleyl alcohol which is contained in sperm blubber oil in a large proportion, appear not to have been obtained as yet by the high pressure hydrogenation of the corresponding fatty acids or their

---

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1077.

(1) *J. Soc. Chem. Ind., Japan*, **30** (1927), 527.

esters, and consequently sperm blubber oil seems to be the only important raw material of the unsaturated alcohols. Under these circumstances, it is desirable, also from the industrial point of view, to gain a fuller information on the unsaturated alcohols in sperm blubber oil.

In these experiments, the unsaponifiable matter was first prepared by heating the sperm blubber oil with barium hydroxide and water under pressure and by subsequent extraction of the product consisting of barium soaps and free unsaponifiable matter with acetone. The acetone extract thus obtained was, however, contaminated with a small amount of barium soaps and unsaponified oil. It was, therefore, refluxed with alcoholic potash to effect a complete saponification of the contaminated oil, after which the product was acidified with hydrochloric acid. The resulting unsaponifiable matter which was contaminated with free fatty acids was taken up with ether, the ethereal solution was washed with an aqueous solution of potassium hydroxide containing a little alcohol in order to remove the free fatty acids as their potassium soaps, and the unsaponifiable matter was obtained from the ethereal solution. The unsaponifiable matter (10 kg.) thus obtained was fractionally distilled, the fraction boiling below 188°/ca. 5 mm. was separated, and the solid portion was removed by cooling the fraction dissolved in acetone. The liquid portion was converted into acetates and fractionated. The higher fraction was removed, and the lower fraction was saponified to yield free alcohols, from which a further quantity of solid portion was removed on cooling the acetone solution. The liquid portion was subjected to a further fractional distillation, by which the fraction boiling below 200°/15 mm. was separately collected. This fraction still contained a considerable amount of saturated alcohols. For a further removal of saturated alcohols, it was converted into acetates and then brominated. The product was distilled so as to remove the saturated acetates as distillate, leaving the bromides of unsaturated acetates as residue which was then debrominated to regenerate the unsaturated acetates. These were saponified, and the free alcohols were subjected to a further distillation in order to remove the high boiling portions. Since the lower fraction was suspected to be contaminated with some hydrocarbons, it was treated with 85% methanol, the insoluble portion removed, and the soluble portion separated. After repeated fractionation there was obtained a fraction corresponding to hexadecenol. The actual yield was only 16 g., but the total quantity contained in the unsaponifiable matter used for these experiments would be far larger than the actual yield. The presence of tetradecenol was not ascertained in these experiments; it could have been present, if any, in a far smaller amount than hexadecenol.

The acetate of hexadecenol was oxidised with potassium permanganate in acetone. Among the oxidation products, *n*-heptoic acid $CH_3 \cdot (CH_2)_5 \cdot COOH$ and acetyl-hydroxynonoic acid $HOOC \cdot (CH_2)_7 \cdot CH_2O \cdot COCH_3$ were identified. Further oxidation of hydroxynonoic acid, obtained by saponification of its acetate, with chromic acid in acetic acid yielded azelaic acid $HOOC \cdot (CH_2)_7 \cdot COOH$. Hence, the constitution of hexadecenol is represented by the formula $CH_3 \cdot (CH_2)_5 \cdot CH=CH \cdot (CH_2)_7 \cdot CH_2OH$. It is thus seen that hexadecenol in sperm blubber oil is identical with zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) in sperm head oil.

Experimental.

1. **Separation of Unsaponifiable Matter.** Sperm blubber oil used for these experiments was procured from the Nihon Hogei K. K. (Japan Whaling Co., Ltd.) and had d_4^{25} 0.8735, n_D^{25} 1.4635, acid value 0.85, saponification value 123.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98%. It deposited a large amount of crystalline solid at the room temperature. The unsaponifiable matter was separated in the following way: every 1 kg. of the oil was mixed with 400 g. of crystalline barium hydroxide (corresponding to an excess of 12%) and 1 l. of water, and the mixture was heated for one hour under 5–6 atm. in an autoclave. The product was taken out from the autoclave, squeezed for the removal of water as far as possible, then mixed with anhydrous sodium sulphate, cut into small pieces and extracted with acetone in an extractor. The acetone extract containing unsaponifiable matter was contaminated with a small amount of barium soaps and unsaponified oil, and on removal of acetone the residue was refluxed with an excess of alcoholic potash in order to effect a complete saponification. The product was then acidified with hydrochloric acid, and the unsaponifiable matter together with a small proportion of free fatty acids were taken up with ether. The ethereal solution was washed with an aqueous solution of potassium hydroxide containing a little alcohol, and the free fatty acids were converted into potassium soaps which were separated from the ethereal solution. The latter was thoroughly washed with water, and the solvent was removed by distillation. The yield of unsaponifiable matter was 10,120 g. (or 36.1%) from 28 kg. of the oil. It had d_4^{25} 0.8443, n_D^{25} 1.4572, acetyl value 186.8 and iodine value 73.9, and deposited a large amount of crystalline solid at the room temperature so that it was not mobile.

2. **Fractionation of Unsaponifiable Matter and Removal of Solid Portion.** The unsaponifiable matter obtained above was subjected to a fractional distillation. A batch of 530 g. was taken in each distillation, and 5 fractions were separately collected; fractions (1) and (2) were collected in an amount of 100 c.c. by volume, fraction (3) 200 c.c., fraction (4) 100 c.c., and fraction (5) consisted of the remainder of the distillate which was obtained by continuing the distillation until nearly nothing distilled further. The pressure was not maintained exactly at 5 mm. in each run, and consequently the boiling points given below were not estimated exactly in the same way in each run. The following results were obtained from 10,070 g. in total.

Fraction	B.p. / 5 mm.	Iodine value	Yield (g.)
(1)	Below 188°	51.8	1,600
(2)	188 - 190°	57.5	1,600
(3)	190 - 192°	68.4	3,190
(4)	192 - 195°	80.6	1,580
(5)	195 - 198°	96.8	1,680
Residue and loss	—	—	420

Fraction (1) was dissolved in 16 l. of 95% acetone, kept at 5–7° over a night, and the crystalline deposit formed was filtered off. It had iodine value 11.5, while the liquid portion (1,140 g.) obtained from the filtrate had iodine value 68.1. The latter was acetylated by heating with acetic anhydride, and the acetates having saponif. value 185.6 were distilled, yielding 829 g. of a fraction boiling below 212°/15 mm. This was saponified, and the free alcohols liberated were dissolved in 95% acetone as before and kept at 0° over a night. The solid portion was removed by filtration, and there was obtained 610 g. of the liquid portion from the filtrate which was then distilled, yielding 238 g. of a fraction boiling below 200°/15 mm. For a further removal of solid portion from this fraction it was dissolved in 95% acetone, cooled down to −10°, and the solid deposit was filtered off. The liquid portion (238 g.) obtained from the filtrate was then dissolved in 90% acetone, cooled down to −12°, and on removal of a further quantity of solid deposit, there was obtained 208 g. of liquid portion from the filtrate. It was distilled once more, and 160 g. of a fraction boiling below 200°/15 mm. and having iodine value 71.2 was separately collected.

3. **Separation of Hexadecenol.** The fraction described above, boiling below 200°/15 mm., was converted into the acetates. These (188 g.) were dissolved in 1.9 l. of ether, cooled down to −10°, and bromine (80 g.) in a slight excess was gradually added with constant stirring in the course of two hours. After standing for a short time, the excess of bromine was removed by washing with sodium thiosulphate solution, and then the ether was distilled off from the solution, giving 257 g. of the product of bromination which consisted of the unchanged saturated acetates and the bromides derived from unsaturated acetates. It was then subjected to distillation in order to drive off the saturated acetates. The distillation was continued up to 160°/2 mm., when the rate of distillation became very slow, and the operation was discontinued. Yield of the residual bromides 198 g. These were mixed with 200 g. of zinc powder, and 300 c.c. of methanol was added. The mixture was heated on the water-bath under a reflux condenser with the addition of 300 c.c. of 5 N hydrogen chloride in methanol in the course of 30 minutes, and after heating for 30 minutes more, the mixture was diluted with water. The oily substances separated were taken up with ether, and the ethereal solution was washed with water and then distilled. The debrominated products thus obtained were found to consist largely of free alcohols formed by the hydrolysis of acetates. They were reconverted into acetates by heating with acetic anhydride, and the latter distilled giving 116 g. of a fraction boiling below 215°/15 mm. The free alcohols obtained by saponifying this

fraction was distilled once more, giving 84 g. of a fraction boiling below 200°/15 mm. By these distillations, there was an indication of contamination of hydrocarbons in the fraction boiling below 200°/15 mm., especially in the lowest boiling portion. In an attempt to remove hydrocarbons the fraction boiling below 200°/15 mm. was shaken out with 900 c.c. of 85% methanol, kept at the room temperature over a night, and separated into the soluble and the insoluble portions. Each portion had the following constants, and the hydrocarbons seemed to be concentrated in the insoluble portion to a certain extent.

	Yield (g)	Iodine value	Acetyl value
Insoluble portion	17.4	95.1	192.4
Soluble portion	64.6	96.7	196.0

The soluble portion was distilled once more, giving 51 g. of a fraction boiling below 197°/15 mm. It was still contaminated with a small proportion of saturated compounds. It was dissolved in 370 c.c. of 90% acetone and cooled down to −20°, by which a small amount of solid deposit was formed. The liquid portion obtained from the filtrate was then subjected to a repeated fractionation, and 16 g. of a fraction boiling at 187-190°/15 mm. was finally separated as hexadecenol $C_{16}H_{32}O$.(2)

d_4^{15} 0.8534, n_D^{15} 1.4600, mol. refraction 77.11 (calc. for $C_{16}H_{32}O$ $\overline{\overline{F}}_1$: 77.14), iodine value 98.0 (calc. 105.7).

Hydrogenation of hexadecenol yielded cetyl alcohol $C_{16}H_{34}O$ which showed acetyl value 197.2 (calc. 197.4), m.p. and mixed m.p. 49.5° after recrystallisation from 95% alcohol. Hexadecenyl acetate $C_{18}H_{34}O_2$ obtained by heating hexadecenol with acetic anhydride had the following constants.

d_4^{15} 0.8760, n_D^{15} 1.4508, mol. refraction 86.73 (calc. for $C_{18}H_{34}O_2$ $\overline{\overline{F}}_1$: 86.51), saponif. value 196.8 (calc. 198.8), iodine value 83.5 (calc. 89.9).

4. **Oxidation of Hexadecenyl Acetate.** Ten grams of hexadecenyl acetate was dissolved in 100 c.c. of acetone, and the solution was heated on the water-bath under reflux condenser with the addition of 30 g. of powdered potassium permanganate in the course of 40 minutes, and the heating was continued for 30 minutes more. Water (250 c.c.) was then added, and a current of sulphur dioxide was passed into the solution until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The solution was shaken with 1 l. of ether in order to extract the oxidation products, and the ethereal solution was then treated with potassium carbonate solution which dissolved out the acidic oxidation products as their potassium salts, leaving the neutral substances in ethereal solution. On removal of ether, there remained 3.2 g. of neutral substances. The aqueous solution containing potassium salts was acidified with hydrochloric acid, the acidic substances liberated were taken up with ether, the ethereal solution

(2) The fraction boiling below 187°/15 mm. was obtained with a yield of 15 g., and had acetyl value 196.1. Though the comparatively low acetyl value might be attributed to a contamination of hydrocarbons, tetradecenol was considered to be present, if any, only in a far smaller amount than hexadecenol in sperm blubber oil.

was washed with water containing sodium chloride, and on distilling off ether from the solution, there was obtained 7.7 g. of acidic substances as an orange yellow liquid. It was fractionated; the fraction (a) boiling below 160°/100 mm., 1.6 g., was first separated, then the fractionation was continued under a lower pressure, and after the fraction boiling below 160°/5 mm., 2.0 g., was set apart, the fraction (b) boiling at 160–190°/5 mm., 2.0 g., was separated. On refractionation of the fraction (a), the portion boiling below 160°/100 mm. was separated which had neutr. value 431.5 (calc. for $C_7H_{14}O_2$: 431.2). The amide prepared from it melted at 94-94.5° after recrystallisation from petroleum ether and no depression of melting point was observed when the substance was admixed with a pure specimen of *n*-heptoic acid amide.[3]

The fraction (b) had neutr. value 269.0 and saponif. value 507.5, and was thought to consist mainly of acetyl-hydroxynonoic acid $C_{11}H_{20}O_4$ (neutr. value 259.6 and saponif. value 519.1). The free hydroxy-acid obtained on saponification of the acetate was purified by washing with petroleum ether, yielding hydroxynonoic acid $C_9H_{18}O_3$ as a faintly yellow, viscous oil having neutr. value 329.2 (calc. 322.2). Acetyl-hydroxynonoic acid regenerated by heating the free hydroxynonoic acid with acetic anhydride showed neutr. value 261.2 and saponif. value 513.5. For a further oxidation of hydroxynonoic acid, 0.8 g. of the substance was dissolved in 30 c.c. of glacial acetic acid, and the solution was heated with the addition of 5 g. of chromic acid on the water-bath under reflux condenser for two hours. The oxidation products were once taken up with 400 c.c. of ether, and after the ethereal solution being washed with water, the ether was removed by distillation, yielding a crystalline residue from which azelaic acid $C_9H_{16}O_4$ was obtained on recrystallising from water; neutr. value 591.2 (calc. 596.5), m.p. and mixed m.p. 105-106°.[4]

Summary.

Hexadecenol has been separated, in a very small yield, from the unsaponifiable matter of sperm blubber oil, and its constitution has been established as $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$. Hence, hexadecenol in sperm blubber oil is proved to be identical with zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) previously found in sperm head oil.

Tokyo Imperial Industrial Research Laboratory,
Shibuya-ku, Tokyo.

(3) *n*-Heptyl aldehyde was separated from the product of dry distillation of castor oil. It was then oxidised into *n*-heptoic acid, from which the amide was prepared; m.p. 94.5–95°.

(4) Azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid.

ATTEMPTED FORMATION OF RINGS ATTACHED TO THE *p*-POSITIONS OF THE PHENYL GROUPS IN 2,2′-DIPHENYLDIPHENYL.

By Shin-ichi SAKO.

Received September 5th, 1935. Published December 28th, 1935.

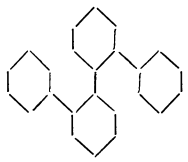
In a previous communication dealing with the relative ease of formation of carbon rings,[1] it was pointed out that the difficulty attending formation of large carbon rings should be attributed mainly to free rotation of atoms constituting open carbon chains, and consequently that this difficulty should be reduced by inhibiting free rotation. One of the examples cited in support of this view was that which was encountered in the facile formation of seven-membered rings attached to the 2,2′-positions of diphenyl. The present paper deals with the case of 2,2′-diphenyldiphenyl (I), in the *p*-positions of the phenyl groups of which are present suitable substituents through which cyclization may be effected.

Although the number of carbon atoms separating the *p*-substituting atoms in the phenyl groups in 2,2′-diphenyldiphenyl exceed that separating the 2,2′-substituting atoms in diphenyl by as many as eight, it is clear that, as a result of inhibition of free rotation, the relative position of the *p*-substituting atoms in the former compound is altered only by free rotation of the benzene nuclei around the common axis of the central diphenyl system, a condition which is precisely the same in the case of 2,2′-substituting atoms in diphenyl. Thus, in regard to one of the main factors which determine the ease of ring formation, there is a close similarity between the 2,2′-positions and the *p*-positions of the phenyl groups. We are however not as yet certain whether substituting atoms in the *p*-positions of the phenyl groups in 2,2′-diphenyldiphenyl can approach each other or not, for, in order to do so, the compound will have to assume a strained configuration. It should be noted that in this case the valency angle will have to be increased in order to bring the *p*-substituting atoms close together, just as Baeyer[2] has erroneously supposed to be the case in alicyclic rings composed of six carbon atoms and more, but in the present case the condition is altogether different and there seems to be no means whereby strain can be relieved.

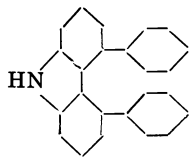
On the other hand, although the supposed condition of 2,2′-diphenyldiphenyl molecule involves strain, this is not large (here it is assumed that the

(1) This Bulletin, **9** (1934), 41.
(2) *Ber.*, **18** (1885), 2277.

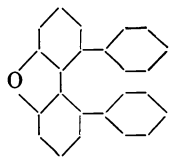
valency deflection is possible only in the planes in which the benzene nuclei lie[3]). Further, a fact from which we may assume that there is a possibility of the *p*-substituting atoms coming close together is to be found in the ready formation of 4,5-diphenyl carbazole (II)[4] and 4,5-diphenyldiphenylene oxide (III)[5] from 2,2′-diamino-6,6′-diphenyldiphenyl, since, as has been shown some time ago,[3] the closure of five-membered rings in these substances must necessarily be accompanied by the two atoms in question being in close proximity.



(I)

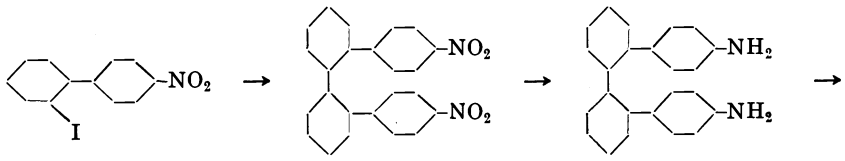


(II)

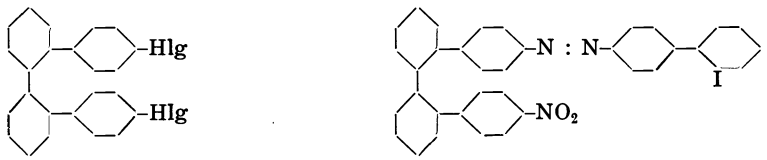


(III)

With these considerations in mind, the possibility of effecting cyclization in 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V), 2,2′-bis-(*p*-aminophenyl)-diphenyl (VI), and 2,2′-bis-(*p*-halogenophenyl)-diphenyl (VII) has been investigated. 4′-Nitro-2-iododiphenyl can be obtained from 4′-nitro-2-aminodiphenyl, and the compound has been treated with copper powder to yield (V), which has been converted successively into (VI) and (VII).



(IV) (V) (VI)



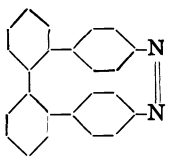
(VII) (VIII)

The yield of (V) has been found to be unexpectedly small. After a large number of comparative experiments, it has been found that the best yield (53% of the theoretical) is obtained when the quantity of copper powder is 1.4 times the theory, a larger amount giving a lower yield. The rather poor

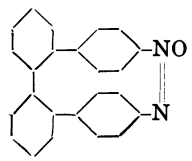
(3) This Bulletin, **9** (1934), 63–64.
(4) This Bulletin, **9** (1934), 70.
(5) This Bulletin, **9** (1934), 72.

yield seems due mainly to the reducing action of copper powder on the nitro-groups, for, in addition to (V), there is also produced a small quantity of a crystalline substance which appears to have the constitution (VIII). Search has naturally been made for the compound (IX) amongst the products, as it has been thought possible that, if the compound (VIII) is producible by the condensation of (IV) with (V) as would be supposed most probable, the compound (IX) may be produced from (V) alone, since, in general, combination of two atoms by an intramolecular reaction leading to a ring compound takes place more readily than that by an intermolecular one, provided of course that in the former case the atoms can approach each other easily. No crystalline substance other than (V) and (VIII) has however been isolated. It is possible that even though the compound (IX), the structure of which is not a stable one, is produced during the reaction, it cannot survive at such a high temperature as employed in this reaction.

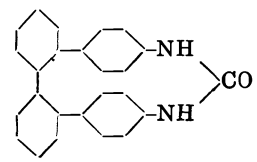
The comparison of the compounds (V), (VI), and (VII) respectively with 2,2′-dinitro-, 2,2′-diamino-, and 2,2′-dihalogeno-diphenyl shows at once that relative positions of the nitro-groups, the amino-groups, and the halogenoradicals in both series of compounds are altered in exactly the same way as already mentioned, and therefore if the methods such as those used for producing (i) phenazone[6] or phenazone oxide[7] from 2,2′-dinitrodiphenyl, (ii) 2-keto-2,3-dihydrodiphenimidine[8] from 2,2′-diaminodiphenyl and urea, (iii) carbazole[9] from 2,2′-diaminodiphenyl, (iv) diphenylene[10] from 2,2′-dibromodiphenyl can be applied to the compounds (V), (VI), and (VII), the result would be the formation of large ring compounds (IX), (X), (XI), (XII) and (XIII).



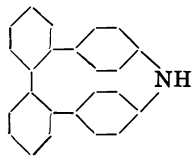
(IX)



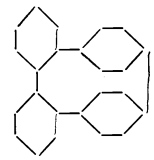
(X)



(XI)



(XII)

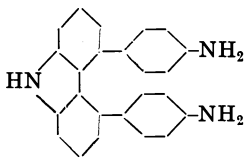


(XIII)

(6) Täuber, *Ber.*, **24** (1891), 3085.
(7) Ullmann and Dieterle, *Ber.*, **37** (1904), 23.
(8) Niementowski, *Ber.*, **34** (1901), 3330.
(9) Täuber, *Ber.*, **24** (1891), 200.
(10) Dobbie, Fox, and Gauge, *J. Chem. Soc.*, **99** (1911), 683.

The strain in substances such as the hypothetical (XII) and (XIII) would undoubtedly be very large, and indeed with a Kekulé nucleus such formulæ can not be constructed. As a matter of fact, 2,2′-bis-(*p*-bromophenyl)-diphenyl and 2,2′-bis-(*p*-iodophenyl)-diphenyl (VII), on treatment with metallic sodium in absolute ether, gives 2,2′-diphenyldiphenyl (I) as the only crystalline product, and no reaction occurs when 2,2′-bis-(*p*-aminophenyl)-diphenyl is heated with hydrochloric acid at high temperatures.

In the case of hypothetical substances (IX), (X) and (XI), however, there appears to be less reason for instability, and if the nitrogen atoms in the compounds (V) and (VI) can only come close together, they may pass into the respective compounds (IX), (X), and (XI). In practice, however, it has been found that such cyclization cannot be effected. Whether this failure is due to the impossibility of bringing the nitrogen atoms close together or to the instability of the hypothetical rings, it is impossible at present to say, but if due to the former cause, it is possible that, in a compound such as (XIV) in which the two amino-groups would be in close proximity, cyclization reactions similar to those which take place in 2,2′-diaminodiphenyl as well as in *o*-phenylenediamine can be applied. It is proposed to investigate the possibility of ring formation in this or similarly constituted compounds.



(XIV)

Experimental.

4′-Nitro-2-aminodiphenyl hydrochloride. Scarborough and Waters,[11] by the nitration of 2-acetamidodiphenyl, obtained 4′-nitro-2-acetamidodiphenyl in 44 per cent. yield. The following method, which is an improvement of theirs, gave 78 per cent. yield.

To a solution of 53 g. of 2-acetamidodiphenyl in 53 c.c. of acetic acid and 106 c.c. of conc. H_2SO_4 was added at 0–2°C. a mixture of 15 c.c. of fuming HNO_3 (d=1.51) and 53 c.c. of acetic acid with stirring. About one hour was required for the addition of the mixed acid. After one more hour's agitation, the mixture was poured on ice, when the product formed a faintly yellow syrup which solidified after a time. The dried crude product weighed 63 g. On crystallization from chloroform, it gave light-yellow thin needles melting at 193°. The yield of pure 4′-nitro-2-acetamidodiphenyl was 50 g.

The acetyl compound was hydrolysed with moderate ease by alcoholic HCl and with difficulty by alkali. As the action of the 10 per cent. alcoholic HCl employed by Scarborough and Waters[11] proved too weak, the hydrolysis was conducted as follows: a suspension of 70 g. of 4′-nitro-2-acetamidodiphenyl in a mixture of 140 c.c. each of EtOH and conc. HCl was refluxed on the water bath for 90 minutes. The original substance disappeared in 15 minutes to be followed after a time by the separation of the crystalline

(11) *J. Chem. Soc.*, **1927**, 95.

4-nitro-2-aminodiphenyl hydrochloride. After cooling the crystals were collected and washed with 20 per cent. HCl solution (Found: Cl, 13.94. Calc. for $C_{12}H_{11}O_2N_2Cl$: Cl, 14.16%). The dried crystals weighed 65 g. The mother liquor, on concentration, gave a second crop, 2.8 g. The hydrochloride readily loses HCl either on heating or on washing with water, showing that it is a weak base.

4'-Nitro-2-iododiphenyl (IV). A mixture of 68 g. of 4'-nitro-2-aminodiphenyl hydrochloride, 100 c.c. of conc. HCl, and 80 g. of cracked ice was, with external cooling by ice, treated with 20.7 g. of solid sodium nitrite with stirring. The diazotized solution was filtered if necessary, treated with a solution of 60 g. of potassium iodide, and allowed to stand for three days until completion of the reaction (the decomposition by heating on the water bath somewhat lowers the yield of the iodo-compound). The crude iodo-compound thus precipitated, 89.7 g., was dissolved in ether and shaken with a KOH solution. After the removal of the ether, the residue was distilled in vacuum. It had b p. 203°/5 mm. On crystallization from EtOH, beautiful yellow needles melting at 100–101.5° separated. The yield of the purified substance was 64.6 g. (Found: C, 44.2; H, 2.7. Calc. for $C_{12}H_8O_2NI$: C, 44.3; H, 2.5%). 4'-Nitro-2-iododiphenyl is very easily soluble in boiling EtOH and sparingly so in the cold.

4'-Amino-2-iododiphenyl, its hydrochloride and the acetyl derivative. A hot solution of 10.8 g. of 4'-nitro-2-iododiphenyl in 100 c.c. of EtOH was mixed with 27 g. of $SnCl_2 \cdot 2H_2O$ and 33 c.c. of conc. HCl, and heated on the water bath for 15 minutes, at the end of which the yellow colour of the original substance had disappeared. The solution was concentrated to one half the original bulk, and, while still hot, diluted with 100 c.c. of water, when 4'-amino-2-iododiphenyl hydrochloride separated at once as colourless needles which were collected and washed with EtOH-water. The hydrochloride thus obtained was pure and weighed 10.6 g. It can be crystallized from EtOH or EtOH-water (Found: Cl, 10.60. Calc. for $C_{12}H_{11}NClI$: Cl, 10.70%).

The free base was obtained as follows: the hydrochloride obtained above was shaken with a sodium hydroxide solution and ether, and the ethereal layer evaporated up. The residual syrup resisted all attempts at crystallization. It was therefore purified by vacuum distillation (Found: I, 43.20. Calc. for $C_{12}H_{10}NI$: I, 43.02%).

The gummy free base on acetylation gave the crystalline acetyl derivative: on treatment of a conc. ethereal solution of 4'-amino-2-iododiphenyl with the calculated quantity of acetic anhydride, 4'-acetamido-2-iododiphenyl separated in colourless needles after a short time. It had m.p. 162–163°C. (Found: I, 37.49. Calc. for $C_{14}H_{12}ONI$: I, 37.66%).

The action of copper powder on 4'-nitro-2-iododiphenyl. Formation of 2,2'-bis-(*p*-nitrophenyl)-diphenyl (V) and 4-(*o*-iodophenyl)-4'-[*o*-(*p*'-nitro-*o*-diphenylyl)-phenyl]-azobenzene (VIII). As stated in the introduction the preparation of 2,2'-bis-(*p*-nitrophenyl)-diphenyl from 4'-nitro-2-iododiphenyl present unexpected difficulties, and, in spite of the many experiments made under a great variety of conditions, no more than a 50 per cent. yield could be obtained. The best result was obtained as follows.

2,2'-Bis-(p-nitrophenyl)-diphenyl (V). Copper powder (1.8 g.) prepared by the method of Piccard and Larsen[12] was added with stirring to 6.5 g. of 4'-nitro-2-iododiphenyl which was heated in an oil bath at 220-225°, and the heating and agitation continued for 80 minutes. After cooling, the solidified mass was extracted with 700 c.c. of C_6H_6. The

(12) *J. Am. Chem. Soc.*, **39** (1917), 2007.

extract was treated with animal charcoal and concentrated until, while heating, the crystals began to separate (about 180 c.c.). The yellow thin needles thus obtained, 2.1 g., was almost pure 2,2′-bis-(*p*-nitrophenyl)-diphenyl. The pure substance obtained by crystallization from benzene melted at 290° (Found : N, 7.2. Calc. for $C_{24}H_{16}O_4N_2$: N, 7.1%). By a couple of analyses on carbon and hydrogen, it was shown that the dinitro-compound is one of those rare organic compounds which do not give the correct figure for carbon, although a good result was obtained for the hydrogen content. About 100 c.c. of boiling benzene is required to dissolve 0.5 g. of this compound.

4-(o-Iodophenyl)-4′-[o-(p′-nitro-o-diphenylyl)-phenyl]-azobenzene (VIII). This substance was contained in the mother liquor of the yellow needles of 2,2′-bis-(*p*-nitrophenyl)-diphenyl described above. On concentration of this solution to about 10 c.c., 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V), 0.14 g., separated, which was filtered off. The filtrate was evaporated off and the residue, after the removal of the alcohol-soluble part by extraction with EtOH, crystallized from 4 c.c. of benzene, inoculation being desirable if possible. The orange crystals of (VIII) thus obtained weighed 0.10 g. It happened at times that the orange crystals were contaminated with the yellow needles of (V). The mechanical separation of the two substances could be effected fairly completely by means of decantation, if proper care was taken that the orange crystals of (VIII) are made to grow large enough. A fact which should be noted in this connection is that, although the orange compound (VIII) used to separate from C_6H_6 in a compact granular form, it crystallized at times in short prisms and rarely in thin needles, and that these forms were capable of coexistence in benzene. The purified substance (VIII) melted, irrespective of crystalline forms, at 312–313° (Found : C, 64.8 ; H, 3.9 ; N, 6.7 ; I, 18.8. Calc. for $C_{36}H_{24}O_2N_3I$: C, 65.8 ; H, 3.7 ; N, 6.4 ; I, 19.3%). Rast's method for molecular weight determination could not be applied because of its slight solubility in camphor. On heating the powdered orange compound with a mixture of stannous chloride, conc. HCl, and acetic acid it disappeared slowly forming a colourless solution. This was probably the indication that the molecule was cleaved at the double bond to give the two amines, a reaction characteristic of an azo-compound. The substance is insoluble or very slightly soluble in usual organic solvents. Ten c.c. of boiling benzene dissolves about 0.1 g. of the orange crystals.

2,2′-Bis-(*p*-aminophenyl)-diphenyl (VI). This substance can be obtained by the reduction of 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V) either with stannous chloride or with sodium sulphide.

Dry HCl was passed into a mixture of 5.3 g. of powdered 2,2′-bis-(*p*-nitrophenyl)-diphenyl, 2.7 g. of stannous chloride, and 150 c.c. of acetic acid, and the mixture heated on the water bath at 60–70°C. The sparingly soluble dinitro-compound slowly disappeared to be replaced by the voluminous, powdery double salt. As the mixture became very thick, frequent shaking was necessary. Heating was continued for some hours till the complete disappearance of the dinitro-compound, HCl being passed in all the time. After cooling, the fine bluish precipitate was collected, dissolved in 150 c.c. of water, treated with an excess of KOH solution, and the liberated base dissolved in ether. On removal of ether, the residue completely crystallized, which was distilled under reduced pressure. It had b.p. 290°/5 mm. The distillate was dissolved in boiling EtOH (36 c.c.), concentrated to about 18 c.c., and allowed to stand for crystallization. Inoculation was found often necessary. The large colourless crystals, 3.9 g., melted at 163-164°C. (Found : N, 8.6. Calc. for $C_{24}H_{20}N_2$: N, 8.3%). By concentration of the mother liquor, some more crystals separated, and the yield was quantitative.

The reduction of the dinitro-compound (V) with sodium sulphide was carried out as follows: a mixture of 2 g. of (V), 7.5 g. of sodium sulphide, 90 c.c. of EtOH, and 30 c.c. of H_2O was refluxed for three hours. The original substance disappeared in 30 minutes. On concentration of the reaction mixture to a small bulk, followed by the addition of water, an oil separated, which solidified at once. It was crystallized from EtOH. The crystals thus formed melted, either alone or when mixed with the diamino-compound obtained by the stannous chloride method described above, at 163–164°C.

2,2'-Bis-(*p*-iodophenyl)-diphenyl (VII). A suspension of 1.7 g. of 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI) in 33 g. of 8 per cent. HCl solution was gently heated with agitation, when the difficultly soluble hydrochloride was deposited in needles. It was then cooled in ice and treated with 0.76 g. of sodium nitrite with agitation. After an hour's agitation, a clear solution resulted, which was treated with a solution of 2.4 g. of KI. It was then allowed to stand at ordinary temperature for two hours and finally heated at 50°C. The brown precipitate thus obtained was dissolved in ether, shaken with a KOH solution, and the ether removed. The residue, 2.6 g., was purified first by vacuum distillation and then by two crystallizations from C_6H_6–EtOH. It was obtained in yellow needles melting at 205–206°C. (Found: I, 44.4. Calc. for $C_{24}H_{16}I_2$: I, 45.5%). It is readily soluble in C_6H_6, less so in ether, and very difficultly soluble in EtOH.

2,2'-Bis-(*p*-bromophenyl)-diphenyl (VII). 2,2'-Bis-(*p*-aminophenyl)-diphenyl (1.7 g.) was gently heated with a 5 per cent. HBr solution. The clear solution thus obtained, on cooling with ice water, separated the dihydrobromide in needles. The latter, on treatment with a solution of 0.76 g. of sodium nitrite, disappeared in a short time. To the bisdiazonium bromide solution was added cuprous bromide, which was prepared by boiling a mixture of 1.26 g. of $CuSO_4 \cdot 5H_2O$, 0.40 g. of copper powder, 2.28 g. of anhydrous NaBr, 0.60 g. of conc. H_2SO_4, and 10 c.c. of water for some hours. The reaction mixture was allowed to stand for decomposition at ordinary temperature. The decomposition proceeded very slowly. After one week, it was heated at 50°, and the precipitated substance collected and extracted with ether. The ether was removed and the residue, on distillation under reduced pressure, gave a crystalline distillate (0.55 g.), which was twice recrystallized from EtOH (10 c.c.). The almost colourless needles thus obtained had m.p. 170–171°C. (Found: Br, 34.0. Calc. for $C_{24}H_{16}Br_2$: Br, 34.5%).

Instead of leaving, as described above, the bis-diazonium bromide solution at ordinary temperature, when it was heated at 50–60°, the decomposition was complete in one hour, but the product was contaminated with a larger quantity of impurities which rendered the purification difficult. In any case, the yield of the desired substance was far from being satisfactory.

The action of sodium on 2,2'-bis-(*p*-iodophenyl)-diphenyl. A solution of one gram of 2,2'-bis-(*p*-iodophenyl)-diphenyl in 150 c.c. of absolute ether was heated under reflux in a water bath at 45° with a large excess of finely divided sodium metal, with constant stirring (mercury seal). The separation of sodium iodide was noticeable after 20 hours' heating. The yellow colour of the solution gradually disappeared. After 63 hours' heating, it was filtered and the filtrate evaporated off. The residue which consisted of beautiful colourless crystals was dissolved in EtOH, treated with animal charcoal to remove a trace of an amorphous matter and the filtrate concentrated to a few c.c. The colourless crystals thus separated melted at 117–118°C. and found by the

mixed melting point method to be identical with 2,2'-diphenyldiphenyl made from 2-iododiphenyl.[13]

The action of metallic sodium on 2,2'-bis-(*p*-bromophenyl)-diphenyl. A solution of 0.4 g. of 2,2'-bis-(*p*-bromophenyl)-diphenyl in 100 c.c. of absolute ether was refluxed in a water bath at 45° for 100 hours with stirring. It was then filtered and the ether removed. The partly solidified residue was collected on a filter, washed first with EtOH and then with petroleum ether. The almost colourless needles thus obtained, 0.21 g., on crystallization from EtOH gave slender needles which proved to be the original dibromo-compound (mixed m.p.). The oily filtrate and the washings were united and the solvents removed. The residual gummy substance persistently resisted crystallization, but when seeded with a crystal of 2,2'-diphenyldiphenyl[13] prepared from 2-iododiphenyl, gradual increase of the crystals was observed, showing the presence of the same substance among the products. That some of the dibromo-compound was acted on by sodium was further shown by the fact that the aqueous solution of the solid separated from the original ethereal solution, on treatment with HNO_3 and $AgNO_3$, deposited AgBr.

Attempts to prepare the hypothetical large ring compounds (IX) and (X). As already described on p. 591, the action of sodium sulphide on 2,2'-bis-(*p*-nitrophenyl)-diphenyl (V) gave rise to the diamino-compound (VI), and not to the cyclic azoxy-compound (X). Another method of preparation of azoxy-compounds, namely, the use of alkaline arsenite[14] as the reducing agent was also attempted, but with indifferent success. Thus, although 2,2'-bis-(*p*-nitrophenyl)-diphenyl (0.5 g.), As_2O_3 (0.5 g.), NaOH (0.6 g.), H_2O (3 c.c.), and toluene (3.0 c.c.) were heated together in an oil bath at 145–160° for 40 hours with stirring, no change occurred, the original substance being recovered almost unchanged (in this reaction, in order to facilitate the reaction, toluene was used as solvent for the dinitro-compound which does not melt at the temperature). The use of alkaline stannite solution in an attempt to obtain the azo-compound (IX)[15] was also a failure.

The action of heat on 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI) hydrochloride. 2,2'-Bis-(*p*-aminophenyl)-diphenyl (VI) and dil. HCl were heated in a sealed tube at high temperatures, but the only crystalline substance isolable was the unchanged diamino-compound.

The action of urea on 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI). 2,2'-Bis-(*p*-aminophenyl)-diphenyl (VI) was heated either with urea alone or with a mixture of urea and *m*-cresol at varied temperatures. The liberation of ammonia gas was observed, but the reaction seemed to be a deep-seated one and no crystalline product could be isolated.

Chemistry Department, Imperial University of Kyushu, Fukuoka.

---

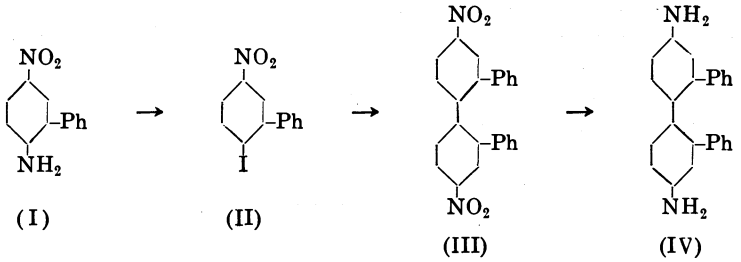
(13) Bowden, *J. Chem. Soc.*, **1931**, 1112.
(14) Loesner, *J. prakt. Chem.*, (2), **50** (1894), 564.
(15) Witt, *Ber.*, **18** (1885), 2912.

THE SYNTHESIS OF 2,2′-DIPHENYLBENZIDINE.

By Shin-ichi SAKO.

Received September 5th, 1935. Published December 28th, 1935.

The synthesis of 2,2′-diphenylbenzidine has been carried out in connection with the other diamino-derivatives[1] of 2,2′-diphenyldiphenyl prepared in this laboratory. The starting substance employed for this synthesis is 2-amino-5-nitro-diphenyl (I) which has been obtained along with 2-amino-3-nitro-diphenyl in the nitration[2] of 2-acetamidodiphenyl. 2-Amino-5-nitro-diphenyl has been converted into 5-nitro-2-iododiphenyl (II) in the usual way, and the latter treated with copper powder to yield 4,4′-dinitro-2,2′-diphenyldiphenyl (III) which, on reduction, gives 2,2′-diphenylbenzidine (IV).



Experimental.

5-Nitro-2-iododiphenyl (II). 2-Amino-5-nitrodiphenyl (I) (21.4 g.) was dissolved in 120 c.c. of conc. H_2SO_4 at ordinary temperature with stirring. The vessel was surrounded by ice water and the solution diluted with 40 g. of ice. With vigorous stirring, 7.2 g. of sodium nitrite were added at once. After some time 60 g. of ice was added in three portions with an interval between each addition. It was finally diluted with a large quantity of ice, filtered, and treated with a solution of 19 g. of potassium iodide in the cold. The iodo-compound separated in an oil which solidified slowly. The crude product, 32 g., was dissolved in ether, and the solution filtered to remove some insoluble matter, shaken with a potassium hydroxide solution and dried. The ether was then evaporated off and the residue distilled under reduced pressure. It had b.p. 191–192°/4 mm. Recrystallized from MeOH it formed light-yellow, long needles melting at 114°C (Found: I, 38.73. Calc. for $C_{12}H_8O_2NI$: I, 39.05%). The yield of the pure substance was 26 g.

4,4′-Dinitro-2,2′-diphenyldiphenyl (III). To 63 g. of 5-nitro-2-iododiphenyl heated in an oil bath at 215–225° was added during 10 minutes 45 g. of copper powder prepared by the method of Piccard and Larsen[3] with stirring, and the mixture heated 20 minutes

(1) This Bulletin, **9** (1934), 70; **10** (1935), 585.
(2) This Bulletin, **9** (1934), 65.
(3) *J. Am. Chem. Soc.*, **39** (1917), 2007.

more. The cooled mass was extracted with a large quantity of boiling benzene. After the removal of benzene, the residue was purified by vacuum distillation. It boiled at 290°/4 mm. On crystallization from benzene, yellow crystals melting at 218–219°C. separated (Found: N, 7.4. Calc. for $C_{24}H_{16}O_4N_2$: N, 7.1%). The yield was 27 g. It is moderately soluble in boiling benzene, and difficultly soluble in cold benzene and hot acetone.

2,2′-Diphenylbenzidine (IV). A suspension of 22 g. of powdered 4,4′-dinitro-2,2′-diphenyldiphenyl (III) in a solution of 100 g. of stannous chloride in 290 c.c. of acetic acid containing dry HCl was heated on the water bath for 8 hours with frequent shaking, HCl being led in all the time. Frequent shaking was necessary because the unchanged dinitro-compound which subsided was apt to be covered by the reaction product which, being almost insoluble, began to separate soon after the start. When the reaction was over, the precipitated double salt was collected, dissolved in 1100 c.c. of water, and made alkaline with a solution of KOH (60 g.). The free base which solidified at once was filtered, dissolved in ether and the solution filtered. The solvent was then removed and the residue, 18 g., on two crystallizations from EtOH, gave large crystals melting at 151–152°C. (Found: N, 8.7. Calc. for $C_{24}H_{20}N_2$: N, 8.3%). The separation of the crystals from the alcoholic solution was very slow. Its solution darkens in colour fairly quickly.

Chemistry Department, Imperial University of Kyushu, Fukuoka.

A RESEARCH ON THE ABSOLUTE SINGLE POTENTIAL OF THE ELECTRODE.

By K. HIROTA and T. MURATA.

Received September 7th, 1935. Published December 28th, 1935.

"The absolute single potential" of an electrode determined by the electrocapillary curve and the drop mercury electrode has been subjected to various objections.[1] The potential across the Helmholz double layer might vanish at the maximum of electrocapillary curve, while the potential due to selective adsortion would persist. The latter effect may be neglected for the drop mercury electrode in the case of rapid flow of mercury; still we are not sure that the potential across the double layer vanishes in this case. We have tried the method described below by which the point of maximum interface tension is determined by means of a rapid jet of mercury into the solution.

(1) Frumkin, *Ergebnisse der exakten Naturwiss*, **7** (1928), 239. "Handbuch der Experimentalphysik, XII Elektrochemie," 2. Teil, 368.

Our method is based upon the following observations: the height of a mercury jet ejected upward through a small nozzle into a solution depends upon the electrical potential applied between the solution and the mercury; and the rate of the mercury flow is practically independent of the potential. It follows that the mercury is imparted with a constant kinetic energy as it leaves the nozzle. The kinetic energy is partly converted into the surface work which depends on the interface tension at the moment it spreads out into small mercury drops, and the rest of the energy determines the height of the mercury jet. The mininum in height should then correspond to the maximum interface tension.

The apparatus used is illustrated in Fig. 1. The mercury was allowed to flow down from a wide vessel and was ejected through an orifice of 0.08 mm.

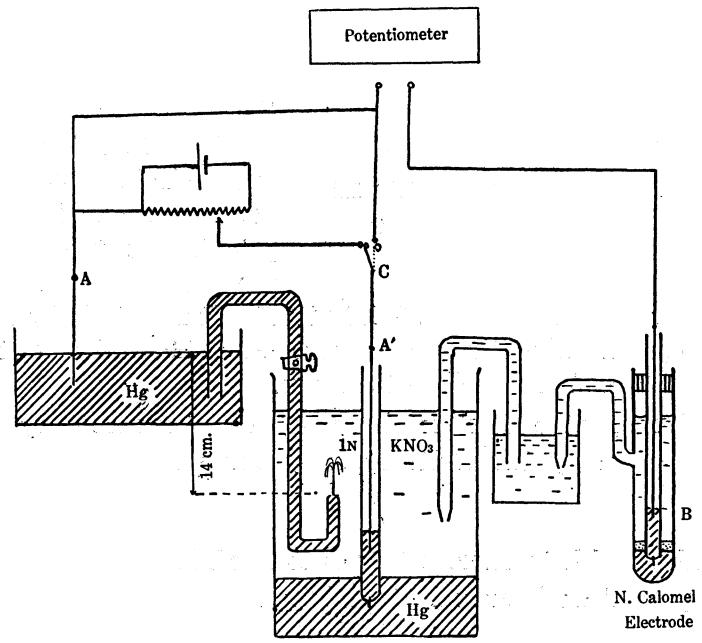


Fig. 1.

diameter into a normal potassium nitrate solution. The mercury head was practically constant during the experiment. The potential varying from zero to 1.5 volts was applied between A and A′, the corresponding potential of mercury jet against a normal calomel electrode B being measured by means of a potentiometer inserted between A and B. The height of the jet was measured with a microcathetometer accurately within 1/100 mm.

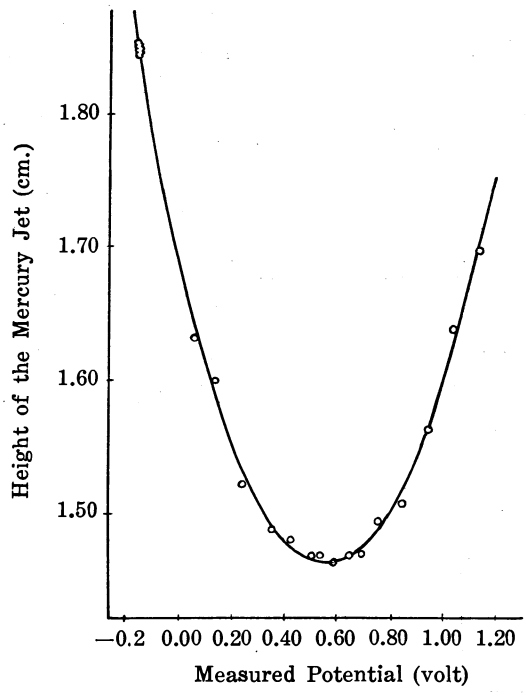


Fig. 2.

The height of the jet was plotted against the measured potential difference between the mercury jet and the normal calomel electrode. One of the series of measurements is shown in Fig. 2. A crowd of points on the upper part of the left branch of the curve shows measurements made in the absence of the applied potential (effected by the commutation C) from time to time between these experiments.

The curve runs parabolic fairly well as is expected from the foregoing reasoning. We obtained therefrom "the absolute single potential" of the normal calomel electrode as the potential at the minimum of the curve. The minimum of this parabola was determined as $+0.560 \pm 0.004$ volt at 20.1°C. by the method of the least square. The other series gave $+0.567 \pm 0.005$ volt at 21.0°C., giving $+0.563 \pm 0.004$ at 20.6°C. as the mean.

This value of "the absolute single potential" agrees very well with former ones given by the electrocapillary curve and the drop mercury electrode.

The authors wish to express thanks to Prof. J. Horiuti for his suggestions in the present work and valuable advices.

Institute of Physical Chemistry,
Hokkaido Imperial University,
Sapporo, Japan.

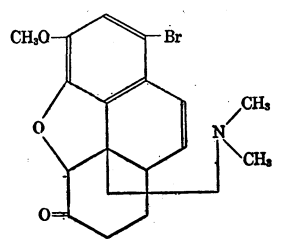
UNTERSUCHUNGEN ÜBER SINOMENIN. XLIII. MITTEILUNG.[1]

Von Kakuji GOTO und Hideo SHISHIDO.

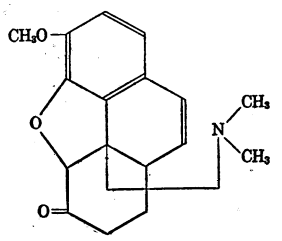
Eingegangen am 11. September, 1935. Ausgegeben am 28. Dezember, 1935.

I. Hofmannscher Abbau von Demethoxy-dihydro-sinomenin.

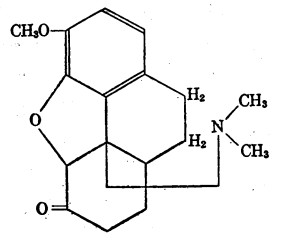
1-Brom-demethoxy-dihydro-sinomenein[2] und sein bromfreies Derivat[2] wurden in die zugehörige Des-N-methyl-basen umgewandelt und mit den entsprechenden Des-N-methyl-basen aus Dihydro-thebain racemisiert. Dabei wurden auch die Dihydro-des-N-methyl-basen (III) aus den beiden Quellen bereitet und racemisiert. Im Übergang von (+)- bzw. (−)-Dihydrokodeinon in die Des-N-methyl-base, hat der Drehungssinn nicht umgekehrt,[3] sondern das Drehungsvermögen stark abmindert. Ob dies von dem Oxyd-ring zwischen C_4 und C_5, oder von dem Drehungssinn von C_5[4] abhängt, ist zur Zeit nicht bekannt. Beim weiteren Abbau von Des-N-methyl-base, können wir noch nicht ein krystallisierender, N-freier Körper erhalten.[5]



I.



II.



III.

Des-N-methyl-1-brom-demethoxy-dihydro-sinomenein (I). 1 g. 1-Brom-demethoxy-dihydro-sinomeneinjodmethylat wurde mit 10 c.c. 2% Natronlauge 5 Min. lang gekocht. Das gebildete Öl wird aus Äthanol umkrystallisiert. Schmp. 130°. Ausbeute 0.3 g. (Gef.: C, 58.00; H, 5.65; Br, 20.19; N, 3.56. Ber. für $C_{19}H_{22}NO_3Br$ (392): C, 58.16; H, 5.61; Br, 20.41; N, 3.57%.) Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = +0.07°$; $[\alpha]_D^{11} = +7.00°$. Diese Substanz bildet ein schön krystallisierendes Jodmethylat (Schmp. 278–279°), aber dessen Abbau noch nicht gelungen ist.

(1) XLII. Mitteilung, Dieses Bulletin, **10** (1935), 481

(2) *Ann.*, **489** (1931), 95.

(3) Thebenon-ringschluss lässt den Drehungssinn umkehren, Goto, *Ann.*, **485** (1931), 252.

(4) Im Morphin ist C_5 als linksdrehend angenommen, Emde, *Helvetica Chimica Acta*, **13** (1930), 1035.

(5) Vgl. M. Freund und E. Speyer, *Ber.*, **53** (1920), 2250.

Des-N-methyl-1-brom-dihydro-kodeinon (I). Darstellung wie oben. Schmp. 132°. (Gef.: N, 3.59. Ber. für $C_{19}H_{22}O_3NBr$ (392): N, 3.57%.) Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = -0.08°$; $[\alpha]_D^{11} = -8.00°$.

***d, l*-Des-N-methyl-1-brom-dihydro-kodeinon.** Racemisiert wie gewöhnlich. Schmp. 148°; $\alpha = \pm 0$.

Des-N-methyl-demethoxy-dihydro-sinomenein (II). Diese Des-N-methyl-base wurde aus Demethoxy-dihydro-sinomenein[6] ganz wie ihr optischer Antipod aus Dihydro-kodeinon[7] dargestellt. Prismen, Schmp. 120°. (Gef.: N, 4.42. Ber. für $C_{19}H_{23}NO_3$ (313): N, 4.46%.) Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = +0.04°$; $[\alpha]_D^{11} = +4.00°$.

Des-N-methyl-dihydro-kodeinon. Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = -0.04$; $[\alpha]_D^{11} = -4.00°$.

***d, l*-Des-N-methyl-dihydro-kodeinon.** Bedingung der Racemisierung wie üblich. Schmp. 114–116°; $\alpha = \pm 0$.

Dihydro-des-N-methyl-demethoxy-dihydro-sinomenein (III). 0.7 g. Des-N-methyl-1-brom-demethoxy-dihydro-sinomenein wird in 100 c.c. 0.3% Salzsäure gelöst und mit 0.1 g. Palladiumchlorür und 0.2 g. palladiniertem $BaSO_4$ im Wasserstoff geschüttelt. Aufnahme des Wasserstoffes 90 c.c. in einer Stunde. Die befreite Base wird aus Äthanol-Äther umkrystallisiert. Schlanke Prismen, Schmp. 93–97°. Ausbeute 0.5 g. Keine Eisenchlorid- und Beilstein-reaktion. Löst sich in konz. Schwefelsäure farblos. (Gef.: C, 72.52; H, 8.15; N, 4.40. Ber. für $C_{19}H_{25}NO_3$ (315): C, 72.38; H, 7.94; N, 4.44%.) Spez. Drehung: 0.2000 g. Subst. in 10 c.c. Äthanol, 1 dm. Rohr, $\alpha = +1.00°$; $[\alpha]_D^{11} = +50.00°$.

Dihydro-des-N-methyl-dihydro-kodeinon (III). 0.8 g. Des-N-methyl-dihydro-kodeinon wird in 100 c.c. 2% Salzsäure gelöst und mit 0.2 g. $PdCl_2$ und 2 g. Kohle in Wasserstoffatmosphäre geschüttelt. Aufnahme des Wasserstoffes kommt zum Stillstand in 20 Min. (75 c.c.). Die Dihydro-des-N-base wird aus Äthanol-äther-gemisch umkrystallisiert. Schlanke Prismen, Schmp. 95–98°C. Eigenschaften wie in der (+)-Substanz. (Gef.: C, 72.66; H, 8.08; N, 4.53. Ber. für $C_{19}H_{25}NO_3$: C, 72.38; H, 7.94; N, 4.44%.) Spez. Drehung: 0.2000 g. Subst. in 10 c.c. Äthanol, 1 dm. Rohr, $\alpha = -1.01°$; $[\alpha]_D^{11} = -50.5°$.

***d, l*-Dihydro-des-N-methyl-dihydro-kodeinon.** Die racemische Substanz wurde dadurch bereitet dass man je 0.2 g. (+)- und (−)-Substanz, in Äthanol gelöst, vereinigte. Beim Einengen des Äthanols und Zusatz von Äther, krystallisierte die racemische Substanz in Rosetten. Ausbeute 0.3 g. Schmp. 113–116°C.; $\alpha = \pm 0$.

II. Katalytische Hydrierung von Thebain.

Bei der Bereitung von Dihydro-thebain nach Wieland und Kotake,[8] haben wir den Fall begegnet, in dem die Reducierung eine sehr lange Zeit in Anspruch nahm und die resultierende Substanz hauptsächlich aus Dihydro-kodeinon bestand. So haben wir einige Versuche über den Einfluss von Salzsäure-konzentration auf die katalytische Reduktion von Thebain gestellt,

(6) Dieses Bulletin, **5** (1930), 96.
(7) M. Freund und E. Speyer, *Ber.*, **53** (1920), 2250.
(8) *Ann.*, **444** (1925), 88.

obgleich es schon darüber eine ausführliche Arbeit von Schöpf[9] gibt. Sogar hat Cahn[10] durch katalytische Reducierung von roter Lösung von Thebain in rauchender Salzsäure Meta-thebainon in 81% Ausbeute erhalten. Unsere Resultate werden kurz in der folgenden Tabelle zusammengefasst.

	Konzentration von HCl	Thebain (g.)	Zeit-dauer	H_2 (c.c.)	Ausbeute
1	10 c.c. rauch. HCl 10 c.c. H_2O } ca. 5 N. (Die Lösung war nur fade gelb gefärbt.)	2	8 St.	135	Meta-thebainon (Schmp. 120–122°) 1.4 g. (75%)
2	20 c.c. ca. 2.5 N HCl	2	6 St.	150	Meta-thebainon (Schmp. 122–123°) 0.1 g. Dihydro-kodeinon (Schmp. 192–194°) 0.55 g. Dihydro-thebainon (Schmp. 153°) 0.15 g.
3	24 c.c. N HCl 5 c.c. H_2O	5	einige Tage	375	Dihydro-thebain 1.7 g. Dihydro-thebainon 0.2 g.

Aus dieser Tabelle ersieht man leicht dass eine stärkere Salzsäure (z.B. 2.5 N) das zuerst gebildete Dihydrothebain in der Kälte verseifen kann. Tatsächlich wurde Dihydro-thebain beim Stehenlassen über Nacht mit 2 N Salzsäure quantitativ ins Dihydro-kodeinon umgewandelt. Thebain selbst bleibt bei derselben Behandlung fast unangegriffen. Jedenfalls scheint die Reducierung von Thebain in konz. Salzsäure eine bequeme Darstellungsmethode von Meta-thebainon zu sein.

III. Isolierung von Demethoxy-dihydro-sinomenin über Bromhydrat.

In der XIX. Mitteilung[11] haben wir über die Mischkrystalle von Demethoxy-dihydro-sinomenin [(+)-Dihydro-thebainon] und Demethoxy-dihydro-sinomeninol [(+)-Dihydro-thebainol] berichtet, welche durch blosse Umkrystallisierung nicht voneinander getrennt werden können. Nun werde es gefunden dass die Trennung sehr leicht durch HBr oder HCl erzielt werden kann. Demethoxy-dihydro-sinomenin-bromhydrat krystallisiert sofort beim Lösen der Base in Bromwasserstoffsäure aus. Dicke Prismen, Schmp. 291° (Zers.). (Gef.: Br, 20.58. Ber. für $C_{18}H_{24}NO_3Br$ (382): Br, 20.94%). Das

(9) Schöpf, *Ann.*, **452** (1927), 244.
(10) R. S. Cahn, *J. Chem. Soc.*, **1933**, 1038.
(11) Dieses Bulletin, **5** (1930), 288.

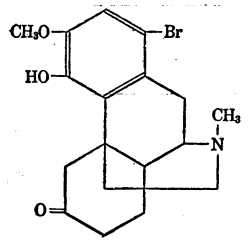
Chlorhydrat ist etwas löslicher. Schlanke Prismen, Schmp. 293° (Zers.). (Gef.: Cl, 10.60. Ber. für $C_{18}H_{24}NO_3Cl$ (337.5): Cl, 10.52%.)

(−)-Dihydro-thebainon bildet auch Bromhydrat und Chlorhydrat, die bei 291° bzw. 293° schmelzen. Diese Eigenschaft kann vorteilhaft benutzt werden, in der Darstellung von Dihydro-thebainon aus Thebain.[12]

(+)- und (−)-Dihydro-thebain, aus ihren Salzen befreit, schmelzen bei 152–153°[13] scharf und bilden das Oxim-chlorhydrat von Schmp. 317°.

IV. *d, l*-1-Brom-dihydro-thebainon.

C. Schöpf[14] gibt dem (−)-1-Brom-dihydro-thebainon (IV) den endgültigen Schmelzpunkt 167° an. Wir haben den Schmelzpunkt von 1-Brom-demethoxy-dihydro-sinomenin als 119° angegeben.[15] Da, aber, nach unseren Erfahrungen die entsprechenden (−)- und (+)-Derivate von Thebain und Sinomenin fast immer einen gleichen Schmp. zeigen, haben wir 1-Brom-demethoxy-dihydro-sinomenin vom Schmp. 167° darzustellen versucht. Und einmal haben wir die Substanz (5 g.) von Schmp. 167° bekommen, aber beim Umkrystallisieren aus Aceton kehrte der Schmp. zu 127° (mit Meniskusbildung bei 167°) zurück.[16] Dieses Verhalten erinnert uns an den zweierlei Schmp. von Sinomenin (159° bzw. 182°). Die Substanz von höherem Schmp. gewinnt man gelegentlich bei der schnellen Befreiung[17] der Base aus dem Chlorhydrat, z.B. Erhitzen auf 100°C. von dem Chlorhydrat mit $NaHCO_3$ in Wasser. Dieses Verfahren glückt, indessen, nicht immer.



IV.

Spez. Drehung von 1-Brom-dihydro-thebainon: 0.1500 g. Subst. in 10 c.c. Methanol+Chloroform, $\alpha = -1.16°$; $[\alpha]_D^{17} = -77.33°$.

Spez. Drehung von 1-Brom-demethoxy-dihydro-sinomenin[18]: 0.1500 g. Subst. in 10 c.c. Methanol+Chloroform, $\alpha = +1.18°$; $[\alpha]_D^{17} = +78.67°$.

Je 0.15 g. (−)- und (+)-1-Brom-dihydro-thebainon wurden in Methanol gelöst und vereinigt. Die racemische Substanz scheidet sich in sechsseitigen Tafeln aus, Schmp. 190–193°; $\alpha = \pm 0$.

---

(12) Freund und Speyer, *Ber.*, **53** (1920), 2261.
(13) Skita's Angabe (Schmp. 137–138°), *Ber.*, **54** (1921), 1561, scheint zu niedrig zu sein.
(14) C. Schöpf und T. Pfeifer, *Ann.*, **483** (1930), 157.
(15) Dieses Bulletin, **5** (1930), 96.
(16) Das Oxim von 1-Brom-demethoxy-dihydro-sinomenin schmilzt bei 177–178° (Gef.: N, 6.77. Ber. für $C_{18}H_{23}O_3N_2Br$: N, 7.01%). Der Schmp. 263° [Dieses Bulletin, **5** (1930), 96] war leider derselbe vom Oximchlorhydrat.
(17) H. Kondo und E. Ochiai empfahlen die Befreiung mit konz. Ammoniak.
(18) Neu gemessen. Frühere Angabe war zu niedrig.

THE DIRECT INTRODUCTION OF DEUTERIUM INTO BENZENE BY HIGH FREQUENCY CURRENT.

By J. HORIUTI and T. KOYANO.

Received November 25th, 1935. Published December 28th, 1935.

It is known that deuterium can be directly introduced into benzene with heavy water at 200°C. in the presence of a metallic catalyst.[1] This method has been successfully applied by H. S. Taylor to the preparation of C_6D_6.[2]

We have found now that under the influence of the electromagnetic oscillator of high frequency deuterium can be introduced into benzene at room temperature, metallic catalyst being used.

In a vessel of 20 c.c. capacity with a flat bottom 0.25 c.c. of pure benzene was sealed together with 0.2 c.c. of 8% heavy water and 0.5 g. of platinum black prepared by reducing platinum chloride with formaldehyde. After the contents were subjected to the influence of high frequency wave for some time, the benzene was burnt and the formed water was analysed for the deuterium content.

In our first experiment the vessel was kept on a pole of a Tesla coil for ten hours and the benzene was found to have been shifted to 0.69% in the deuterium content. No temperature change was observed during the treatment. In the second experiment the vessel was kept between poles of the high frequency oscillator of 4 meter wave length. The vessel was cooled with water during the treatment. The deuterium content of the benzene was 0.41%.

Benzene was also treated similarly with ordinary water and it was found that physical constants were unaffected within the limit of the experimental errors: the density and the freezing point agreed with those of untreated benzene within 10^{-4} and 1/10°C. respectively.

It was found that even under the influence of the high frequency oscillator the exchange reaction did not take place without the catalyst. Further studies on the introduction of deuterium into organic compounds by this simple method will be carried on in our laboratory.

We wish to thank the Nippon Gakujutsu-Shinkôkai for a financial grant.

Chemical Department, Faculty of Science,
Hokkaido Imperial University,
Sapporo, Japan.

1) J. Horiuti and M. Polanyi, *Nature*, **134** (1934), 377; *Trans. Faraday Soc.*, **30** (1934), 1164.

2) P. I. Bowman, W. S. Benedict, H. S. Taylor, *J. Am. Chem. Soc.*, **57** (1935), 960.